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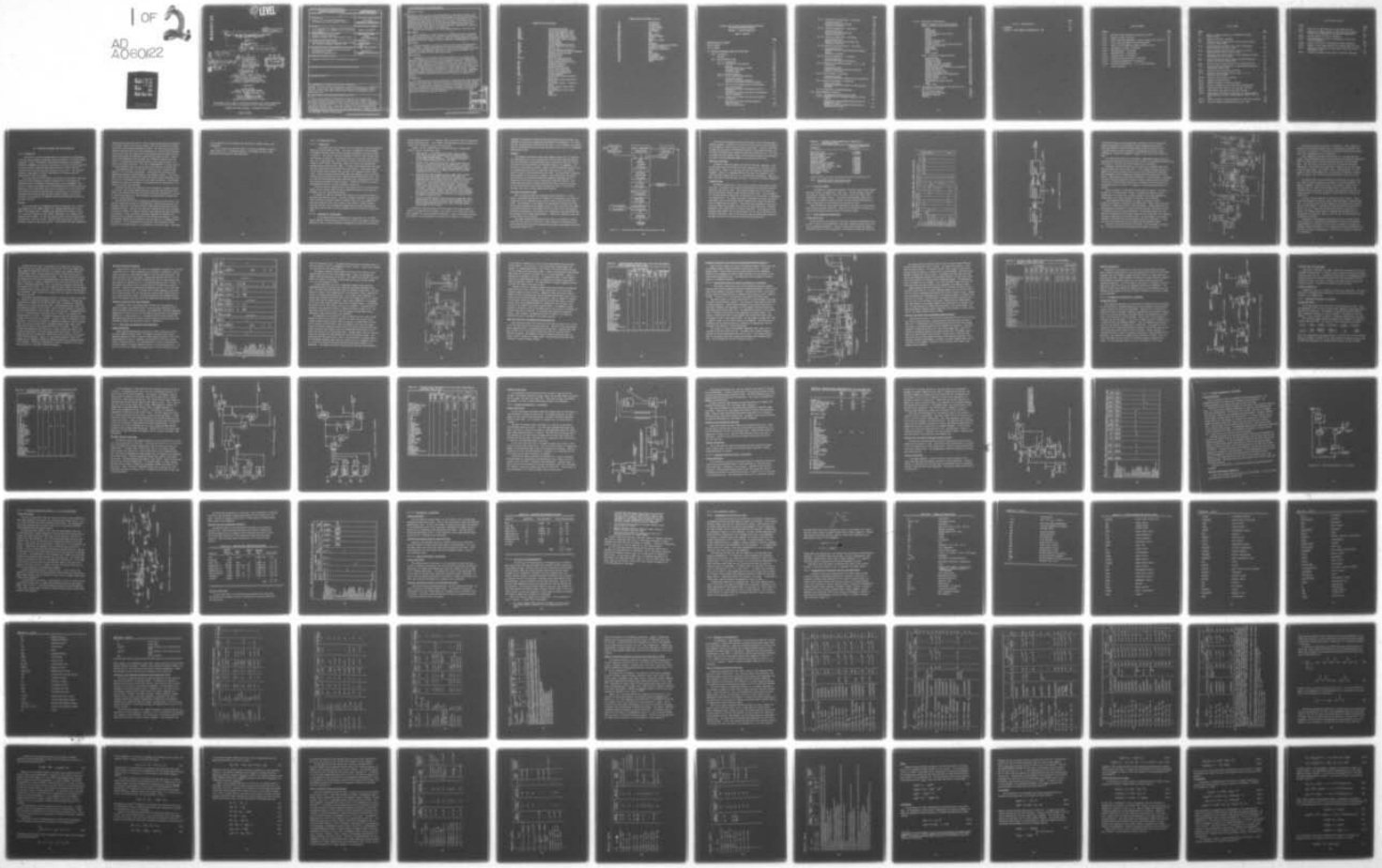

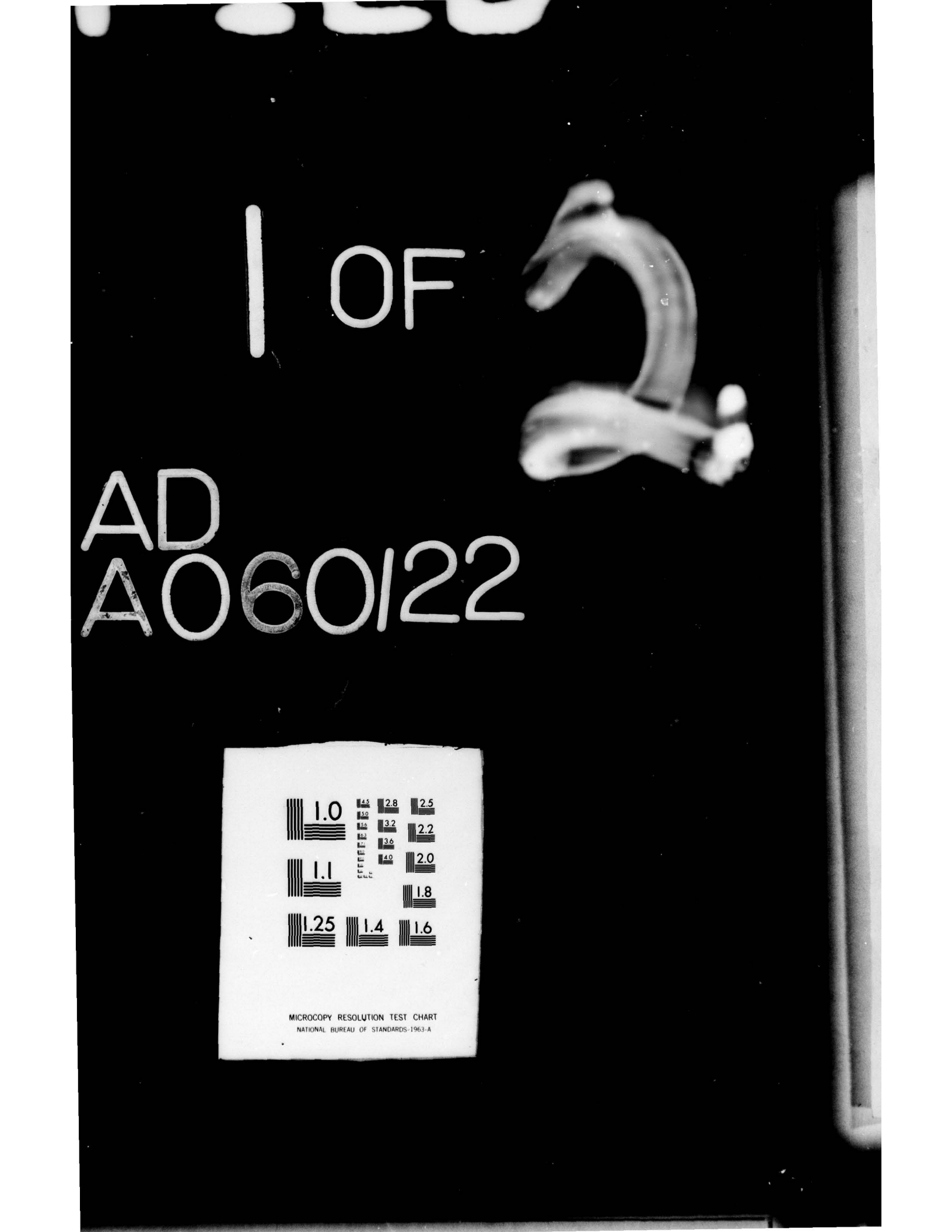
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VOLUME 2

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This work is directed toward better definition of the specific air pollutants generated from the production of RDX and TNT, together with their attendant raw material manufacture and recovery processes, and the incineration of offgrade and used materials. Plant visits were made to discuss operations and acquire available data. These data, together with survey reports by the USAEHA and technology reports from the arsenals, were used to develop a state-of-knowledge emissions inventory projected to 'mobilization' production rates.

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Individual emission sources were characterized to the extent possible. The considerable data gaps were identified and flagged for further investigation. A methodology was applied to develop estimates of concentrations of the various compounds that might arise in the air over the plant. The chemical and toxicological characteristics of known emitted compounds were used and their relevant chemical reactivity under photochemical and at ground state was reviewed by literature search. The various possible transformation processes were catalogued. Data gaps were indicated.

Based on this assessment, the following recommendations were developed.

TNT PROCESS

Source sampling of a single continuous process line should be conducted in depth to provide data in the identify of pollutants and their relation to process parameters and source controls. These data are prerequisite to further assessment of the air chemistry through dispersion and photochemical modeling.

RDX PROCESS

Further development of currently available process and source emissions data is needed. Source characteristics and process conditions developed herein should be defined and confirmed for use in future assessments. Specific compounds in source emissions need fugitive emissions and emissions from process vents should both be sampled and tested.

RDX CHEMISTRY

Assessment of the potential pollutant reactions in air indicates that known carcinogens may be formed: N-nitrosodimethylamine from dimethylamine emissions and N-nitrosomethylamine from methyamine emissions. Modeling will provide further guidance on the emissions likely to be present in the environment and enable investigators to select test methodology for individual compounds. Sampling should then be employed to define further the emission rates for organic compounds and to quantify each nitrogen oxide species. Further assessment of the potential for formation of toxic levels of these substances using photochemical-diffusion modeling is recommended as the next immediate effort in order to set guidelines for laboratory studies and ambient air testing.

INCINERATION

The trend toward air curtain incinerators, instead of the better controlled SITPA II and Rotary Kiln incinerators, presents the possibility that emissions problems will still exist, since such problems persist among municipal incinerators. A strong effort in computer modeling of combustion product generation in the incineration of explosives and propellants is needed to determine the fuel and air feed rates and temperatures required to optimize incinerator operation and minimize pollutant emissions.

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ABBREVIATIONS AND ACRONYMS

AAP	Army Ammunition Plant
HAAP	Holston Army Ammunition Plant
JAAP	Joliet Army Ammunition Plant
RAAP	Radford Army Ammunition Plant
NAAP	Newport Army Ammunition Plant
VAAP	Volunteer Army Ammunition Plant
USAEHA	United States Army Environmental Hygiene Agency
TNT	Trinitrotoluene
RDX	Cyclotrimethylenetrinitramine
NEDS	National Emissions Data System
TPD	Tons per day
SPS	Source Performance Standards
NAAQS	National Ambient Air Quality Standards
N&P	Nitration and Purification
SA	Spent Acid Tanks
ST	Settling Tanks
NAC/SAC	Nitric Acid Concentration/ Sulfuric Acid Concentration
DSN	Direct Strong Nitric Acid Plant
RWP	Red Water Processing
FB	Finishing Building
AOP	Ammonia Oxidation Plant
NAC	Nitric Acid Concentrator
SAC	Sulfuric Acid Concentrator
SAR	Sulfuric Acid Regeneration
TNM	Tetranitromethane
SC/SA	Single Contact/Single Absorption Acid Plant
DC/DA	Double Contact/Double Absorption Acid Plant
CAR	Carcinogenic effects - producing cancer
CNS	Central nervous system effects
EYE	Eye effects
GIT	Gastrointestinal tract effects
ham	hamster
hmn	human
ihl	Inhalation

ABBREVIATIONS AND ACRONYMS (cont'd)

ims	Intramuscular
ipl	Intraplueral
ipr	Intraperitoneal
IRR	Irritant effects
itr	Intratracheal
IVN	Intravenous
MAN	Man
MTH	Mouth effects
MUT	Mutagenic effects
mus	mouse
NEO	Neoplastic effects
orl	Oral
par	Parenteral
PNS	Peripheral nervous system effects
PSY	Psychotropic effects
PUL	Pulmonary system effects
rat	Rat
rbt	Rabbit
SKN	Skin effects
scu	Subcutaneous
TER	Teratogenic effects
unk	Unreported route
wmn	Woman

SPECIFIC AIR POLLUTANTS FROM MUNITIONS PROCESSING
AND THEIR ATMOSPHERIC BEHAVIOR

VOLUME 2 -- RDX/HMX PRODUCTION

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6.0 EMISSIONS ASSESSMENT FROM PLANT OPERATIONS

6.A.0 INTRODUCTION

The Office of the Army Surgeon General is responsible for development of health and environmental guidelines governing emissions of military-related compounds. The U.S. Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) has reported an evaluation of the air pollution potential of seven substances emitted at Army ammunition plants (AAP's) for which emissions and air quality standards currently do not exist.[1] The evaluation provides a background for further investigations of possible needs for appropriate air quality standards.

This study provides a continuation of the effort to establish a data base from which either discharge or ambient standards for air pollutants not addressed by the Environmental Protection Agency can be recommended. The study is limited to the production of cyclotrimethylenetrinitramine (RDX); the production of trinitrotoluene (TNT); and the incineration of waste materials. The investigation required consideration of the nature of the explosives manufacturing processes and the emissions controls applied, the possible emissions, their potential for chemical reaction and photochemical reaction, and their toxicity.

APPROACH

Visits were made to army ammunition plants at Kingsport, Tenn.--Holston Army Ammunition Plant (HAAP); Radford, Va.--Radford Army Ammunition Plant (RAAP); Chattanooga, Tenn.--Volunteer Army Ammunition Plant (VAAP); Joliet, Ill.--Joliet Army Ammunition Plant (JAAP); and Newport, Ind.--Newport Army Ammunition Plant (NAAP). At each the processing and operating practices were discussed with plant specialists. Available data were acquired relating to emissions sources and emissions controls. The available data were augmented by

survey and test data from the U.S. Army Environmental Hygiene Agency (USAEHA), by relevant reports from Picatinny Arsenal, and from the technical reference facilities of the Defense Documentation Center. The data were assessed where possible to project emissions source characteristics (stack height, diameter, eixt gas flow rate, gas composition) to be expected when the explosives-manufacturing processes were operated at mobilization production rates. Mobilization rates themselves were not based upon information obtained from the plants. In developing the projected emissions, many extensive gaps in the existing data were identified. This led to recommendations for future work to fill the information gaps and provide much needed emissions inventory data.

Waste materials were, at the time of the plant visits, burned on open ground, or in air curtain incinerators. Enclosed burning techniques were undergoing evaluation and development at the arsenals, however. Visits were made to the Picatinny Arsenal and Tooele Army Depot to obtain additional available data for assessment of emissions from closed incineration. Considerable attention was given to assessment of the methodologies for calculation of the products of controlled combustion.

Although the emissions inventories thus developed are incomplete because of data gaps, and include elements necessarily derived from theoretical principles, one inventory (RDX) provided enough approximate information to justify a limited investigation of likely atmospheric concentrations of emitted substances of plant boundaries.

For both RDX and TNT, the literature was searched to collect data on the chemical properties and potential photochemistry, ground state chemistry, and secondary reactions of both the positively identified emissions and selected suspected emissions. Reaction rate data were compiled to the extent available. The extensive numbers of chemical reactions thus obtained have been interpreted in three ways. First, potentially hazardous compounds are identified by assessing the toxicological properties of the reactants and products. Second, the reactions themselves are screened to provide some focus on expected principal products. Third, methodologies were applied toward estimating concentrations of emitted pollutants at the boundary of a mobilized plant. Additional

work on modeling the air chemistry over the plant is needed, however, and recommended.

This is Volume 2 of the Final Report, the study of RDX/HMX is covered. Other Volumes are: 1--Executive Summary, 3--TNT Production, and 4--Open Burning and Incineration of Waste Munitions.

6.A.1 THE PRODUCTION OF RDX

6.A.1.1 Introduction

An estimated emissions inventory for the production of RDX was developed based upon existing data for HAAP. This plant is currently the sole producer of RDX-HMX explosives, which are the principal ingredients of a total of some 75 products. The site was visited on September 21 and 22, 1976. At that time, one line was in operation. At 10:30 am on the 21st, there was a sun-lit haze over the "B" operating area. Each of the six stacks of the coal-fired boilers showed a visible plume. Visible NO_x plumes rose from the one operating 50 ton/day ammonia oxidation plant (AOP). A visible whitish-brown plume rose from the acid concentration unit (magnesium nitrate process). Proprietary changes in the overhead vapor condenser were reported to be underway to mollify the plume. Fugitive emissions with an amine odor were detected at the E Building; the wash tank vent gases had an odor resembling formaldehyde-formic acid. The air outside the G Building was heavy with amine odors, uncharacteristic of the main processing function of these buildings. Inside the G Building, fugitive cyclohexanone and acetic acid were evident by their odor.

In Area A, odors of organic esters were strong in the acid refining areas. Ketene was not noticed around the acetic anhydride synthesis area, which was evidently very well sealed and maintained.

A request was made for available data relevant to the characterization of emissions and emissions sources. The data ultimately received in response were used in efforts to construct tables of emission rates, exit gas compositions, and source characteristics (e.g., stack or vent location, height, diameter, exit gas velocity), and relationships between emission rates and production rates that could be used to project recorded values to mobilization production rates.

6.A.1.2 Assessment of the Data Base

The available data were incomplete and inconsistent and, in general, process material balances were not available to serve as estimators of emissions. HAAP has no heat or material balances or adequate flow sheets for the existing

acetic anhydride process (J. T. Bearden, letter of June 23, 1972 to Contracting Officers Representative). They estimate that 500 manhours would be required to develop this information for just this one system.

Examples of the incompleteness of the data were met in almost every effort to assess the emissions rates:

1. Evans et. al., in reporting the pollution status at HAAP, fails to list the acid concentration units associated with acetic anhydride manufacture.[2] These are located in Building 6, according to other references. The extent of emissions and the source characteristics are not known.

2. Jackson lists nonparticulate emission rates (source emissions data) for a source identified only as HDCNoA-2-3.[3] It may be inferred that the data relate to the acid concentrators for the acetic anhydride stills, except that the drawing presented indicates that the feed is 60 percent acetic acid, as do the drawings for A-2-5 and A-2-7.

3. Source emission data documents issued by HAAP contain several inconsistencies between emissions-source flow rates and emissions rates. For example, data for the condenser vent at the azeotropic distillation column (HDC A-2-8) show a flow rate of 0.01 cu ft/sec, which converts to 0.012 cu ft/sec at exit gas temperature. The moisture content, 80 grains per dry cu ft at 60°F, converts to 20 vol percent moisture. Subtracting the moisture, there remains a daily organic vapor output of 1.74 moles. Using the reported gas composition, this translates to 157 lb/day of organic vapors, versus the 200 lb/day reported. These data thus show an internal inconsistency of over 25 percent. For eight stills operating at mobilization, the reported values could be 344 lb/day too high.

4. The methyl nitrate emission rate from the acid azeotropic distillation columns is reported to be 533 lb/day,[4] whereas the source emissions data show only 48 lb/day at 1970 production rates,[4] a value which extrapolates to only 96 lb/day at the mobilization rates assumed for this report.

Although the data base lacked sufficient detail and accuracy needed to prepare a refined emissions inventory, the location of all sources was available, together with gross estimates of emissions. Since an emissions inventory was essential to any assessment of the plant's air chemistry, a preliminary

inventory was developed in which the best data available were collected, and extended as necessary by engineering calculations and assumptions. This inventory was thus utilized for the rest of the study. It also provides an organized means for developing more precise data, source by source, which is a recommended future area of work.

Approach

The elements of emissions-source data needed to assess the air chemistry were enumerated, and a source inventory was constructed by compiling whatever data were available, using assumptions about a source when data were lacking, and reconciling inconsistencies by engineering analysis and judgement. This was done to serve several purposes: obtain a state-of-knowledge inventory; use it to guide the scope of the air chemistry study; and use it to identify specific needs for further emissions source data. In the following discussion, the development of the emissions inventory is described process by process. Descriptions of the processing operations themselves have been kept to a minimum consistent with clarity of definition of emissions sources. Flow sheets shown were based on USAEHA drawings[6] which were revised to bring up to date and modified to show emissions sources not shown in the original drawings, which were oriented toward water pollution.

The Production Process at HAAP

RDX is produced at HAAP by the Bachman continuous process. In this process, hexamethylenetetramine (or "hexamine") is nitrolyzed in a mixture of strong nitric acid, ammonium nitrate, glacial acetic acid, and acetic anhydride. The components of the reaction are separated and recovered for reuse. The principal advantage of the Bachman process is that the yield of RDX based on hexamine conversion is high (about twice that of the nitric acid process). The major disadvantage of the process is its complexity, requiring manufacture and recovery of the various feed chemicals. Figure 6.A-1 presents an overview of the process flow at Holston.

The acetic anhydride manufacturing area, Area A, is physically located some miles from the rest of the plant. Acetic anhydride is made from acetic acid reclaimed from the explosive manufacturing process, and makeup acetic acid is purchased commercially.

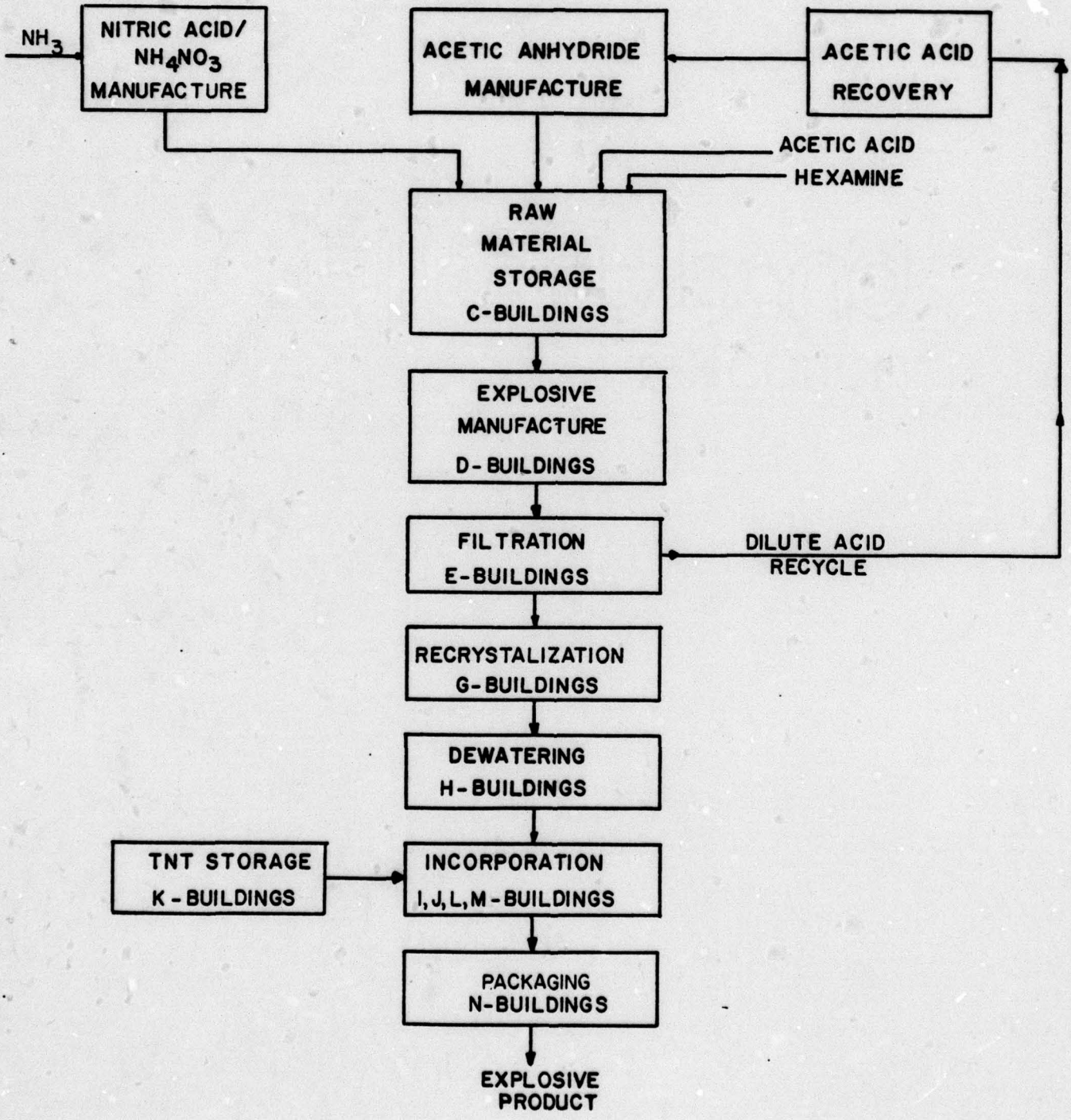


Figure 6.A-1. Overview of RDX manufacturing operations at HAAP.

Nitric acid and ammonium nitrate are produced in Area B from purchased anhydrous ammonia. Synthesis is carried out in the acid area and the products are transported to the raw material area (C Buildings). From the C Buildings through the N Buildings, the processing facilities are arranged serially and the feeds and products move sequentially down the production line. The liquid is removed from the reaction slurry at the filtration operation (E Buildings) and acetic acid and anhydrous ammonia are recovered at the B line.

Overview of the Plant

The HAAP is located in Hawkins and Sullivan Counties, Tennessee. There are two plant areas, A (Sullivan Co.) and B (Hawkins Co.). Both are on the Holston River. Area A is a 134-acre plot near the Tennessee Eastman plant at Kingsport. Area B is a separate 6369 acre plot near the confluence of the north and south forks of the river, a few miles west of Kingsport. HAAP has a mean elevation of 1260 feet above sea level. An area map is shown in Appendix 4.

Production Rates

The emission rates given in this report are based on mobilization production rates. In general, this required extrapolation from the rate at which a particular data set was taken. The production capability of the plant was taken to be 670,000 lbs/day of RDX and 8000 lbs/day of HMX. This corresponds to 1,120,000 lbs/day of Composition B production if all of the RDX is compounded into Composition B. The production rates at individual units were calculated from factors used by the Holston Defense Corporation to relate feed material rates to Composition B production. These factors are presented in Table 6A-1. As actual Composition B production utilizes only about 80 percent of the RDX production, this simplification introduces some error. On the positive side, emission rates based on this factoring process can be clearly defined and are internally consistent. Most of the emissions data were taken when production was about one half of the planned maximum rates described above.

TABLE 6A-1. FACTORS TO CONVERT COMPOSITION B PRODUCTION TO FEED MATERIAL RATES

Production	Fraction of Composition B Production
Weak Nitric Acid	0.7593000
Ammonia Recovered at Bldg A-1 (as 100% Ammonia)	0.0151250
Anhydrous Ammonia Used	0.3000000
Crude RDX, batches	0.0001340
Hexamine, pounds	0.2317200
Hexamine/Acetic Acid, pounds	0.6050000
Nitric Acid (99%), pounds	0.7460000
Nitric Acid/Ammonia Nitrate, pounds	0.8140000
Acetic Anhydride, pounds	1.1919000
Acetic Acid, pounds	0.4086200
Cyclohexanone, pounds	0.0071000
TNT, pounds	0.3900000

Notes: Assume 4500 pounds crude RDX per batch.
Assume 850 pounds crude HMX per batch.

6.A.1.3 Emissions Summary

The known and characterized emissions from HAAP, based on mobilization production rates, are summarized in Table 6A-2. The most prevalent emissions are oxides of nitrogen (NO_x), acetic acid vapor, nitric acid fumes, light hydrocarbons, and methyl nitrate. The explosive manufacturing operations in D Buildings, the ammonia oxidation process, and the anhydride manufacturing process produce most of the emissions from the Holston Plant.

Fugitive emissions from processing operations contribute to the pollutant load, but have not been quantified. These arise from materials handling, and from periodic dumping of waste solvents into disposal ponds.

6.A.1.4 Acetic Anhydride Manufacturing

Process Description

Three operations are conducted in the acetic anhydride manufacturing area at HAAP: acetic acid concentration, crude acetic anhydride manufacturing, and acetic anhydride purification. These are supported by producer gas manufacturing and several utilities operations. The production operations take place

TABLE 6A-2. SUMMARY OF EMISSIONS FROM HAAP (POUNDS PER 24-HOUR DAY)

Component	Acetic Anhydride Manufacture			Nitric Acid Manufacture			Acid Recovery B-Line		Explosive Production by Building								Steam Generation					TOTALS
	Acid Conc.	Ac_2O Mfg.	Ac_2O Ref.	AOP	MAG	AMP	HNO3 Rec.	Acid Rec.	C	D	E	G	H	I,J,K,M	P	N	Stacks 1,2,3,4	Stacks 5,6	Stack 7	B200	B222	
1 Particulates																						14749
2 CO_2																	$1.9x10^6$	$1x10^6$	$0.9x10^6$	$9x10^6$	$0.9x10^6$	$5.6x10^6$
3 SO_2																	5852	3218	2778	4000	900	16749
4 NO_2 NO $_x$				15480	3008					21640							8780	4830	4171	6400		64309
5																						
6 CO		12197																				12197
7 Methane		1955																				1955
8 Non-methane HC	1596	1128	184																			2908
9 Acetic Acid	21		28					6730	1050	4608	60											12497
10 Acetone												2242										2242
11 Cyclohexanone												2514										2514
12 n-Propyl acetate	908		226																			1134
13 Methyl acetate	288			72						373												733
14 n-Propyl formate	256		64																			320
15 Acetic anhydride									50	180												230
16 Formic acid										141												141
17 Toluene												55										55
18 Butanol												8										8
19 Me.eth.ketone												6										6
20 Isobutyl acetate												2										2
21 Phenol																						0.8
22 Trace org.	.12		.12																			2
TOTAL 8 - 22																						2806
23 Ammonia							260	130														390
24 Nitric acid				23	3576	150			660													4409
25 Methyl nitrate	128		32							1398												1558
26 Nitromethane	24		6																			80
27 Explosives (particulate)														1	1	0.3						7.3
28 Hydrogen		418																				418
29 Methylamine							18															18

Basis: 670,000 lb/day HDX, 8,000 lb/day HNX, factored to 1,120,000 lb/day Composition B.

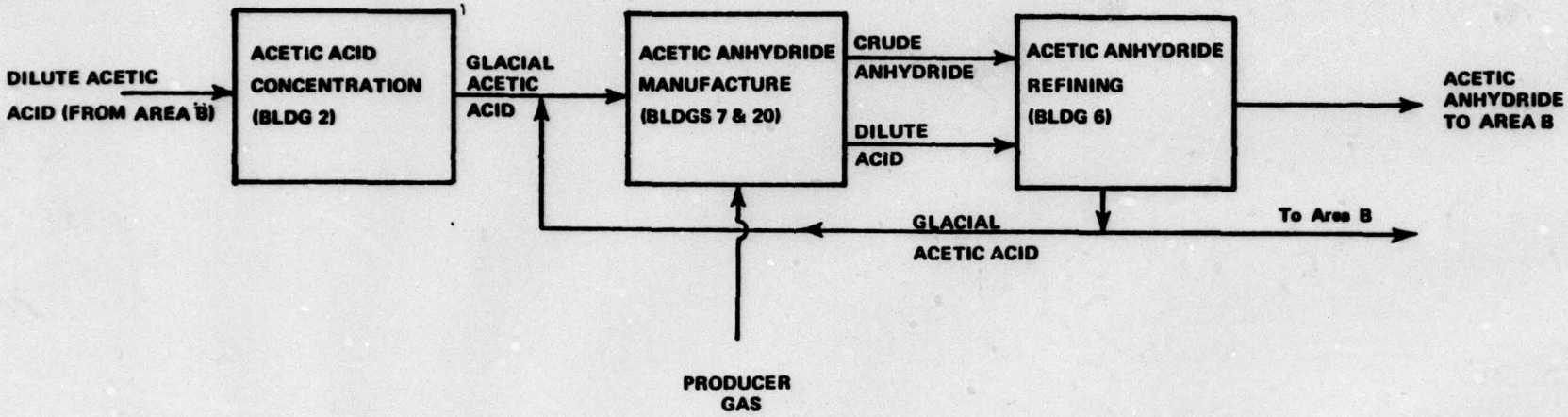


Figure 6.A-2. Summary of Area A flow plan.

in Building 2 (acetic acid concentration), Buildings 7 and 20 (crude acetic anhydride manufacture), and Building 6 (acetic anhydride purification). Using the production figures discussed above, the base production rate is 1,335,000 lbs/day of acetic anhydride, or 40,000,000 lbs of acetic anhydride/month. Figure 6.A-2 presents a summary of the flow plan by production area.

The distillation facilities in Building 2 concentrate dilute acetic acid returned from the primary distillation line (B-line) in the explosives manufacturing area, Area B. There are eight distillation units in Building 2.

Azeotropic distillation techniques are necessary to separate water from the acid within the finite column size. A third element (n-propyl acetate) is added to the acetic acid-water mixture to form the azeotrope with the water. This azeotrope is taken overhead and condensed forming two immiscible liquid phases. These phases are separated by decantation. The water phase is subjected to solvent recovery operations to recover as much n-propyl acetate as possible. A flow plan of the Building 2 operations is presented as part of Figure 6.A-3. Concentrated acetic acid (99+ %) is removed as the column bottoms and sent to storage.

Solids accumulate in the bottom of the column and reboiler. As shown in Figure 6.A-3, a bleed stream of sludge is drained every couple of hours, accumulated in a storage tank, and then charged to the sludge evaporator to recover acetic acid vapors overhead for feed back into the process.

Acetic anhydride manufacturing is housed in Buildings 7 and 20. Figure 6.A-3 presents a flow plan of the operations. Glacial acetic acid from Building 2 is vaporized and fed to cracking furnaces. Eighty percent of the entering acetic acid vapor is cracked to ketene and water, and about 2 percent is cracked into various light hydrocarbons. The unreacted acetic acid and water are condensed out of the vapor stream and sent to Building 6 for recovery. The vapor stream enters the scrubbing train. In the scrubbers, crude acetic anhydride is formed by the reaction between acetic acid and ketene. In addition, the light hydrocarbons are separated from the anhydride stream.

There are 32 cracking furnaces in Building 7 and 16 furnaces in Building 20. In each building, one gas scrubbing train serves two furnaces.

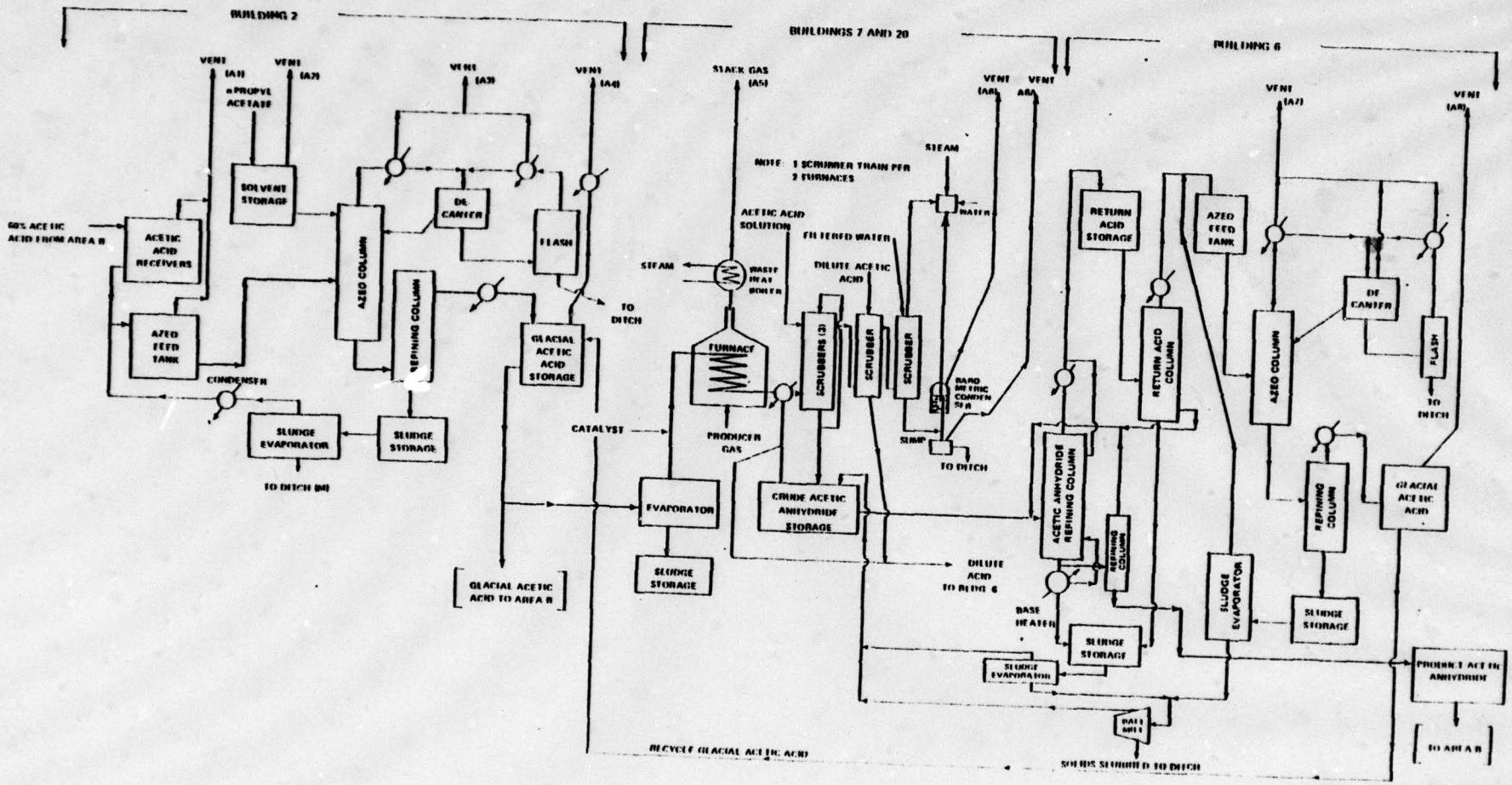


Figure 6.A-3. Acetic anhydride manufacture - Area A, showing total emissions.

Two distinct operations take place in Building 6: acetic anhydride is refined by distillation and acetic acid is concentrated by azeotropic distillation as in Building 2. There are nine anhydride refining units and two acetic acid concentration units in Building 6.

Acetic anhydride is refined by distillation in a two-stage refining column. The crude anhydride feed (containing acetic acid and other impurities) enters the lower stage of the refining column directly from the storage tanks. Two base heaters are used to maintain the column at the proper temperature. The refined acetic anhydride is removed from the lower stage of the refining column. This product stream is further refined in a small column to remove colored impurities. The pure acetic anhydride is removed from the bottom of this refining column and stored for later use in Area B.

The overhead vapor from the anhydride refining column contains acetic acid, about 15 percent anhydride, and numerous low boiling compounds. The vapor is condensed, a portion refluxed to the anhydride column, and the remainder sent to a return acid stripping column. The bottoms of the stripping column are returned to the feed of the anhydride column, and the overhead product is fed to an azeotropic distillation unit to recover the acetic acid.

As before, solids accumulate in the heaters of this process. These solids are periodically bled off, stored, then evaporated in sludge evaporators. The overhead vapors from the evaporators are condensed and recovered for use in the process. In Building 6 the solids from the evaporators are fed to a ball mill, where they are physically broken up under heat and vacuum. The overhead vapor stream is condensed and recovered for use in the process; the solids are slurried out of the ball mill periodically and discharged to the ditch.

In addition to the manufacturing operations, Area A includes several utility operations. Refrigeration requirements for cooling the anhydride scrubber medium in Buildings 7 and 20 are met by mechanical refrigeration equipment located in Building 5. Five steam-driven Freon refrigeration units cool the glycol heat exchange medium. Each unit has a capacity of 500 tons of refrigeration.

Process steam for Area A is generated in the steam plant, Building 8. There are seven coal burning boilers in Building 8; six are the stoker-fired type capable of generating 130,000 lbs of steam/hr under normal conditions (160,000 lbs/hr peak), and the seventh boiler burns pulverized coal and is rated at 160,000 lbs/hr (190,000 lbs/hr peak). The stoker-fired boilers have the capability of burning tar sludge generated in the manufacture of producer gas in Building 10. Steam is generated at the boiler house at 400 psig and 575°F; a 100 psig system (440 ± 10°F) is provided by expanding the high pressure steam across a valve. On a full production basis, about 12 million pounds of steam are used in Area A each day. This requires that about 320 tons/day of coal be burned. About 16,000 lbs of producer gas tar sludge are also burned in the boilers each day.

The producer gas manufacturing facilities in Area A are housed in Building 10: there are 12 Semet-Solvay Model 10 Koller gas producers. Producer gas (heating value between 165 and 185 Btu/cubic foot) is produced by incomplete combustion of a special gasification coal. Approximately 56 cubic feet of gas are produced per pound of coal burned. Each of the gas producers is presently rated at approximately 2 million cubic feet of gas per day. To manufacture the gas, air is blown through a saturation tower in which it is contacted with sparged steam at 6-7 psig. The steam-air mixture leaves the saturation column at about 120°F and enters the furnaces. No other sources of combustion air are permitted. The coal in the furnace is incompletely combusted, and the products leave the furnace at about 1100°F, proceeding through a dust removal water spray and tar trap to a main header which serves six furnaces. The gas is scrubbed continuously by water sprays as it passes through the header to the primary scrubber where it is again contacted with water sprays. The gas is compressed and then scrubbed again before being sent to Building 7 for burning in the cracking furnaces. There is no gas storage capacity in Area A and producer gas is produced on demand as required by the acetic anhydride manufacturing process. Producer gas requirements have been estimated at 14.3 cubic feet per pound of crude acetic anhydride produced.

Emissions from Area A Processes

Known emissions sources from Area A are summarized in Figure 6.A-3, the flow diagram for Area A. Source characteristics are shown in Table 6A-3. Some of these characteristics have been estimated in lieu of actual source data. The known emissions are of three types. Storage tank emissions such as A-1, A-2, A-4, and A-8 are due to diffusion through the tank vent (a minor source) and mass transfer by saturated air as it is displaced when the tank is filled. The maintenance of constant levels in these tanks will minimize this source of emissions. Vents of non-condensible hydrocarbons such as A-3, A-6, and A-6A, are a major emission source. Flue gases such as that produced by the acetic acid cracking furnace (A-5) and the flue gas from the Area A steam plant are also a major emissions source. Emissions generated by the handling of coal both at the producer gas plant and at the steam plant have not been included.

Controls on Emissions from Area A Processes

Atmospheric vents from storage tanks in Area A are not controlled. A steam jet scrubber and scrubber column is used on waste cracked gas in the acetic anhydride manufacturing process. Non-condensible, insoluble hydrocarbon components of the vent gas are not collected and go directly to the atmosphere. Producer gas is water-washed as it is produced, and this should prevent the emission of many hydrocarbon species from the anhydride cracking furnace and considerably reduce the particulate loading in Stream A-5.

6.A.1.5 Nitric Acid and Ammonium Nitrate Manufacture

Process Description

Three separate manufacturing operations are used to manufacture nitric acid and ammonium nitrate at HAAP. The ammonia oxidation plant converts anhydrous ammonia and water to medium strength (about 60 percent) nitric acid. Concentrated nitric acid is produced by an extractive distillation process based on magnesium nitrate. The concentrated nitric acid is contacted with anhydrous ammonia to produce ammonium nitrate in a third processing unit. The nitric acid units are capable of producing about 1 million lbs/day of nitric

TABLE 6A-3. EMISSIONS SOURCE CHARACTERISTICS, ACETIC ANHYDRIDE MANUFACTURING, AREA A, HAAP

	Acetic Acid Concentration, A2				Acetic Anhydride Manufacture Building 7			Building 20			Producer Gas Building 10		Acetic Anhydride Refining, Bldg. 6	
	Feed Tank Vent A1	Sol. Sto. Vent A2	Cond. Vent A3	Glac. Acid Sto. A4	Stack Gas A5	Para. Seal Vent A6	Drain Sump Vent A6A	Stack Gas A5	Bara. Seal Vent A6	Drain Sump Vent A6A	Stoker Vent	Decant. and Evap.	Condenser Vent A7	Acid Storage A8
Height, ft			125		150	83	83	150	83	83	40		125	
Inside diameter (tip), ft			0.5		8	0.5	0.67	8	0.5	0.67	0.5		0.5	
Flow, Exit Temperature cft/s			0.0131		980	1	0.005	321	1.4	0.067	7.3		0.0131	
Exit Temperature, °F			150		343	212	212	343	212	212	80		150	
Gas Velocity, ft/sec			0.067		19	5.03	0.136	2.8	7.12	0.19	37.1		0.067	
Number of Sources	8	8	8	8	1	2	2	1	1	1	1		2	2
Moisture Volume, %			26			36	36		36	36			26	
Emissions, lb/day														
1 Particulates														
2 CO_2						1755	84		2480	119	2980			
3 SO_2														
4 NO_2 NO_x											0.26	U		
5 NO												N		
6 CO						230	11		325	16	11374	K		
7 Methane						343	17		486	23	726	N		
8 Non-methane HC						761	37		1076	52		O		
9 Acetic Acid	1.25			1.4	U			U				W		14
10 Acetone					N			N				N		
11 Cyclohexanone					K			K						
12 n-Propyl Acetate		0.5	113		N			N					113	
13 Methyl Acetate			36		O			O					36	
14 n-Propyl Formate			32		W			W					32	
15 Acetic Anhydride					N			N						
16 Formic Acid														
17 Toluene														
18 Butanol														
19 Me. Eth. Ketone														
20 Isobutyl Acetate														
21 Phenol											0.8			
22 Trace Organics			0.12										0.12	
Total 8 - 22														
23 Ammonia														
24 Nitric Acid														
25 Methyl Nitrate			16										16	
26 Nitromethane			3										3	
27 Explosives (particulate)														
28 Hydrogen											418			

acid (as 100 percent acid). The ammonium nitrate process can produce about 1.4 million lbs/day of nitric acid/ammonium nitrate solution. Figure 6.A-4 includes the flow plans for the three processes.

The ammonia oxidation plants produce dilute nitric acid which is later concentrated into the nitric acid concentrators. There are two operable ammonia oxidation processes at the plant: Four DuPont units housed in Building 302-B, are rated at 50 tons/day of 100 percent acid; and a new 300 ton/day unit, put into operation in 1974.

In both processing units air is compressed, heated, then mixed with superheated ammonia and passed over a specially developed proprietary catalyst. Nitrogen oxide (NO) and water vapor are formed by the reaction. As this mixture is cooled in the condensers and in the absorption column, oxidation of the NO to nitrogen dioxide (NO_2) occurs. As the water vapor condenses, it absorbs some nitrogen dioxide and forms nitric acid (HNO_3) which is air lifted through the column by compressed air. Water (steam condensate) is introduced at the top of the column to absorb most of the nitrogen dioxide. The reactions which take place in this process unit are all exothermic. The heat which is released in the absorption column is removed by internal cooling coils. The waste gases from the top of the column are expanded through power recovery compressors before being vented to the atmosphere.

The magnesium nitrate process is used to concentrate nitric acid at HAAP. Magnesium nitrate has a chemical attraction for water, and is used in the ternary system, magnesium nitrate-nitric acid-water, to remove water from the acid by extractive distillation. Weak (61 percent) nitric acid and concentrated (72 percent) magnesium nitrate solution are fed to the top of the three-stage stripping column together with the intermediate (80-90 percent) nitric acid from the base of the rectifying column. Overhead vapors from the stripping column are condensed and then divided into reflux and product streams. The product portion (99 percent nitric acid) is cooled further in cascade coolers. The uncondensed overhead vapors from the strong nitric acid condensers are led to a rectifying column and scrubbed with water before being vented to the atmosphere. The bottoms from the stripping column, which have been denitrated

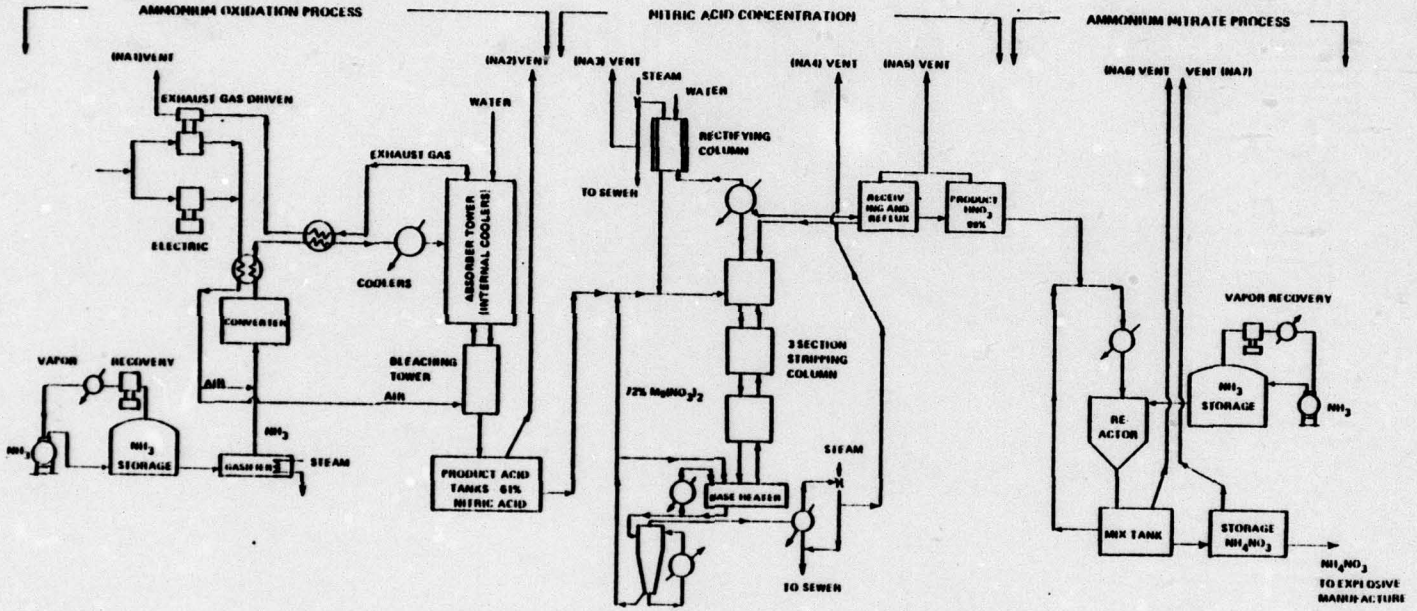


Figure 6.A-4. Nitric acid and ammonium nitrate manufacture.

to less than 0.1 percent nitric acid, contain approximately 60 percent magnesium nitrate. This solution is first concentrated to approximately 64 percent in a steam-heated reboiler (base heater) which also supplies the heat for the stripping and rectifying columns. Further concentration to the original feed stream of 72 percent is carried out in a vacuum evaporator. Water is removed and discharged to the sewer. As magnesium nitrate is not consumed in the process, fresh magnesium nitrate is added only to replace losses due to leaks and equipment cleaning. The concentrated (72 percent) magnesium nitrate solution will freeze unless kept at 100°C.

Ammonium nitrate is produced at HAAP by the direct reaction of anhydrous ammonia and nitric acid, with the reaction taking place in a circulating stream of ammonium nitrate solution. Ammonium nitrate from the mix tank is pumped into the circulating loop, and concentrated (99 percent) nitric acid is mixed with the solution through a mixing nozzle. Heat is removed in a series of five water cooled heat exchangers and the solution then enters a cyclone reactor where liquid anhydrous ammonia is sprayed into the solution. Gasification of the ammonia and further reaction occurs. The ammonium nitrate solution is returned to the mix tank where part of the solution is withdrawn to storage tanks and the remainder is circulated back through the production process. Once produced, the ammonium nitrate is shipped to the explosive manufacturing area (C Buildings) in railroad tank cars.

Emissions from Nitric Acid/Ammonium Nitrate Production

Known emissions sources from the nitric acid area are identified on Figure 6.A-4, the flow diagram for the processing area. Table 6A-4 shows the emission source characteristics, as estimated from available data. Emissions NA2, NA5, NA6, and NA7 are all from vented storage tanks and are relatively small. Emission stream NA1, the exhaust gas from the ammonia oxidation process absorber, contains primarily nitrogen oxides. NA3 and NA4 are both vents from steam jets on process exhaust streams.

TABLE 6A-4. EMISSIONS SOURCE CHARACTERISTICS, NITRIC ACID AND AMMONIUM NITRATE MANUFACTURE, AREA B, HAAP

	NITRIC ACID MANUFACTURE					AMMONIUM NITRATE	
	AOP, B-302		MAG, Bldg. 304				
	Absorber Vent NA1	Acid Tanks NA2	Jet Discharge NA3	Base Heater Vent NA4	Sto. Tank Vents NA5	Mix Tank Vent NA6	Storage Tank Vent NA7
Height, ft	34	12	129		12		
Inside diameter (tip), ft	1.3	0.2	0.53	U	0.2		
Flow, Exit Temperature cft/s	72.1		4	N			
Exit Temperature, °F	110		212	K			
Gas Velocity, ft/sec	54.3		18.1	N			
Number of Sources	9	9	8	O	8	4	4
Moisture Volume, %			60	W			
				N			
Emissions, lb/day							
1 Particulates							
2 CO_2							
3 SO_2			0.3				
4 NO_2 NO_x	1720		376				
5 NO							
6 CO							
7 Methane							
8 Non-methane HC							
9 Acetic Acid							
10 Acetone							
11 Cyclohexanone							
12 n-Propyl Acetate							
13 Methyl Acetate							
14 n-Propyl Formate							
15 Acetic Anhydride							
16 Formic Acid							
17 Toluene							
18 Butanol							
19 Me. Eth. Ketone							
20 Isobutyl acetate							
21 Phenol							
22 Trace Organics							
Total 8 - 22							
23 Ammonia							
24 Nitric Acid		2.5	424		23	12.5	25
25 Methyl Nitrate							
26 Nitromethane							
27 Explosives (particulate)							
28 Hydrogen							
29 Methylamines							

Controls on Emissions from the Nitric Acid/Ammonium Nitrate Production

Vapor recovery systems are used on the anhydrous ammonia railway tank cars and storage systems, preventing emissions from those sources. The other storage tanks in this process area are vented directly to the atmosphere. Steam jet type scrubbers are used to reduce emissions from two sources in the nitric acid concentration area. The exhaust gas from the ammonia oxidation process is discharged untreated.

6.A.1.6 Primary Distillation for Acetic Acid Recovery - B Buildings

The primary distillation units at the B Buildings receive contaminated weak acid from the explosive filtration section and separate it into dilute acetic acid, ammonia, and sludge fractions. The weak acid feed is principally dilute acetic acid containing 0.5-3.0 percent nitric acid and a small amount of RDX-HMX. Figure 6.A-5 is a flow plan of the primary distillation area.

The feed solution is initially neutralized in a crude treatment tank using 50 percent sodium hydroxide solution. The solution is then stored and fed into a primary evaporator. Approximately 80 percent of the entering weak acid is vaporized, condensed, and recovered as a clear aqueous distillate containing approximately 60 percent acetic acid. The remaining 20 percent of the original feed is withdrawn from the base of the evaporator as primary sludge. This sludge is diluted with water to approximately 30 to 35 percent acetic acid, then heated to 100°C, then cooled to 30°C. As the sludge is cooled, RDX slurry is added as "seed" to aid crystallization of the RDX-HMX. The explosives are separated from the solution either by a cyclone or by decantation, and are returned to the explosive filtration buildings.

The filtrate is then fed to secondary evaporators which again split it into acetic acid and sludge portions. The acetic acid is again condensed overhead and stored before being sent back to Area A. The sludge portion is fed to a stripping column where sparged steam removes the remaining acetic acid. This recovered acid is also returned to Area A.

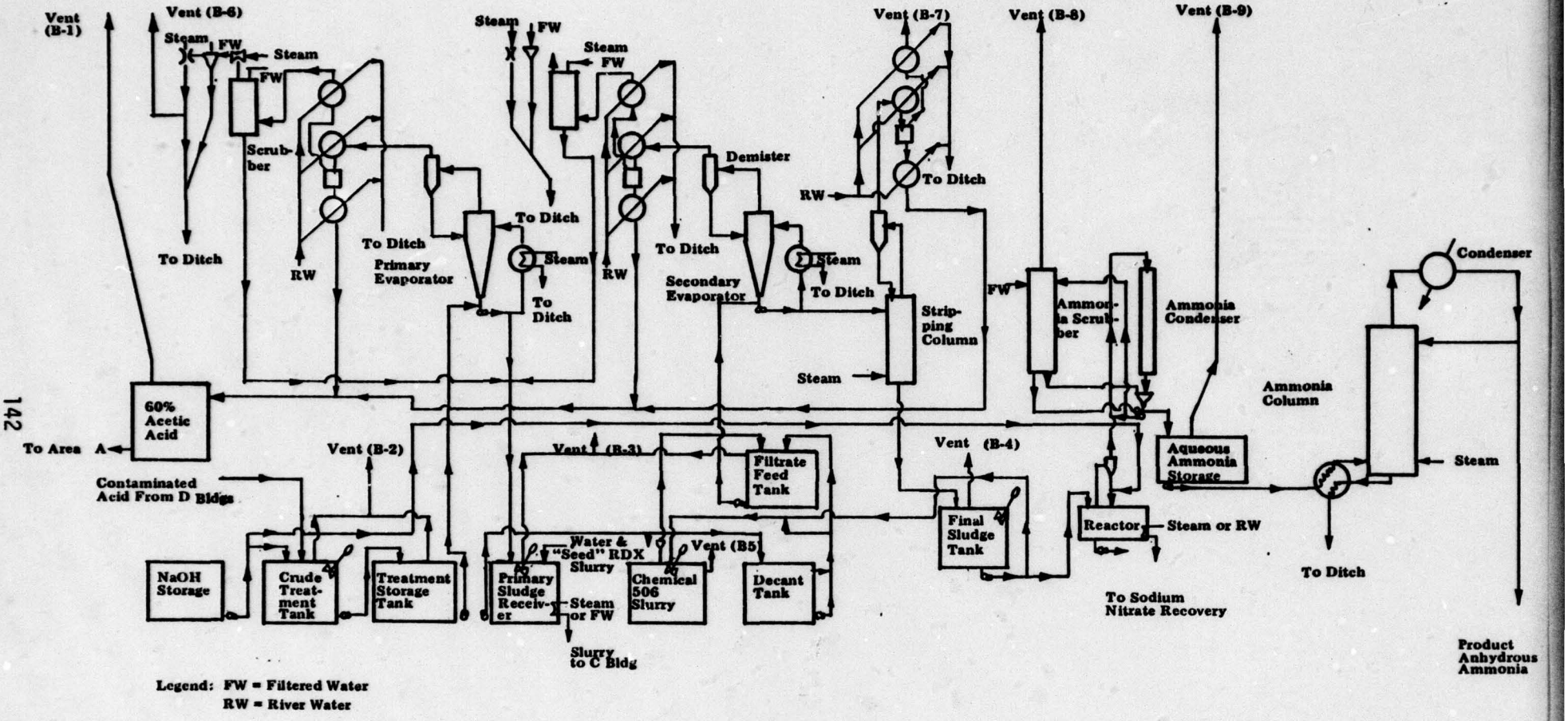


Figure 6.A-5. Acetic acid and anhydrous ammonia recovery, B-line.

The sludge from the stripping column is fed to a batch reactor where 50 percent sodium hydroxide slurry is added. The reactor also contains a "heel" from the previous batch. The ammonium nitrate in the sludge is converted to sodium nitrate and ammonia, the acetic acid to sodium acetate, and the residual RDX-HMX to ammonia and sodium nitrate. The ammonia and water vapor from the reactor are condensed overhead, and the aqueous ammonia is stored before being sent to Building A-1 for concentration to anhydrous ammonia. Non-condensable gases are vented from the scrubber. All of the operations described above are batch operations with the exception of the evaporators and ammonia columns.

Aqueous ammonia from the B Buildings (12 to 15 percent nitrogen as NH_3) is distilled in Building A-1 to recover anhydrous ammonia for sale as fertilizer. The feed stream is preheated before being fed into the recovery column. Sparged steam accomplishes the stripping action, and anhydrous ammonia is obtained from the top of the column. The distillate is condensed and then either fed into a railroad tank car or refluxed to the column. Methylamine and dimethylamine which were present in the aqueous ammonia feed stream (about 2-4 percent of the total nitrogen content) are wasted from the column in the bottom stream. The recovered anhydrous ammonia contains impurities which prevent its being used as feed to the ammonia oxidation plant at HAAP.

Emissions from Acetic Acid and Anhydrous Ammonia Recovery

Known emission sources from B-Line are summarized on Figure 6.A-5, the flow plan for the processing area. Emissions source characteristics are given in Table 6A-5. The emissions from this processing area are either from storage tank vents or uncollected emissions from scrubbers and steam jets. Emissions streams B1 through B5 and B9 are all vents from storage tanks. Vent B2 is especially noteworthy because of the high emission rate. Presumably, this is due to the neutralization reaction which is taking place in the two tanks. Vents B6 and B7 are both acetic acid vapors which were not collected in the upstream scrubbers and condensers. Vent B8 is primarily ammonia which was not collected in the scrubber. Vent B10 is the light ends vent stream on the ammonia column condenser.

TABLE 6A-5. EMISSIONS SOURCE CHARACTERISTICS OF ACETIC ACID AND AMMONIA RECOVERY, B-LINE, AREA B, HAAP

	ACID RECOVERY								AMMONIA RECOVERY	
	Sto. Tank Vent B1	Treat Tank Vent B2	Sludge Tank Vent B3	Final Sludge Tank Vent B4	Slurry Tank Vent B5	Acid Scrub. Vent B6	Strip. Col. Vent B7	NH_3 Scrub. Vent B8	NH_3 Storage Vent B9	NH_3 Col. Vent B10
Height, ft	18	18	18	18	18		34	34	34	34
Inside diameter (tip), ft	0.2	0.2	0.2	0.2	0.2		0.2	0.2	0.2	0.2
Flow, Exit Temperature cft/s	0.00006	0.06	0.0004		0.0004		0.0001	0.007	0.0035	0.011
Exit Temperature, °F	60	60	60	60	60		60	60	60	60
Gas Velocity, ft/sec	0.02	1.2	0.012		0.012		0.002	0.23	0.12	0.34
Number of Sources	9	9	5	1	1	9	5	5	5	5
Moisture Volume, %										
Emissions, lb/day										
1 Particulates										
2 CO_2										
3 SO_2										
4 NO_2 NO_x										
5 NO										
6 CO										
7 Methane										
8 Non-methane HC										
9 Acetic Acid	7.5	714	5.2	0.1	5	?	1			
10 Acetone										
11 Cyclohexanone										
12 n-Propyl Acetate										
13 Methyl Acetate										
14 n-Propyl Formate										
15 Acetic Anhydride										
16 Formic Acid										
17 Toluene										
18 Butanol										
19 Me. Eth. Ketone										
20 Isobutyl Acetate										
21 Phenol										
22 Trace Organics										
Total 8-22										
23 Ammonia								26	13	39
24 Nitric Acid										
25 Methyl Nitrate										
26 Nitromethane										
27 Explosives (Particulate)										
28 Hydrogen										
29 Methylamines		18								

Controls on Emissions

The majority of the emissions in this area are from uncontrolled atmospheric vents on storage tanks, by far the largest emission being from the crude treatment tank and treatment storage tank which follow the contaminated acid neutralization step. Water scrubbers followed by two-stage steam jets equipped with barometric condensers control the vent streams from the primary and secondary evaporators. The final stage of the acetic acid recovery, the stripping column, vents directly to the atmosphere following its condensers. The ammonia scrubber vents uncollected ammonia directly to the atmosphere, and the condenser on the ammonia distillation column in Bulding A-1 also vents directly to the atmosphere.

6.A.1.7 Raw Materials Storage Area - C Buildings

Process Description

The C Buildings are used to mix and prepare raw materials for distribution to the D Buildings. Secondary operations at the C Buildings include preparing lacquer mixtures for use at the G Buildings. Figure 6.A-6 is a flow plan of operations at the C Buildings. Ammonium nitrate/nitric acid solutions from the nitric acid area are received in railroad tank cars and unloaded into storage tanks for distribution to the D Buildings. Acetic acid is also received in railroad tank cars from Area A. This acid is stored, and some is measured into a dissolver along with powdered hexamine. After the hexamine has dissolved in the acid, the solution is dumped into a storage tank. The contents of this storage tank are circulating continuously through a distribution loop, and the D Buildings draw solution from the loop as required. Acetic anhydride is received from Area A of HAAP via pipeline and stored in tanks outside of the C Buildings. The anhydride is pumped to the D Buildings as needed. There are five C Buildings, one for every two D Buildings (explosive manufacturing areas). At full production rates, all five C Buildings will be in use.

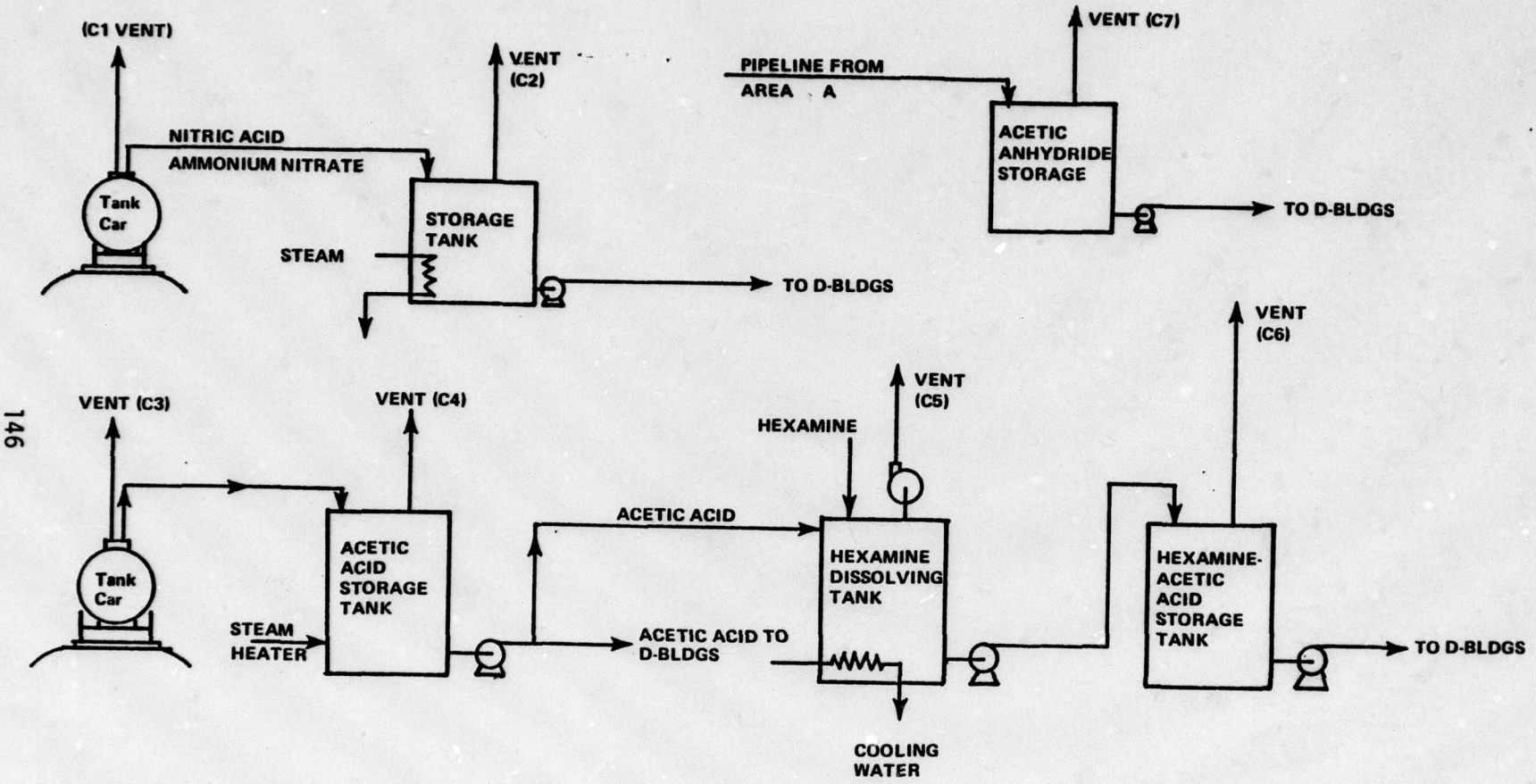


Figure 6.A-6. Raw material storage - C Buildings.

Emissions from the C Buildings

The emissions from the C Buildings (Table 6A-6) are primarily vents from atmospheric storage tanks. A blower is used to remove vapor from the hexamine dissolving tank (vent C5). The emissions from the nitric acid/ammonium nitrate solution have not been completely characterized, but are thought to consist primarily of nitric acid vapor. Similarly, the vapor from the acetic acid/ hexamine solution is thought to be primarily acetic acid vapor.

Controls on Emissions

Storage tank vents in the Building C area are not controlled. The rate of emissions is dependent on the temperature of the stored solution and on level changes in the storage tank.

6.A.1.8 Explosive Manufacture - D Buildings

Process Description

Two principal explosives, RDX and HMX, are manufactured at HAAP. These are compounded with TNT or any of several other compounds to make Composition B and specialty explosives. The processes for manufacturing RDX and HMX are nearly identical except for the relative amounts of raw materials which are reacted. In fact, some HMX is present in commercial grade RDX and vice versa.

The D Buildings house nitrators (reactors) where hexamine is nitrated to produce crude RDX or HMX. The reaction for RDX is essentially as follows:

$$C_6H_{12}N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2O \rightarrow 2C_3H_6O_6N_6 + 12CH_3COOH$$

Hexamine	Acid Nitric	Ammonium Nitrate	Acetic Anhydride	RDX	Acid Acetic

HMX is also produced from the same reactants. By varying the ratios of ammonium nitrate to hexamine, the reaction can favor either the formation of RDX or HMX. The operating temperatures of the RDX and HMX reactors are also different.

TABLE 6A-6. EMISSIONS SOURCE CHARACTERISTICS OF THE RAW MATERIALS AREA - C BUILDINGS (5), AREA B, HAAP

	RAW MATERIALS			AREA BUILDINGS C		
	NH_4NO_3 Tank Car Vent C1	NH_4NO_3 Sto. Tank Vent C2	Acetic Acid Tank Vent C3	Acetic Acid Sto. Vent C4	Hexamine Soln. Mix Tank C5	Acetic Anhydride Sto. Vent C7
Height, ft	18	18	18	18	18	18
Inside diameter (tip), ft	0.2	0.2	0.2	0.2	0.2	0.2
Flow, Exit Temperature cft/s	0.044	0.0008	0.016	0.004	0.08	0.002
Exit Temperature, °F	60	60	60	60	60	60
Gas Velocity, ft/sec	1.4	0.25	0.5	0.125	2.5	0.073
Number of Sources	1	1	1	1	1	1
Moisture Volume, %						
Emissions, lb/day						
1 Particulates						
2 CO_2						
3 SO_2						
4 NO_2 NO_x						
5 NO						
6 CO						
7 Methane						
8 Non-methane HC						
9 Acetic Acid			200	50	950	
10 Acetone						
11 Cyclohexanone						
12 n-Propyl Acetate						
13 Methyl Acetate						
14 n-Propyl Formate						
15 Acetic Anhydride						50
16 Formic Acid						
17 Toluene						
18 Butanol						
19 Me. Eth. Ketone						
20 Isobutyl Acetate						
21 Phenol						
22 Trace Organics						
Total 8-22						
23 Ammonia						
24 Nitric Acid	560	100				
25 Methyl Nitrate						
26 Nitromethane						
27 Explosives (Particulates)						
28 Hydrogen						
29 Methylamines						

In the manufacture of these explosives the following solutions are fed to a reactor: (a) hexamine/acetic acid; (b) nitric acid/ammonium nitrate; (c) acetic acid; and (d) acetic anhydride. The reaction is exothermic, and the heat evolved is removed by the reactor jacket cooling water and by internal cooling coil rather than by reactor leg. The slurry from the reactor enters a temperature-controlled age tank where further reaction occurs. Slurry from the age tank drains to four simmer tanks in series (HMX production involves two simmer tanks in parallel) where dilution liquor is added to maintain an acetic acid concentration of 63 ± 3 percent. The solution is simmered at a temperature of 108°C and is then cooled to 50°C. The last simmer tank serves as a holding tank from which the slurry is pumped to the E Buildings. The RDX production lines are all continuous operations, while the HMX production lines contain batch units. There are seven D Buildings which are used for production of HMX, one containing a single batch unit and one containing two. At full production, all of the D Buildings will be in use, producing about 670,000 lbs/day of RDX and about 8,000 lbs/day HMX. Figure 6.A-7 is a flow plan of RDX manufacture in the D Buildings, and Figure 6.A-8 is a similar flow plan of HMX manufacture.

Emissions from the D Buildings

The emission sources from the RDX production units are summarized on Figure 6.A-7 and characterized in Table 6A-7. The principle emissions are from the vent off the scrubber which controls the emissions from the reactor age tanks and simmer tanks. The vapor steam is high in NO_x, acetic acid, methyl nitrate, methyl acetate, and formic acid. Vents from the acetic acid, hexamine/acetic acid, and nitric acid/ammonium nitrate storage tanks are thought to be negligible at the D Buildings. The acetic anhydride storage tank, however, vents about 150 lbs/day. The HMX manufacturing process is very similar. Again, the principal emissions are from the scrubber vent. As the HMX process is a batch process, the emissions per pound of product are considerably higher than those for the RDX process. Again, the acetic anhydride storage tank is the only one with significant emissions, although a vent is indicated on the dilution liquor tank for HMX manufacture.

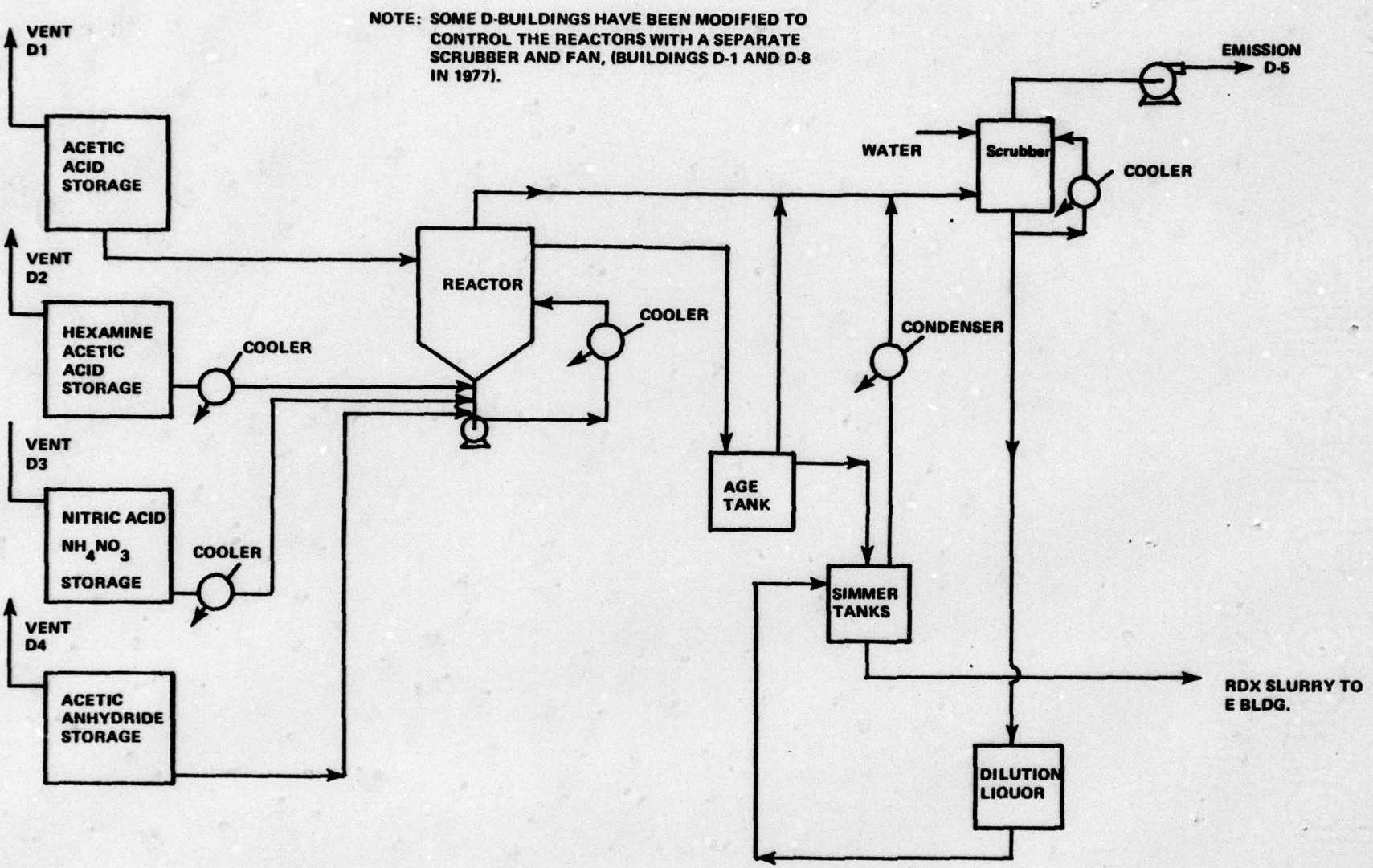


Figure 6.A-7. RDX manufacture - D Buildings.

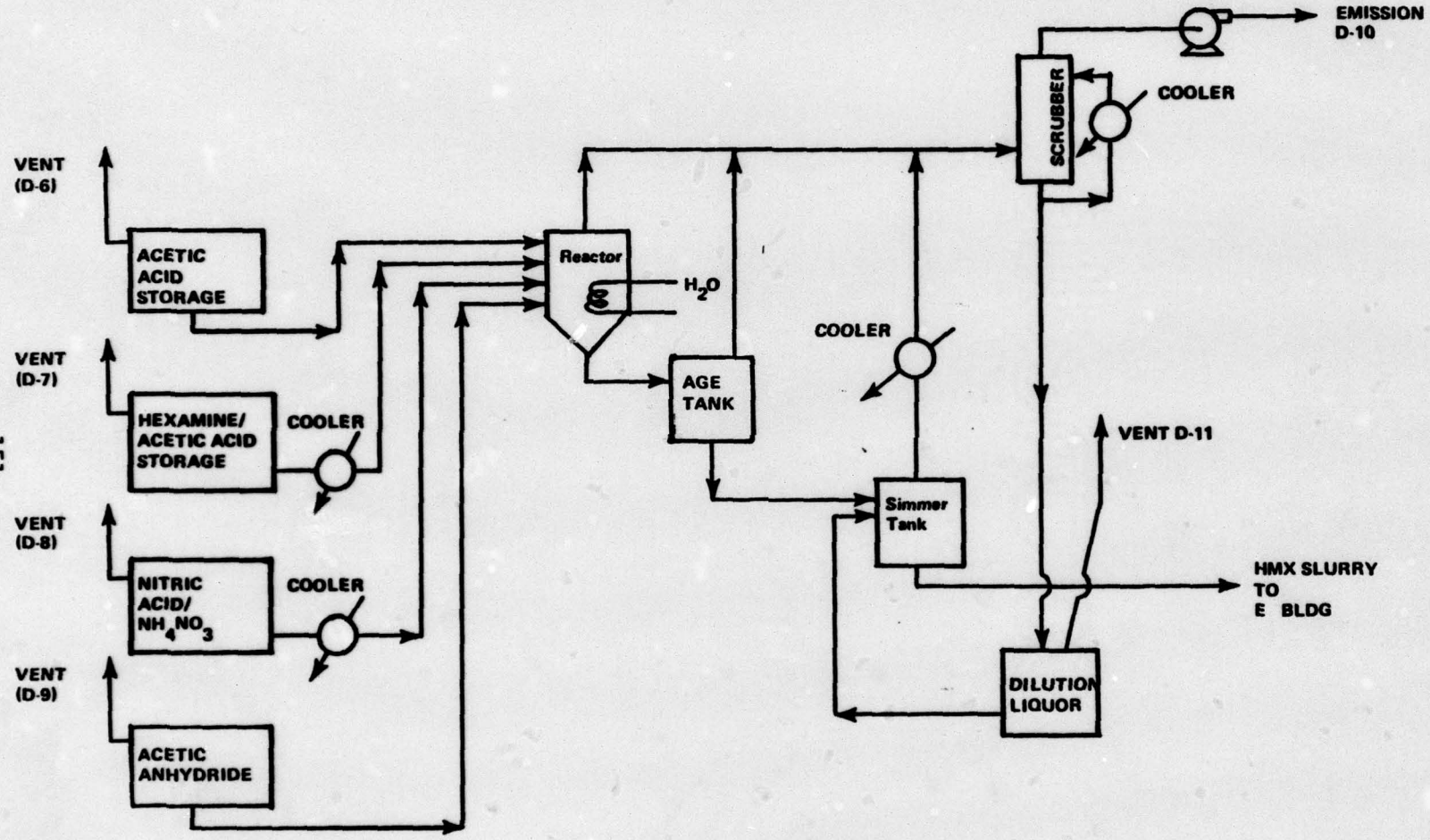


Figure 6.A-8. HMX manufacture - D Buildings.

TABLE 6A-7. EMISSIONS SOURCE CHARACTERISTICS OF THE RDX-HMX MANUFACTURING, D BUILDINGS, AREA B, HAAP

	RDX					HMX		
	Acetic Acid Sto. Vent D1	Hexamine Soln. Sto. Vent D2	NH_4NO_3 Soln. Sto. Vent D3	Anhydride Storage Vent D4	Reactor Vent D5	D5 ≈ D1 D6 ≈ D2 D7 ≈ D3	Anhydride Storage Vent D9	Reactor Vent D10
Height, ft				18	56.5		18	56.5
Inside diameter (tip), ft				0.2	2.83		0.2	2.83
Flow at Exit Temp., cf/sec				0.001	4.97		0.001	4.97
Exit Temperature, °F				60	120		60	120
Gas Velocity, ft/sec				0.03	0.80		0.03	0.80
Number of Sources				8	8		1	1
Moisture Volume, %								
Emissions, lb/day								
1 Particulates								
2 CO_2								
3 SO_2								
4 NO_2								
5 NO NO_x					2300			3240
6 CO								
7 Methane								
8 Non-methane HC								
9 Acetic Acid					512			512
10 Acetone								
11 Cyclohexanone								
12 n-Propyl Acetate								
13 Methyl Acetate					41			45
14 n-Propyl Formate								
15 Acetic Anhydride				20			20	
16 Formic Acid								
17 Toluene								
18 Butanol								
19 Me. Eth. Ketone								
20 Isobutyl Acetate								
21 Phenols								
22 Trace Organics								
Total 8 - 22								
23 Ammonia								
24 Nitric Acid								
25 Methyl Nitrate					157			142
26 Nitromethane								
27 Explosives (Particulate)								
28 Hydrogen								
29 Methylamines								

Controls on Emissions

As the emissions from storage tank vents are small, they are not controlled. Considerable amounts of organic vapors and nitrogen oxides are emitted by the reactor, age tank, and simmer tank. These vapor streams are combined and treated in a water scrubber before being vented to the atmosphere.

6.A.1.9 Explosive Washing Area - E Buildings

Process Description

At the E Buildings, crude RDX or HMX slurry pumped from the D Buildings or the B Buildings is washed to remove acids. The washed explosives are then pumped in slurry form to the G Buildings. The entire E Buildings operation involves three steps: (a) filtering, (b) washing, and (c) reslurrying for transfer.

When RDX is received at the E Buildings it is received in two batches totaling 4500 pounds (dry basis). The first batch averages 2500 pounds (dry basis), and this is settled and filtered as described below before the second batch (2000 pounds dry basis) is received. The settling and filtering step is then repeated for the second batch combined with the first batch before proceeding with the next step. When HMX slurry is received at the E Buildings it is received in one 850 pound batch (dry basis).

In the first step, the slurry is allowed to settle and a vacuum is then drawn on the tank (see Figure 6.A-9). Most of the acid solution is removed and pumped to the B Buildings where acids and explosives are recovered. When the second batch of RDX from the D Buldings is received, it is combined with the first batch and the vacuum filtration is repeated.

The discussion above referred to RDX batches only. The acid withdrawn from HMX batches is approximately 80 percent acetic acid, rather than the 60 percent acetic acid which is withdrawn from RDX batches. Dilution liquor is used to dilute the 80 percent acid to about 60 percent so that the B Buildings will receive a relatively uniform feed from all E Buildings. This dilution of the contaminated acid is shown as dashed lines on Figure 6.A-9.

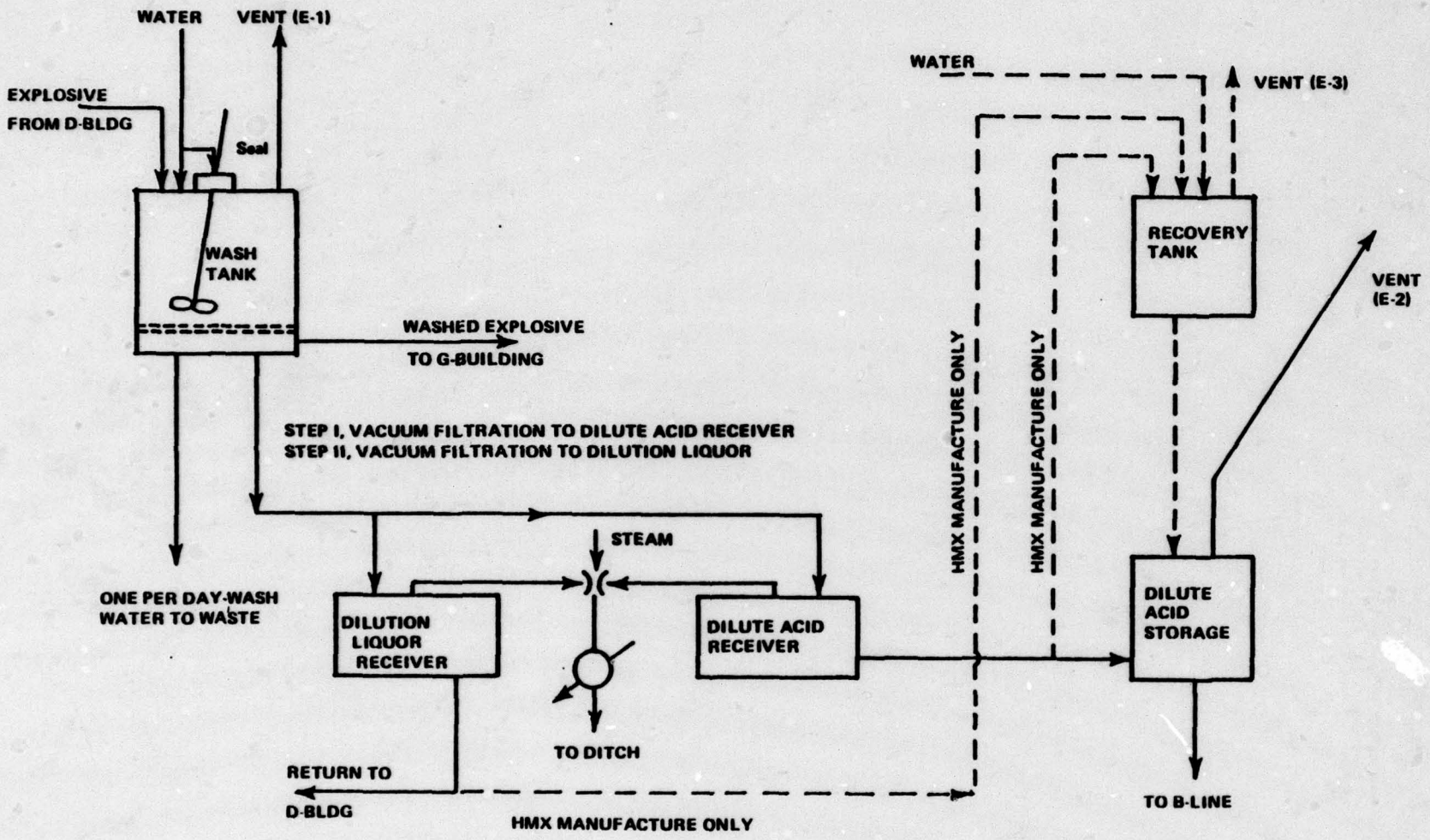


Figure 6.A-9. Explosive wash - E Buildings.

In the second processing step, the cake remaining from step one is washed with filtered water. A vacuum is again drawn on the wash tank and the filtrate is sent to the D Buildings as dilution liquor. The third processing step is to reslurry the explosive cake with filtered water. This slurry is agitated and pumped to the G Buildings.

At each E Building, approximately one wash tank per day is cleaned with steam and filtered water in a "warm water wash" operation.

With minor difference all E Buildings house essentially identical operating units. There are six E Buildings each of which contains six vacuum wash tanks. There are two E Buildings which contain seven wash units, and two E Buildings which contain eight vacuum units. In general, two of the E Buildings are used for HMX production, the others for RDX production.

Emissions from the Explosive Wash Step

Three vent streams have been noted from the explosive wash area. These are the vent on the wash tank, the vent on the dilute acid storage tank, and for HMX production, the vent on the recovery tank. These emission sources are summarized in Figure 6.A-9. Emission sources characteristics are given in Table 6A-8. The vent on the dilute acid storage is much more significant than the other two.

Controls on Emissions

All of the emissions from the E Buildings are from uncontrolled atmospheric storage tanks. As most of the process takes place under a vacuum, process emissions are minimal.

6.A.1.10 Explosive Recrystallization - G Buildings

Process Description

The G Buildings are used for recrystallization of explosives, but many of them contain other equipment which is used occasionally. Only the recrystallization step is discussed in this section. Crude RDX or HMX from an E Building is dissolved and recrystallized to form the crystalline size and configuration desired for the product explosive. Figure 6.A-12 is a flow plan of the processing area. The washed RDX or HMX slurry is received by pipeline

TABLE 6A-8. EMISSION SOURCE CHARACTERISTICS OF THE E BUILDINGS (10)

	Wash Vent E1	Acid Storage E2	Recovery Tank E3
Height, ft	18	18	18
Inside diameter (tip), ft	0.2	0.2	0.2
Flow, Exit Temperature cft/s		0.005	
Exit Temperature, °F	60	60	60
Gas Velocity, ft/sec		0.15	
Number of Sources	10	10	1
Moisture Volume, %			
Emissions, lb/day			
1 Particulates			
2 CO_2			
3 SO_2			
4 NO_2 NO_x			
5 NO^2			
6 CO			
7 Methane			
8 Non-methane HC			
9 Acetic Acid	0.1	6.0	0.1
10 Acetone			
11 Cyclohexanone			
12 n-propyl acetate			
13 Methyl Acetate			
14 n-propyl formate			
15 Acetic Anhydride			
16 Formic Acid			
17 Toluene			
18 Butanol			
19 Me. eth. ketone			
20 Isobutyl Acetate			
21 Phenol			
22 Trace Organics			
Total 8-22			
23 Ammonia			
24 Nitric Acid			
25 Methyl Nitrate			
26 Nitromethane			
27 Explosives (particulate)			
28 Hydrogen			

and fed into a dissolver containing a specified amount of cyclohexanone, acetone, or toluene, depending on the type of crystallization desired. The dissolver contents are simmered and then transferred into a preheated still. The solvent is distilled off, condensed, and then either returned to the dissolver or sent to a decant tank. Vapors from the primary condenser, together with vapors from the dissolver, are condensed in a secondary condenser and returned to the dissolver. Uncondensed vapors are vented through a flame arrestor to the atmosphere. After distillation is complete, the batch is cooled and then dewatered at either the G Buildings or the H Buildings.

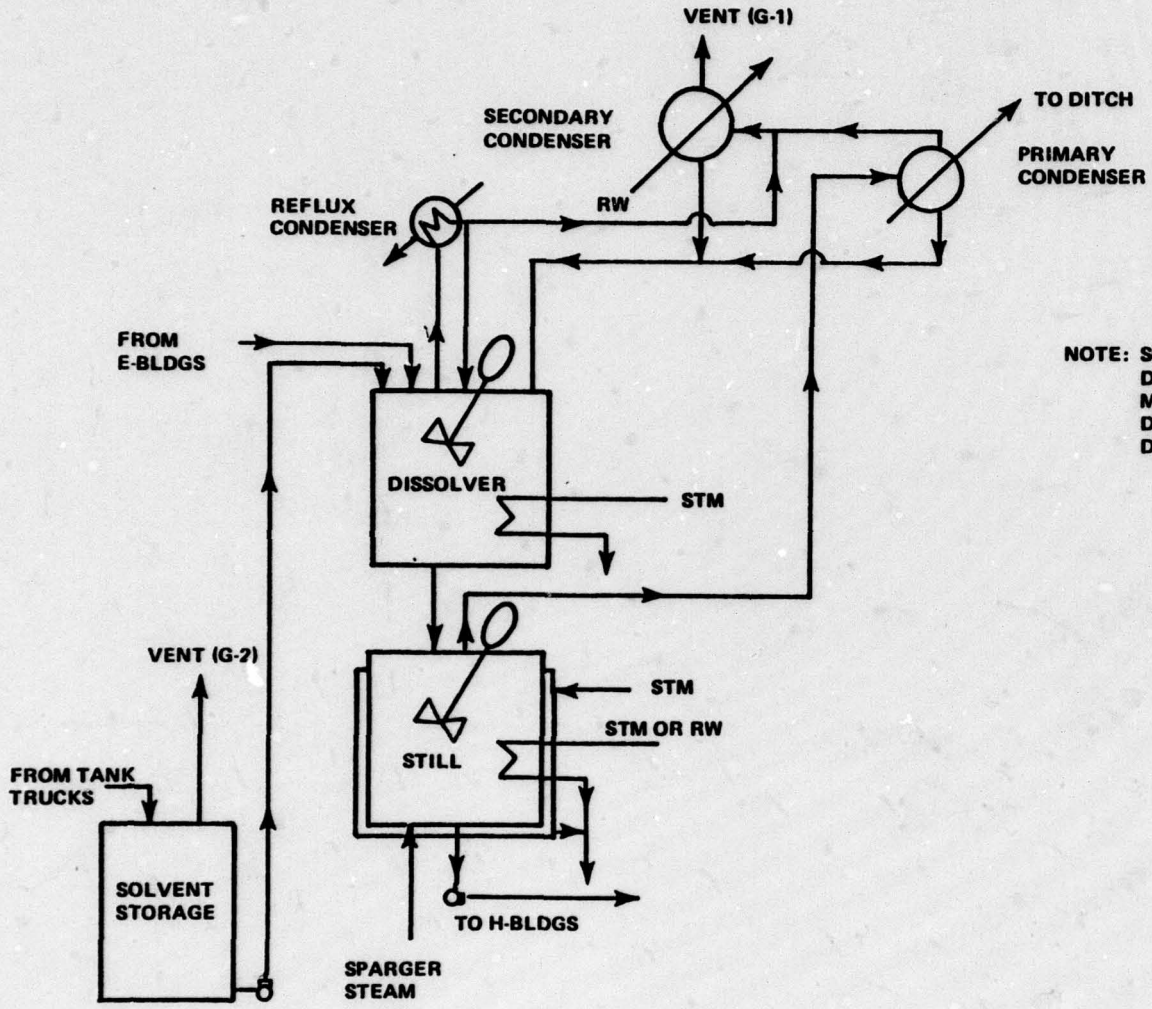
There are five G Buildings which are generally used for the recrystallization of RDX in cyclohexanone. They each contain four units (dissolver and still), and three solvent storage tanks. Four other operable dissolver and still units are located in two other Buildings. The remaining four G Buildings contain similar equipment, and they also contain additional equipment such as dewatering facilities, vacuum stills or compound equipment. At full design rates, all of the G Buildings would be in use. Cyclohexanone is used for redissolving RDX and is, therefore, the most prevalent solvent. Acetone (used with HMX products) and toluene are also commonly used.

Emissions from the Explosive Recrystallization Process

The emissions from the explosive recrystallization step (Figure 6.A-10) depend on which solvent is used. The emission rates characterized in Table 6A-9, are for production at a given product slate. There are also emissions from the solvent storage tanks. For cyclohexanone, these are estimated to be about four pounds per day.

Controls on Emissions

A two-stage condenser is used to collect as much as possible of the vapors emanating from the dissolver and stills in the G Buildings. Collected solvent is returned to the dissolver, and the uncollected vapor is discharged through a flame arrestor to the atmosphere. The solvent storage tank vents are not controlled.



NOTE: SOME G BUILDINGS UTILIZE AN EXTERNAL DECANTER VESSEL TO RECEIVE THE PRIMARY CONDENSER CONDENSATE. THE CONDENSATE IS THEN PUMPED BACK TO THE DISSOLVER.

Figure 6.A-10. Explosive recrystalization - G Buildings.

TABLE 6A-9. EMISSION SOURCE CHARACTERISTICS OF THE RDX-HMX MANUFACTURING, G BUILDINGS, AREA B, HAAP

	Cond. Vent G1,2,4,7, 8,9	Feed Tank G1,2,7,8 9	Tank Vents G1,2,4,7 8,9	Cond. Vent G6	Feed Tank G6	Cond. Vent G4,6, 10,10A	Tank Vent G4,6, 10,10A	Tank Vent G6	Cond. Vent G4,6, 10	Tank Vent G4,6, 10	Cond. Vent G4,6, 10A	Sep. Vent G4, 10A	Tank Vent G4, 10A	Tank Vent G4,6
Height, ft	52.5	52.5	14.5	52.5	14.5	52.5	15.5	15.5	52.5	15.5	55.5	51.8	14	11.2
Inside diameter (tip), ft	0.333	0.156	0.156	0.033	0.156	0.333	0.156	0.156	0.333	0.156	0.333	0.167	0.19	0.333
Flow, Exit Temperature cft/s	0.072	0.018	0.016	0.072	0.016	0.081	0.019	0.019	0.015	0.019	0.08	0.024	0.014	0.044
Exit Temperature, °F	100	100	90	100	90	100	90	90	100	90	90	100	90	90
Gas Velocity, ft/sec	0.083	0.094	0.082	0.083	0.083	0.093	1	1	0.17	0.93	0.92	0.83	0.5	0.5
Number of Sources	22	20	62	3	3	3	3	2	6	14	4	3	3	4
Moisture Volume, %														
Emissions, lb/day														
1 Particulates														
2 CO_2														
3 SO_2														
4 NO_2 NO_x														
5 NO														
6 CO														
7 Methane														
8 Non-methane HC														
9 Acetic Acid														
10 Acetone						106	94.5	94.5	106	94.5				
11 Cyclohexanone	27	77.8	0.71	27	0.95									
12 n-Propyl Acetate														
13 Methyl Acetate														
14 n-Propyl Formate														
15 Acetic Anhydride														
16 Formic Acid														
17 Toluene											4.2	4.2	2.3	3.7
18 Butanol											2			
19 Me. Eth. Ketone												2		
20 Isobutyl Acetate												0.7		
21 Phenol														
22 Trace Organics														
Total 8-22														
23 Ammonia														
24 Nitric Acid														
25 Methyl Nitrate														
26 Nitromethane														
27 Explosives (Particulate)														
28 Hydrogen														
29 Methylamines														

6.A.1.11 Explosive Dewatering - H Buildings

Process Description

The H Buildings are used for dewatering and grinding explosives. The dewatering process also takes place in several of the G Buildings. The grinding operations are normally done only at the H Buildings.

Explosive slurry from the G Buildings is received in the H Building receiving tank. It is then either dewatered immediately or ground to specified particle sizes and then dewatered. If grinding is not required, the slurry is dropped into nutsches (receiving carts) equipped with vacuum probes. Vacuum is applied to the probes to remove water from the explosives. This water collects in the vacuum tank and is then pumped to a settling tank where most of the entrained explosive particles settle out. These solids are recycled to the receiving tank. Overflow water from the settling tank drains to a catch basin and then to the industrial waste sewer. The dewatered explosives are then either transported to the incorporation buildings or reslurried for grinding in a Cowles Dissolver. Figure 6.A-11 is a flow plan of the H Buildings.

Grinding of explosives to the correct particle size can be accomplished in two ways, one method requiring only one dewatering, and the other requiring two dewatering operations. In the first method, explosive slurry from the receiver tanks is cycled through pumps fitted with an orifice on the pump discharge. Explosives are broken down to the required particle size as they pass through the orifice. The ground explosives are recycled to the receiver tanks and then dewatered in nutsches as described above. In the second method, the explosives are first dewatered, and then reslurried and fed to a Cowles Dissolver. Grinding to the required particle size occurs in the dissolver due to high sheer agitation. The ground explosives are returned to the receiver tanks and are again dewatered.

There are 10 Buildings, all containing essentially the same dewatering equipment.

Emissions from Explosive Dewatering

There are no known emission sources at the H Buildings. The vent from the vacuum pump has not been characterized.

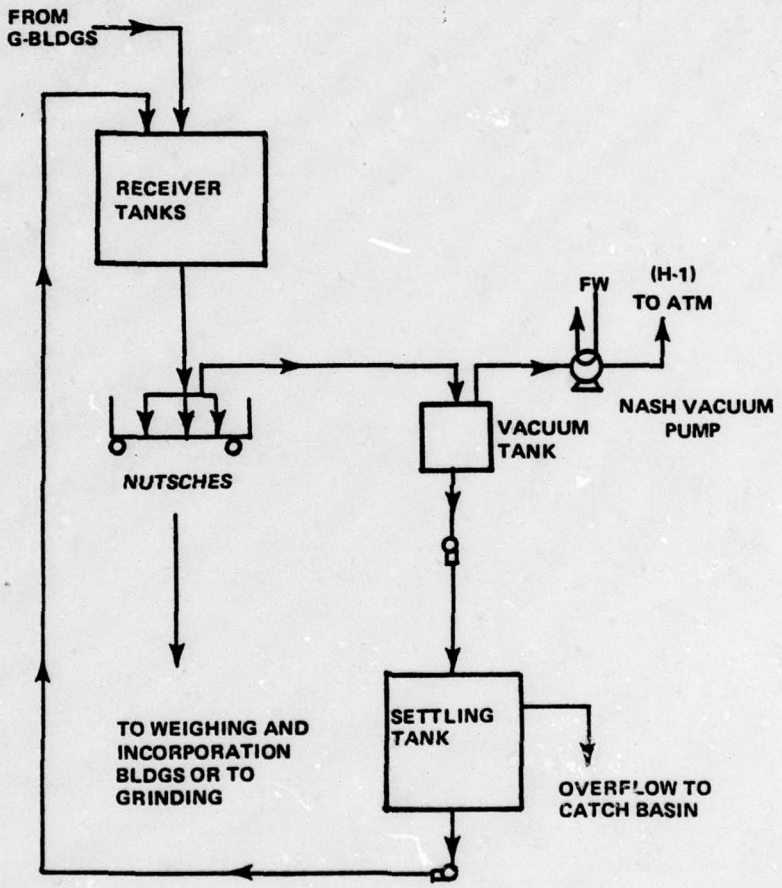


Figure 6.A-11. Grinding and dewatering - H Building.

6.A.1.12 Explosive Incorporation Process - I, J, L, and M Buildings

Process Description

The term "incorporation" refers to the mixing of two or more compounds to make other compounds (such as RDX, TNT, and wax to make Composition B). All I, J, L, and M Buildings are called Incorporation Buildings. The incorporation and drying processes which are used in the various Incorporation Buildings differ depending upon the product desired.

The most prevalent process is that used for making Composition B and similar explosives. Nutches (hoppers) of wet RDX (about 59.5 percent water by weight) are received from the H Buildings, and melt kettles of dry TNT are received from the A Buildings. Each of the mixing buildings consists of two process lines. Each line consists of two incorporation kettles, one holdup kettle, a casting pot, and a casting belt. Figure 6.A-12 is a flow plan of the process. Steam hoses are attached to the TNT melting pots and the TNT is melted. The TNT is then poured into the heated incorporation kettle. Wet RDX is shoveled into the incorporation kettles and the resulting water is decanted to the sewer. The temperature is then increased, wax is added, and the kettle contents are agitated and then emptied into the holdup tank. The mixture then flows to the casting pot where it is dropped onto a casting belt. The strands of explosives solidify on the cool belt and break apart as they drop into a hopper at the end of the belt. Hoppers from the Incorporation Buildings are sent to the N Buildings for packaging and shipment.

A second processing approach is kettle drying. In this process, the explosive is shoveled into the drying kettles, where heating and mixing ensue. Water vapors and dust from the kettles are drawn off to a scrubber before being vented to the atmosphere.

A third process is bed drying. The operation is similar to kettle drying, except that the explosive is shoveled onto perforated trays and then placed under a hood. Hot air is circulated through the explosive from the underside of the trays, and the vapors and dust are drawn through scrubbers before being vented to the atmosphere.

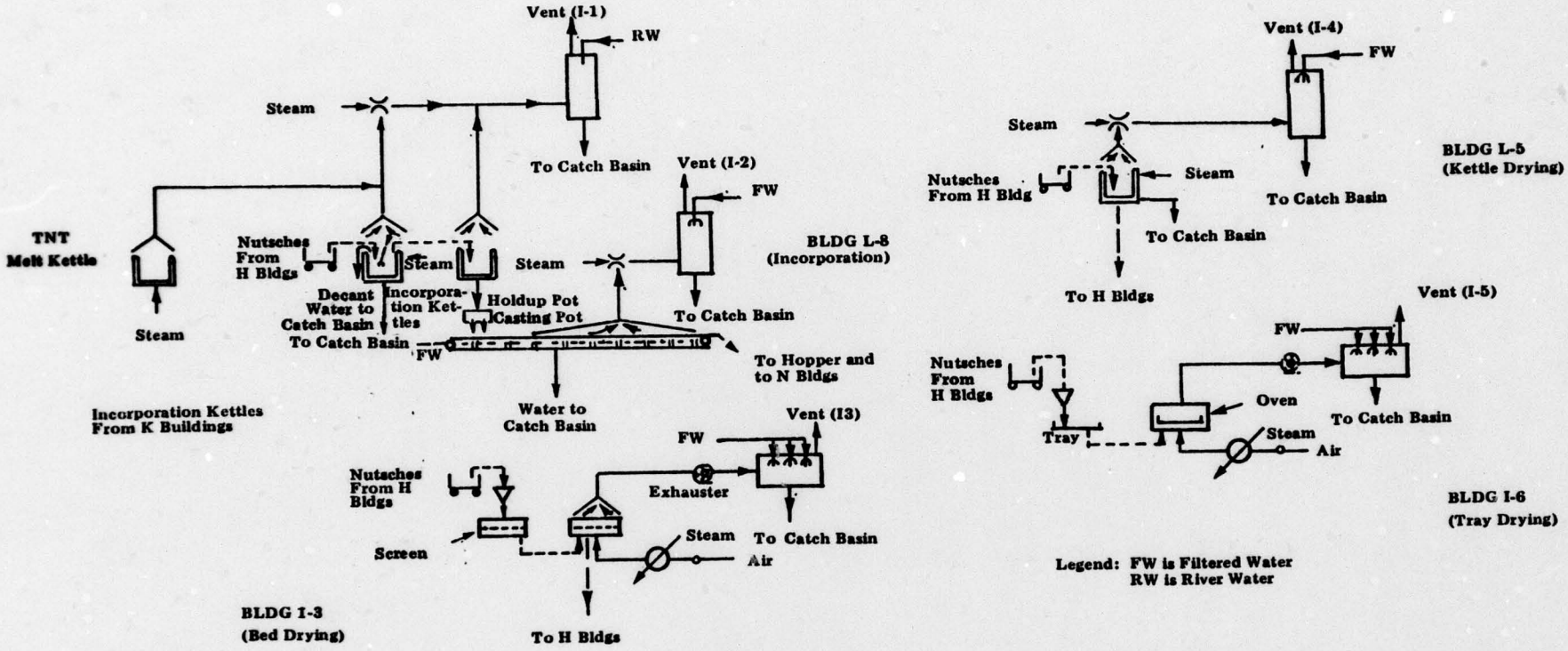


Figure 6.A-12. Explosive incorporation - I, J, L, and M Buildings.

The fourth drying operation is tray drying. Here the explosive is shoveled onto trays that are placed in drying ovens where hot air circulates over the trays. The hot air exhaust from the ovens is drawn through a scrubber before being vented to the atmosphere.

Emissions from the Incorporation Buildings

The emission points in the Incorporation Buildings are indicated on Figure 6.A-12. Table 6A-10 shows the emission per batch of products; for the given product slate the average of total emissions were about 1 lb/day. All of the known emissions are vent streams off product drying systems. Table 6A-11 gives estimated source characteristics for these and other sources.

TABLE 6A-10. EMISSIONS FROM INCORPORATION BUILDINGS

Explosive	Average Daily Production	Batch Size	Batch / day	Emission / batch	Emission/day
PBX's	300	varies	< 1	0.0056 lbs	< 0.01
Crude HMX	2,200			0	0 lbs
Octol 75/25	11,200	1460	8	0.0284 lbs	0.2 lbs
Composition B	896,000	1422.5 lbs	630	0.00035 lbs	0.2 lbs
Composition B-4	87,400	1412 lbs	62	0.000145 lbs	0.01 lbs
Composition C-4	2,200	800	2.8	0.0566 lbs	0.2 lbs
Desensitized RDX	9,000	4500 lbs	2	0.0056 lbs	0.01 lbs
A-Products	32,500	4700 lbs	6.9	0.0056 lbs	0.04 lbs
Cyclotol	56,000	?	?	?	?
				TOTAL	< 1 lb

Controls on Emissions

All the dryer hoods in the Incorporation Buildings contain entrained particulate, and scrubbers are used to remove most of this particulate from the vent stream.

TABLE 6A-11. EMISSION SOURCE CHARACTERISTICS OF THE I,J,L,M BUILDINGS, AREA B, HAAP

	IJLM BLDGS		STORAGE TANKS				STEAM GENERATION				
	Dryer IJLM	Vent K	Acetone IV-7-P 10-G-A	Toluene IV-9-Q IV-GT1	Gasoline	Fuel Oil 10-116L IV-567M	Stacks 1,2,3,4	Stacks 5,6	Stack 7	B200	B222 Gas Fired
Height, ft	55.3	55.3	18	18	18	18	115	115	115	115	100
Inside diameter (tip),ft	0.333	0.333	0.2	0.2	0.2	0.2	7	7	7	7	5.75
Flow, Exit Temperature cft/s							810	810	810	724	467
Exit Temperature, °F	100	100	60	60	60	66	470	470	470	465	550
Gas Velocity, ft/sec							21	21	21	18.8	18
Number of Sources	1	1	1	2	2	2	4	2	1	2	3
Moisture Volume, %											
Emissions, lb/day											
1 Particulates							1525	1677	2898	900	
2 CO_2							$.47 \times 10^6$	$.52 \times 10^6$	$.9 \times 10^6$	$.45 \times 10^6$	$.29 \times 10^6$
3 SO_2							1463	1609	2799	2000	323
4 NO_2 NO_x							2195	2415	4171	3200	
5 NO											
6 CO											
7 Methane											
8 Non-methane HC					7	85					
9 Acetic Acid											
10 Acetone			2.2								
11 Cyclohexanone											
12 n-Propyl Acetate											
13 Methyl Acetate											
14 n-Propyl Formate											
15 Acetic Anhydride											
16 Formic Acid											
17 Toluene				0.3							
18 Butanol											
19 Me. Eth. Ketone											
20 Isobutyl Acetate											
21 Phenol											
22 Trace Organics											
Total 8-22											
23 Ammonia											
24 Nitric Acid											
25 Methyl Nitrate											
26 Nitromethane											
27 Explosives (Particulate)	1 (RDX)	1 (TNT)									
28 Hydrogen											
29 Methylamines											

6.A.1.13 TNT Handling - K Buildings

Process Description

The K Buildings are used primarily for the receipt of TNT, although some packaging of explosives is done. There is one K Building for every two explosives manufacturing lines. The TNT used at HAAP is manufactured at other installations. It is delivered by truck to the K Buildings, unpackaged, and dumped into melt kettles to be transported to the Incorporation Buildings. Each melt kettle holds about 550 pounds of TNT. At full production rates, about 400,000 pounds per day of TNT is handled at the K Buildings.

Emissions and Emission Control at the K Buildings

Explosive dust generated during the unloading operation is drawn into a hood and through a scrubber before being vented to the atmosphere. The scrubber water flows into a catch basin before being released to the sewer. Particulate emissions from the scrubber have been estimated at about 1 lb/day at full production rates.

6.A.1.14 Explosive Packaging - N Buildings

Process Description

The processing which takes place in the N Buildings involves receiving barrels or nutsches of explosives from the Incorporation Buildings, packing the explosives, and loading the packages onto trucks for shipment to local storage or to railroad loading docks. The weighing facilities at the N Buildings can also be used for weighing small quantities of special product ingredients. At most of the N Buildings, the barrels or nutsches are lifted to the second floor where the explosives are dumped into a hopper prior to packaging.

Emissions and Emission Control at the Packaging Buildings

Table 6A-12 presents estimated emissions from the packaging buildings. The table is based on a particular product slate. The emissions indicated are particulates in the gas stream leaving the scrubbers which are located in each N Building. Dust which is generated during the explosive packaging operation is drawn into hoods and then to scrubbers.

TABLE 6A-12. EMISSIONS FROM PACKAGING BUILDINGS

Explosive	Batches/Day	Emissions/Batch	Average Emissions/Day
PBX's	< 1	0.0056 lbs	≈ 0 lbs
Crude HMX	?	0	0 lbs
Octol 75/25	8	0.00094 lbs	0.01 lbs
Composition B	630	0.00035 lbs	0.22 lbs
Composition B-4	62	0.000145 lbs	0.01 lbs
Composition C-4	2.8	0	0
Desensitized RDX	2	0.0056	0.01 lbs
A-Products	6.9	0.0056	0.04 lbs
Cyclotol	?	?	?
		TOTAL	0.30 lbs/day

6.A.1.15 Conclusions and Recommendations

The emissions from the production of RDX-Composition B at HAAP at mobilization rates have been estimated using currently available process and source emissions data. Emission rates are given (Table 6A-2) for the twenty-nine pollutants identified through reported sampling and testing studies. Included are the conventional substances for which standards exist, and reactive organic solvents and reaction byproduct substances, which can undergo reaction in the air and sunlight. Emissions source characteristics have been tabulated. Fugitive emissions have not been considered. Based on the results, steam generation accounts for essentially all the particulates and SO_x emissions. The processes greatest emission rates are: NO_x (64,000 lb/day); hydrocarbons and reactive organic solvents (23,000 lb/day); nitric acid (4,400 lb/day); and reaction byproducts (1,600 lb/day including an estimated 390 lb/day of ammonia and 18 lb/day of nitrosamines).

While this inventory appears to be suitable for a first assessment of the air chemistry, it needs further development:

1. All source characteristics should be reviewed on location to confirm source heights, diameters, exit gas temperatures and flow rates.

2. The emissions from process vents showing any significant flow rate should be further identified by sampling and testing, using a chemical identification scheme in which the sample is fractionated into characteristic groups of compounds with gas chromatographic techniques, and the fractions examined further for specific compounds.[5]

3. The process conditions should be recorded whenever future source samples are taken.

4. Material balances should be developed to more precisely define and confirm emissions rates.

5. Fugitive emissions should be sampled and tested using evacuated containers for "grab" samples.

Further sampling and testing of emissions sources is needed to determine what specific substances there may be in those gross emissions of organic compounds now identified only as classes of compounds. Distinction between NO_2 and NO is desirable if the air chemistry is to be better defined.

The fact that mobilization rates may not be attained need not be an obstacle to further definition of emissions. Most of the process steps are performed with several similar units, all of which would be operating at mobilization. At least one of these units is frequently operated at its anticipated rate under mobilization. Where all the units have similar emissions, sources, and controls, the one unit could usually be sampled so as to be representative of the others.

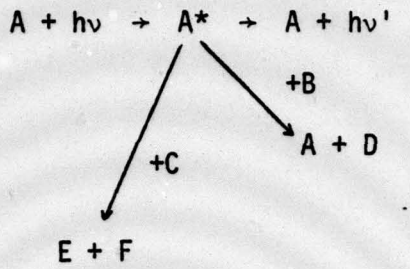
6.A.2 PLANT ATMOSPHERIC CHEMISTRY

6.A.2.1 Introduction and Definition of Terms

In the following sections the properties and atmospheric chemistry of the compounds emitted from Army ammunition plants are discussed. The structure, molecular weight, boiling point, melting point, density, vapor pressure, and uv-visible characteristics are given for each compound. Of these properties, the vapor pressure and uv-visible characteristics are important in determining the atmospheric chemistry of each compound. The vapor pressure determines the highest possible concentration that a compound can attain in the atmosphere. For example, a compound with a vapor pressure of 76 mm Hg at 25°C may have a maximum concentration of 10^{-1} atm or 10^{5} ppm. The second property, the uv-visible characteristics of a compound, indicates whether a particular compound absorbs light within the photochemistry of the troposphere. If a compound does absorb within this region, it may react photochemically as well as nonphotochemically with other species in the atmosphere.

The remaining sections deal with the chemistry of the emissions from explosive manufacturing. The reactions of these compounds with nonradical species are considered first. These reactions can potentially occur with or without light. For each specific reaction, the rate expression temperature and other conditions under which the rate constant was derived, and the rate constant itself, are tabulated. The second order rate constants are given in units of (cm^3 $molecule^{-1}$ sec^{-1}) or (ppm^{-1} min^{-1}). To convert from the former units to the latter, it was assumed that the value of the given rate constant is the same as that obtained under standard conditions of 298°K and one atmosphere pressure. Conversion factors can be found in the tables. In addition to kinetic data, reaction products are mentioned if they are known.

Photochemical reactions are discussed next. Only those compounds that absorb light within the region of 290-800 nm are considered. Depending on the energy (wavelength) of the absorbed light, the reactions will result either in the formation of an excited species (A*) or in bond cleavage. The excited state species will either return to the ground state (A) or react with another species in the atmosphere (B or C).



Reactions which involve bond cleavage may result in the formation of a highly reactive species such as a hydroxyl radical (OH) or atomic oxygen (O). Because these species are highly reactive, they will react almost immediately with other species present in the atmosphere.

$$A\text{-}OH + h\nu \rightarrow A + OH$$

$$B + OH \rightarrow \text{products}$$

Kinetic data, rate expressions, and constants are available for these secondary reactions. If the kinetic data are not known, available thermochemical data are given. Alternatively, kinetic data of model compounds (*i.e.*, compounds which are similar in structure to the desired compound) are given.

Table 6A-13 lists the symbols and abbreviations used in the following sections. Table 6A-14 contains a list of compounds and radical species.

6.A.2.2 Characteristics of Compounds Emitted in the RDX Process

Emissions from sources characteristic of the RDX process at HAAP include (in order of decreasing importance as indicated in Table 6A-2) a mixture of nitrogen oxides composed of nitric oxide, nitrogen dioxide, and nitrous oxide; sulfur dioxide; particulates; acetic acid; carbon monoxide; nitric acid; a mixture of volatile organics (possibly composed of acetaldehyde, acetone, methane, ethane, methanol, and methyl acetate); acetone; cyclohexanone; methyl nitrate; n-propyl acetate; methyl acetate; ammonia; n-propyl formate; acetic anhydride; formic acid; toluene; nitromethane; a mixture of methylamine and dimethylamine; a mixture of butanol, n-propanol, methanol

(Text continued on page 177.)

TABLE 6A-13. SYMBOLS AND ABBREVIATIONS

uv	ultraviolet
mm Hg ≡ torr	millimeters mercury
atm	atmosphere
ppm	parts per million, 1 ppm = 10^{-6} atm
°C	degrees centigrade
°K	degrees Kelvin, 0°C = 273°K
sec	second
min	minute
msec	millisecond
hr	hour
nm	nanometer, 1 nm = 10 Å = 10^{-9} m
cm^3	cubic centimeter
A*	excited state species
$h\nu$	light, E = $h\nu$ where h = 6.62×10^{-27} erg-sec
λ(nm)	wavelength
λ_{max}(nm)	wavelength of maximum absorption
ε	absorption coefficient, liter/mole-cm
ℓ	liter
Φ	quantum yield, number of molecules decomposed or formed per quantum of light absorbed
z	solar zenith angle
g/mole	gram-molecular weight
g/ml	grams per milliliter
g/ℓ	grams per liter
TPD	tons per day
kcal	kilocalories, 10^3 calories
kcal/mol	kilocalories per mole
D°	bond dissociation energy
ΔH_f	heat formation

TABLE 6A-13. (cont'd)

k	rate constant
$t_{1/2}$	half life, $t_{1/2} = 0.693/k$
glpc	gas-liquid phase chromatograph
epr	electron paramagnetic resonance
NO_x	nitrogen oxides
TNM	tetranitromethane
MNT	mononitrotoluene
DNT	dinitrotoluene
TNT	trinitrotoluene
PFN	peroxy formyl nitrate
PAN	peroxy acetyl nitrate
PBN	peroxy benzoyl nitrate
PSS	photostationary state
NEDS	National Emissions Data System
SPS	source performance standards
NAAQS	National Ambient Air Quality Standards
TLV	threshold level value

TABLE 6A-14. SELECTED COMPOUNDS AND RADICAL SPECIES

$HCOO_2NO_2$	peroxy formyl nitrate (PFN)
HCO	formyl radical
COOH	carboxy radical
HCO_2	formate radical
$HCOO_2$	peroxy formyl radical
$^1CH_2$	singlet methylene
$^3CH_2$	triplet methylene
CH_2NO_2	nitromethyl radical
HCOOH	formic acid
CH_3	methyl radical
CH_3NO	nitrosomethane
CH_3ONO	methyl nitrite
CH_3ONO_2	methyl nitrate
$CH_3O_2NO_2$	peroxy methyl nitrate
CH_3O	methoxy radical
CH_2OH	hydroxymethyl radical
CH_3O_2	methyl peroxy radical
CH_3NH	methylamino radical
CH_2NH_2	aminomethyl radical
CH_3OH	methanol
CH_3O_2H	methyl peroxide
CH_3NHOH	oxime of methylamine
$(CHO)_2$	glyoxal

TABLE 6A-14. (cont'd)

$C_2H_2O_4S$	sulfoacetic anhydride
$CH_3COO_2NO_2$	peroxy acetyl nitrate (PAN)
CH_3CO	acetyl radical
CH_3CO_2	acetate radical
CH_2COOH	carboxymethyl radical
C_2H_4	ethylene
CH_3COO_2H	peracetic acid
CH_3CH_2	ethyl radical
$(CH_3)_2N$	dimethylamino radical
$(CH_3)_2NNO$	N-nitroso dimethylamine
$CH_3O_2CH_3$	dimethyl peroxide
$(CH_3)_2NOH$	oxime of dimethylamine
CH_3NHCH_2OH	methyl hydroxymethyl amine
C_3H_4	allene
CH_2CHCHO	acrolein
CH_3COCHO	methyl glyoxal, pyruvic aldehyde
CH_2CH_2OCO	2-oxetanone
CH_3CH_2CO	propionyl radical
CH_3COCH_2	acetonyl radical
C_3H_6	propylene
C_4H_6	1,3-butadiene
$CH_3COCOCH_3$	biacetyl
CH_3COCH_2COOH	acetoacetic acid
C_5H_8O	cyclopentanone

TABLE 6A-14. (cont'd)

C_5H_{10}	cyclopentane
$CH_2CH(CH_2)_2CH_3$	1-pentene
C_6H_4O	benzoquinone
C_6H_5	phenyl radical
$C_6H_4(OH)(NO_2)$	nitrophenol
C_6H_5OH	phenol
$C_6H_4(OH)_2$	catechol, resorcinol, hydroquinone
$C_6H_8O_2$	cyclohexadione
$CH_2CH(CH_2)_3CHO$	5-hexenal
$HO_2C(CH_2)_4CO_2H$	adipic acid
$C_6H_5COO_2NO_2$	peroxy benzoyl nitrate (PBN)
C_6H_5CO	benzoyl radical
C_6H_5CHO	benzaldehyde
$C_6H_5CH_2$	benzyl radical
$(CH_3)C_6H_4(NO_2)$	nitrotoluene
$(CH_3)C_6H_3(NO_2)(OH)$	nitrocresol, methyl nitrophenol
$C_6H_5CH_2ONO_2$	benzyl nitrate
$(CH_3)C_6H_4(OH)$	cresol
$C_6H_4(OH)(CH_2OH)$	hydroxybenzyl alcohol
$C_8H_8O_4$	dehydroacetic acid
H	hydrogen atom
NH	imino radical
HNO	nitroxyl radical
HNO_2	nitrous acid
HO_2NO_2	pernitric acid

TABLE 6A-14. (cont'd)

HO	hydroxyl radical
HO_2	hydroperoxy radical
H_2	hydrogen molecule
NH_2	amino radical
H_2O	water
H_2O_2	hydrogen peroxide
$HOSO_2$	sulfo radical
H_2SO_4	sulfuric acid
$NH_3 \cdot SO_2$	amidosulfurous acid
NH_4NO_3	ammonium nitrate
$(NH_3)_2 \cdot SO_2$	ammonium amido sulfite
NO_2*	excited state nitrogen dioxide
NO_3	nitrogen trioxide
N_2	molecular nitrogen
N_2O_3	dinitrogen trioxide
N_2O_4	dinitrogen tetroxide
N_2O_5	dinitrogen pentoxide
$O, O(^3P)$	ground state atomic oxygen
$O(^1D)$	excited state atomic oxygen
$O_2(^3\Sigma_g^{-1})$	ground state molecular oxygen
$O_2(^1\Sigma_g^{+})$, $O_2(^1\Delta_g)$	excited state molecular oxygen
O_3	ozone

TABLE 6A-14. (cont'd)

S	sulfur atom
SO	sulfur oxide
$SO_2(^3B_1)$	sulfur dioxide in the triplet excited state
$SO_2(^1B_1)$	sulfur dioxide in the singlet excited state
SO_3	sulfur trioxide

methyl formate, and formaldehyde; methyl ethyl ketone; explosives (particulates); isobutyl acetate; and phenol. Hexamine is also emitted from HAAP; however, the emission rate of this amine was not available, and may be negligible. Ketene and diketene may also be emitted due to abnormal process operations.

Properties of the Compounds Emitted During the Manufacture of RDX

Table 6A-15 summarizes some of the physical properties of the identified emissions characteristic of the RDX process. Included are the molecular weight, boiling point, melting point, density, vapor pressure, and uv-visible characteristics of each of the 35 emitted compounds. For convenience, the compounds are listed according to type: compounds which only contain carbon and hydrogen; compounds which contain carbon and oxygen; compounds which contain carbon, hydrogen, and oxygen (alcohols, phenol, aldehydes, ketones, carboxylic acids, esters, and acetic anhydride); compounds which contain nitrogen and hydrogen (ammonia, dimethylamine, methylamine, and hexamine); compounds which contain nitrogen and oxygen (nitrogen oxides, nitric acid, and organic derivatives of the nitrogen oxides); and compounds which contain sulfur (sulfur dioxide).

Since the vapor pressure of a compound indicates its maximum possible concentration in the gas phase, this property is vital in determining the importance of a compound in the atmosphere. For the most part, the compounds emitted from HAAP are either gases or volatile organic compounds. These compounds will

TABLE 6A-15. PHYSICAL PROPERTIES OF EMISSIONS FROM RDX MANUFACTURE

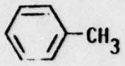
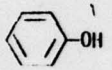
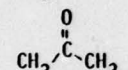
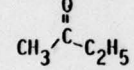
No.	Compound	Chemical Formula	Molecular Weight (g/mole)[a]	Boiling Point (°C)	Melting Point (°C)	Density (g/ml)	Vapor Pressure (mmHg)[b]	Estimated Vapor Pressure (mmHg)[c]	UV - vis Absorption Between 290 - 800 nm[d]
1	Methane	CH_4	16.04	-161.49	-182.48	0.415^{-164}	----	----	0[g]
2	Ethane	CH_3-CH_3	30.07	- 88.63	-182.8	0.572_4^{-108}	3.26×10^4 (25°)	----	0[g]
3	Toluene		92.13	110.6	- 95	0.8669^{20}	36.7 (30°)	29.3 (25°)	0[g]
4	Carbon monoxide	CO	28.01	-191.5	-199	1.250	----	----	0[g]
5	Methanol	CH_3OH	32.04	64.96	97.8	0.7914_4^{20}	123 (25°)	----	0[g]
6	n-propanol	$CH_3CH_2CH_2OH$	60.09	97.1	-127	0.7796_4^{20}	20.1 (25°)	----	0[g]
7	n-butanol	$CH_3CH_2CH_2CH_2OH$	74.12	117.5	- 89.8	0.8098_4^{20}	6.4 (25°)	-----	0[h]
8	Phenol		94.11	182	43	1.0722^{20}_{20}	0.40 (27°)	0.67 (25°)	x[g]
9	Formaldehyde	HCHO	30.03	- 21	- 92	0.815^{-20}	----	----	x[g]
10	Acetaldehyde	CH_3CHO	44.05	20.08	-124.6	0.7834_4^{18}	912 (25°)	----	x[g]
11	Acetone		58.08	56.2	- 95.35	0.7908^{20}	400 (39.5°)	231 (25°)	x[g]
12	Methylethyl ketone		72.11	79.6	- 87	0.8054_2^{20}	95.4 (25°)	----	x[g]

TABLE 6A-15. (cont'd)

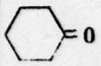
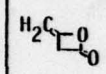
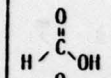
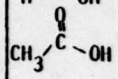
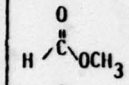
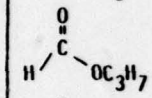
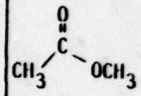
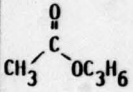
No.	Compound	Chemical Formula	Molecular Weight (g/mole)[a]	Boiling Point (°C)	Melting Point (°C)	Density (g/ml)	Vapor Pressure (mmHg)[b]	Vapor Pressure (mmHg)[c]	UV - vis Absorption Between 290 - 800 nm[d]
13	Cyclohexanone		98.14	155.65	- 16.4	0.9978_4^{20}	5 (26.4)	4 (25°)	x[g]
14	Ketene	$CH_2=C=O$	42.04	- 56	-151	-----	----	----	x[g]
15	Diketene (4-methylene-2-oxetanone)		84	127.4	- 6.5	1.0897_{20}^{20}	8 (20°)	----	x[i]
16	Formic acid		46.03	100.7	8.4	1.220_4^{20}	40.7 (25°)	----	0[g]
17	Acetic acid		60.05	118.5	16.60	1.0491_4^{20}	15.1 (25°)	----	0[g]
18	Methyl formate		60.05	31.5	- 99	0.9742_4^{20}	617 (25°)	----	0[g]
19	n-propyl formate		88.11	81.3	- 92.9	0.9006_4^{20}	63.9 (20°)	83.8 (25°)	0
20	Methyl acetate		74.08	57	- 98.1	0.9723_4^{20}	169.8 (20°)	217 (25°)	0[g]
21	n-propyl acetate		102.13	101.6	- 95	0.8884_4^{20}	25.1 (20°)	34.7 (25°)	0[j]

TABLE 6A-15. (cont'd)

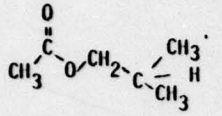
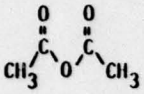
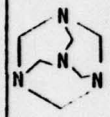
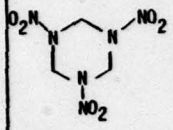
No.	Compound	Chemical Formula	Molecular Point (g/mole)[a]	Boiling Point (°C)	Melting Point	Density (g/ml)	Vapor Pressure (mmHg)[b]	Estimated Vapor Pressure (mmHg)[c]	UV - vis Absorption Between 290 - 800 nm[d]
22	Isobutyl acetate		116.16	117.2	- 98.58	0.874_4^{20}	10 (12.8°)	17.5 (25°)	0[j]
23	Acetic anhydride		102.09	136.4	- 73.1	1.0820_4^{20}	5 (24.8°)	----	0[g]
24	Ammonia	NH_3	17.03	- 33.35	- 77.7	0.7710	7.55×10^3(25°)	----	0[g]
25	Methyl amine	CH_3NH_2	31.06	- 6.3	- 93.5	0.699^{-11}	3.8×10^3 (36°)	2.84×10^3(25°)	0[g]
26	Dimethylamine	$(CH_3)_2NH$	45.08	7.4	- 96	0.6804_4	1.52×10^3(25°)	----	0[g]
27	Hexamine (hexamethylenetetramine; 1,3,5,7-tetraazatricyclo [3.3.1.$1^{3,7}$] decane)		140.19		280 sublime	1.331^{-5}	$0.81\text{-}5.24 \times 10^{-4}$ (7.9-25.3°)	----	0[k]
28	Nitric oxide	NO	30.01	-151.8	-163.6	1.3402	----	----	0[g]
29	Nitrogen dioxide	NO_2	46.01	21.2	- 11.20	1.4494_{20}^{20}	910 (25°)	----	x[g]
30	Nitrous oxide	N_2O	44.01	- 88.5	- 90.8	$1.977_{760}^{0,e}$	4.34×10^4(25°)	----	0[g]
31	Nitromethane	CH_3	61.04	100.8	- 28.5	1.1354_4^{22}	27.8 (20°)	39.1 (25°)	x[g]
32	Nitric acid	HNO_3	63.01	83	- 42	1.5027_4^{25}	47.9 (20°)	64.6 (25°)	x[i]

TABLE 6A-15. (cont'd)

No.	Compound	Chemical Formula	Molecular Weight (g/mole)[a]	Boiling Point (°C)	Melting Point (°C)	Density (g/ml)	Vapor Pressure (mmHg)[b]	Estimated Vapor Pressure (mmHg)[c]	UV - vis Absorption Between 290 - 800 nm[d]
33	Methyl nitrate	CH_3ONO_2	77.04	65[f]	-108	1.2032^{25}	156.85 (25°)	----	x[g]
34	RDX (hexahydro-1,3,5-trinitro-s-triazine)		222.12	---	203.5	1.82^{20}	3.16×10^{-7} (56°)	----	x[m]
35	Sulfur dioxide	SO_2	64.06	-10	- 72.7	2.927[e]	2.895×10^{3} (25°)	----	x[g]

[a]Except for Compound 15, the molecular weights, boiling points, melting points, and densities are from Reference 1; the properties of Compound 15 are from Reference 2.

[b]The vapor pressures of Compounds 2,24,29,30, and 35 are from Reference 3; those of Compounds 3,11,22, and 31 from Reference 4. The vapor pressure of the following Compounds are from Reference 5: 5,6,7,8,10,12,13,16,17,18,19,20,21,23,25, and 26. The vapor pressure of Compound 15 is from Reference 6; that of Compound 27 is from Reference 7; that of Compound 32 from Reference 1; that of Compound 33 from Reference 8; and that of Compound 34 from Reference 9.

[c]The vapor pressure at 25°C for Compounds 3,8,11,19,20,22, and 31 were estimated using the method of Dreisbach; see Reference 10. The vapor pressure for nitric acid at 25° was estimated from the vapor pressures at 20° and 30°C; that for methylamine was estimated from the vapor pressures at 10.1° and 36°C.

[d]The mark (x) indicates that the compound absorbs light within the 290-800 nm region; a zero (o) indicates it does not.

[e]The densities of nitric oxide, nitrous oxide, and sulfur dioxide are in g/ℓ.

[f]Methyl nitrate explodes upon boiling and melting; it is an explosive vapor.

[g]The uv-visible spectrum of this compound is from Reference 11.

[h]The spectrum of butanol was obtained from Reference 12.

[i]The uv-vis spectrum of diketene was found in Reference 13.

[j]The uv-vis spectrum of this ester is from Reference 14.

[k]The uv-vis spectrum of hexamine was found in Reference 15.

[l]The spectrum of nitric acid was obtained from Reference 16.

[m]The uv-vis spectrum of cyclonite was obtained from Reference 17.

affect the chemistry of the atmosphere above HAAP. However, hexamine and RDX have very low vapor pressures at 25°C (5.24×10^{-4} mm (25°) and 3.16×10^{-7} mm (56°), respectively) and the concentration of each of the compounds cannot exceed one ppm (0.69 and 4.16×10^{-4} ppm, respectively). Because the concentration of these compounds will be low, their chemistry will have little effect on the atmosphere above HAAP and will not be considered in this investigation.

Methods of Detecting Compounds Emitted During the Manufacture of RDX

The compounds emitted at HAAP can be divided into those compounds which are well known and those which are not. The first class consists of hydrocarbons, aldehydes, ammonia, nitrogen oxides, nitric acid, and sulfur dioxide. Detection methods for these common emissions have been reviewed recently and will not be reviewed here.[18]

The second class is composed of low molecular weight organic compounds: alcohols, ketones, ketene, diketene, carboxylic acids, esters, acetic anhydride, amines, nitromethane, and methyl nitrate. Detection of these compounds may involve adsorbing the compounds onto some polymeric material (e.g., Tenax GC[19]), desorbing the organic vapors,[20] and analyzing them using a gas liquid phase chromatograph (glpc) equipped with a flame ionization detector interfaced with a mass spectrometer. Hundreds of compounds present in the air have been successfully detected in this manner.[21,22,23]

However, it is not known whether this method will be successful in the detection of ketene and diketene, two relatively reactive compounds (see Section 6.A.2.2). Both compounds can be detected in the atmosphere by passing air through a sulfuric acid solution to which resorcinol is added. The intensity of the blue-violet fluorescence of the resulting solution is measured to determine the concentration of ketene and diketene. The analysis reportedly can detect ketene and diketene at the 0.02 ppm level. To determine the concentration of diketene in the atmosphere, the air is initially passed through water to destroy any ketene which may be present. Sulfuric acid and resorcinol are added, and the intensity of the fluorescence is again measured.[24]

6.A.2.3 Atmospheric Transformations

The atmospheric transformations of the emissions at HAAP fall into two main categories: ground state reactions (reactions which occur without light) and light-induced reactions. Among the reactions considered will be those that occur between a particular pollutant and a compound normally present in the atmosphere and those between two pollutants. Reactions that occur because of the presence of light ($290 \leq \lambda \leq 800$ nm) are excited state reactions and may be further classified into those which directly occur because of light ($A + h\nu \rightarrow A^* \rightarrow$ products) and those which indirectly occur because of light ($x + h\nu \rightarrow x^*$, $x^* + A \rightarrow$ products). Known or potential secondary reactions will also be considered.

Known or Potential Ground State Reactions

Ground state reactions that are likely to occur in the atmosphere above HAAP are listed in Table 6A-16. Also listed are their rate expressions, the conditions under which the rate expressions and constants were determined, the rate constants at a particular temperature, and the literature reference. Those reactions in which one of the reactants is a carbon-containing compound are listed first and are followed by nitrogen- and sulfur-containing compounds.

The role of each of the tabulated reactions is, of course, dependent on the presence or absence of other reactive species and their absolute concentrations. Over the course of a day, as concentrations change due to reactions, meteorological mixing, and the diurnal variation in solar intensity, the importance of each reaction also changes. To assess the relative importance of any reaction at a given time for a particular pollutant matrix requires the use of computerized chemical/diffusion models.

Many of the organic compounds emitted from HAAP are known to react with ozone to yield oxidized products such as carbon monoxide, carbon dioxide, water, hydrogen peroxide, carboxylic acids, and peroxy acids (see Table 6A-15). Of these reactions, only the rate constants for the ozonolysis of carbon monoxide, methane, toluene, formaldehyde, and acetaldehyde have been determined in the gas phase. The remaining rate constants were determined in carbon tetrachloride solvent. If the rate constants determined for the reactions occurring in solution are similar to those in the gas phase and if the rate constants

TABLE 6A-16. KNOWN GROUND STATE REACTIONS OF EMISSIONS FROM HAAP

No.	Reaction	Rate Expression	Condition	T(K)	Rate Constant[a] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constant[a] $k\frac{l}{ppm\text{-}min}$	Ref.
1	$CH_4 + O_3 \rightarrow CO, CO_2, HCOOH, H_2O$	$k_1[CH_4][O_3]$		310	4.3×10^{-24}	6.4×10^{-9}	25
2	$C_2H_6 + O_3 \rightarrow$ products	$k_2[C_2H_6][O_3]$		---	---	---	---
3	$C_7H_8 + O_3 \rightarrow$ products	$k_3[C_7H_8][O_3]$		298	1.2×10^{-20}	1.8×10^{-5}	26
4	$CO + O_3 \rightarrow CO_2 + O_2$	$k_4[CO][O_3]$		296	$<4 \times 10^{-25}$	$<6 \times 10^{-10}$	27
5	$CH_3OH + O_3 \rightarrow HCOOH, H_2O_2$	$k_5[CH_4O][O_3]$		---	---	---	28
6	$C_3H_7OH + O_3 \rightarrow$ products	$k_6[C_3H_8O][O_3]$		---	---	---	---
7	$C_4H_9OH + O_3 \rightarrow$ products	$k_7[C_4H_{10}O][O_3]$	in CCl_4	298	6.47×10^{-22}	9.6×10^{-7}	29
8	$C_6H_5OH + O_3 \rightarrow$ products	$k_8[C_6H_6O][O_3]$		---	---	---	---
9	$HCHO + O_3 \rightarrow HO + HCO_3 \rightarrow HO_2 + HCO_2$	$k_9[CH_2O][O_3]$	400 torr	298	$\sim 2.1 \times 10^{-24}$	$\sim 3.1 \times 10^{-9}$	30
10	$CH_3CHO + O_3 \rightarrow CH_3CO_2H, CH_3CO_3H$	$K_{10}[C_2H_4O][O_3]$		298	3.4×10^{-20}	5.0×10^{-5}	26,31
11	$CH_3CHO + N_2O_5 \rightarrow CH_3CH(ONO_2)_2$	$k_{11}[C_2H_4O[N_2O_5]$	in N_2	<273	---	---	32
12	$(CH_3)_2CO + O_3 \rightarrow$ products	$k_{12}[C_3H_6O][O_3]$		---	---	---	---
13	$CH_3COC_2H_5 + O_3 \rightarrow CH_3COCOCH_3, RO_2R_1\ H_2O_2$	$k_{13}[C_4H_8O][O_3]$	in CCl_4	298	1.9×10^{-24}	2.8×10^{-9}	33
14	$C_6H_{10}O + O_3 \rightarrow HO_2C(CH_2)_4CO_2H$	$k_{14}[C_6H_{10}O][O_3]$	in CCl_4	293	9.8×10^{-24}	1.4×10^{-8}	34,35
15	$CH_2CO + H_2O \rightarrow CH_3CO_2H$	$k_{15}[C_2H_2O][H_2O]$		550	2.0×10^{-23}	3.0×10^{-8}	36

TABLE 6A-16. (cont'd)

No.	Reaction	Rate Expression	Condition	T(K)	Rate Constant[a] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constant[a] $k\frac{1}{ppm\text{-}min}$	Ref.
16	$CH_2CO + ROH \rightarrow ROCOCH_3$	$k_{16}[C_2H_2O][ROH]$		---	---	---	37
17	$2CH_2CO + RCHO \rightarrow RCHCHCOCH_3 + CO_2$	$k_{17}[C_2H_2O]^2[RCHO]$		---	---	---	37
18	$CH_2CO + (CH_3)_2CO \xrightarrow{H^+} CH_2C(CH_3)O_2CCH_3$	$k_{18}[C_2H_2O][C_3H_6O]$	acid catalyzed	---	---	---	37
19	$2CH_2CO \rightarrow C_4H_4O_2$	$k_{19}[C_2H_2O]^2$	6-155 torr	498	1.2×10^{-46}	1.8×10^{-31}	38
20	$CH_2CO + HCOOH \rightarrow (CH_3CO)_2O, CH_3COOH$	$k_{20}[C_2H_2O][CH_2O_2]$		428	3.98×10^{-21}	5.9×10^{-6}	39
21	$CH_2CO + CH_3COOH \rightarrow (CH_3CO)_2O$	$k_{21}[C_2H_2O][C_2H_4O_2]$		428	1.7×10^{-21}	2.5×10^{-6}	40
22	$CH_2CO + RNH_2 \rightarrow RNHCOCH_3$	$k_{22}[C_2H_2O][RNH_2]$		---	---	---	37
23	$CH_2CO + SO_3 \rightarrow \underline{CH_2CO_2SO_2}$	$k_{23}[C_2H_2O][SO_3]$		---	---	---	37
24	$CH_2CO + H_2SO_4 \rightarrow CH_3CO_2SO_2CH_2CO_2H$	$k_{24}[C_2H_2O][H_2SO_4]$		---	---	---	37
25	$C_4H_4O_2 + O_3 \rightarrow CH_3COCHO, CH_3CHO$	$k_{25}[C_4H_4O_2][O_3]$		---	---	---	37
26	$C_4H_4O_2 + H_2O \rightarrow CH_3COCH_2COOH$	$k_{26}[C_4H_4O_2]$	in 40:60 v/v dioxane H_2O	298	3.5×10^{-5}	2.1×10^{-3}	41
27	$C_4H_4O_2 + ROH \rightarrow CH_3COCH_2CO_2R$	$k_{27}[C_4H_4O_2][ROH]$		---	---	---	37
28	$C_4H_4O_2 + RCHO \xrightleftharpoons{\Delta} CH_3COCHCHR + CO_2$	$k_{28}[C_4H_4O_2][RCHO]$		---	---	---	37

TABLE 6A-16. (cont'd)

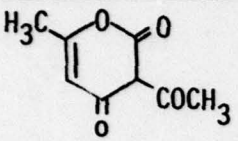
No.	Reaction	Rate Expression	Condition	T(K)	Rate Constant[a] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constant[a] $k\frac{l}{ppm\text{-}min}$	Ref.
29	$2C_4H_4O_2 \rightarrow$ 	$k_{29}[C_4H_4O_2]^2$		---	---	---	37
30	$CH_3CO_2H + O_3 \rightarrow CH_3CO_3H + O_2$	$k_{30}[C_2H_4O_2][O_3]$	in CCl_4	293	1.7×10^{-22}	2.5×10^{-7}	44,42
31	$(CH_3CO)_2O + H_2O \rightarrow 2CH_3CO_2H$	$k_{31}[C_4H_6O_3]$	in water	298	2.663×10^{-3}	1.598×10^{-1}	43
32	$2NH_3 + 4O_3 \rightarrow NH_4NO_3 + 4\ O_2 + H_2O$	---		---	---	---	44
33	$3NH_3 + 2SO_2 \rightleftarrows (NH_3 \cdot SO_2) + [(NH_3)_2 \cdot SO_2)]$	$k_{33}[NH_3][SO_2]$		296	$2\text{-}10 \times 10^{-16}$	$3\text{-}15 \times 10^{-1}$	45,46
34	$CH_3NH_2 + O_3 \rightarrow CH_3NHOH, CH_3NO, CH_3NO_2$	$k_{34}[CH_5N][O_3]$	in pentane	---	---	---	47
35	$(CH_3)_2NH + O_3 \rightarrow (CH_3)_2NOH, CH_3HNCH_2OH$	$k_{35}[C_2H_7N][O_3]$		---	---	---	47
36	$(CH_3)_2NH + HONO \rightarrow (CH_3)_2NNO + H_2O$	$k_{36}[C_2H_7N][HON_2]$		296	5.4×10^{-17}	8.0×10^{-2}	48
37	$NO + O_3 \rightarrow NO_2 + O_2$	$k_{37}[NO][O_3]$		298	1.80×10^{-14}	2.66×10	49
38	$2NO + O_2 \rightarrow 2NO_2$	$k_{38}[NO]^2[O_2]$		298	1.96×10^{-38}	7.1×10^{-10}	27
39	$NO + NO_2 = N_2O_3$	$k_{39} = \frac{[N_2O_3]}{[NO][NO_2]}$		298	2.12×10^{-20}	5.22×10^{-7}	50
40	$NO + NO_2 + O_2 \rightarrow NO_2 + NO_3$	$k_{40}[NO][NO_2][O_2]$		300	3.04×10^{-40}	1.1×10^{-10}	27

TABLE 6A-16. (cont'd)

No.	Reaction	Rate Expression	Condition	T(K)	Rate Constant[a] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constant[a] $k\frac{l}{ppm\text{-}min}$	Ref.
41	$NO + NO_2 + H_2O \rightarrow 2HNO_2$	$k_{41}[NO][NO_2][H_2O]$		300	$\leq 4.4 \times 10^{-40}$	$\leq 1.6 \times 10^{-11}$	51
42	$NO + NO_3 \rightarrow 2NO_2$	$k_{42}[NO][NO_3]$	1 atm N_2	297	8.7×10^{-12}	1.3×10^{4}	52
43	$2NO_2 + M \rightarrow N_2O_4 + M$	$k_{43}[NO_2]^2[M]$	$M = N_2$	300	2.64×10^{-36}	9.61×10^{-8}	27
44	$NO_2 + O_2 \rightarrow NO + O_3$	$k_{44}[NO_2][O_2]$		298	2.8×10^{-49}	4.1×10^{-34}	27
45	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$k_{45}[NO_2][O_3]$		298	3.3×10^{-17}	4.9×10^{-2}	27
46	$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$	$k_{46}[NO_2][NO_3]$		300	8.16×10^{-15}	1.21×10	27
47	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$k_{47}[NO_2][NO_3]$	$M = N_2O_5$, NO	300	3.8×10^{-12}	5.6×10^{3}	27
48	$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	$k_{48}[NO_3]^2$		300	2.2×10^{-16}	3.3×10^{-1}	27
49	$N_2O_4 + M \rightarrow 2NO_2 + M$	$k_{49}[N_2O_4][M]$	$M = N_2$	300	3.8×10^{-15}	5.6	27
50	$N_2O_3 + H_2O \rightarrow 2HNO_2$	$k_{50}[N_2O_3][H_2O]$		298	1.98×10^{-17}	2.94×10^{-2}	50
51	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$k_{51}[N_2O_5]$	$M = N_2O_5$, NO	300	2.3×10^{-1}	1.4×10	27
52	$N_2O_5 + H_2O \rightarrow 2HNO_3$	$k_{52}[N_2O_5][H_2O]$		300	$<1 \times 10^{-20}$	$<1.5 \times 10^{-5}$	27
53	$2HONO \rightarrow NO + NO_2 + H_2O$	$k_{53}[HNO_2]^2$		300	$\leq 1 \times 10^{-20}$	$\leq 1.5 \times 10^{-5}$	51
54	$HNO_2 + HNO_3 \rightarrow 2NO_2 + H_2O$	$k_{54}[HNO_2][HNO_3]$		300	1.55×10^{-17}	2.30×10^{-2}	53
55	$NO_3 + O_2 \rightarrow NO_2 + O_3$	$k_{55}[NO_3][O_2]$		300	7×10^{-34}	1×10^{-18}	27
56	$NO_2 + SO_2 \rightarrow NO + SO_3$	$k_{56}[NO_2][SO_2]$		300	$<2 \times 10^{-24}$	$<3 \times 10^{-9}$	27

TABLE 6A-16. (cont'd)

No.	Reaction	Rate Expression	Condition	T(K)	Rate Constant[a] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constant[a] $k\frac{1}{ppm\text{-}min}$	Ref.
	$NO_2 + SO_2 \rightarrow NO + SO_3$	$k_{56}[NO_2][SO_2]$	water vap. present	300	2×10^{-18}	3×10^{-3}	138
57	$NO_3 + SO_2 \rightarrow NO_2 + SO_3$	$k_{57}[NO_3][SO_2]$		300	$<7 \times 10^{-21}$	$<1 \times 10^{-5}$	27
58	$N_2O_5 + SO_2 \rightarrow N_2O_4 + SO_3$	$k_{58}[N_2O_5][SO_2]$		300	$<4 \times 10^{-23}$	$<6 \times 10^{-8}$	27
59	$SO_2 + O_3 \rightarrow SO_3 + O_2$	$k_{59}[SO_2][O_3]$		300	$\leq 10^{-22}$	$\leq 10^{-7}$	54
60	$SO_2, O_2, H_2O \xrightarrow{\text{soot}} H_2SO_4$	---		---	---	---	55
61	$SO_3 + H_2O \rightarrow H_2SO_4$	$k_{61}[SO_3][H_2O]$	1-1.3 torr	298	9.1×10^{-13}	1.4×10^{3}	56

[a]The rate constants for reactions 26, 31, and 51 are pseudo-first order and units for these reactions are sec^{-1} and min^{-1}. The units for the rate constants for reaction numbers 38, 40, 41 and 43 are given in $cm^6/molecule^2\text{-}sec$ and $ppm^{-2}\text{-}min^{-1}$. The equilibrium constant, k_{39} is given in $cm^3/molecule$ and ppm^{-1}. To convert from units of cm^3-molecule-sec to ppm-min, it was first assumed that the given values of the rate constants in the former units are the same as those under standard conditions, T = 298°K and P = 1 atm. The following conversions were used: to convert $cm^3/molecule$ to ppm^{-1}, multiply the values of the rate constant in $cm^3/molecule$ by 2.46×10^{13}; $cm^3/molecule\text{-}sec$ by 1.478×10^{15}; and $cm^6/molecule^2\text{-}sec$ by 3.64×10^{28}. A complete listing of reactions and rate constants can be found in Appendix 1.

[b]Reaction 15 is a heterogeneous reaction, and the value of k_{15} given here is that which was determined in an unpacked vessel.

[c]The identification of the products formed in the ozonolysis of this amine was not available; therefore, the products formed were assumed to be analogous to those formed in the ozonolysis of various butylamines.

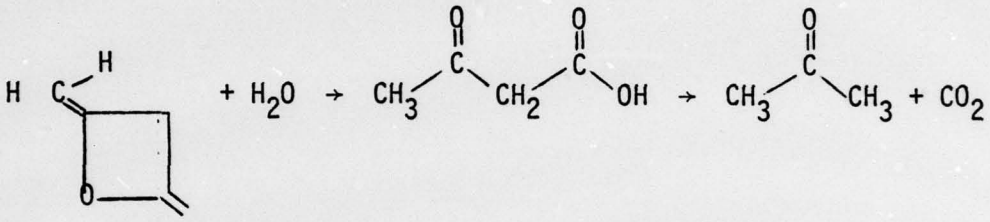
[d]For reactions 43 and 49, $k_{43\text{-}49} = k_{43/k_{49}} = 7.06 \times 10^{-20} cm^3/molecule = 1.74 \times 10^{-6}$ ppm^{-1}.

[e]For reactions 45 and 55, $k_{45\text{-}55} = k_{45/55} = 7.14 \times 10^{16}$.

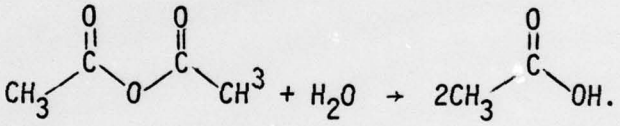
[f]The rate constant, k_{54}, is an upper limit.

which were not available in the literature are of the same magnitude as the known rate constants, it may be assumed that the oxidation of these compounds by ozone will proceed rather slowly. Whether this is a reasonable assumption is not known.

In contrast, the hydrolyses of diketene and acetic anhydride occur at a rapid rate. Water reacts with diketene initially to form acetoacetic acid which later decomposes into acetone and carbon dioxide and with acetic anhydride to form acetic acid:

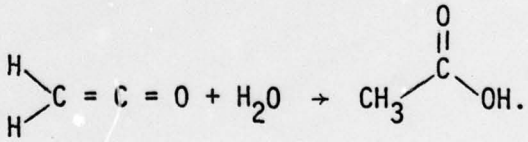


(26)



(31)

Ketene is fairly rapidly hydrolyzed to acetic acid. If the concentration of water in the atmosphere is 10,000-30,000 ppm, half of the ketene in the atmosphere will hydrolyze within 13-38 hours.



(15)

Although the homogeneous dimerization of ketene occurs at an insignificant rate at room temperature, the rate of the heterogeneous reaction may be quite rapid.[38] With the high rate of particulate emission at HAAP, the dimerization of ketene on particle surfaces may thus be important to the chemistry of this atmosphere. Other reactions involving ketene and diketene may also be fast; however, little information is available on the rates of these reactions.

In addition to the preceding reactions of the organic compounds emitted at HAAP, dimethylamine can react with the nitrous acid in the air to form N-nitroso dimethylamine:[48]

$$(CH_3)_2NH + HONO \rightarrow (CH_3)_2NNO + H_2O. \quad (36)$$

Some work with gas-phase systems is currently being conducted by EPA.[141] In this study, gaseous dimethylamine, $(CH_3)_2NH$, has been shown to react with gaseous nitrous acid, HONO, in air to yield N-nitrosodimethylamine, $(CH_3)_2N$-NO. This ongoing research has shown that, in a humid atmosphere containing dimethylamine, NO, NO_2, and HONO at concentrations of 0.5 to 2 ppm, the amine reacted at a rate of about 4 percent per minute yielding N-nitrosodimethylamine as the major reaction product. In the absence of HONO and humidity, the rate was lower by a factor of approximately four. It now appears that a much more intense look will have to be taken at the concentration of nitrosamine precursors in pollutant atmospheres. Thus, knowledge of the environmental concentrations of nitric oxide, nitrogen dioxide, nitrous acid, nitrites, nitrates, and primary secondary, tertiary, and quarternary amines will be required.

The concentration of the nitrosamine will build up at night. In light, however, both the nitrosamine and nitrous acid will photodissociate. Hence, the nitrosamine concentration will diminish during the daylight hours. Half-lives of 30 to 60 minutes have been observed in ambient irradiations conducted in Teflon bags.[48]

Primary amines such as methylamine may also react with nitrous acid to form a nitrosamine which may then tautomerize to the diazohydroxide:[57]

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad N - N = O \\ \diagup \\ H \end{matrix} \rightarrow CH_3 - N = N - OH. \quad (62)$$

In solution, this species is known to decompose into nitrogen, methyl carbonium ion, and hydroxide ion:[58]

$$CH_3 - N = N - OH \rightarrow CH_3^+ + N_2 + OH^-.$$

In the atmosphere it may similarly decompose into nitrogen, methyl radical, and hydroxyl radical, although no rate data were found:

$$CH_3 - N = N - OH \rightarrow CH_3 + N_2 + OH. \quad (63)$$

Investigations of the pyrolysis of nitrosamines have shown that these same radical species originate from the decomposition of the diazohydroxide tautomer. To date, there is no evidence as to the existence of the parent compound, H_2NNO.[57]

The chemical formation of nitrosamines has been the subject of numerous studies that have recently been reviewed by Mirvish.[138] Although most of the reported studies have been concerned with condensed-phase reactions systems, the formation of nitrosamine in the gas phase has been demonstrated.[139,140] Neurath et. al.[140] showed that the formation of nitrosamines from secondary amines requires an equimolar mixture of nitrogen oxides. This reaction, which occurs in the gaseous phase, can be represented as follows:

$$2\ R_2NH + NO + NO_2 \rightarrow 2\ R_2NNO + H_2O.$$

Bretschneider and Matz[139] showed that diethylamine and nitrogen dioxide (NO_2) at concentrations of 50 to 100 parts per million (ppm) reacted within seconds to form measurable levels of nitrosamine.

Ammonia in the atmosphere above HAAP will react with ozone and sulfur dioxide to form particulate products. Initially the ozone reacts with ammonia to form nitric acid. The nitric acid then reacts with another equivalent of ammonia to form ammonium nitrate which eventually coagulates to form particles:[44]

$$NH_3 + 4\ O_3 \rightarrow HNO_3 + H_2O + 4\ O_2 \quad (32a)$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \rightarrow \text{particles}. \quad (32b)$$

In the reaction between ammonia and sulfur oxide, amidosulfurous acid and ammonium amidosulfite are initially formed:

$$NH_3 + SO_2 \rightarrow [NH_3 \cdot SO_2] + [(NH_3)_2 \cdot SO_2]. \quad (33)$$

Depending on the surrounding oxygen and water concentrations, these compounds condense to form aerosols composed of such compounds as ammonium sulfate, $(NH_4)_2SO_4$; ammonium sulfamate, $NH_4NH_2SO_3$; sulfamic acid, NH_2SO_3H; ammonium azide, NH_4N_3; ammonium amidosulfite, $NH_4NH_2SO_2$; ammonium pyrosulfate, $(NH_4)_2S_2O_7$, and amidosulfate hydrazide, $N_3H_7SO_4$.[46]

Based on the rate constants given in Table 6A-15, and computer models of atmospheric chemistry,[59] the reactions of the nitrogen oxides and their acids that appear to be most important in the chemistry of the atmosphere above HAAP include the reaction between nitric oxide and ozone; nitric oxide and oxygen; nitric oxide, nitrogen dioxide, and water; nitric oxide and nitrogen trioxide; nitrogen dioxide and ozone; nitrogen dioxide and nitrogen trioxide; dinitrogen pentoxide and water; as well as the dissociation of dinitrogen pentoxide.

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (37)$$

$$2NO + O_2 \rightarrow 2\ NO_2 \quad (38)$$

$$NO + NO_2 + H_2O \rightarrow 2HONO \quad (41)$$

$$NO + NO_3 \rightarrow 2\ NO_2 \quad (42)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (45)$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \quad (47)$$

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \quad (52)$$

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M \quad (51)$$

The remaining reactions of the nitrogen oxides and their acids (reactions 39, 40, 43, 44, 46, 48, 50, 53, 54, and 55) are believed to be less important.

The SO_2 emitted will react rapidly only with NO_2; assuming 10-fold dilution of power plant plumes and 100-fold dilution of D Building plumes, this reaction could be producing SO_3 at a rate of 70 ppm/min. The trioxide species will quickly react with water to form sulfuric acid (reaction 61). In addition it has also been demonstrated that sulfur dioxide is oxidized to sulfuric acid in the presence of soot particulates in the atmosphere (reaction 60).[55] Since a large quantity of particulates is emitted from the power plants at HAAP, this heterogeneous reaction may influence the atmospheric chemistry of emissions from this installation.

Known or Potential Excited State Reactions

Of the 35 compounds emitted from HAAP, 13 absorb light within the 290-800 nm wavelength region. These photo acceptors are phenol, formaldehyde, acetaldehyde, acetone, methyl ethyl ketone, cyclohexanone, ketene, diketene, nitrogen dioxide, nitric acid, nitromethane, methyl nitrate, and sulfur dioxide. For these compounds, the photolyses likely to occur in the atmosphere are listed in Table 6A-17. The majority of these photolyses result in the breaking of bonds. For these reactions, the bond dissociation energies (kcal/mole), the maximum wavelength necessary for the occurrence of bond dissociation, quantum yields (Φ = number of molecules decomposed or formed per quantum of absorbed light), and rate of product formation or decomposition (sec^{-1}) are given. The remaining photolyses only result in the formation of an excited state species (A*). The known quantum yields or rates of product formation or decomposition are also given for these reactions. Much information is available on the photochemistry of formaldehyde, acetaldehyde, acetone, methyl ethyl ketone, cyclohexanone, N-nitrosodimethylamine, ketene, nitrogen dioxide, nitrogen trioxide, dinitrogen pentoxide, nitrous acid, nitric acid, nitromethane, methyl nitrite, ozone, and sulfur dioxide. However, little is known of the gas-phase photochemistry of phenol, diketene, and methyl nitrate. Therefore, the photochemistry of these compounds in solution, the photochemistry of model compounds, and the gas-phase decomposition of these compounds have been considered to lend insight into the possible photochemistry of these compounds in the atmosphere.

TABLE 6A-17. PHOTOCHEMICAL REACTIONS OF EMISSIONS FROM HAAP

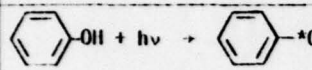
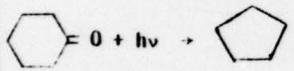
No.	Reaction	Range of Absorption Spectrum (nm)	Bond Dissociation Energy (kcal/mole)[a]	Max.λ (nm) Required for Bond Dissociation[a]	T(K)	Quantum Yields $\Phi_{products}$	Rate of Product Formation or Decomposition $k(sec^{-1})$[e]
64		~240 - 320[d]	----	----	----	----	----
65-a	H_2-CO + hν → H_2 + CO	240 - 365[d]	----	----	----	Φ= 0.62(λ320)[e]	8.7×10^{-5}(z=40°)[f]
65-b	H-CHO + hν → H + CHO	----	87.1	<328	----	Φ= 0.38(λ320)	3×10^{-5}(z=40°)[f]
66-a	CH_3H-CO + hν → CH_4 + CO	230 - 350[d]	----	----	----	Φ= 0(λ313)[g]	4.1×10^{-7}[g]
66-b	CH_3-CHO + hν → CH_3 + CHO		83.0	<345	----	Φ= 0.05 (λ313)	2.8×10^{-6}
66-c	CH_3CHO + hν → CH_3CHO*	----	----	----	----	Φ= 0.84 (λ313)	----
67-a	CH_3CO-CH_3 + hν → CH_3CO + CH_3	220 - 330[d]	80.6	<365	298	$\Phi_{products}$ = 0.5 (λ315)[n]	1.4×10^{-5}(z=40°)[f]
67-b	CH_3-$COCH_3$ + hν → 2CH_3 + CO	----	93.9	<305	----	----	----
67-c	H-CH_2COCH_3 + hν → H + CH_2COCH_3	----	97.8	<293	----	----	----
68-a	CH_3CO-C_2H_5 + hν → CH_3CO + C_2H_5	220 - 330[d]	79.5	<360	----	Φ_a/Φ_b=(λ290-320)[i]	1.4×10^{-5}(z=40°)[f]
68-b	CH_3-COC_2H_5 + hν → CH_3 + COC_2H_5	----	----	----	----	----	----
69-a		240 - 325[d]	8.2	<3490	----	Φ= 0.05 (λ302)[j]	

TABLE 6A-17. (cont'd)

No.	Reaction	Range of Absorption Spectrum (nm)	Bond Dissociation Energy (kcal/mole)[a]	Max.λ (nm) Required for Bond Dissociation[a]	T(K)	Quantum Yield $\Phi_{products}$	Rate of Product Formation or Decomposition $k(sec^{-1})$[e]
69-b	+ hν → $CH_2 = CH(CH_2)_2CH_3$ + CO	----	21.7	<1320	----	Φ= 0.15(λ302)	----
69-c	+ hν → $CH_2 = CH(CH_2)_3CHO$	----	23.6	<1210	----	Φ= 0.28 (λ302)	
69-d	+ hν → $CH_2 = CH_2$ + CH_3CH = CH_2 + CO	----	44.1	<649	----	----	----
70-a	$CH_2 = CH(CH_2)_3CHO$ + hν → $CH_2CHCHCH_2$ + CH_3CHO	~230 - 340[d,k]	----	----	----	Φ= 0.36(λ312)[ℓ]	----
70-b	$CH_2 = CH(CH_2)_3CHO$ + hν → CH_3CHCH_2 + CH_2CHCHO	----	----	----	----	Φ= 0.25(λ312)	----
71-a	CH_2CHCHO + hν → polymer	240 - 385[d]	----	----	----	Φ= 0.39(λ366)[m]	5.1×10^{-4}(z=40°)[n]
71-b	CH_2CHCHO + hν → CH_2CH_2 + CO	----	----	----	----	----	----
72-a	CH_2CO + hν → CH_2CO^* → $^3CH_2$ + CO	260 - 370[d]	79	<367	----	----	----
72-b	CH_2CO + hν → CH_2CO^* → $^1CH_2$ + CO		95	<301	----	----	----
73	$C_4H_4O_2$ + hν → products	290 - 355[o]	----	----	----	----	----

TABLE 6A-17. (cont'd)

No.	Reaction	Range of Absorption Spectrum (nm)	Bond Dissociation Energy (kcal/mole)[a]	Max.λ (nm) Required for Bond Dissociation[a]	T(K)	Quantum Yields Φproducts	Rate of Product Formation or Decomposition $k(sec^{-1})$[e]
74	$(CH_3)_2NNO + h\nu \rightarrow (CH_3)_2N + NO$	320 - 390[p]	----	----	----	$\Phi=0.01(350<\lambda<380)$[p]	----
75-a	$NO-O + h\nu \rightarrow NO + O(^3p)$	180 - 410[g]	73.19	<390	300	$\Phi_o \sim 1(\lambda 295\text{-}410)$[m]	$8 \times 10^{-3}(z=40°)$[f]
75-b	$NO_2 + h\nu \rightarrow NO_2^*$	----	----	----	----	----	$2.27 \times 10^{-2}(z=40°)$[f]
76	$NO_2-O + h\nu \rightarrow NO_2 + O(^3p)$	450 - 680[r]	50.5	567	----	----	$2.6 \times 10^{-2}(\lambda 450\text{-}578)$[g] $4.34 \times 10^{-2}(\lambda 579\text{-}680)$
77	$N_2O_5 + h\nu \rightarrow$ products	210 - 380[r]	----	----	----	----	----
78-a	$HO-NO + h\nu \rightarrow HO + NO$	200 - 270[t] 314 - 393	49.9	<574	----	$\Phi_{OH} = 0.92(365)$[t]	$2.5 \times 10^{-3}(z=30°)$[t]
78-b	$H-ONO + h\nu \rightarrow H + NO_2$	----	79.0	<362	----	----	----
79	$HO-NO_2 + h\nu \rightarrow HO + NO_2$	185 - 335[s]	49.52	<578	----	$\Phi_{OH}=1(\lambda 300)$[v]	$\leq 3.5 \times 10^{-6}(\lambda<330°)$[F]
79-b	$HNO_2-O + h\nu \rightarrow HNO_2 + O(^3p)$		72.8	<393	----	----	----
79-c	$H-ONO_2 + h\nu \rightarrow H + NO_3$	----	101.4	<283	----	----	----
79-d	$HNO_2-O + h\nu \rightarrow HNO_2 + o(^1D)$	----	118.1	<242	----	----	----
80-a	$CH_3NO_2 + h\nu \rightarrow CH_2O + HNO$	240 - 330[d]	----	----	320	$\Phi_{CH_2O}=0.20(\lambda 313)$[w]	$4.5 \times 10^{-5}(z=40°)$[n,x]
80-b	$CH_3-NO_2 + h\nu \rightarrow CH_3NO + O(^3p)$	----	60.1	476	----	$\Phi_{CH_3} \sim 0.6(\lambda 313)$	----

TABLE 6A-17. (cont'd)

No.	Reaction	Range of Absorption Spectrum (nm)	Bond Dissociation Energy (kcal/mole)[a]	Max. λ (nm) Required for Bond Dissociation[a]	T(K)	Quantum Yields $\Phi_{products}$	Rate of Product Formation or Decomposition $k(sec^{-1})$[e]
80-c	$CH_3NO\text{-}O + h\nu \rightarrow CH_3NO + O(^3P)$	----	93.5	<306	----	$\Phi_{CH_3NO} = 0.06(\lambda 313)$	----
81-a	$CH_3ONO_2 + h\nu \rightarrow CH_2O + HONO$	200 - 320[d]	----	----	----	$\Phi = 0.094$[y]	$2.1 \times 10^{-6}(z=40°)$[n,x]
81-b	$CH_3O\text{-}NO_2 + h\nu \rightarrow CH_3O + NO_2$		31.1	<920	----	$\Phi = 0.134$	
81-c	$CH_3ONO\text{-}O + h\nu \rightarrow CH_3ONO + O(^3P)$	----	72.6	394	----	$\Phi = 0.240$	----
82	$CH_3ONO + h\nu \rightarrow CH_3O + NO$	290 - 410[d]	40.7	703	----		$1.64 \times 10^{-3}(z=40°)$[n,x]
83-a	$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g^-)$	200 - 350[d] 450-700	25.4	1120	----	$\Phi = 1(450<\lambda<750)$[s]	$3.39 \times 10^{-4}(450<\lambda<750)$[s]
83-b	$O_3 + h\nu \rightarrow O(^3P) + O_2(^1\Delta_g)$	----	48.0	595	----	$\Phi = 1(310<\lambda<350)$[s]	
83-c	$O_3 + h\nu \rightarrow O(^1D) + O(^3\Sigma_g^-)$	----	70.7	404	----	----	----
83-d	$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta_g)$	----	93.2	306	---	$\Phi = 1(250<\lambda<310)$[3]	

TABLE 6A-17. (cont'd)

No.	Reaction	Range of Absorption Spectrum (nm)	Bond Dissociation Energy (kcal/mole)[a]	Max. λ (nm) Required for Bond Dissociation[a]	T(K)	Quantum Yields Φproducts	Rate of Product Formation or Decomposition k(sec^{-1})[e]
84-a	$SO_2(^1A_1) + h\nu \rightarrow SO_2^* (^3B_1)$	370 - 400[z]	----	----	----	$\Phi_{SO_3} = 0.108$[z]	----
84-b	$SO_2(A_1) + h\nu \rightarrow SO_2^* (^1B_1)$	240 - 320	----	----	----	$\Phi_{SO_3} = 0.09$	----

[a]For reactions 65,66,67,68,80,81, and 82, the bond dissociation energies at T=300°K were calculated using the tables of thermochemical data in Reference 10. For reactions 75,76,78,79, and 83, the data was obtained from Reference 27.

[b]The values for the maximum wavelength necessary for the occurrence of bond dissociation were calculated using the relationship, $\lambda(nm) = 2.86 \times 10^4/D°$, where D° = bond dissociation energy in kcal/mole.

[c]A complete list of reactions and rate constants can be found in Appendix I.

[d]The absorption spectrum of this compound is from Reference 11.

[e]The quantum yields for the formaldehyde photolysis are from Reference 63.

[f]See Reference 59.

[g]The quantum yields and rates for the photolysis of acetaldehyde were found in Reference 64.

[h]The quantum yield for the acetone photolysis was obtained from Reference 65.

[i]The quantum yield for the photolysis of methyl ethyl ketone was from Reference 66.

[j]The quantum yields for the photolysis of cyclohexanone were from Reference 61.

[k]The absorption spectrum of 5-hexenal was not available. Hence, it was assumed that it absorbs within the 230-340 nm region, the region in which simple aldehydes absorb.

[l]The quantum yields for the photolysis of 5-hexenal were obtained from Reference 67.

[m]See Reference 11.

[n]See Reference 68.

[o]The absorption spectrum of diketene was obtained from Reference 13.

[p]The absorption spectrum of nitrosamine was obtained from Reference 69. The quantum yield is from the same reference.

[q]The absorption spectrum of nitrogen dioxide was found in Reference 70.

[r]The absorption spectrum of this nitrogen dioxide was found in Reference 70.

[s]See Reference 27.

[t]The uv-visible spectrum of nitrous acid was obtained from Reference 72. Values for the hydroxyl radical quantum yields and rate of decomposition were obtained from the same reference.

[u]The uv-visible spectrum of nitric acid was obtained from Reference 16.

[v]The quantum yield for the nitric acid photolysis was obtained from Reference 73.

[w]The quantum yields for the photolysis of nitromethane was from Reference 74.

[x]The given rate constant is that for the analogous ethyl compound.

[y]The given quantum yields are those obtained in the photolysis of ethyl nitrate; see Reference 75.

[z]See Reference 76 for the absorption spectrum of sulfur dioxide. The quantum yields can also be found in this reference.

Phenol

Because the vapor pressure of phenol is low (0.67 mm at 25°C), the photolysis of this compound has been studied in water solution. In the presence of light ($h\nu$), phenol is activated into an electronically excited state ($C_6H_5OH^*$). This excited state species may then react with water to form the excited state anion ($C_6H_5O^{-*}$) and a hydronium ion. The excited state anion may then decay to the ground state anion ($C_6H_5O^-$) which may react with water to reform phenol.[11]

$$C_6H_5OH + h\nu \rightarrow C_6H_5OH^* \quad (64)$$

$$C_6H_5OH^* + H_2O \rightleftarrows C_6H_5O^{-*} + H_3O^+$$

$$C_6H_5O^{-*} \rightarrow C_6H_5O^- + h\nu'$$

$$C_6H_5O^- + H_2O \rightarrow C_6H_5OH + OH^-$$

Formaldehyde

In the presence of light, formaldehyde can photodissociate via two pathways. At wavelengths less than 328 nm, formaldehyde can dissociate either into molecular hydrogen and carbon monoxide or into atomic hydrogen and the formyl radical:*

$$H_2CO + h\nu \rightarrow H_2 + CO \quad (65\text{-a})$$

$$H\text{-}CHO + h\nu(\lambda<328) \rightarrow H + CHO. \quad (65\text{-b})$$

---

*The value of 328 nm is based on the value of the H-CHO bond dissociation energy suggested by Benson.[60] Calvert suggests a dissociation energy of $\leq$ 81.5 kcal/mole.[63] Thus, the maximum wavelength required for the occurrence of bond dissociation is now 350 nm.

Although the sum of quantum yields for reactions 65-a and 65-b is approximately equal to one over the entire absorption band, the ratio of these quantum yields ($\Phi_{65\text{-}b}/\Phi_{65\text{-}a}$) varies from zero at 365 nm to five at 280 nm.[63] Over the wavelength region of 290-365 nm, the ratio of the quantum yield for reaction 65-b to that of 65-a is 1:2. In the atmosphere with a solar zenith angle of 40° (z = 40°), the rate constants for these photolyses have been estimated (See Table 6A-17). Assuming that the formaldehyde in the atmosphere is only removed photochemically, the half life for formaldehyde was estimated from the rate constants of reactions 65-a and 65-b ($t_{1/2} = 0.693/k$). In 5760 sec, half of the formaldehyde in the atmosphere decomposes into hydrogen molecules and carbon monoxide or hydrogen atoms and formyl radicals.[63]

Acetaldehyde

The acetaldehyde in the atmosphere may directly photodissociate into methane and carbon monoxide or into methyl and formyl radicals:

$$CH_3CHO + h\nu \rightarrow CH_4 + CO \qquad (66\text{-a})$$

$$CH_3CHO + h\nu(\lambda<345) \rightarrow CH_3 + CHO \qquad (66\text{-b})$$

However, from the quantum yields given in Table 6A-17, it appears that these reaction pathways are of little importance. Instead, the acetaldehyde is excited into an electronically excited singlet state ($^1CH_3CHO$). This excited state species may then decay into a triplet species ($^3CH_3CHO$). The excited triplet species may either decay to the ground state or react with molecular oxygen to form methyl and hydroperoxy radicals and carbon monoxide.

$$\left.\begin{aligned} CH_3CHO + h\nu &\rightarrow {}^1CH_3CHO \\ {}^1CH_3CHO &\rightarrow {}^3CH_3CHO \end{aligned}\right\} \Phi = 0.84\ (\lambda 313\ nm) \qquad (85)$$

$$^3CH_3CHO + O_2 \rightarrow CH_3CHO + O_2 \quad (86\text{-a})$$

$$^3CH_3CHO + O_2 \rightarrow CH_3 + CO + HO_2 \quad k = 8.7 \times 19^{-6} sec^{-1} \ (z=0°) \quad (86\text{-b})$$

Compared to the quantum yields of the two preceding photodissociation pathways (reactions 66-a and 66-b), it appears that the formation of triplet acetaldehyde and its subsequent oxidation is the chief pathway for the photodecomposition of acetaldehyde.[64]

Acetone and Methyl Ethyl Ketone

In the presence of light, acetone can photodissociate into methyl, acetyl, and acetonyl radicals; hydrogen atoms; and carbon monoxide:

$$CH_3CO\text{-}CH_3 + h\nu \ (\lambda<365) \rightarrow CH_3CO + CH_3 \quad (67\text{-a})$$

$$CH_3\text{-}CO\text{-}CH_3 + h\nu \ (\lambda<305) \rightarrow 2CH_3 + CO \quad (67\text{-b})$$

$$H\text{-}CH_2COCH_3 + h\nu \ (\lambda<293) \rightarrow H + CH_2COCH_3. \quad (67\text{-c})$$

At 25°C with a wavelength of 315 nm, the quantum yield for the photolytic decomposition of acetone is 0.5; above 100°C, the sum of the quantum yields for pathways 67-a and 67-b is equal to 1.0. Hence it appears that pathway 67-c is relatively unimportant in the photodecomposition of acetone. Indeed the products identified in the flash photolysis of acetone at 25°C verify this fact. Ethane, which is formed by the combination of two methyl radicals, is the major product. Only small amounts of acetaldehyde, formed from the hydrogen abstraction reaction between an acetyl radical and acetone; biacetyl, formed by the combination of two acetyl radicals; and methyl ethyl ketone, formed by the combination of methyl and acetonyl radicals, are also produced.[65]

Methyl ethyl ketone is known to photodissociate either into acetyl and ethyl radicals or into propionyl and methyl radicals:

$$CH_3CO\text{-}C_2H_5 + h\nu\ (\lambda<360) \rightarrow CH_3CO + C_2H_5 \qquad (68\text{-a})$$

$$CH_3\text{-}COC_2H_5 + h\nu \rightarrow CH_3 + COC_2H_5. \qquad (68\text{-b})$$

From the ratio of the quantum yield of pathway 68-a to that of 68-b, it appears that methyl ethyl ketone will most likely photodissociate into acetyl and ethyl radicals.

Cyclohexanone

Like acetone, cyclohexanone can dissociate via a number of pathways; in the gas phase carbon monoxide, ethylene, propylene, cyclopentane, 1-pentene, and 5-hexenal are formed:

$$(CH_2)_5CO + h\nu\ (\lambda<3490) \rightarrow (CH_2)_5 + CO \qquad (69\text{-a})$$

$$(CH_2)_5CO + h\nu\ (\lambda<1320) \rightarrow CH_2 = CH(CH_2)_2CH_3 + CO \qquad (69\text{-b})$$

$$(CH_2)_5 + h\nu\ (\lambda<1210) \rightarrow CH_2 = CH(CH_2)_3CHO \qquad (69\text{-c})$$

$$(CH_2)_5CO + h\nu\ (\lambda<649) \rightarrow CH_2 = CH_2 + CH_3\text{-}CH = CH_2 + CO. \qquad (69\text{-d})$$

From photochemical investigations of cyclohexanone, it was found that the yields of the various products showed a wavelength and pressure dependence. At shorter wavelengths or higher energies, the quantum yields of cyclopentane and 1-pentene are greater than at longer wavelengths [Φ = 0.21 and 0.47 (λ289), respectively; Φ = 0.03 and 0.04 (λ313), respectively]. In contrast, the quantum yield of 5-hexenal is greater at the longer wavelengths [Φ = 0.17 (λ289) and Φ = 0.32 (λ313)].[61] With the addition of a foreign gas such as oxygen, carbon dioxide, or more cyclohexanone, the yields of 1-pentene and cyclopentane decreased, while the yield of 5-hexenal increased (77-a,b). Hence, at atmospheric pressure, 5-hexenal may be the major product formed in the photolysis of cyclohexanone.

The 5-hexenal is known to react photochemically to form either 1,3-butadiene and acetaldehyde or propylene and acrolein:[67]

$$CH_2 = CH(CH_2)_3CHO + h\nu \rightarrow CH_2 = CH\text{-}CH = CH_2 + CH_3CHO \quad (70\text{-a})$$

$$CH_2 = CH(CH_2)_3CHO + h\nu \rightarrow CH_3CH = CH_2 + CH_2 = CHCHO. \quad (70\text{-b})$$

Of these products, the acetaldehyde, propylene, and acrolein are known to be highly reactive. The acetaldehyde can react photochemically or with oxygen atoms and hydroxyl radicals. Its reactions are discussed herein. The propylene cannot photodissociate; however, it can react with ozone, oxygen atoms or hydroxyl radicals:[27]

$$C_3H_6 + O_3 \rightarrow \text{products} \quad k = 1.1 \times 10^{-17}\ cm^3/\text{molecule-sec} \quad (87)$$

$$C_3H_6 + O(^3P) \rightarrow \text{products} \quad k = 3.6 \times 10^{-12} cm^3/\text{molecule-sec} \quad (88)$$

$$C_3H_6 + OH \rightarrow \text{products} \quad k = 1.53 \times 10^{-11} cm^3/\text{molecule-sec} \quad (89)$$

Some of these products include carbon dioxide, formaldehyde, acetaldehyde, formic acid, and acetic acid.[59] The acrolein may also react with these species[78] or it may photodissociate into ethylene and carbon monoxide or polymerize.[11]

$$CH_2CHCHO + O_3 \rightarrow \text{products} \quad (90)$$

$$CH_2CHCHO + O\ (^3P) \rightarrow \text{products} \quad k = 3.85 \times 10^{-13} cm^3/\text{molecule-sec} \quad (91)$$

$$CH_2CHCHO + OH \rightarrow \text{products} \quad (92)$$

$$CH_2CHCHO + h\nu \rightarrow \text{polymer} \quad (71\text{-a})$$

$$CH_2CHCHO + h\nu \rightarrow CH_2CH_2 + CO. \quad (71\text{-b})$$

The 1,3-butadiene cannot react photochemically; however, it may react with hydroxyl radicals, for example, to form a substituted allyl radical:

$$CH_2CHCHCH_2 + OH \rightarrow CH_2CH\cdot CHCH_2OH. \quad (93)$$

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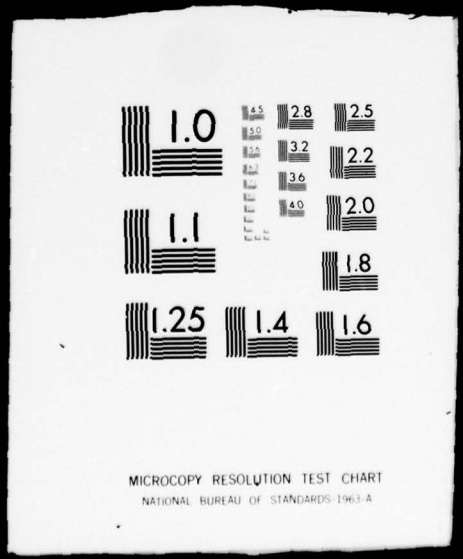


This radical may react with molecular oxygen and nitric oxide. The species formed may then decompose into acrolein and hydroxymethyl radicals. It is believed that butadiene and other 1,3-diolefins are a major source of acrolein in the atmosphere.[59]

Ketene

Ketene may photodissociate into either triplet or singlet methylene and carbon monoxide:[62]

$$CH_2CO + h\nu\ (\lambda<367) \rightarrow {}^3CH_2 + CO \qquad (72\text{-a})$$

$$CH_2CO + h\nu\ (\lambda<301) \rightarrow {}^1CH_2 + CO. \qquad (72\text{-b})$$

Triplet methylene, a species in which the two unshared electrons are unpaired is formed at both high and low wavelengths; whereas singlet methylene, a species in which the unshared electrons are paired, is formed only at the lower wavelengths ($\lambda<301$ nm). The products formed in the photolysis of ketene at wavelengths of 313, 334, and 366 nm, and at different concentrations of ketene reflect this behavior.

At the two more energetic wavelengths, the excited states decompose into ethane, acetylene, and ethylene as well as carbon monoxide. With the addition of oxygen, the yields of ethane and acetylene are eliminated, since these two products are formed from the triplet methylene:

$$^3CH_2 + CH_2CO \rightarrow CH_3 + CHCO \qquad (94)$$

$$2CH_3 \rightarrow C_2H_6 \qquad (95)$$

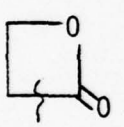
$$2CHCO \rightarrow C_2H_2 + 2CO. \qquad (96)$$

The addition of oxygen also reduces the yield of ethylene but does not wipe it out completely. Hence, it is believed that this product is formed from both singlet and triplet methylene.

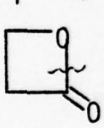
In the photolysis at 366 nm, the quantum yields for the products are much lower. Since the extinction coefficient of ketene is much lower than that at 313 nm [$\varepsilon \sim 0.07$ ℓ/mole-cm (λ366 nm) vs. $\varepsilon \sim 3.2$ ℓ/mole-cm (λ313 nm)][11], fewer radicals will be available to react. Hence ethane and acetylene were not detected as products in the photolysis of ketene at this wavelength.

Diketene

Information on the photochemistry of diketene was not available in the literature, therefore, the photochemistry of a model compound, 2-oxetanone, will be considered. In the photolysis of 2-oxetanone; carbon monoxide, carbon dioxide, ethylene, acetaldehyde, and polymer are produced. At 25°C, the quantum yields for this reaction are quite low, $\Phi_{CO} \sim 0.04$ and $\Phi_{CO_2} \sim 0.01$.[11] It can be assumed that these products may arise by ring cleavage, either between the methylene and carbonyl carbons (A) or between the oxygen and carbonyl carbon (B) to yield one of two diradical intermediates. These intermediates then decompose into products:



$$+ h\nu \rightarrow \cdot CH_2CH_2O\overset{O}{\overset{\|}{C}}\cdot \rightarrow CH_2CH_2 + CO_2 \qquad (A)$$

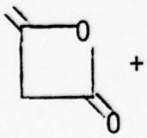


$$+ h\nu \rightarrow \cdot OCH_2CH_2\overset{O}{\overset{\|}{C}}\cdot \rightarrow \cdot OCH_2\dot{C}H_2 + CO. \qquad (B)$$

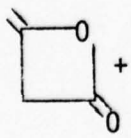
$$\downarrow$$

$$OCHCH_3$$

Diketene, 4-methylene-2-oxetanone, may decompose in an analogous manner.

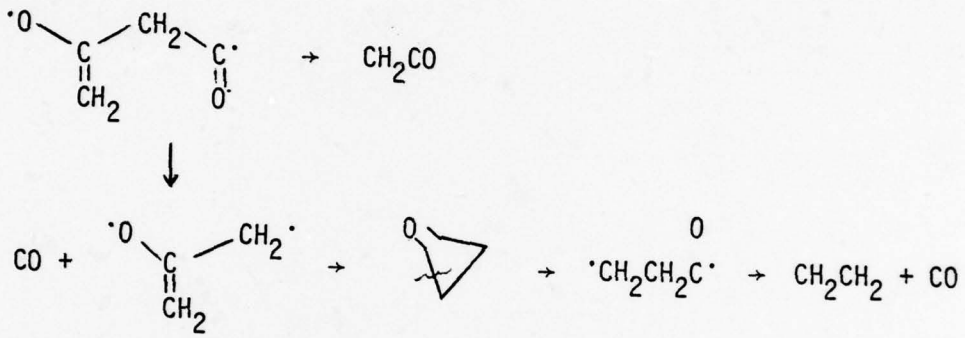


$$+ h\nu \rightarrow \cdot CH_2-\underset{\underset{CH_2}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}\cdot \rightarrow CH_2CCH_2 + CO_2 \qquad (73\text{-a})$$

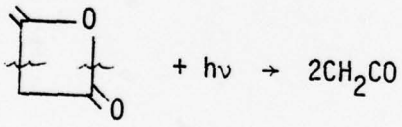


$$+ h\nu \rightarrow \cdot O-\underset{\underset{CH_2}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}\cdot \rightarrow \cdot O-\underset{\underset{CH_2}{\|}}{C}-CH_2 + CO. \qquad (73\text{-b})$$

Cleavage between the methylene and carbonyl carbons may result in the formation of allene and carbon dioxide. The formation of products via cleavage between the oxygen and carbonyl carbon is less clear. This diradical may directly decompose into ketene or into another diradical and carbon monoxide. The second diradical may momentarily form cyclopropanone which, in turn may decompose into ethylene and carbon monoxide:



Perhaps diketene can directly form ketene through a concerted mechanism:



All of this is purely speculation.

N-Nitroso Dimethylamine

In the presence of light, N-nitroso dimethylamine may photodissociate into the dimethylamino radical and nitric oxide:[69]

$$(CH_3)_2NNO + h\nu \rightarrow (CH_3)_2N + NO. \qquad (74)$$

In the atmosphere, the dimethylamino radical is capable of abstracting a hydrogen atom from such species as the hydroperoxy radical or formaldehyde:*

$$(CH_3)_2N + HO_2 \rightarrow (CH_3)_2NH + O_2 \quad \Delta H = -45.5 \text{ kcal/mole} \tag{97}$$

$$(CH_3)_2N + HCHO \rightarrow (CH_3)_2NH + CHO \quad \Delta H = -10.9 \text{ kcal/mole}. \tag{98}$$

Nitrogen Dioxide

Light can affect nitrogen dioxide in two ways. At wavelengths less than 390 nm, photodissociation can occur to yield nitric oxide and ground state atomic oxygen:

$$NO\text{-}O + h\nu \ (\lambda<390) \rightarrow NO + O(^3P). \tag{75-a}$$

In the atmosphere with a solar zenith angle of 40°C, the rate constant for the formation of nitric oxide and atomic oxygen is approximately $8 \times 10^{-3} sec^{-1}$. By calculating the half life of this reaction, it was determined that half of the nitrogen dioxide present in the atmosphere is photodissociated within 90 sec.

Competing reactions, however, are important in dictating the behavior of nitrogen dioxide in the atmosphere. In the absence of organic vapors, the atomic oxygen produced in nitrogen dioxide photolysis interacts with atmospheric molecular oxygen to generate small concentrations of ozone. The following are the major reactions that occur under these conditions:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{75-a}$$

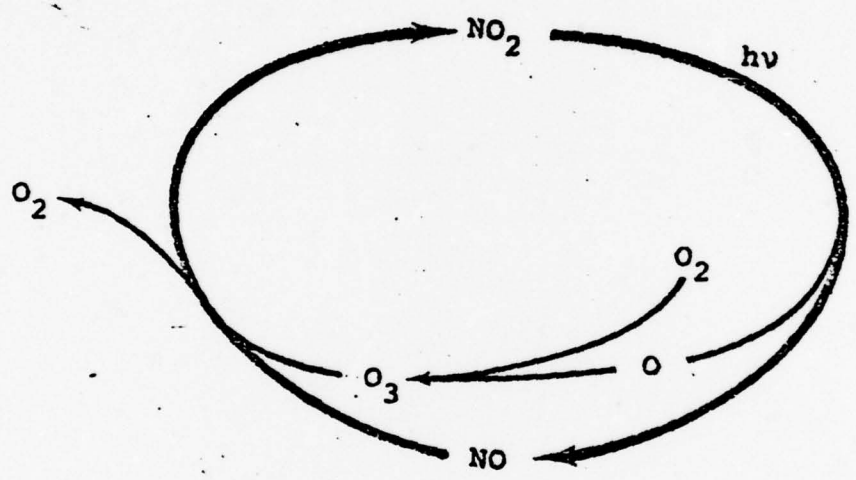
$$O + O_2 + M \rightarrow O_3 + M \tag{99}$$

$$O_3 + NO \rightarrow NO_2 + O_2. \tag{37}$$

*The enthalpies of the compounds and radicals in reactions 97 and 98 are from tables in Reference 11.

This sequence is represented below as a cycle. The condition under which the photolysis of nitrogen dioxide balances the nitric oxide oxidation by ozone is known as a photostationary state (PSS). Under the PSS assumption, the following equation may be written.

$$\frac{k_{75\text{-}a}}{k_{37}} = \frac{[NO][O_3]}{[NO_2]} .$$



Near the equinox, a $k_{75\text{-}a}$ value representative of the 4-hour period encompassing solar noon at Research Triangle Park, North Carolina would be approximately $8 \times 10^{-3} sec^{-1}$. Table 6A-18 shows the ozone levels calculated from the PSS assumption for an atmosphere initially contaminated by various levels of only nitrogen dioxide and at a light intensity equal to $8 \times 10^{-3} sec^{-1}$. Thus, for an organic-free atmosphere, slightly less than 0.4 ppm of NO_2 would be required to generate the oxidant standard (0.08 ppm), and almost insignificant quantities of ozone would result from initial nitrogen dioxide levels below 0.01 ppm.

TABLE 6A-18. OZONE LEVELS CALCULATED FROM PSS FOR AN IRRADIATED ($k_{75\text{-}a} = 8 \times 10^{-3}$ sec^{-1}) ORGANIC FREE ATMOSPHERE INITIALLY CONTAMINATED BY VARIOUS LEVELS OF NO_2

Initial $[NO_2]$, ppm	$[O_3]$, ppm
2.74	0.222
0.400	0.0848
0.250	0.067
0.100	0.042
0.050	0.03
0.025	0.0212
0.010	0.0134
0.0050	0.0095
0.0025	0.0067

At wavelengths greater than 390 nm, photodissociation cannot occur and light only serves to activate nitrogen dioxide into an excited state:*

$$NO_2 + h\nu(\lambda<390 \text{ nm}) \rightarrow NO_2^* \qquad (75\text{-b})$$

This excited NO_2^* species can then transfer its excess energy to another species present in the atmosphere. To date several studies of such quenching have been conducted on this excited state species. Transfer of energy to nitrogen dioxide, carbon dioxide, or oxygen may only result in the formation of ground state nitrogen dioxide:[59,79]

*Although wavelengths of light above 390 nm are not energetic enough to produce nitric oxide and atomic oxygen from ground nitrogen dioxide, excited state nitrogen dioxide (NO_2^*) can photodissociate at wavelengths up to 430 nm.

$$NO_2^* + NO_2 \rightarrow 2NO_2 \qquad k = 9.8 \times 10^{-12}\ cm^3/molecule\text{-}sec \qquad (100\text{-}a)$$

$$NO_2^* + CO_2 \rightarrow NO_2 + CO_2 \qquad k = 8.8 \times 10^{-12}\ cm^3/molecule\text{-}sec \qquad (101)$$

$$NO_2^* + O_2 \rightarrow NO_2 + O_2 \cdot \qquad (102\text{-}a)$$

In addition to the formation of ground state nitrogen dioxide, the transfer of energy to nitrogen dioxide, carbon monoxide, and oxygen may also result in further photochemical reactivity. The excited state nitrogen dioxide species can react with a molecule of ground state nitrogen dioxide to form nitric oxide and oxygen,[79] it can react with carbon monoxide to form nitric oxide and carbon dioxide,[80] or it can react with ground state molecular oxygen (triplet oxygen) to form nitrogen dioxide and singlet oxygen.[59]

$$NO_2^* + NO_2 \rightarrow 2NO + O_2 \qquad \Phi_{O_2} = 0.0055\ (\lambda 450) \qquad (100\text{-}b)$$

$$k = 4.2 \times 10^{-14}\ cm^3/molecule\text{-}sec$$

$$NO_2^* + CO \rightarrow NO + CO_2 \qquad k = 2.2 \times 10^{-16}\ cm^3/molecule\text{-}sec \qquad (103)$$

$$NO_2^* + O_2(^3\bar{g}) \rightarrow NO_2 + O_2\ (^1\bar{g}) \qquad \Phi_{O_2}(^1\bar{g}) \sim 0.04\ (\lambda 400) \qquad (102\text{-}b)$$

$$k \approx 1.15 \times 10^{-4} sec^{-1}$$

Although these reactions are possible, they are not very efficient. The quantum yields for the reactions of the excited state nitrogen dioxide species with ground state nitrogen dioxide and oxygen are low. Only 0.55 percent of the excited nitrogen dioxide species react with ground state nitrogen dioxide to form nitric oxide. Similarly, only 4 percent of these exicted species react with ground state molecular oxygen to form excited state oxygen.

Nitrogen Trioxide and Dinitrogen Pentoxide

At wavelengths below 567 nm, nitrogen trioxide is known only to photodissociate into nitrogen dioxide and ground state atomic oxygen:[27]

$$NO_3 + h\nu\ (\lambda<567) \rightarrow NO_2 + O(^3P)\,. \qquad (76)$$

The lifetime of nitrogen trioxide in the atmosphere is short. Depending on the wavelength of light absorbed, the half life of this species in the atmosphere is 16 to 2.66 sec. Hence, it appears that any nitrogen trioxide formed in the atmosphere may quickly photodissociate into nitrogen dioxide and atomic oxygen.

In contrast, the photolysis of dinitrogen pentoxide is not important in the chemistry of the atmosphere because the amount of light absorbed by this species is small. The products formed in this photolysis are nitrogen dioxide, nitrogen trioxide, and atomic oxygen:[59]

$$N_2O_5 + h\nu\ (\lambda<1290) \rightarrow NO_2 + NO_3 \qquad (77\text{-a})$$

$$N_2O_5 + h\nu\ (\lambda<394) \rightarrow 2NO_2 + O(^3P)\,. \qquad (77\text{-b})$$

Nitrous and Nitric Acid

Two photodissociation mechanisms are possible in the photochemistry of nitrous acid.[72] Bond breaking can occur either between the oxygen and nitrogen atoms to produce hydroxyl radicals and nitric oxide or between the hydrogen and oxygen atoms to produce atomic hydrogen and nitrogen dioxide:

$$HO\text{-}NO + h\nu\ (\lambda<475) \rightarrow HO + NO \qquad (78\text{-a})$$

$$H\text{-}ONO + h\nu\ (\lambda<362) \rightarrow H + NO_2\,. \qquad (78\text{-b})$$

From the reported quantum yield in Table 6A-17, the first route is more important. From the rate of formation of hydroxyl radicals ($k = 2.5 \times 10^{-1}$), the half life of nitrous acid in sunlight ($z = 30°$) will be approximately 280 sec.

The photochemistry of nitric acid is somewhat similar to that of nitrous acid in that numerous photodissociation mechanisms are possible.[16] Photodissociation may result in the formation of hydroxyl radicals and nitrogen dioxide, nitrous acid and ground state atomic oxygen [$O(^3P)$, hydrogen atoms and nitrogen trioxide, or nitrous acid and excited state atomic oxygen, $O(^1D)$]:

$$HO - NO_2 + h\nu \ (\lambda<578) \rightarrow HO + NO_2 \qquad (79\text{-a})$$

$$HNO_2 - O + h\nu \ (\lambda<393) \rightarrow HNO_2 + O(^3P) \qquad (79\text{-b})$$

$$H - ONO_2 + h\nu \ (\lambda<283) \rightarrow H + NO_3 \qquad (79\text{-c})$$

$$HNO_2 - O + h\nu \ (\lambda<242) \rightarrow HNO_2 + O(^1D). \qquad (79\text{-d})$$

Also like nitrous acid, only one mechanism is important in describing the photochemistry of nitric acid. At wavelengths below 325 nm, nitric acid photodissociates to form hydroxyl radicals and nitrogen dioxide.[73] However, unlike nitrous acid, the rate of formation of hydroxyl radicals is much slower. As a result of this slow rate of hydroxyl radical formation, the half life of nitric acid is quite long ($t_{1/2} = 2 \times 10^5$ sec).[59]

Nitromethane

Nitromethane absorbs light within the 240-330 nm region and photodissociates into formaldehyde and nitroxyl radicals, methyl radicals and, nitrogen dioxide or nitrosomethane and atomic oxygen:

$$CH_3NO_2 + h\nu \ (\lambda<1320) \rightarrow CH_2O + HNO \qquad (80\text{-a})$$

$$CH_3\text{-}NO_2 + h\nu \ (\lambda<476) \rightarrow CH_3 + NO_2 \qquad (80\text{-b})$$

$$CH_3NO\text{-}O + h\nu\ (\lambda<306) \rightarrow CH_3NO + O(^3P). \qquad (80\text{-}c)$$

In the gas-phase photolysis of nitromethane at 313 nm and 55°C, methyl nitrite, formaldehyde, nitrosomethane, nitric oxide, and nitrous oxide are the main products formed ($\Phi_{CH_3ONO} = 0.22$, $\Phi_{CH_2O} = 0.22$, $\Phi_{CH_2O} = 0.20$, $\Phi_{CH_3NO} = 0.06$, $\Phi_{NO} = 0.10$, and $\Phi_{NO_2} = 0.05$). Minor products include hydrogen, nitrogen, water, carbon monoxide, carbon dioxide, methane, ethane, methanol, and methyl nitrate.

From their studies of the photochemistry of nitromethane, Honda, et. al.[74] have shown that reactions 80-a and 80-b, with quantum yields of $\Phi_{CH_2O} = 0.20$ and $\Phi_{CH_3} = 0.6$, are the major modes of decomposition. Reaction pathway 80-c in which nitrosomethane is directly formed from nitromethane is relatively unimportant.

The formaldehyde and nitrogen dioxide formed during the photolysis of nitromethane will also undergo photodecomposition, the formaldehyde either into hydrogen and carbon monoxide or into hydrogen atoms and formyl radicals and the nitrogen dioxide intc nitric oxide and oxygen atoms. The methyl radical formed in reaction 80-b may react with nitric oxide to form nitrosomethane or with nitrogen dioxide to form methyl nitrite or nitromethane. In the presence of excess nitric oxide, the nitrosomethane will eventually decompose into methyl radicals, nitrogen trioxide, and nitrogen or methyl nitrate and nitrogen. The nitroxyl radical can react with itself to form water and nitrous oxide, or with oxygen to form nitric oxide and the hydroperoxy radical.

$$CH_3 + NO \rightarrow CH_3NO \qquad (104)$$

$$CH_3 + NO_2 \rightarrow CH_3ONO \qquad (105\text{-}a)$$

$$CH_3 + NO_2 \rightarrow CH_3NO_2 \qquad (105\text{-}b)$$

$$CH_3NO + 2NO \rightleftarrows CH_3\text{-}\underset{\displaystyle NO}{\underset{|}{N}}\text{-}ONO \rightarrow CH_3N_2NO_3 \qquad (106)$$

$$CH_3N_2NO_3 \rightarrow CH_3 + NO_3 + N_2 \qquad (107\text{-}a)$$

$$2HNO \rightarrow H_2O + N_2O. \qquad (108\text{-a})$$

$$HNO + O_2 \rightarrow NO + HO_2 \qquad k < 2 \times 10^{-20} \text{ cm}^3\text{/molecule-sec} \qquad (108\text{-b})$$

Because of the high concentration of oxygen in the atmosphere, the methyl radicals formed in reaction 80-b will chiefly react with molecular oxygen to form methyl peroxy radicals:

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad k = 1.2 \times 10^{-12} \text{ cm}^3\text{/molecule-sec} \qquad (109)$$

This radical species will react further with other species such as nitric oxide, nitrogen dioxide, ozone, hydroperoxy radicals, and itself. These reactions are discussed in Section 6A.2.2.3.

Methyl Nitrate

The photolysis of methyl nitrate at 253.7 nm yielded nitric oxide, nitrogen dioxide, carbon monoxide, carbon dioxide, nitrogen, and hydrogen.[81] However, in this investigation nothing was found on the possible mechanisms which may have been involved. In the photolysis of ethyl nitrate, possible mechanisms of photochemical decomposition were found and these are now discussed.

Ethyl nitrate can photochemically decompose into acetaldehyde and nitrous acid, ethoxy radicals and nitrogen dioxide, or ethyl nitrite and atomic oxygen:[75]

$$C_2H_5ONO_2 + h\nu \rightarrow CH_3CHO + HONO$$

$$C_2H_5ONO_2 + h\nu \rightarrow C_2H_5O + NO_2$$

$$C_2H_5ONO_2 + h\nu \rightarrow C_2H_5ONO + O(^3P)$$

The major products formed in the gas phase photolysis of this nitrate include ethyl nitrite, acetaldehyde, nitrogen dioxide, and oxygen. In the presence of nitric oxide and other radical scavengers, the yields of ethyl nitrite and acetaldehyde are not reduced. Hence, these products are believed to form directly from the photolysis. In fact, in the presence of a small amount of nitric oxide, the yields of these compounds increase. This increase is accounted for by the possible reactions between the ethoxy radical and nitric oxide:

$$C_2H_5O \rightarrow C_2H_5ONO$$

$$C_2H_5O + NO \rightarrow CH_3CHO + HNO.$$

Similarly, methyl nitrate may decompose into formaldehyde and nitrous acid, methoxy radicals and nitrogen dioxide, and methyl nitrite and atomic oxygen:

$$CH_3ONO_2 + h\nu \rightarrow CH_2O + HONO \qquad (81\text{-a})$$

$$CH_3O\text{-}NO_2 + h\nu\ (\lambda<920) \rightarrow CH_3O + NO_2 \qquad (81\text{-b})$$

$$CH_3ONO\text{-}O + h\nu\ (\lambda<394) \rightarrow CH_3ONO + O(^3P). \qquad (81\text{-c})$$

From these reactions, it can be assumed that the major products formed in the photolysis of methyl nitrate may include methyl nitrite, formaldehyde, nitrogen dioxide, and oxygen. The remaining products observed in the photolysis of methyl nitrate at 253.7 nm are assumed to be the products of secondary reactions, such as the photolysis of formaldehyde or nitrogen dioxide.

Except for methyl nitrite, the photochemistry of the products formed in the photolysis of methyl nitrate has been previously discussed. The methyl nitrite will photodissociate into the methoxy radical and nitric oxide:[11]

$$CH_3ONO + h\nu\ (\lambda<703) \rightarrow CH_3O + NO. \qquad (82)$$

In the atmosphere, the half life of this species is 2 minutes, compared to 3.8 days, the half life of methyl nitrate. The shorter photolytic half life of organic nitrites compared to organic nitrates is analogous to the situation found in nitrous and nitric acids (i.e., the half life of nitrous acid is 6 minutes, compared to nitric acid with a half life of 55 hours).

Ozone

The products formed in the photolysis of ozone are wavelength dependent. Based on the bond dissociation energies (see Table 6A-17), ground state atomic oxygen and either ground or excited state molecular oxygen can form from the absorption of light within the 450-700 nm wavelength region. However, the quantum yields given in Table 6A-17 for the photodissociation of ozone indicates that most of the light absorbed within this region leads to the formation of ground state atomic oxygen and ground state molecular oxygen (reaction 83-a).

The more energetic products can form from the absorption of light within the 200-350 nm region. From the quantum yields for reactions 83-b, 83-c, and 83-d in Table 6A-16, it can be seen that the ozone preferentially photodissociates into ground state atomic oxygen and excited state molecular oxygen between wavelengths of 310 and 350 nm and excited state atomic oxygen and excited state molecular oxygen between 250 and 310 nm.

Rate constants were estimated for the formation of ground state atomic oxygen, excited state atomic oxygen, and excited state molecular oxygen from the photolysis of ozone in sunlight ($z = 40°$). The rate expressions for the formation of these products from the ozone photolysis are given below:[59]

$$\frac{d[O\ (^3P)]}{dt} \sim 3.5 \times 10^{-4}\ [O_3]\ \text{sec}^{-1}$$

$$\frac{d[O(^1D)]}{dt} \sim 5.7 \times 10^{-5}\ [O_3]\ \text{sec}^{-1}$$

$$\frac{d[O_2(^1\Delta_g)]}{dt} \sim 7.2 \times 10^{-5}\ [O_3]\ \text{sec}^{-1}.$$

Sulfur Dioxide

Within the 290-800 nm region, the photolysis of sulfur dioxide can only result in the formation of excited state species. The bond dissociation energy

for $SO_2 \rightarrow SO + O(^3P)$ is 131.993 kcal/mole, and for bond dissociation to occur, a wavelength of 216 nm or less is required. In the 370-400 nm region, the absorption of light results in the formation of an excited triplet state species; and in the 240-320 nm region, both excited triplet and singlet state species may be formed:[76]

$$SO_2(^1A_1) + h\nu\ (\lambda 370 - 400) \rightarrow SO_2^*\ (^3B_1) \qquad (84\text{-a})$$

$$SO_2(^1A_1) + h\nu\ (\lambda 240 - 320) \rightarrow SO_2^*\ (^1B_1). \qquad (84\text{-b})$$

These excited state species can then react with ground state sulfur dioxide to form sulfur trioxide and sulfur oxide or decompose into a less energetic species:[82]

$$SO_2^*(^3B_1) + SO_2(^1A_1) \rightarrow SO_3 + SO(^3\Sigma^-) \qquad k = 7 \times 10^{-14}\ cm^3/molecule\text{-}sec \qquad (110)$$

$$SO_2^*(^1B_1) + SO_2(^1A_1) \rightarrow SO_3 + SO(^3\Sigma^-) \qquad k = 3.7 \times 10^{-12}\ cm^3/molecule\text{-}sec \qquad (111\text{-a})$$

$$SO_2^*(^1B_1) + SO_2(^1A_1) \rightarrow SO_2^*(^3B_1) + SO_2(^1A_1) \qquad k = 3.0 \times 10^{-2} cm^3/molecule\text{-}sec \qquad (111\text{-b})$$

$$SO_2^*(^1B_1) \rightarrow SO_2 + h\nu \qquad k = 8.8 \times 10^4\ sec^{-1} \qquad (112\text{-a})$$

$$SO_2^*(^1B_1) \rightarrow SO_2^*\ (^3B_1) \qquad k = 2 \times 10^3\ sec^{-1} \qquad (112\text{-b})$$

$$SO_2^*(^3B_1) \rightarrow SO_2 + h\nu \qquad k = 1.4 \times 10^2\ sec^{-1} \qquad (113\text{-a})$$

$$SO_2^*(^3B_1) \rightarrow SO_2 \qquad k = 1.3 \times 10^2\ sec^{-1} \qquad (113\text{-b})$$

$$SO_2^*(^3B_1) + M \rightarrow SO_2 + M \qquad k = 1.4 \times 10^{-13}\ cm^3/molecule\text{-}sec. \qquad (113\text{-c})$$

The sulfur oxide species formed can further react with itself to form sulfur dioxide and sulfur or with sulfur trioxide to form two equivalents of sulfur dioxide:[76]

$$2SO \rightarrow SO_2 + S \text{ [or}(SO_2)] \qquad k < 3 \times 10^{-15} \text{ cm}^3\text{/molecule-sec} \qquad (114)$$

$$SO + SO_3 \rightarrow 2SO_2 \qquad k = 2.0 \times 10^{-15} \text{ cm}^3\text{/molecule-sec.} \qquad (115)$$

Known or Potential Secondary Reactions

In the two preceding sections, the known and potential ground state and excited state reactions of compounds emitted during the production of RDX were discussed. These reactions will produce other species in the atmosphere: atomic hydrogen, molecular hydrogen, hydroxyl radicals, hydroperoxy radicals, hydrogen peroxide, atomic oxygen at two different energy levels, molecular oxygen, ozone, carbon monoxide, carbon dioxide, triplet and singlet methylene, methyl radicals, ethyl radicals, ethylene, allene, cyclopentane, 1-pentene, formyl radicals, formate radicals, peroxy formyl radicals, acetyl radicals, propionyl radicals, acetonyl radicals, organic peroxides, peracetic acid, pyruvic aldehyde, biacetyl, 5-hexenal, esters of acetoacetic acid, adipic acid, dehydroacetic acid, nitrosomethane, methyl nitrite, sulfoacetic anhydride, nitrogen trioxide, dinitrogen trioxide, dinitrogen pentoxide, nitroxyl radicals, nitrous acid, sulfur oxide, sulfur trioxide, sulfuric acid, and of course, water. These newly formed species, some of which are highly reactive, may combine with each other or with emitted compounds. The known or potential reactions which may occur between these reactive species and the compounds originally emitted are listed in Table 6A-19. For the known reactions, the rate expression, conditions under which the rate expressions and constants were determined, the rate constants at a particular temperature, and the literature reference are also shown. For potential reactions for which the rate constants are not available, the heat of formation or the rate constant of an analogous reaction involving a similar compound are reported as evidence of feasibility.

TABLE 6A-19. KNOWN OR POTENTIAL SECONDARY REACTIONS OF EMISSIONS FROM HAAP

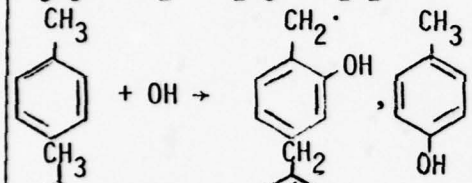
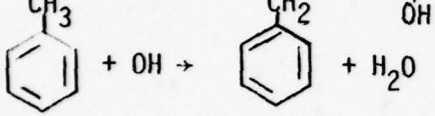
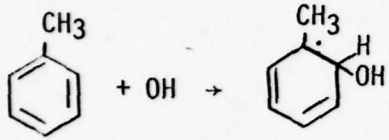
No.	Reaction	Rate Expression	Condition	T(K)	Rate Constants[a,b,c,d,e] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constants[a,b,c,d,e] $k\frac{l}{ppm\text{-}min}$	Ref.
116	$CH_4 + O(^3P) \rightarrow CH_3 + OH$	$k_{116}[CH_4][O]$		350	7.8×10^{-17}	1.2×10^{-2}	27
117	$CH_4 + OH \rightarrow CH_3 + H_2O$	$k_{117}[CH_4][OH]$	1 atm	298	7.6×10^{-15}	1.1×10	83
118	$C_2H_6 + O(^3P) \rightarrow C_2H_5 + OH$	$k_{118}[C_2H_6][O]$		300	9.4×10^{-16}	1.4	27
119	$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$k_{119}[C_2H_6][OH]$		295	2.64×10^{-13}	3.9×10^{2}	84
120	$C_6H_6 + HO_2 \rightarrow C_2H_5 + H_2O_2$	$k_{120}[C_2H_6][HO_2]$		300	1.1×10^{-22}	1.6×10^{-7}	27
121		$k_{121}[C_7H_8][O]$		298	7.5×10^{-14}	1.1×10^{2}	85,86
122-a		$k_{121a}[C_7H_8][OH]$		298	1×10^{-12}	1.5×10^{3}	87
122-b		$k_{122b}(C_7H_8][OH]$		298	6.4×10^{-12}	9.5×10^{3}	87
123	$CO + OH \rightarrow CO_2 + H$	$k_{123}[CO][OH]$	1 atm	298	$\frac{1.4 \times 10^{-13}}{2.7 \times 10^{-13}}$	$\frac{2.07 \times 10^{2}}{4.0 \times 10^{2}}$	27 83
124	$CO + HO_2 \rightarrow CO_2 + OH$	$k_{124}[CO][HO_2]$		300	$<1 \times 10^{-19}$	$<1.5 \times 10^{-4}$	27

TABLE 6A-19. (cont'd)

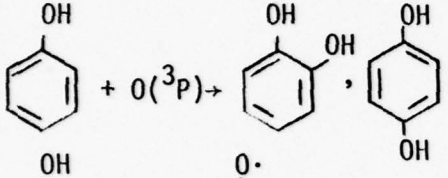
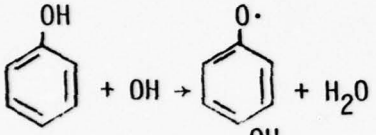
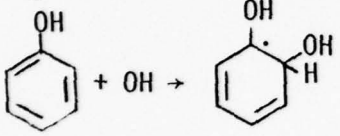
No.	Reaction	Rate Expression	Condition	T(K)	Rate Constants[a,b,c,d,e] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constants[a,b,c,d,e] $k\frac{l}{ppm\text{-}min}$	Ref.
125	$CH_3OH + O(^3P) \rightarrow CH_2OH + OH$	$k_{125}[CH_4O][CO]$		298	6.2×10^{-14}	9.2×10	88
126	$CH_3OH + OH \rightarrow CH_2OH + H_2O$	$k_{126}[CH_4O][OH]$		292	9.5×10^{-13}	1.4×10^{3}	89
127	$RCH_2OH + ((^3P) \rightarrow RCHOH + OH$	$k_{127}[RCH_2OH][CO]$		298	1.0×10^{-13}	1.5×10^{2}	90
128	$C_3H_7OH + OH \rightarrow C_3H_6OH + H_2O$	$k_{128}[C_3H_8O][OH]$		292	3.8×10^{-12}	5.6×10^{3}	89
129	$C_4H_9OH + OH \rightarrow C_4H_8OH + H_2O$	$k_{129}[C_4H_{10}O][OH]$		292	6.8×10^{-12}	1.0×10^{4}	89
130		$k_{130}[C_6H_5O][O]$		---	---	---	---
131-a		$k_{131a}[C_6H_5O][OH]$		---	---	---	91
131-b		$k_{131b}[C_6H_5O][OH]$		299	3.2×10^{-11}	4.7×10^{4}	92
132	$CH_2O + O(^3P) \rightarrow CHO + OH$	$k_{132}[C_6H_5O][OH]$		300	1.6×10^{-13}	2.4×10^{2}	27
133	$CH_2O + OH \rightarrow CHO + H_2O$	$k_{133}[CH_2O][OH]$		300	1.4×10^{-11}	2.1×10^{4}	27
134	$CH_2O + HO_2 \rightarrow CHO + H_2O_2$	$k_{134}[CH_2O][HO_2]$		300	2.7×10^{-17}	4.0×10^{-2}	27

TABLE 6A-19. (cont'd)

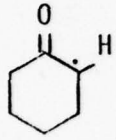
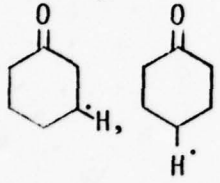
No.	Reaction	Rate Expression	Condition	T(K)	Rate Constants[a,b,c,d,e] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constants[a,b,c,d,e] $k\frac{l}{ppm\text{-}min}$	Ref.
135	$CH_3CHO + O(^3P) \rightarrow CH_3CO + OH$	$k_{135}[C_2H_4O][O]$		300	4.78×10^{-13}	7.07×10^{2}	93
136	$CH_3CHO + OH \rightarrow CH_3CO + H_2O$	$k_{136}[C_2H_4O][OH]$	1 atm	298	2.0×10^{-11}	3.0×10^{4}	94
137	$(CH_3)_2CO + O(^3P) \rightarrow CH_2COCH_3 + OH$	$k_{137}[C_3H_6O][CO]$		298	4.2×10^{-11}	6.2×10^{4}	95
138	$(CH_3)_2CO + OH \rightarrow CH_2COCH_3 + H_2O$	$k_{138}[C_3H_6O][OH]$		298	$\sim 1.3 \times 10^{-12}$	$\sim 1.9 \times 10^{3}$	95
139	$CH_3COCH_2CH_3 + O(^3P) \rightarrow CH_3COCHCH_3 + OH$	$k_{139}[C_4H_8O][O]$		---	---	---	---
140	$CH_3COCH_2CH_3 + OH \rightarrow CH_3COCHCH_3 + H_2O$	$k_{140}[C_4H_8O][OH]$		305	3.3×10^{-12}	4.9×10^{3}	96
141	$+ O(^3P) \rightarrow C_6H_9O + OH$	$k_{141}[C_6H_{10}O][O]$		---	---	---	---
142-a	$+ OH \rightarrow$  $+ H_2O$	$k_{142a}[C_6H_{10}O][OH]$		---	1.3×10^{-12}	1.9×10^{3}	97
142-b	$+ OH \rightarrow$  $, H_2O$	$k_{142b}[C_6H_{10}O][OH]$		---	5×10^{-2}	7.4×10^{3}	97

TABLE 6A-19. (cont'd)

No.	Reaction	Rate Expression	Condition	T(K)	Rate Constants[a,b,c,d,e] $k\frac{cm^3}{molecule\text{-}sec}$	$k\frac{l}{ppm\text{-}min}$	Ref.
143	$CH_2CO + O(^3P) \rightarrow 2CHO$	$k_{143}[C_2H_2O][O]$		293	5.7×10^{-13}	8.4×10^{2}	98
144	$CH_2CO + OH \rightarrow$ products	$k_{144}[C_2H_2][OH]$		---	$\sim 1.7 \times 10^{-12}$	$\sim 2.5 \times 10^{3}$	98
145	$C_4H_4O_2 + O(^3) \rightarrow$ products	$k_{145}[C_4H_4O_2][O]$		---	---	---	---
146	$C_4H_4O_2 + OH \rightarrow$ products	$k_{146}[C_4H_4O_2][OH]$		---	---	---	---
147	$HCOOH + O(^3P) \rightarrow COOH + OH$	$k_{147}[CH_2O_2][O]$		300	ΔH=-9.7kcal/mole	---	60
148	$HCOOH + OH \rightarrow$ products	$k_{148}[CH_2OH_2][OH]$	pH 2-5	298	2.3×10^{-13}	3.4×10^{2}	99
149	$CH_3COOH + O(^3P) \rightarrow CH_2COOH + OH$	---		300	$\Delta H \sim$-4.5 kcal/mole		60
150	$CH_3COOH + OH \rightarrow$ products	$k_{150}[C_2H_4O_1][OH]$	pH 2	293	3.2×10^{-14}	4.7×10	99
151	$HCOOR + O(^3P) \rightarrow COOR + OH$	$k_{151}[HCO_2R][O]$	$R = CH_3$	300	$\Delta H \sim$-9.7kcal/mole		60
152	$HCOOR + OH \rightarrow COOR + H_2O$	$k_{152}[HCO_2R][OH]$	$R = CH_3$	300	$\Delta H \sim$-28.8kcal/mole		60
153	$CH_3COOCH_2R + O(^3P) \rightarrow CH_3CO_2CHR+OH$	$k_{153}[C_3H_5O_2R][O]$	R = H	300	$\Delta H \sim$-4.5kcal/mole		60
154	$CH_3COOCH_2R + OH \rightarrow CH_3CO_2CHR + H_2O$	$k_{154}[C_3H_5O_2R][OH]$	R = H	300	$\Delta H \sim$-21.5kcal/mole		60
155	$NH_3 + O(^3P) \rightarrow NH_2 + OH$	$k_{155}[NH_3][O]$		300	1.0×10^{-16}	1.5×10^{-1}	27
156	$NH_3 + OH \rightarrow NH_2 + H_2O$	$k_{156}[NH_3][OH]$		298	1.64×10^{-13}	2.42×10^{2}	100
157	$CH_3NH_2 + OH \rightarrow$ products	$k_{157}[CH_5N][OH]$		298	2.20×10^{-11}	3.26×10^{4}	101
158	$(CH_3)_2NH + OH \rightarrow$ products	$k_{158}[C_2H_7N][OH]$		298	$>2.2 \times 10^{-11}$	$>3.3 \times 10^{4}$	101
159	$NO + O\ (^3P) + M \rightarrow NO_2 + M$	$k_{159}[NO][O]$	$M = N_2$	295	3.0×10^{-11}	4.4×10^{3}	102

TABLE 6A-19. (cont'd)

No.	Reaction	Rate Expression	Condition	T(K)	Rate Constants[a,b,c,d,e] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constants[a,b,c,d,e] $k\frac{l}{ppm\text{-}min}$	Ref.
160	$NO + OH + M \rightarrow HONO + M$	$k_{160}[NO][OH]$	$M=N_2,O_2$ 1 atm	298	$\frac{5.6 \times 10^{-12}}{1.17 \times 10^{-11}}$	$\frac{8.3 \times 10^{3}}{1.73 \times 10^{4}}$	27 83
161-a	$NO + H_2O \rightarrow NO_2 + OH$	$k_{161a}[NO][HO_2]$		298	1.6×10^{-12}	2.4×10^{3},f	27
161-b	$NO + HO_2 + M \rightarrow HONO_2 + M$	$k_{161b}[NO][HO_2]$	$M=N_2,O_2$ 1 atm	298	1.8×10^{-13}	2.7×10^{2},f	104
162-a	$NO_2 + O(^3P) \rightarrow NO + O_2$	$k_{162a}[NO_2][O]$		293-339	9.12×10^{-12}	1.35×10^{4}	105
162-b	$NO_2 + O(^3P) + M \rightarrow NO_3 + M$	$k_{162b}[NO_2][O][M]$	$M = N_2$	298	1.0×10^{-31}	3.6×10^{3}	27
163	$NO_2 + OH + M \rightarrow HNO_3 + M$	$k_{163}[NO_2][OH]$	$M = N_2$	296	$\frac{4.5 \times 10^{-12}}{1.6 \times 10^{-11}}$	$\frac{6.6 \times 10^{3}}{2.4 \times 10^{4}}$	27 106a
164-a	$NO_2 + HO \rightarrow HNO_2 + O_2$	$k_{164a}[NO_2][HO_2]$		300	$\sim 3 \times 10^{-14}$	$\sim 4 \times 10^{9}$	27
164-b	$NO_2 + HO_2 \quad HO_2NO_2$	$k_{164b}[NO_2][HO_2]$		298	4.83×10^{-13}	7.15×10^{2},g	107
165	$N_2O + OH \rightarrow N_2 + HO_2$	$k_{165}[N_2O][OH]$		298	3.8×10^{-17}	5.6×10^{-2}	108
166	$NO_3 + HO_2 \rightarrow HNO_3 + O_2$	$k_{166}[NO_3^2][HO_2]$		298	1.69×10^{-12}	2.5×10^{3}	59
167	$N_2O_5 + O(^3P) \rightarrow$ products	$k_{167}[N_2O_5][O]$		300	$<2 \times 10^{-13}$	$<3 \times 10^{2}$	27
168	$HNO_2 + O(^3P) \rightarrow NO_2 + OH$	$k_{168}[HNO_2][O]$		300	$\geq 1.5 \times 10^{-14}$	$\geq 2.2 \times 10$	27
169	$HNO_2 + OH \rightarrow NO_2 + H_2O$	$k_{169}[HNO_2][OH]$	1 atm	300	2.2×10^{-12}	3.3×10^{3}	104
170	$HNO_3 + O(^3P) \rightarrow NO_3 + OH$	$k_{170}[HNO_3][O]$		300	1.5 x 10-14	<2.2 x 10	27

TABLE 6A-19. (cont'd)

No.	Reaction	Rate Expression	Condition	T(K)	Rate Constants[a,b,c,d,e] $k\frac{cm^3}{molecule\text{-}sec}$	Rate Constants[a,b,c,d,e] $k\frac{l}{ppm\text{-}min}$	Ref.
171	$HNO_3 + OH \rightarrow NO_3 + H_2O$	$k_{171}[HNO_3][OH]$		295	9.5×10^{-14}	1.4×10^{2}	109
172	$CH_3NO_2 + O(^3P) \rightarrow CH_2NO_2 + OH$	$k_{172}[CH_3NO_2^2[O]$		295	3.2×10^{-15}	4.7	110
173	$CH_3NO_2 + OH \rightarrow CH_2NO_2 + H_2O$	$k_{173}[CH_3NO_2^2[OH]$		292	9.1×10^{-13}	1.4×10^{3}	111
174	$CH_3ONO_2 + O(^3P) \rightarrow CH_2ONO_2 + OH$	$k_{174}[CH_3NO_3][O]$		300	3.7×10^{-15}	5.5	112
175	$CH_3ONO_2 + OH \rightarrow CH_2ONO_2 + H_2O$	$k_{175}[CH_3NO_2][OH]$		---	---	---	---
176	$O_2 + O(^3P) + M \rightarrow O_3 + M$	$k_{176}[O_2][O][M]$	$M = N_2$	300	5.8×10^{-34}	2.1×10^{-5}	27
177	$O_3 + OH \rightarrow O_2 + HO_2$	$k_{177}[O_3][OH]$		300	5.7×10^{-14}	8.3×10	27
178	$O_3 + HO_2 \rightarrow 2\ O_2 + OH$	$k_{178}[O_3][HO_2]$		300	1.5×10^{-15}	2.2	27
179	$SO_2 + O(^3P) + M \rightarrow SO_3 + M$	$k_{179}[SO_2][O][M]$	$M = N_2$	300	7.8×10^{-34}	2.8×10^{-5}	27
180	$SO_2 + OH + M \rightarrow HOSO_2 + M$	$k_{180}[SO_2][OH]$	$M = N_2$ 1 atm	297	6.0×10^{-13}	8.9×10^{2}	113
181	$SO_2 + HO_2 \rightarrow SO_3 + OH$	$k_{181}[SO_2][HO_2]$		300	9×10^{-16}	1.3	27
182	$SO_3 + O(^3P) \rightarrow SO_2 + O_2$	$k_{182}[SO_3][O]$		300	5.7×10^{-17}	8.4×10^{-2}	27

TABLE 6A-19. (cont'd)

No	Reaction	Rate Expression	Condition	T(K)	Rate Constants[a,b,c,d,e] $k\frac{cm^3}{molecule\text{-}sec}$	$k\frac{1}{ppm\text{-}min}$	Ref.
183	$SO + O_2 \rightarrow SO_2 + O(^3P)$	$K_{183}[SO][O_2]$		300	$<8 \times 10^{-17}$	$<1 \times 10^{-1}$	27
184	$SO + O_3 \rightarrow SO_2 + O_2$	$k_{184}[SO][O_3]$		300	7.55×10^{-14}	1.12×10^{2}	27

[a]The rate constants for reactions 162-b, 176, and 179 are in units of $cm^6/molecule^2$-sec. A complete listing of reactions and rate constants can be found in Appendix 1.

[b]To convert from units of $cm^3/molecule$-sec to ppm^{-1}-min^{-1}, multiply the former unit by 1.478×10^{15}; to convert from $cm^6/molecule^2$-sec to ppm^{-2}-min^{-1}, multiply by 3.64×10^{28}.

[c]In reaction 127, R = CH_3.

[d]The rate constant for reaction 131-b is the rate constant for the addition of hydroxyl radicals to o-cresol.

[e]The rate constants for reactions 138 and 144 are estimated.

[f]Since reaction 161-a is the predominant reaction pathway between nitric oxide and hydroperoxy radicals, reaction 161-b may have little importance in atmospheric chemistry. Hence, $k_{161b} \sim 0$, see Reference 103.

[g]Since reaction 164-b is the predominant reaction pathway between nitrogen dioxide and hydroperoxy radicals, reaction 164-a may have little importance in atmospheric chemistry. Hence $k_{164a} \sim 0$, see Reference 103.

Carbon Monoxide

Compared to the ground state reactions, the reactions between an emitted compound and a particular reactive species are generally much faster and, as a result, of more importance to the chemistry of this atmosphere. For example, carbon monoxide, a species which reacts slowly with ozone and is unreactive to light at these wavelengths, reacts rapidly with hydroxyl radicals to form atomic hydrogen and the relatively unreactive species, carbon dioxide.[83] The atomic hydrogen then reacts quickly with species present in the atmosphere. A dominant reaction is that between atomic hydrogen and molecular oxygen to yield hydroperoxy radicals:[59]

$$H + O_2 + M \rightarrow HO_2 + M \ (M = O_2, N_2) \quad k = 4.67 \times 10^{-32} \text{ cm}^6/\text{molecule}^2\text{-sec} \quad (185)$$

It has been noted, in both smog chamber and computer simulation studies,[59] that the presence of small amounts of carbon monoxide in a moist, NO_x-polluted, and hydrocarbon-free atmosphere enhances the reactivity of the system. This increased activity is evidenced by increased concentrations of nitrogen dioxide, ozone, and atomic oxygen, and the formation of hydrogen peroxide. The increase in nitrogen dioxide and ozone concentrations is the direct result of the presence of the carbon monoxide, the formation of the hydroperoxy radical, and the subsequent oxidation of nitric oxide to nitrogen dioxide:[27]

$$NO + HO_2 \rightarrow NO_2 + OH. \quad (161\text{-a})$$

The newly formed hydroxyl radical will eventually react with a species present in the atmosphere, conceivably with another carbon monoxide molecule to repeat the cycle of reactions 123, 185, and 161-a.[59]

Methane and Ethane

Since the atmospheric chemistries of methane and ethane are similar, the decomposition of these two hydrocarbons (RCH_3, where R + H or CH_3) will be discussed concurrently. Both hydrocarbons initially react with oxygen atoms, hydroxyl radicals, or hydroperoxy radicals to form either the methyl or ethyl radicals (RCH_2). The dominant reaction is that between the hydrocarbon and hydroxyl radical.

$$RCH_3 + O(^3P) \rightarrow RCH_2 + OH \quad (186)$$

$$RCH_3 + OH \rightarrow RCH_2 + H_2O \quad (187)$$

$$RCH_3 + HO_2 \rightarrow RCH_2 + H_2O_2 \,. \quad (188)$$

The majority of the alkyl radicals then react with oxygen to form the alkyl peroxy radical (RCH_2O_2):[114,59]

$$RCH_2 + O_2(M) \rightarrow RCH_2O_2(M) \quad (M=N_2)\ k_{R=H}=1.2 \times 10^{-12} cm^3/molecule\text{-}sec \quad (109)$$

$$k_{R=CH_3} = 6.8 \times 10^{-12} cm^3/molecule\text{-}sec \,.$$

A small fraction of the methyl and ethyl radicals, however, may react with atomic oxygen[115] or ozone[116] to form the corresponding aldehyde, i.e., formaldehyde in the case of the methyl radical and acetaldehyde in the case of the ethyl radical. The alkyl species also may react with nitrogen dioxide to yield an alkoxy radical and nitric oxide.[27]

$$RCH_2 + O(^3P) \rightarrow RCHO + H \quad k_{R=H} = 1.2 \times 10^{-10}\ cm^3/molecule\text{-}sec \quad (189)$$

$$RCH_2 + O_3 \rightarrow RCH_2O + O_2 \quad k_{R=H} = 1.6 \times 10^{-13}\ cm^3/molecule\text{-}sec \quad (190)$$

$$RCH_2 + NO_2 \rightarrow RCH_2O + NO \quad k_{R=H} = 3.3 \times 10^{-11}\ cm^3/molecule\text{-}sec \,. \quad (191)$$

Because the concentration of molecular oxygen is much greater than that of atomic oxygen, ozone, or nitrogen dioxide, the reaction between the alkyl radical and molecular oxygen is the dominant reaction occurring in the atmosphere.

The alkyl peroxy radical formed in reaction 109 will further react with ozone[116], hydroperoxy radical[27], alkyl peroxy radical[115,59], nitric oxide[117,59], or nitrogen dioxide.[117,118] In the atmosphere, the reaction with nitric oxide is expected to dominate.

$$RCH_2O_2 + O_3 \rightarrow \text{products} \qquad k_{R=H} = 2.4 \times 10^{-17} cm^3/\text{molecule-sec} \qquad (192)$$

$$RCH_2O_2 + HO_2 \rightarrow RCH_2O_2H + O_2 \qquad k_{R=H} = 6.7 \times 10^{-14} cm^3/\text{molecule-sec} \qquad (193\text{-a})$$

$$\rightarrow RCH_2O + OH \qquad (193\text{-b})$$

$$RCH_2O_2 + R'CH_2O_2 \rightarrow RCH_2O + R'CH_2O + O_2 \quad (R'=H)\ k_{R=H} = 1.6 \times 10^{-13} cm^3/\text{molecule-sec} \qquad (194\text{-a})$$

$$(R'=\text{alkyl})\ k_{R=H} \sim 6.8 \times 10^{-14} cm^3/\text{molecule-sec}$$

$$\left.\begin{array}{l} \rightarrow RCH_2OH + RCHO + O_2 \\ \rightarrow (RCH_2O)_2 + O_2 \end{array}\right\} (R'=H)\ k_{R=H} = 3.05 \times 10^{-13} cm^3/\text{molecule-sec} \qquad (194\text{-b})$$

$$RCH_2O_2 + NO \rightarrow RCH_2O + NO_2 \qquad k_{R=H} = 1.2 \times 10^{-12}\ cm^3/\text{molecule-sec} \qquad (195)$$

$$k_{R=H} = 3.2 \times 10^{-13}\ cm^3/\text{molecule-sec}$$

$$RCH_2O_2 + NO_2 \rightarrow RCH_2O_2NO_2 \qquad k_{R=H} \sim 1.2 \times 10^{-12}\ cm^3/\text{molecule-sec} \qquad (196\text{-a})$$

$$\xrightarrow{NO} RCH_2ONO + NO_3 \qquad (197)$$

$$\xrightarrow{NO_2} RCH_2ONO_2 + NO_3 \qquad (198)$$

$$\rightarrow RCHO + HONO_2\ . \qquad (196\text{-b})$$

The alkoxy radical formed in these preceding reactions will most likely react with oxygen, nitric oxide, or nitrogen dioxide.[59,17]

$$RCH_2O + O_2 \rightarrow RCHO + HO_2 \qquad k_{R=H} = 1.8 \times 10^{-15} cm^3/molecule\text{-}sec \qquad (197)$$

$$k_{R=CH_3} \sim 3.8 \times 10^{-17} cm^3/molecule\text{-}sec$$

$$RCH_2O + NO \rightarrow RCH_2ONO \qquad k_{R=H} \sim 1.7 \times 10^{-13} cm^3/molecule\text{-}sec \qquad (198\text{-}a)$$

$$k_{R=CH_3} \sim 1.4 \times 10^{-13} cm^3/molecule\text{-}sec$$

$$\rightarrow RCH_2O + HNO \qquad k_{R=H} \sim 2.9 \times 10^{-14} cm^3/molecule\text{-}sec \qquad (198\text{-}b)$$

$$k_{R=CH_3} \sim 3 \times 10^{-14} cm^3/molecule\text{-}sec$$

$$RCH_2O + NO_2 \rightarrow RCH_2ONO_2 \qquad k_{R=H} = 3.3 \times 10^{-13} cm^3/molecule\text{-}sec \qquad (199\text{-}a)$$

$$k_{R=CH_3} \sim 2.0 \times 10^{-13} cm^3/molecule\text{-}sec$$

$$\rightarrow RCHO + HONO \qquad k_{R=H} = 3.3 \times 10^{-14} cm^3/molecule\text{-}sec \qquad (199\text{-}b)$$

$$k_{R=CH_3} \sim 4.0 \times 10^{-14} cm^3/molecule\text{-}sec .$$

In addition, the methoxy radical is also known to react with carbon monoxide, methane, and formaldehyde.[59]

$$CH_3O + CO \rightarrow CH_3 + CO_2 \qquad k = 5.5 \times 10^{-14} \ cm^3/molecule\text{-}sec \qquad (200)$$

$$CH_3O + CH_4 \rightarrow CH_3OH + CH_3 \qquad k = 9.5 \times 10^{-21} \ cm^3/molecule\text{-}sec \qquad (201)$$

$$CH_3O + CH_2O \rightarrow CH_3OH + CHO \qquad k = 1.0 \times 10^{-15} \ cm^3/molecule\text{-}sec. \qquad (202)$$

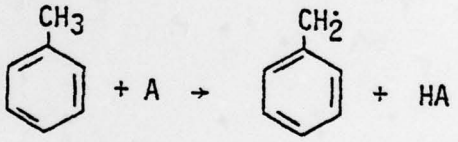
The ethoxy radical also may decompose into formaldehyde and methyl radicals:[59]

$$CH_3CHO \rightarrow CH_3 + CH_2O \qquad k = 3.3 \times 10\ sec^{-1} \tag{203}$$

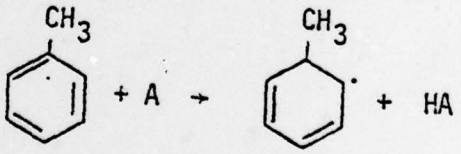
The fate of the products formed in the decomposition of the alkoxy radicals (formaldehyde, acetaldehyde, methyl nitrite, ethyl nitrite, nitroxyl radicals, methyl nitrate, ethyl nitrate, nitrous acid, and methanol) will be discussed in the following sections.

Toluene and Phenol

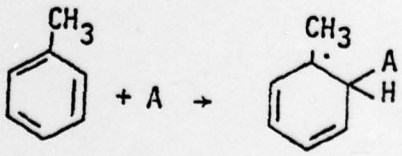
Toluene can react with such reactive species as ozone, atomic oxygen, hydroxyl radicals, and other free radicals. Both hydroxyl radicals and atomic oxygen are thought to react by hydrogen abstraction from either the methyl or phenyl portion of the molecule as well as by addition to the aromatic ring.



(C)



(D)

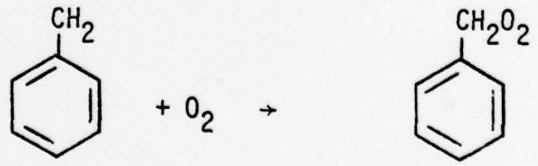


(E)

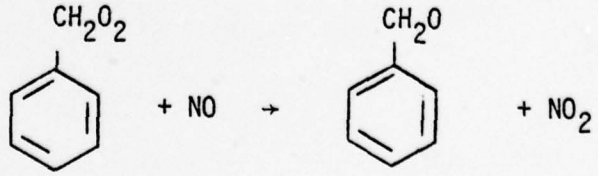
Since the dissociation energy of the methyl carbon-hydrogen bond is less than that of the phenyl carbon-hydrogen bond ($D^{\circ}_{H_2C-H}$ = 88.3 kcal/mole and $D^{\circ}_{C_{Ar}-H}$ = 110.5 kcal/mole*)[179], it is believed that hydrogen abstraction from the methyl group is the more important of the two abstraction pathways.

The products identified in the oxidation of toluene by atomic oxygen indicate that the oxygen initially attacks the aromatic ring and the intermediate subsequently rearranges to form cresols, most of which were identified as the ortho and para isomers. Of the cresols formed, the quantity of ortho-cresol was found to be three or four times that of para-cresol. The meta isomer formed less than 4 percent of the total concentration of cresol isomers. In addition to these cresol isomers, polymer material also forms.[120]

From thermochemical data,[60] it is believed that the oxygen atom may also abstract a hydrogen atom from the methyl group to form the benzyl and hydroxyl radicals (ΔH_f = -17.2 kcal/mole). The benzyl radical may then react with molecular oxygen to form the peroxy benzyl radical. This species may oxidize nitric oxide yielding the benzyloxy radical and nitrogen dioxide in a reaction analogous to that of the methyl peroxy radical (reaction 195). The benzyloxy radical may then react with molecular oxygen or nitrogen dioxide. Benzaldehyde is formed by the reaction with oxygen via a route that is analogous to that of the methoxy radical to formaldehyde (reaction 197). The reaction of the benzyloxy radical with nitrogen dioxide yields benzyl nitrate via a route analogous to that for methyl nitrate formation (reaction 199-a). In most cases the formation of benzaldehyde should be the dominant pathway.

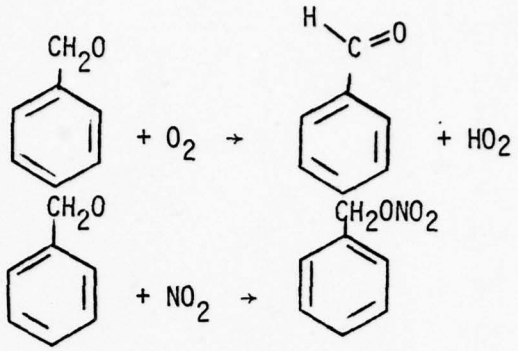


(204)



(205)

*Bond dissociation energy for benzene.



(206)

(207)

The benzaldehyde may absorb light to form an electronically excited molecule which generally does not decompose but returns to the ground state:[59]

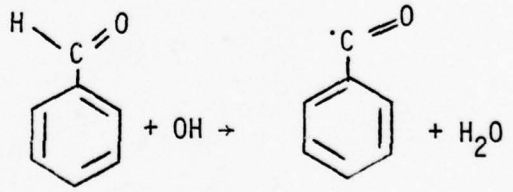
$$C_6H_5CHO + h\nu \rightarrow C_6H_5CHO^* \quad (208)$$

$$C_6H_5CHO^* + M \rightarrow C_6H_5CHO + M. \quad (209)$$

However, the excited benzaldehyde may react with oxygen to form ground state benzaldehyde and singlet oxygen:[59]

$$C_6H_5CHO^* + O_2 \rightarrow C_6H_5CHO + O_2\ (^1\Delta_g). \quad (210)$$

In addition to its photochemical reactions, the benzaldehyde may react with oxygen atoms or hydroxyl radicals, for example, to form a benzoyl radical:



(211)

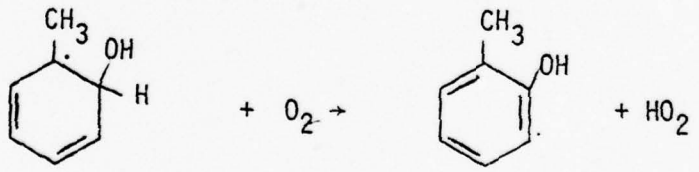
Like the formyl radical in the oxidation of methane (reactions 236 and 239) the benzoyl radical may further react to produce peroxybenzoyl nitrate (PBN):[59]

$$C_6H_5\overset{\overset{O}{\|}}{C}\cdot + O_2 \rightarrow C_6H_5\overset{\overset{O}{\|}}{C}O_2 \qquad (212)$$

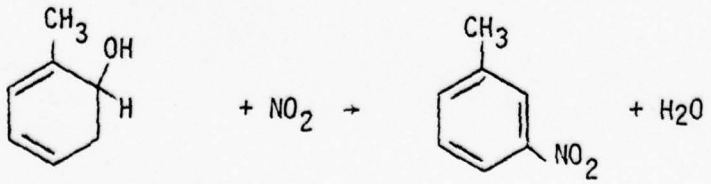
$$C_6H_5\overset{\overset{O}{\|}}{C}O_2 + NO_2 \rightarrow C_6H_5\overset{\overset{O}{\|}}{C}O_2NO_2 \qquad (213)$$

Although it is believed that only trace quantities of this compound will form, it is a recognized irritant at low concentrations.

The hydroxyl radical, the dominant reactive species in the atmospheric oxidation, may also abstract a methyl hydrogen or add onto the aromatic ring.[87] It has been suggested that at room temperature abstraction is a minor pathway and that addition to the ring occurs over 80 percent of the time. Abstraction of a methyl hydrogen would eventually lead to the formation of benzaldehyde and to subsequent products such as PBN. Addition of a hydroxyl radical to the aromatic ring results in the formation of a hydroxyl radical-toluene adduct which has a lifetime of 1-30 msec.[87] The adduct may then decompose back to toluene and hydroxyl radical or it may lead to the formation of new products by reaction with molecular oxygen and nitrogen dioxide:



(214)

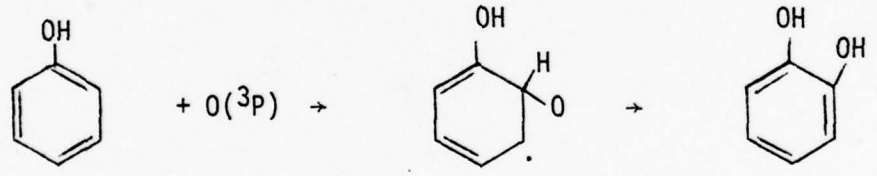


(215)

The favored pathway at low NO_x concentrations should yield cresols. For high nitrogen dioxide concentrations, the pathway to nitrotoluenes may be important.

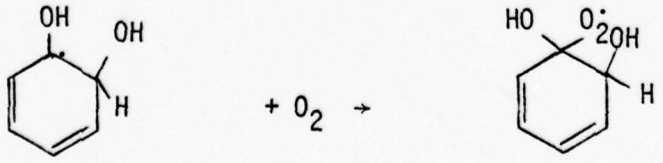
Photooxidation of toluene in the presence of nitrogen oxides has been reported to produce considerable quantities of carbon dioxide and carbon monoxide.[121] Other species have been identified: formaldehyde, formic acid, glyoxal, methylglyoxal, PAN, cresols, benzaldehyde, hydroxyl benzyl alcohols, nitrotoluenes, nitrocresols, and benzyl nitrate.[121-124] Many of these products are compatible with the reactions proposed above. The large yields of carbon dioxide and carbon monoxide and the identification of other simple oxidation product species suggest alternative reaction pathways involving ring opening steps in the subsequent oxidation of the adduct.[121] The mechanism describing photooxidation of aromatic hydrocarbons is highly uncertain and is currently under investigation.

Oxygen atoms and hydroxyl radicals may also react with phenol via addition to the aromatic ring. The radical species formed with the addition of oxygen may decompose into catechol, resorcinol, or hydroquinone (1,2-; 1,3-; and 1,4-dihydroxybenzene; respectively).

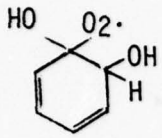


(130)

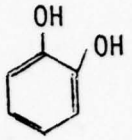
The addition of hydroxyl radical to the ring leads to the formation of an adduct which may either decompose back to phenol and hydroxyl radical or react with molecular oxygen or nitrogen dioxide.



(216)

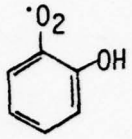


$\xrightarrow{-HO_2}$

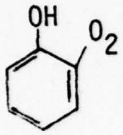


(217-a)

$\xrightarrow{-H_2O}$

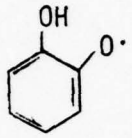


(217-b)

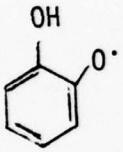


+ NO →

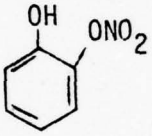
NO_2 +



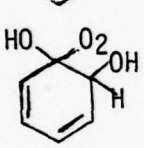
(218)



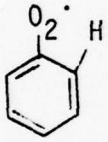
+ NO_2 →



(219)



$\xrightarrow{-H_2O_2}$



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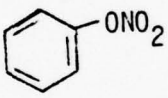
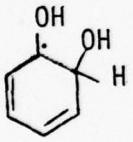
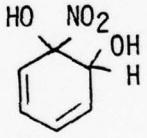


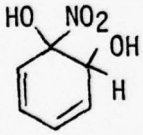
(217-c)



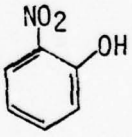
+ NO_2 →



(220)

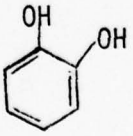


$\xrightarrow{-H_2O}$



(221-a)

$\xrightarrow{-HNO_2}$



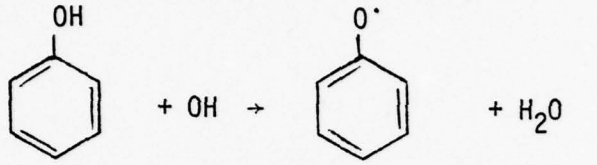
(221-b)

$\xrightarrow{-HONO_2}$

(221-c)

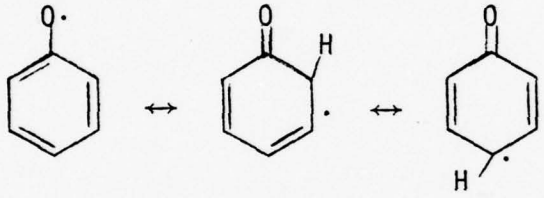
The favored pathway at low NO_x concentration should yield dihydroxybenzenes. For high nitrogen dioxide concentrations, the pathway to nitrophenols and dihydroxybenzenes may be important.

At room temperature, the hydroxyl radical may also abstract the phenolic hydrogen atom to produce the phenoxyl radical and water:[91]

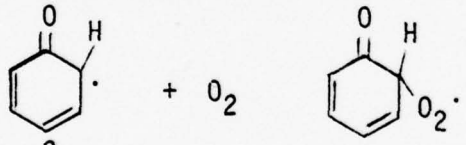


(131-a)

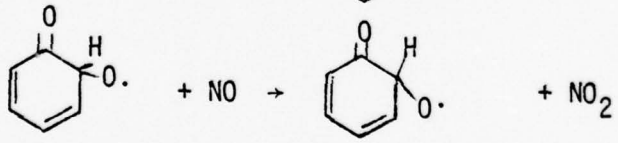
This radical is resonance stabilized; therefore, it should be relatively stable.



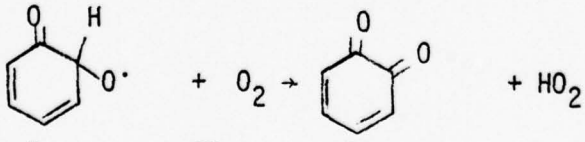
Because the phenoxy radical is resonance stabilized, the addition of molecular oxygen or nitrogen dioxide to the ortho and para positions will be enhanced. Addition of oxygen to the ortho carbon may lead to the formation of 1,2-benzoquinone or 2-hydroxy phenyl nitrate.



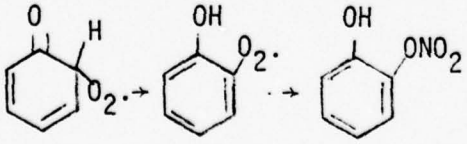
(222)



(223)

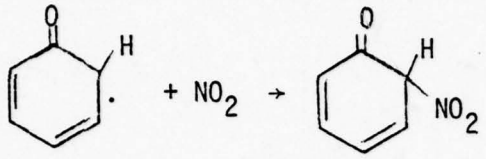


(224)



(225,218,219)

The nitrophenol may be formed by the attack of nitrogen dioxide at the ortho carbon.



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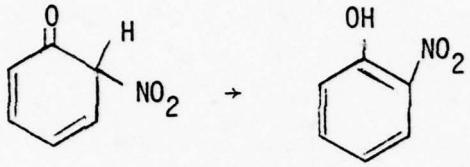


(226)

With the addition of oxygen to the para carbon, 1,4-benzoquinone and 4-hydroxyphenyl nitrate may be produced (see reactions 222-225), and with the addition of nitrogen dioxide, 4-nitrophenol (see reactions 225 and 226). The benzoquinones, nitrophenols, and dihydroxy-benzenes will further decompose into smaller molecules by their reaction with light, ozone, oxygen atoms, or hydroxyl radicals.

Methanol, Propanol and Butanol

As in the case of the hydrocarbons, oxygen atoms or hydroxyl radicals initially abstract hydrogen atoms from the alcohols (RCH_2OH, where R = H, CH_3, C_2H_5, or C_3H_7):[88-90]

$$RCH_2OH + O(^3P) \rightarrow \dot{R}CHOH + OH \quad (227)$$

$$RCH_2OH + OH \rightarrow \dot{R}CHOH + H_2O\,. \quad (228)$$

This hydroxyalkyl radical may then combine with molecular oxygen to form the peroxy hydroxyalkyl radical:[59]

$$RCHOH + O_2 \rightarrow R\text{-}\underset{\displaystyle H}{\overset{\displaystyle O_2}{\underset{|}{\overset{|}{C}}}}\text{-}OH \qquad k_{R=H} \sim 6.8 \times 10^{-12}\ cm^3/molecule\text{-}sec \qquad (229)$$

$$k_{R=CH_3} \sim 6.8 \times 10^{-12}\ cm^3/molecule\text{-}sec$$

$$CH_3CHCH_2OH \rightarrow CH_3CH(O_2)\ CH_2OH \qquad k \sim 6.8 \times 10^{-12}\ cm^3/molecule\text{-}sec\ .$$

Since the concentration of oxygen molecules is greater than that of most other species, a large percentage of the hydroxyalkyl radicals is expected to react in this manner. The peroxy radical may then oxidize nitric oxide to nitrogen dioxide:[59]

$$R\text{-}\underset{\displaystyle H}{\overset{\displaystyle O_2}{\underset{|}{\overset{|}{C}}}}\text{-}OH + NO \rightarrow R\text{-}\underset{\displaystyle H}{\overset{\displaystyle O}{\underset{|}{\overset{|}{C}}}}\text{-}OH + NO_2 \qquad k_{R=H} \sim 3.3 \times 10^{-12}\ cm^3/molecule\text{-}sec \qquad (230)$$

$$k_{R=CH_3} \sim 3.3 \times 10^{-12}\ cm^3/molecule\text{-}sec$$

$$CH_3CH(O_2)CH_2OH + NO \rightarrow CH_3CH(O)CH_2OH + NO_2\cdot$$

The newly formed radical species may further react with molecular oxygen to form an organic acid and hydroperoxy radical:[59]

$$R\text{-}\underset{\displaystyle H}{\overset{\displaystyle O}{\underset{|}{\overset{|}{C}}}}\text{-}OH + O_2 \rightarrow R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OH + HO_2 \qquad k_{R=H} \sim 2.6 \times 10^{-15}\ cm^3/molecule\text{-}sec \qquad (231)$$

$$k_{R=CH_3} \sim 1.4 \times 10^{-14}\ cm^3/molecule\text{-}sec\ .$$

Formaldehyde and Acetaldehyde

Formaldehyde and acetaldehyde (RCHO, where R=H or CH_3) are also known to react with oxygen atoms,[27,93] hydroxyl radicals,[27,94] hydroperoxy radicals,[27,59] and nitrogen trioxide[59] present in the atmosphere. These highly reactive species abstract a hydrogen atom from the carbonyl portion (-CHO) of the molecule to produce the formyl radical (CHO) in the case of formaldehyde and the acetyl radical (CH_3CO) in the case of acetaldehyde:

$$RCHO + O(^3P) \rightarrow RCO + OH \qquad k_{R=H} = 1.6 \times 10^{-13} cm^3/molecule\text{-}sec \qquad (232)$$

$$k_{R=CH_3} = 3.2 \times 10^{-13} cm^3/molecule\text{-}sec$$

$$RCHO + OH \rightarrow RCO + H_2O \qquad k_{R=H} = 1.4 \times 10^{-11} cm^3/molecule\text{-}sec \qquad (233)$$

$$k_{R=CH_3} = 1.5 \times 10^{-11} cm^3/molecule\text{-}sec$$

$$RCHO + HO_2 \rightarrow RCO + H_2O_2 \qquad k_{R=H} = 1.4 \times 10^{-17} cm^3/molecule\text{-}sec \qquad (234)$$

$$k_{R=CH_3} \sim 7.4 \times 10^{-18} cm^3/molecule\text{-}sec$$

$$RCHO + NO_3 \rightarrow RCO + HONO_2 \qquad k_{R=H} = 8.1 \times 10^{-16} cm^3/molecule\text{-}sec \qquad (235)$$

$$k_{R=CH_3} \sim 4.1 \times 10^{-14} cm^3/molecule\text{-}sec.$$

Both the formyl and acetyl radicals will react with molecular oxygen to yield the peroxy formyl and peroxy acetyl radicals, respectively:[59]

$$CHO + O_2 \rightarrow HCOO_2 + M \qquad k = 6.8 \times 10^{-14} cm^3/molecule\text{-}sec \qquad (236\text{-}a)$$

$$CH_3CO + O_2 \rightarrow CH_3COO_2 \qquad k = 6 \times 10^{-12} cm^3/molecule\text{-}sec \qquad (237)$$

The formyl radicals may also react with oxygen to form carbon monoxide and the hydroperoxy radical:[59]

$$CHO + O_2 \rightarrow CO + HO_2 \qquad k = 1.7 \times 10^{-13}\ cm^3/molecule\text{-}sec \qquad (236\text{-}b)$$

These peroxy radicals will further react with nitric oxide and nitrogen dioxide. In the reaction between the peroxy formyl radical and nitrogen oxides, the formate radical and peroxy formyl nitrate (PFN) may be formed:

$$HCOO_2 + NO \rightarrow HCO_2 + NO_2 \qquad k = 6.2 \times 10^{-13} cm^3/molecule\text{-}sec \qquad (238)$$

$$HCOO_2 + NO_2 \rightarrow H\text{–}C(=O)\text{–}O\text{–}O\text{–}N(=O)_2 \qquad k = 3.3 \times 10^{-13} cm^3/molecule\text{-}sec \qquad (239)$$

The formate radicals will finally decompose into carbon dioxide and hydrogen atoms or the former and hydroperoxy radicals:

$$HCO_2 \rightarrow CO_2 + H \qquad k = 2.5 \times 10^{8}\ sec^{-1} \qquad (240)$$

$$HCO_2 + O_2 \rightarrow CO_2 + HO_2 \qquad k = 3.3 \times 10^{-14} cm^3/molecule\text{-}sec \qquad (241)$$

Since peroxy formyl nitrate (PFN) has not been detected in smog chamber studies in which it might have been expected to appear, it is assumed that its concentration is small or that it is very unstable and exists only as a transient species. PFN is estimated to decompose into the formate radical and nitrogen dioxide or carbon dioxide and nitric acid:[59]

$$HCOO_2NO_2 + NO \rightarrow [HCOO_2NO] + NO_2 \qquad k = 1.1 \times 10^{-16}\ cm^3/molecule\text{-}sec \qquad (242)$$

$$[HCOO_2NO] \rightarrow HCO_2 + NO_2 \qquad (243\text{-}a)$$

$$[HCOO_2NO] + h\nu \rightarrow HCO_2 + NO_2 \qquad (243\text{-}b)$$

$$HCOO_2NO_2 \rightarrow CO_2 + HONO_2 \qquad k = 7 \times 10^{6} sec^{-1}. \qquad (244)$$

The peroxy acetyl radical will competitively react with both of the nitrogen oxides. It may react with nitric oxide to yield the acetate radical and nitrogen dioxide:[125]

$$CH_3COO_2 + NO \rightarrow CH_3CO_2 + NO_2 \qquad k = 1.6 \times 10^{-12} cm^3/molecule\text{-}sec \qquad (245)$$

Like the formate radical, the acetate radical will then decompose:[59]

$$CH_3CO_2 \rightarrow CH_3 + CO_2 \qquad k = 2.2 \times 10^{10} sec^{-1}. \qquad (246)$$

The peroxy acetyl radical may also react with nitrogen dioxide to form peroxy acetyl nitrate (PAN):

$$CH_3COO_2 + NO_2 \rightarrow CH_3C(=O)OONO_2 \qquad k = 5.0 \times 10^{-13} cm^3/molecule\text{-}sec. \qquad (247)$$

The PAN exists in a dynamic equilibrium with the peroxy acetyl radical and nitrogen dioxide:[125]

$$CH_3COO_2NO_2 \rightarrow CH_3COO_2 + NO_2 \qquad k = 3.5 \times 10^{-4} sec^{-1}. \qquad (248)$$

If nitric oxide is present in the atmosphere, it will react with the peroxy acetyl radical (reaction 245). Hence, the equilibrium will be shifted away from the formation of PAN, and its concentration in the atmosphere will drop.* When

*If any radical species (e.g., HO_2, HCO_3, CH_3O_2) are in the atmosphere, they too may react with the peroxy acetyl radical and shift the equilibrium away from PAN formation.

the nitric oxide is nearly all oxidized to nitrogen dioxide, the formation of PAN will increase.[59]

If the levels of nitrogen oxides in the atmosphere are low, the peroxy acetyl radicals may react with such radicals as the hydroperoxy, peroxy formyl, methyl peroxy, and peroxy acetyl radicals.[59] These reactions, however, should not be very important, since the concentration of nitrogen oxides in the atmosphere above HAAP should be quite high.

$$CH_3COO_2 + HO_2 \rightarrow CH_3COO_2H + O_2 \quad k = 2.6 \times 10^{-14} cm^3/molecule\text{-}sec \qquad (249\text{-}a)$$

$$\rightarrow CH_3CO_2 + O_2 + OH \qquad (249\text{-}b)$$

$$CH_3COO_2 + HCOO_2 \rightarrow CH_3CO_2 + O_2 + HCO_2 \quad k = 2.6 \times 10^{-15} cm^3/molecule\text{-}sec \qquad (250)$$

$$CH_3COO_2 + CH_3O_2 \rightarrow CH_3CO_2 + O_2 + CH_3O \quad k = 2.6 \times 10^{-14} cm^3/molecule\text{-}sec \qquad (251)$$

$$2CH_3COO_2 \rightarrow 2CH_3CO_2 + O_2 \quad k = 2.6 \times 10^{-15} cm^3/molecule\text{-}sec \qquad (252)$$

Acetone, Methyl Ethyl Ketone, and Cyclohexanone

The oxygen atoms and hydroxyl radicals in the atmosphere may also abstract hydrogen atoms from the ketones: acetone,[95] methyl ethyl ketone,[96] and cyclohexanone.[97] In the acyclic ketones, the point of attack is at a hydrogen atom bonded to a carbon adjacent to the carbonyl group. In methyl ethyl ketone, abstraction occurs from the ethyl branch of the ketone since the carbon-hydrogen bond of the secondary carbon ($COCH_2CH_3$) is weaker than that of the primary carbon ($COCH_3$). In contrast, any one of the ten hydrogens on cyclohexanone is vulnerable to attacks by these reactive species. Hence, the following reactions are expected to occur in the atmosphere:

$$CH_3COCH_3 + O(^3P) \rightarrow CH_2COCH_3 + OH \qquad (137)$$

$$CH_3COCH_3 + OH \rightarrow CH_2COCH_3 + H_2O \qquad (138)$$

$$CH_3COCH_2CH_3 + O(^3P) \rightarrow CH_3COCHCH_3 + OH \quad (139)$$

$$CH_3COCH_2CH_3 + OH \rightarrow CH_3COCHCH_3 + H_2O \quad (140)$$

$$C_6H_{10}O + O\ (^3P) \rightarrow C_6H_9O + OH \quad (141)$$

$$C_6H_{10}O + OH \rightarrow C_6H_9O + H_2O\ . \quad (142)$$

As in the cases of the alkyl, hydroxymethyl, formyl, and acetyl radicals, molecular oxygen is expected to combine with the acetonyl, 2-butanonyl,[59] and cyclohexanonyl radicals to form the respective peroxy radicals:

$$CH_2COCH_3 + O_2 \rightarrow O_2CH_2COCH_3 \quad (253)$$

$$CH_3COCHCH_3 + O_2 \rightarrow CH_3COCH(O_2)CH_3 \quad k \sim 6.8 \times 10^{-12} cm^3/molecule\text{-}sec \quad (254)$$

$$C_6H_9O + O_2 \rightarrow C_6H_9OO_2\ . \quad (255)$$

Most of these peroxy radicals will then be reduced by nitric oxide:

$$O_2CH_2COCH_3 + NO \rightarrow OCH_2COCH_3 + NO_2 \quad (256)$$

$$CH_3COCH(O_2)CH_3 + NO \rightarrow CH_3COCH(O)CH_3 + NO_2 \quad k \sim 3.2 \times 10^{-13} cm^3/molecule\text{-}sec \quad (257)$$

$$C_6H_9O\ O_2 + NO \rightarrow C_6H_9OO + NO_2\ . \quad (258)$$

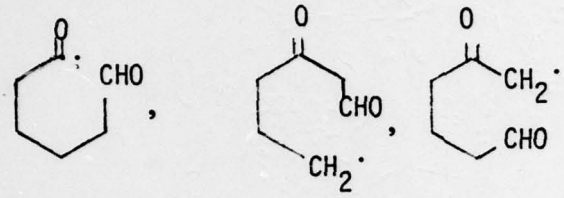
These newly formed radicals can then decompose or react with molecular oxygen in the following manners:

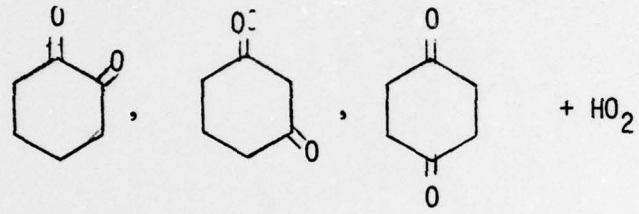
$$CH_3COCH_2O \rightarrow CH_3CO + CH_2O \quad k = 7.2 \times 10^8\ sec^{-1} \quad (259\text{-}a)$$

$$CH_3COCH_2O + O_2 \rightarrow CH_3COCHO + HO_2 \quad (259\text{-}b)$$

$$CH_3COCH(O)CH_3) \rightarrow CH_3CO + CH_3CHO \qquad (260\text{-a})$$

$$CH_3COCH(O)CH_3 + O_2 \rightarrow CH_3COCOCH_3 + HO_2 \quad k \sim 2.2 \times 10^{-16} cm^3/molecule\text{-}sec \qquad (260\text{-b})$$

$C_6H_9OO \rightarrow$  (261-a)

$C_6H_9OO + O_2 \rightarrow$  (261-b)

It can be seen that the alkoxy radical formed from acetone may eventually decompose into acetyl radicals and formaldehyde (259-a) or into pyruvaldehyde (259-b), methyl ethyl ketone into acetyl radicals and acetaldehyde (260-a) or into biacetyl (260-b), and cyclohexanone into other radical species or into diketones.

Of course, these species will also decompose. Previously, the decomposition pathways of acetyl radicals, formaldehyde, and acetaldehyde were discussed. Consistent with acetaldehyde, the pyruvaldehyde may be speculated to photolyze or react with species in the atmosphere:

$$CH_3COCHO + h\nu \rightarrow CH_3CO + CHO \qquad (262)$$

$$CH_3COCHO + O\ (^3P) \rightarrow CH_3COCO + OH \qquad (263)$$

$$CH_3COCHO + OH \rightarrow CH_3COCO + H_2O \qquad (264)$$

$$CH_3COCO + O_2 \rightarrow CH_3COO_2 \qquad (265)$$

$$CH_3COO_2 + NO \rightarrow CH_3COCOO + NO_2 \qquad (266)$$

$$CH_3COCOO \rightarrow CH_3CO + CO_2. \qquad (267)$$

The biacetyl formed from methyl ethyl ketone may also decompose photochemically:[59,68]

$$CH_3COCOCH_3 + h\nu(\lambda<392.8) \rightarrow 2CH_3CO \quad k = 1.7 \times 10^{-4}sec^{-1} \quad \Phi = 0.06\ (\lambda 313) \tag{268}$$

It may react with oxygen atoms or hydroxyl radicals:

$$CH_3COCOCH_3 + O(^3P) \rightarrow CH_2COCOCH_3 + OH \tag{269}$$

$$CH_3COCOCH_3 + OH \rightarrow CH_2COCOCH_3 + H_2O \tag{270}$$

$$CH_3COCOCH_2 + O_2 \rightarrow CH_3COCOCH_2O_2 \tag{271}$$

$$CH_3COCOCH_2O_2 + NO \rightarrow CH_3COCOCH_2O \tag{272}$$

$$CH_3COCOCH_2O \rightarrow CH_3COCO + CH_2O \tag{273}$$

The diketones and radical species may also decompose through a series of reactions with radical species [$O(^3P)$ and OH], molecular oxygen, and nitric oxide to yield such products as cyclopentanone, 4-pentenal, glyoxal, formyl radicals, and carbon dioxide.

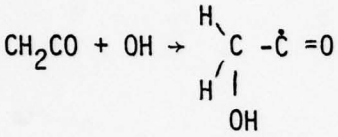
Ketene and Diketene

Instead of abstracting hydrogen atoms, oxygen atoms and hydroxyl radicals combine with ketene to form a radical species. An oxygen atom adds to ketene, and the molecule subsequently rearranges to form an excited glyoxal molecule which immediately decomposes into formyl radicals:[98]

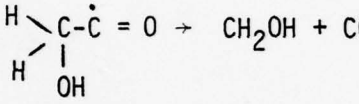
$$CH_2CO + O(^3P) \rightarrow HCOCOH^* \tag{143}$$

$$HCOCOH^* \rightarrow 2\ HCO\cdot \tag{274}$$

Likewise a hydroxyl radical also adds to ketene. It may either attach itself to the methylene or carbonyl carbon. If the hydroxyl radical adds to the methylene carbon, the adduct may cleave to yield the hydroxymethyl radical and carbon monoxide:

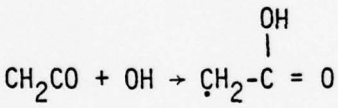


(275-a)

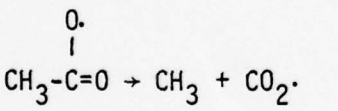


(276-b)

If, on the other hand, it adds to the carbonyl carbon, the hydrogen atom of the hydroxyl group may shift to the methylene carbon, and the resulting adduct may then decompose into the methyl radical and carbon dioxide:



(275-b)



(276-b)

Since the hydroxyl radical is an electrophile, it should attach itself to the most electronegative carbon. In the case of ketene, this carbon is the methylene carbon. Therefore, the first pathway is believed to be preferred.

In the reaction between diketene and these reactive species, three modes of attack are possible. The oxygen atoms or hydroxyl radicals may add to either vinylic carbon or abstract a hydrogen atom from the methylene carbon. Some of the

products of the decomposition may include such species as carbon monoxide, carbon dioxide, formaldehyde, hydroxymethyl radicals, formate radicals, hydroxyl radicals, and hydroperoxy radicals.

Formic and Acetic Acids

The oxygen atoms and hydroxyl radicals present in the atmosphere may abstract one of two hydrogen atoms in formic acid. If the hydrogen bonded to the oxygen atom is abstracted, the formate radical is formed. If, on the other hand, the hydrogen bonded to the carbon atom is abstracted, the carboxy radical is formed. Based on available thermochemical data,[60] only the hydroxyl radical is capable of abstracting the hydrogen bonded to the oxygen atom. (For $HCOOH + O(^3P) \rightarrow HCO_2 + OH$, $\Delta H + 4.3$ kcal/mole; for $HCOOH + OH \rightarrow HCO_2 + H_2O$, $\Delta H = -14.5$ kcal/mole). However, abstraction of the hydrogen bonded to the carbon atom is energetically more feasible. Hence, it is believed that both the oxygen atom and hydroxyl radical will preferentially abstract this hydrogen atom.

$$HCOOH + O(^3P) \rightarrow COOH + OH \qquad \Delta H = -9.7 \text{ kcal/mole} \tag{147}$$

$$HCOOH + OH \rightarrow COOH + H_2O \qquad \Delta H = -26.7 \text{ kcal/mole.} \tag{148}$$

The carboxy radical may then react with such species as molecular oxygen, atomic oxygen, or hydroxyl radicals. Since the concentration of molecular oxygen in the atmosphere is much greater than the concentrations of the two other species, the reaction between the carboxy radical and molecular oxygen will be of greatest importance. The reaction between these two species yields a peroxy carboxy radical (O_2CO_2H). This radical may then react with nitric oxide to form a radical species which may decompose into hydroxyl radicals and carbon dioxide.

$$COOH + O_2 \rightarrow O_2COOH \tag{277}$$

$$O_2COOH + NO \rightarrow OCOOH + NO_2 \tag{278}$$

$$OCOOH \rightarrow CO_2 + OH \cdot \tag{279}$$

The reaction between the carboxy radical and atomic oxygen may lead directly to the formation of the hydroxyl radical and carbon dioxide. Similarly, the reaction between the carboxy and hydroxyl radicals may yield water and carbon dioxide.

$$COOH + O(^3P) \rightarrow CO_2 + OH \qquad (280)$$

$$COOH + OH \rightarrow CO_2 + H_2O. \qquad (281)$$

In acetic acid, there are also two types of hydrogen atoms which may be abstracted by either oxygen atoms or hydroxyl radicals. If the hydrogen bonded to the oxygen atom is abstracted, the acetate radical is produced. If the hydrogen bonded to the carbon atom is abstracted, the carboxymethyl radical (CH_2COOH) is produced. From available thermochemical data*, it appears that abstraction of the hydrogen bonded to the carbon atom is preferred.

$$CH_3COOH + O(^3P) \rightarrow CH_2COOH + OH \quad \Delta H \sim -4.5 \text{ kcal/mole} \qquad (149)$$

$$CH_3COOH + OH \rightarrow CH_2COOH + H_2O \quad \Delta H \sim -21.5 \text{ kcal/mole}. \qquad (150\text{-a})$$

The carboxymethyl radical which is formed may combine with molecular oxygen to yield the peroxy carboxy-methyl radical. This radical may then react with nitric oxide to form a species which decomposes into formaldehyde and the carboxy radical.

$$CH_2COOH + O_2 \rightarrow O_2CH_2COOH \qquad (282)$$

$$O_2CH_2COOH + NO \rightarrow OCH_2COOH + NO_2 \qquad (283)$$

$$OCH_2COOH \rightarrow CH_2O + COOH. \qquad (284)$$

*The heat of formation of the CH_2COOH radical was not available; therefore, its heat of formation was approximated from the bond strength of the carbon-hydrogen bond in acetone (i.e., the bond strength of the carbon-hydrogen bond in acetic acid was assumed to be the same as that in acetone, $D° \sim 98$ kcal/mole).[60] Since both acetone and acetic acid are somewhat similar in structure ($XCOCH_3$, $X = CH_3$ or OH), and since both of the radicals formed are resonance stabilized, it is believed that approximately the same amount of energy would be required to break the carbon-hydrogen bond in acetone and acetic acid.

The hydroxyl radical is also capable of abstracting the hydrogen atom from the acetate radical.[60] This radical may then decompose into the methyl radical and carbon dioxide.

$$CH_3COOH + OH \rightarrow CH_3COO + H_2O \quad \Delta H = -9.2 \text{ kcal/mole} \qquad (150\text{-b})$$

$$CH_3CO_2 \rightarrow CH_3 + CO_2. \qquad (246)$$

The oxygen atom is incapable of abstracting this hydrogen atom (ΔH = 8.6 kcal/mole).[60]

Formate and Acetate Esters

Little is known of the reactions between oxygen atoms or hydroxyl radicals with esters. Hence, the chemistry of these two reactive species with the alcohol (RO-) and acid (R'CO-) portion of an ester will be considered.

Like formic acid, oxygen atoms and hydroxyl radicals can abstract one of two types of hydrogens in the formate esters (HCOOR, R = CH_3 or n-C_3H_2). If the reaction is thermodynamically feasible, these species can abstract a hydrogen atom from the alcohol portion of the ester or the hydrogen atom from the acid portion. Abstraction of hydrogen from the alcohol portion leads to the formation of a radical which may then decompose into a formyl radical and aldehyde (F). Abstraction of the hydrogen from the formate group leads to the formation of a radical which may decompose into carbon dioxide and an alkyl radical (G).

$$HCOOCH_2R + X \ (X=O, OH) \rightarrow HCO_2\dot{C}HR + HX \qquad (F)$$

$$HCO_2CHR \rightarrow HCO + OCHR$$

$$HCOOCH_2R + X \rightarrow \dot{C}O_2CH_2R + HX \qquad (G)$$

$$CO_2CH_2R \rightarrow CO_2 + CH_2R.$$

If the bond strength of the carbon-hydrogen bond in the alcohol ($H\text{-}CH_2OH$, $D° \sim 94$ kcal/mole)* is approximately the same as that of the corresponding bond in methyl formate ($HCO_2CH_2\text{-}H$) and if the bond strength of the carbon-hydrogen bond in formic acid (H-COOH, $D° = 92.6$ kcal/mole)[60] is approximately the same as that of the corresponding bond in the formate ester ($H\text{-}CO_2CH_3$), then the site of abstraction of the oxygen atom or hydroxyl radical in methyl formate may be known. Since the bond strength of the carbon-hydrogen bond in formic acid is less than that in methanol, the oxygen atom and hydroxyl radical should preferentially abstract the hydrogen atom of the formate group (G).

$$HCOOCH_3 + O(^3P) \rightarrow COOCH_3 + OH \quad \Delta H \sim 11.8 \text{ kcal/mole} \qquad (151)$$

$$HCOOCH_3 + OH \rightarrow COOCH_3 + H_2O \quad \Delta H \sim -28.8 \text{ kcal/mole}. \qquad (152)$$

In the acetate esters, (CH_3COOR, R = CH_3, $\Delta\text{-}C_3H_7$, or $i\text{-}C_4H_9$), oxygen atoms and hydroxyl radicals can abstract either the hydrogen of the alcohol portion of the ester or the hydrogen of the acid portion (CH_3CO). Abstraction of a hydrogen in the alcohol portion of the ester (methyl acetate) leads to the formation of a radical which may decompose into the acetyl radical and an aldehyde (H). Abstraction of an acetate hydrogen leads to the formation of an alkoxy radical (I) and ketene.

$$CH_3COOCH_2R + X \ (X=O, OH) \rightarrow CH_3CO_2\dot{C}HR + HX \qquad (H)$$

$$CH_3CO_2CHR \rightarrow CH_3CO + OCHR$$

$$CH_3COOCH_2R + X \rightarrow \dot{C}H_2CO_2CH_2R + HX \qquad (I)$$

$$CH_2CO_2CH_2R \rightarrow CH_2CO + OCH_2R.$$

*The bond dissociation energy of the carbon-hydrogen bond in methanol was assumed to be approximately the same as that in dimethyl ether ($CH_3OCH_3 \rightarrow CH_2OCH_3 + H$, $\Delta H = 94$ kcal/mole).[60]

Based on the relative bond strengths of the carbon-hydrogen bond in methanol and acetic acid, ($H\text{-}CH_2OH$, $D°\sim94$ kcal/mole and $H\text{-}CH_2COOH$, $D°\sim98$ kcal/mole),[60] it appears that both the oxygen atom and hydroxyl radical should abstract the hydrogen atom from the alcohol portion of the ester (H).

$$CH_3COOCH_3 + O(^3P) \rightarrow CH_3COOCH_2 + OH \quad \Delta H \sim -4.5 \text{ kcal/mole} \tag{153}$$

$$CH_3COOCH_3 + OH \rightarrow CH_3COOCH_2 + H_2O \quad \Delta H \sim -21.5 \text{ kcal/mole}. \tag{154}$$

Laity and coworkers[122] also suggested that the hydroxyl radical, for example, abstracts hydrogen from the alcohol portion of the ester (H). However, Kirillov and Shilov[126] reported that, in aqueous solution, the hydroxyl radical abstracts a hydrogen from the acetate portion of the molecule (I).

Ammonia, Methylamine, and Dimethylamine

Ammonia also will react with oxygen atoms and hydroxyl radicals to give the amino radical:[27,100]

$$NH_3 + O(^3P) \rightarrow NH_2 + OH \tag{155}$$

$$NH_3 + OH \rightarrow NH_2 + H_2O \cdot \tag{156}$$

Although ammonia does not react with the hydroperoxy radical, it does complex with it:[126]

$$NH_3 + HO_2 \rightarrow NH_3 \cdot HO_2 \cdot \tag{285}$$

In the presence of ammonia, the rate of the reaction of the hydroperoxy radical with itself increases; therefore, it is possible that the rates of all hydroperoxy reactions may also increase.

The amino radical may then react with nitric oxide, oxygen atoms, and hydroxyl radicals to yield nitrogen. water, nitroxyl radicals, hydrogen atoms, amino radicals, ammonia, and oxygen atoms:[27]

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad k = 8 \times 10^{-12} cm^3/molecule\text{-}sec \qquad (286)$$

$$NH_2 + O(^3P) \rightarrow HNO + H \qquad (287\text{-}a)$$

$$\rightarrow NH + OH \qquad k = 3.5 \times 10^{-12}\ cm^3/molecule\text{-}sec \qquad (287\text{-}b)$$

$$NH_2 + OH \rightarrow NH_3 + O \qquad k = 1.0 \times 10^{-3}\ cm^3/molecule\text{-}sec\ . \qquad (288)$$

The nitroxyl radical will further decompose into nitric oxide and hydroperoxy radical or into nitric oxide and atomic hydrogen:[59]

$$HNO + O_2 \rightarrow NO + H_2O \qquad k < 2.0 \times 10^{-20} cm^3/molecule\text{-}sec \qquad (289)$$

$$HNO + h\nu\ (\lambda 502\text{-}750) \rightarrow NO + H \qquad k = 1.7 \times 10^{-3} sec\ (z = 40°)\ . \qquad (290)$$

The imino radical also decomposes.

Both oxygen atoms and hydroxyl radicals can abstract hydrogen atoms from methylamine and dimethylamine. In methylamine, oxygen atoms are capable of abstracting the hydrogen bonded to the carbon atom. The more energetic hydroxyl radicals are capable of abstracting the hydrogen bonded to either the carbon or nitrogen atoms. Since the strength of the carbon-hydrogen bond is less than that of the nitrogen-hydrogen bond, (for $H\text{-}CH_2NH_2$, ΔH = 92.6 kcal/mole; for $CH_3NH\text{-}H$, ΔH = 102.6 kcal/mole) abstraction of the methyl hydrogen is believed to be preferred.[60]

$$CH_3NH_2 + O(^3P) \rightarrow CH_2NH_2 + OH \qquad \Delta H = -9.7\ kcal/mole \qquad (291\text{-}a)$$

$$CH_3NH_2 + O(^3P) \rightarrow CH_3NH + OH \qquad \Delta H + 0.3\ kcal/mole \qquad (291\text{-}b)$$

$$CH_3NH_2 + OH \rightarrow CH_2NH_2 + H_2O \qquad \Delta H = -26.7\ kcal/mole \qquad (157\text{-}a)$$

$$CH_3NH_2 + OH \rightarrow CH_3NH + H_2O \qquad \Delta H = -16.7\ kcal/mole \qquad (157\text{-}b)$$

The aminomethyl (CH_2NH_2) radical formed in these reactions may combine with molecular oxygen to yield a peroxy radical, which may subsequently react with nitric oxide. The resulting radical species may then decompose into formaldehyde and the amino radical.

$$CH_2NH_2 + O_2 \rightarrow O_2CH_2NH_2 \quad (292)$$

$$O_2CH_2NH_2 + NO \rightarrow OCH_2NH_2 + NO_2 \quad (293)$$

$$OCH_2NH_2 \rightarrow CH_2O + NH_2. \quad (294)$$

If the carbon-hydrogen and nitrogen-hydrogen bond strengths in dimethylamine are approximately equal to those in methylamine, a similar sequence of reactions can be envisioned (reactions 157-a and -b, 291-a and -b, 292-294). However, in the case of dimethylamine, formaldehyde and the methylamino radical (CH_3NH) will be formed instead of the former and the amino radical.

Nitrogen Oxides

The atmospheric reactions of the nitrogen oxides are quite fast. Nitric oxide can react with oxygen atoms,[102] or hydroperoxy radicals[27] to form nitrogen dioxide, with hydroperoxy radicals to form nitric acid[104] (a minor product in the reaction between nitric oxide and hydroperoxy radicals), and with hydroxyl radicals to form nitrous acid.[27,83] In addition to these reactions, it was previously mentioned that nitric oxide is also oxidized to nitrogen dioxide by alkyl peroxy radicals (RO_2). Nitric oxide can also react with alkoxy radicals (RO) to form alkyl nitrites or aldehydes and nitroxyl radical and with peroxy alkyl carbonyl radicals (RCO_3) to form alkyl substituted formate radicals (RCO_2) and nitrogen dioxide.

Nitrogen dioxide reacts quickly with oxygen atoms to form either nitric oxide and oxygen[105] or nitrogen trioxide,[27] with hydroxyl radicals to form nitric acid,[27,106-a] and with hydroperoxy radicals to form either pernitric acid[107] or nitrous acid and oxygen.[27] Like nitric oxide, nitrogen dioxide can also react with alkoxy radicals to form alkyl nitrates or aldehydes and nitrous acid. Reactions between this nitrogen oxide and peroxy alkyl carbonyl radicals

result in the formation of PAN or analogues of PAN. (See the section on the secondary reactions of formaldehyde and acetaldehyde for the reactions leading to the formation of PAN (reactions 136, 237, and 245-248)).

In contrast to the reactions of nitric oxide and nitrogen dioxide, the reactions of nitrous oxide occur at a much slower rate. The rate constants of many of the atmospheric reactions are comparable to the rate constant of the reaction between nitrous oxide and atomic oxygen at 1200°K ($k = 1.3 \times 10^{-5}$ cm^3/molecule-sec).[27] At 298°K, the rate of reaction between nitrous oxide and hydroxyl radical is faster ($k = 3.8 \times 10^{-17}$ cm^3/molecule-sec);[108] however, it is not believed to be of much importance to the overall atmospheric chemistry.

Nitrogen trioxide may react with hydroperoxy radicals to form nitric acid and molecular oxygen;[59] dinitrogen pentoxide may react with atomic oxygen.[27]

Nitrous and Nitric Acids

Nitrous acid decomposes into nitrogen dioxide by its reaction with oxygen atoms and hydroxyl radicals.[27,104] Similarly nitric acid decomposes into nitrogen trioxide by the action of these two reactive species.[27,109] The reactions of nitric acid and these reactive species are slower than the respective reactions of nitrous acid.

Pernitric Acid

Recently kinetic and spectroscopic evidence has been reported for the formation of pernitric acid from the reaction of nitrogen dioxide with hydroperoxy radicals.[107] Although this reaction was believed to form nitrous acid,[104] the major product has been shown to be pernitric acid. The sequence of steps describing major formation and destruction pathways of pernitric acid are listed below.[127]

$$HO_2 + NO_2 \rightarrow HO_2NO_2 \qquad (164\text{-b})$$

$$HO_2NO_2 \rightarrow NO_2 + HO_2 \qquad k = 4.7 \times 10^{-2} sec^{-1} \qquad (295)$$

$$HO_2NO_2 \rightarrow HNO_2 + O_2 \qquad k = 1.6 \times 10^{-2} sec^{-1}. \qquad (296)$$

Pernitric acid is highly unstable and should play an important role in atmospheric chemistry by serving as a temporary sink for oxides of nitrogen.

Nitromethane and Methyl Nitrate

In addition to reacting photochemically, nitromethane may react with oxygen atoms[110] and hydroxyl radicals:[111]

$$CH_3NO_2 + O(^3P) \rightarrow CH_2NO_2 + OH \quad (172)$$

$$CH_3NO_2 + OH \rightarrow CH_2NO_2 + H_2O. \quad (173)$$

The nitromethyl radical may then combine with molecular oxygen to form the nitromethyl peroxy radical and may be subsequently reduced by nitric oxide to form the nitromethoxy radical:

$$NO_2CH_2 + O_2 \rightarrow NO_2CH_2O_2 \quad (297)$$

$$NO_2CH_2O_2 + NO \rightarrow NO_2CH_2O + NO_2. \quad (298)$$

This radical may decompose into formaldehyde and nitrogen dioxide:

$$NO_2CH_2O \rightarrow CH_2O + NO_2. \quad (299)$$

The methyl nitrate in the atmosphere may decompose in a similar manner. Initially the molecule may be attacked by oxygen atoms[112] or hydroxyl radicals:

$$CH_3ONO_2 + O(^3P) \rightarrow CH_2ONO_2 + OH \quad (174)$$

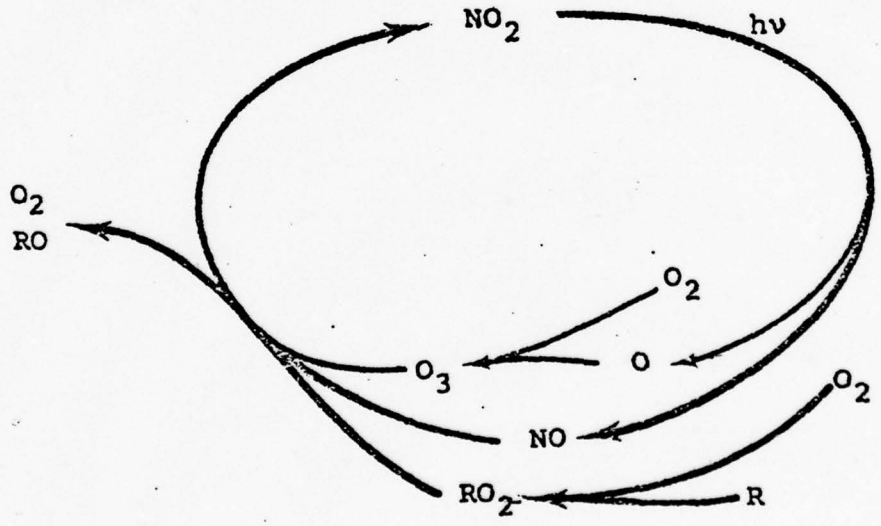
$$CH_3ONO_2 + OH \rightarrow CH_2ONO_2 + H_2O. \quad (175)$$

The radical formed may quickly decompose into formaldehyde and nitrogen dioxide:

$$CH_2ONO_2 \rightarrow CH_2O + NO_2. \quad (300)$$

Ozone

Ozone is exclusively a secondary pollutant. If organic vapors and nitrogen dioxide are irradiated with sunlight, the processes initiated by the photolysis of nitrogen dioxide can generate significant quantities of ozone. The intervention of organic vapors into the NO_x-O_3 cycle is illustrated below. In this cycle, free radicals (R) are generated from hydrocarbons by processes following the photolysis of nitrogen dioxide. These free radicals combine with atmospheric oxygen to form peroxy radicals (RO_2) which are capable of oxidizing nitric oxide to nitrogen dioxide. Each oxidation of nitric oxide to nitrogen dioxide by a nonozone species allows the accumulation of an ozone molecule. To illustrate, consider from Table 6A-18 that in the absence of organics 0.25 ppm NO_2 would generate 0.062 ppm ozone. However, it has been reported that 0.2 ppm NO_x and 12 ppm n-butane generated 0.65 ppm ozone after six hours of irradiation.[128]



The sequence of photolytic and secondary reactions directly or indirectly involving ozone are listed below. Ozone is formed by the rapid reaction of atomic oxygen with molecular oxygen. Ozone may absorb light and photolyze to yield atomic oxygen (see section entitled "Known Potential Excited State Reactions"). The ground state atomic oxygen, $O(^3P)$, can react with molecular oxygen to reform ozone. If the light is of sufficient energy, the photolysis of ozone can yield excited state atomic oxygen, $O(^1D)$. This species can undergo collisional deactivation with air to yield ground state atomic oxygen or it can react with water vapor to yield two hydroxyl radicals.[27]

$$O + O_2 + M \rightarrow O_3 + M \qquad (176)$$

$$O_3 + h\nu \rightarrow O_2 + O(^3P) \qquad (83\text{-a})$$

$$\rightarrow O_2 + O(^1D) \qquad (83\text{-c})$$

$$O(^1D) + M \rightarrow O(^3P) + M \qquad M = N_2,\ k = 5.4 \times 10^{-11} cm^3/molecule\text{-}sec \qquad (301)$$

$$O(^1D) + H_2O \rightarrow 2\ OH \qquad k = 3.5 \times 10^{-10} cm^3/molecule\text{-}sec. \qquad (302)$$

Ozone can also react with hydroxyl and hydroperoxy radical species.[27] The reaction with the hydroxyl radical species yields the hydroperoxy radical which, in turn, can react with itself to yield hydrogen peroxide,[27] with either nitric oxide or nitrogen dioxide as mentioned earlier, or with ozone to reform hydroxyl radicals.

$$O_3 + OH \rightarrow O_2 + HO_2 \qquad (177)$$

$$O_3 + HO_2 \rightarrow OH + 2O_2 \qquad (178)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad k = 5.6 \times 10^{-12} cm^3/molecule\text{-}sec \qquad (303)$$

Sulfur Oxides

The major fate of the sulfur oxides in the atmosphere is conversion to sulfates with subsequent sulfate deposition. There are five broad mechanisms of this conversion: direct photooxidation, indirect photooxidation, air oxidation in liquid droplets, catalyzed oxidation in liquid droplets, and catalyzed oxidation on dry surfaces. The major pathway in the pollutant matrix of munitions facilities should be indirect photooxidation. This process occurs in hydrocarbon-NO_x-SO_2 photochemical systems when the oxidation is mediated by secondary reactions involving radicals.

The sulfur oxides can react with atomic oxygen, hydroxyl radicals, and hydroperoxy radicals. With atomic oxygen, sulfur dioxide reacts to form sulfur trioxide;[27] the sulfur trioxide may then react with water to form sulfuric acid.[56] Sulfur dioxide can also react with the more reactive species as the hydroxyl[113] or hydroperoxy radicals[27] to produce the $HOSO_2$ species or sulfur trioxide and hydroxyl radical, respectively. Although the detailed oxidation mechanisms remain poorly defined, the fate of the sulfur oxides is conversion to sulfates.

6.A.2.4 Environmental Consequences of the Emissions from RDX Manufacturing at HAAP

A summary of the emissions and emission rates from HAAP is presented in Table 6A-20. These primary pollutants are classified into three groups. The first classification is comprised of those species designated as air pollutants by the United States Environmental Protection Agency (EPA). The second group consists of organic compounds such as solvents or byproducts released during RDX manufacturing processes. The third and final group includes miscellaneous species not considered in the first group.

TABLE 6A-20. EMISSIONS SUMMARY FROM RDX MANUFACTURING AT HAAP[a]

Compound		Emission Rate lb/day	Emission Rate ton/year
GROUP I.	EPA Criteria Pollutants		
	Particulates	14,749	2,692
	Sulfur Oxides	16,969	3,097
	Carbon Monoxide[b]	12,197	2,226
	Nitrogen Oxides[b]	64,526	11,776
	Nonmethane Hydrocarbons	2,908	531
GROUP II.	Organics TOTAL	(21,746)	(3,969)
	Acetic Acid	12,746	2,281
	Acetic Anhydride	430	42
	Formic Acid	141	26
	Isobutyl Acetate	2	0.4
	n-Propyl Acetate	1,134	207
	n-Propyl Formate	320	58
	Methyl Acetate	733	134
	Cyclohexanone	2,278	416
	Acetone	2,754	503
	Methyl ethyl Ketone	6	1
	Methyl Nitrate	1,558	284
	Nitromethane	30	5
	Methyl and Dimethylamine	18	3
	Toluene	52	9
	Phenol	0.8	0.1
	Trace Organics (Butanol, Propanol, Methanol, Methyl Formate, Formaldehyde)	10	2
GROUP III.	Miscellaneous Species		
	Methane	1,955	357
	Hydrogen	418	76
	Carbon Dioxide	2,250,000	410,625
	Ammonia	390	71
	Nitric Acid	4,409	805
	Explosives (Particulates)	2.3	0.4

[a]Assumes full mobilization as defined in Section 6.A.1

[b]Calculated as NO_2

EPA Criteria Pollutants

A qualitative evaluation of the impact of the EPA-designated air pollutants on the local environment can now be made by comparing the emission rates from HAAP with county-wide emission rates. Since only a small fraction of the total area of both counties is covered by HAAP, the munition facility may be considered as a point source or a group of point sources relative to the total county areas. In this comparison using NEDS data, it should be noted that the potential for elevated ambient pollutant concentrations in the vicinity of or downwind from the munition installation is not considered. The plant and counties emission rates are presented in Table 6A-21. From the available data, it appears that the emissions from HAAP make up a small fraction of the total emissions from Sullivan and Hawkins Counties. However, the county emission rates in Table 6A-21 were developed for RDX plant operation at less than full capacity. If HAAP does operate at full mobilization, the countywide emission rate estimates as well as the percentage of the county-wide emissions due to HAAP would increase.

EPA regulations include source performance standards (SPS) which specify the maximum permissible emission rates for several types of industries. Currently, these regulations have not been established for the explosives manufacturing industry. To set HAAP emission rates (Table 6A-20) into perspective, capacities of sources subject to EPA SPS with emissions equivalent to HAAP are presented in Table 6A-22. It has been found that the nitrogen oxide emissions from HAAP are equivalent to those from a coal fired boiler in a power plant having a capacity of 360 megawatts or a nitric acid plant which produces 21,509 TPD. On this basis, the nitrogen oxide emissions appear to be significant and are expected to have a noticeable impact on the local environment.

A major issue for EPA criteria pollutants (Group I in Table 6A-20) is the question of compliance with air quality standards. National Ambient Air Quality Standards (NAAQS) are given in Table 6A-23, nondegradation guidelines in Table 6A-24. An estimate of ground level concentrations can be made for the primary

TABLE 6A-21. COMPARISON OF HAAP EMISSIONS TO COUNTY WIDE EMISSIONS (TONS/YEAR)

Location	Particulates	SO_2	CO	NO_x	HC
HAAP[a]					
Area A[a,b]	1.108	2,209	217	1,726	1,782
Area B[a,c]	1,592	2,879	208	3,495	1,038
Total[a]	2,700	5,088	425	5,221	2,820
RTI Estimate[d]	2,692	3,097	2,226	11,776	4,500[e]
Sullivan Co.[a]	31,024	42,289	71,009	28,965	23,350
Hawkins Co.[a]	19,116	62,541	15,139	38,594	4,469
Total[a]	50,140	104,830	86,148	67,559	27,819
%[f]	5.4	4.9	0.5	7.7	10.1

[a]Data were retrieved from EPA's National Emissions Data System (NEDS); see Reference 129. NEDS is a computerized data bank which holds detailed emissions inventory data for each county in the country. It should be noted that differences in practices of reporting and updating emissions data may prevent comparisons on the same bases.

[b]Located in Sullivan Co.

[c]Located in Hawkins Co.

[d]RTI's emissions estimate assumes full mobilization.

[e]Includes 3969 tons/year of organic solvents.

[f]This value is the percent contribution of the army installation to county wide emissions for the two county area, with HAAP not at mobilization.

TABLE 6A-22. CAPACITIES OF SOURCES SUBJECT TO EPA PERFORMANCE STANDARDS WITH EMISSIONS EQUIVALENT TO THE HAAP RDX INSTALLATION

Pollutant	Emission Rate lb/day	Source Category	Emission Regulation[a]	Equivalent Capacity
Particulate	14,749	Coal-fired boiler	0.1 lb/10^6BTU	576 MW[b]
SO_2	16,969	Coal-fired boiler	1.2 lb/10^6BTU	55 MW
		Sulfuric Acid Plant	4 lb/ton	4242 TPD
CO	12,197			
NO_x	64,526	Coal-fired boiler	0.7 lb/10^6BTU	360 MW
		Nitric Acid Plant	3.0 lb/ton	21,509 TPD
HC	24,654			

[a]See Reference 130.

[b]MW = megawatt; conversion assumes power plant efficiency of 32 percent.

TABLE 6A-23. NATIONAL AMBIENT AIR QUALITY STANDARDS[a]

Pollutant	Averaging Time	Maximum Concentration	
		Primary Standard[b]	Secondary Standard[c]
Suspended particulate matter	Annual	75 $\mu g/m^3$	60 $\mu g/m^3$
	24 hr	260 $\mu g/m^3$	150 $\mu g/m^3$
Sulfur oxides	Annual	0.03 ppm	0.02 ppm
	24 hr	0.14 ppm	0.10 ppm
	3 hr		0.5 ppm
Carbon monoxide	8 hr	9 ppm	9 ppm
	1 hr	35 ppm	35 ppm
Nitrogen oxides	Annual	0.05 ppm	0.05 ppm
Nonmethane hydrocarbons	3 hr (6-9 am)	0.24 ppm	0.24 ppm
Photochemical oxidants as ozone	1 hr	0.08 ppm	0.08 ppm

Additional standards have been proposed for asbestos, beryllium, mercury, and lead; they are being prepared for fluorides, polycyclic organic compounds, odors (including hydrogen sulfide), chlorine, hydrogen chloride, arsenic, cadmium, copper, manganese, nickel, vanadium, zinc, barium, boron, chromium, selenium, pesticides, radioactive substances, and aeroallergens.

[a]See Reference 131.

[b]Primary standards have been established to protect public or human health.

[c]Secondary standards have been established to protect soil, water, vegetation, materials, and animals as well as to maintain personal comfort, weather, and visibility.

TABLE 6A-24. MAXIMUM ALLOWABLE INCREASE IN CONCENTRATION FOR SO_2 AND PARTICULATE MATTER[a]

Pollutant	Class I ($\mu g/m^3$)	Class II ($\mu g/m^3$)	Class III[b] ($\mu g/m^3$)
Particulate matter			
Annual average	5	10	60
24 hr maximum	10	30	150
Sulfur dioxide			
Annual average	2	15	(0.02 ppm)
24 hr maximum	5	100	(0.10 ppm)
3 hr maximum	25	700	(0.5 ppm)

[a]See Reference 132. The recently promulgated nondegradation regulations affect only new sources, in contrast to NAAQS which affect both existing and new sources. These regulations require weighing the incremental deterioration against social and economic considerations and limiting increases in sulfur dioxide and particulate matter concentrations within each of three classification areas. The nondegradation guidelines will not allow industrial development in areas designated Class I, will permit a modes increase in industrial development in Class II areas , and will allow industrial development in Class III areas as long as NAAQS are met.

[b]Federal Secondary Ambient Air Quality Standard.

pollutants by employing well established meteorological dispersion models.* For secondary pollutants (pollutants that are formed in atmospheric reactions), models coupling both chemistry and meteorology are required. Because of the inherent inaccuracies of dispersion modeling and the many assumptions that are made (e.g., assumptions involving the plant location, the plant characteristics, and the emission source characteristics), the accuracy of ambient air

*Meteorological dispersion models can be applied to primary pollutants only if these pollutants are assumed to be nonreacting.

concentration estimates from such meteorological models is limited to ± 200-300 percent. The dispersion analysis does, however, give a general feeling for the effect that an industry has on air quality, and these analyses are often used to assess the environmental impact of new industries by comparison of predicted air quality with applicable standards.

In this study, a meteorological model for non-reactive emissions was employed to estimate pollutant concentrations at various distances downwind of their sources.[137]

HAAP presents a problem in modeling because of its two separate areas. To simplify matters, the bend in the Holston River was ignored and Area A was assumed to be directly upstream from Area B. A particular stable set of meteorological conditions was also assumed. Using these assumptions, the ground level concentrations (specifically, at 1.5 meters height) at various locations along the downwind boundary of Area B were calculated. These maximum plant boundary concentrations ($\mu g/m^3$ and ppm) for the emissions from Areas A and B are presented in Table 6A-25.

Of the EPA criteria pollutants, the concentrations of particulates, sulfur dioxide, carbon monoxide and nonmethane hydrocarbons fall within the permissible concentration levels established by EPA in the NAAQS (see Table 6A-23). However, the ambient concentration of nitrogen dioxide at the boundary of HAAP exceeds this permissible level by a factor of approximately 55. At full mobilization, it appears that the nitrogen dioxide emissions from HAAP will have a significant impact on the environment of the surrounding area. If any new RDX facility is to be built, it would have to be built in a Class III area, since the ambient particulate concentration is greater than that established for areas designated as Class I and II (see the nondegradation guidelines in Table 6A-24). This assumes the projections of the model are valid. With a factor of 55 for the concentration excess, the assumption seems reasonable.

Once in the atmosphere, the ultimate fate of these EPA criteria pollutants is fairly straightforward. The particulate material will be deposited on the earth's surface. The sulfur dioxide will be oxidized to sulfates and sulfuric acid which will form aerosols. The fate of these aerosols will then include rainout or dry deposition. The carbon monoxide in the atmosphere will be oxidized to carbon dioxide. The fate of the nitrogen oxides (nitric oxide

TABLE 6A-25. MAXIMUM "GROUND LEVEL" CONCENTRATIONS NOTED AT BOUNDARY[a,b]

Compound		Area A $\mu g/m^3$	Area B $\mu g/m^3$	Total $\mu g/m^3$	Total ppm
Group I.	EPA Criteria Pollutants				
	Particulates	141.5	9.93	151.4	---
	Sulfur Oxides	134.4	33.4	167.8	6.4×10^{-2}
	Carbon Monoxide	403.3	---	403.3	3.52×10^{-1}
	Nitrogen Dioxide	220.8	4872	5093	2.72
	Nonmethane Hydrocarbons	5.32	17.0	22.3	3.42×10^{-3}
GROUP II.	Organics	Total (136.5)	Total (1984)	2120	1.94[c]
	Acetic Acid	1.71	1807	1809	5.76×10^{-1}
	Acetic Anhydride	---	87.7	87.7[d]	2.10×10^{-2}
	Formic Acid	---	13.4	13.4	7.14×10^{-3}
	Isobutyl Acetate	---	1.48×10^{-1}	1.48×10^{-1}	3.12×10^{-5}
	n-Propyl Acetate	40.1	---	40.1	9.63×10^{-3}
	n-Propyl Formate	2.20	---	2.20	6.13×10^{-4}
	Methyl Acetate	2.47	6.90	9.37	3.10×10^{-3}
	Cyclohexanone	---	[illegible]3	153	3.82×10^{-2}
	Acetone	---	187	187	7.90×10^{-2}
	Methyl ethyl Ketone	---	4.22×10^{-1}	4.22×10^{-1}	1.67×10^{-4}
	Methyl Nitrate	1.10	119.1	120.2	3.82×10^{-2}
	Nitromethane	2.09×10^{-1}	8.92×10^{-1}	1.10	4.43×10^{-4}
	Methyl & Dimethylamine	---	2	2	---

TABLE 6A-25. (cont'd)

Compound	Area A $\mu g/m^3$	Area B $\mu g/m^3$	Total $\mu g/m^3$	Total ppm
Toluene	---	3.05	3.05	8.11×10^{-4}
Phenol	2.65×10^{-2}	---	2.65×10^{-2}	6.91×10^{-6}
Trace Organics (Butanol, Propanol, Methanol, Methyl Formate, Formaldehyde)	88.64	6.11×10^{-1}[d]	89.25	1.36×10^{-1}[e]
Group III. Miscellaneous Species				
Methane	64.0	---	64.0	9.86×10^{-2}
Hydrogen	13.8	---	13.8	1.69×10^{-1}
Carbon Dioxide	47,760	15,050	62,810	35.0
Ammonia	---	38.8	38.8	5.60×10^{-2}
Nitric Acid	---	550.3	550.3	2.14×10^{-1}
Explosives (Particulates)	---	1.65×10^{-1}[f]	1.65×10^{-1}	---

[a] "Ground Level" = 1.5 m

[b] Assumes full mobilization

[c] ppm carbon

[d] The ambient concentrations ($\mu g/m^3$) for a particular compound should be consistent with the emission rate given in Table 6A-19 varying somewhat with source height, velocity, and temperature. The value of the ratio between the emission rate (tons/year) and ambient concentration ranges from 2 to 7 for all the emitted compounds except acetic anhydride and trace organics. For acetic anhydride and trace organic emissions, this ratio has values of 0.5 and 0.02, respectively. It is believed that the calculated ambient concentration of these compounds is higher than it actually would be.

[e] Calculated using the molecular weight of methane.

[f] Consists of 6.6×10^{-2} $\mu g/m^3$ RDX and 9.86×10^{-2} $\mu g/m^3$ TNT.

and nitrogen dioxide) will involve conversion to nitric acid and nitrates with subsequent removal by rainout and dry deposition. The hydrocarbons will be oxidized into carbon dioxide, water, and aerosols.

In addition, the hydrocarbons and nitrogen oxides are also precursors of the secondary pollutant and photochemical oxidant, ozone. Ozone is generated and accumulates in the cyclic process illustrated under the Section Known or Potential Secondary Reactions. In the cycle, free radicals (R) are generated from organic compounds by processes following the photolysis of nitrogen dioxide. These free radicals combine with atmospheric oxygen to form peroxy radicals (RO_2) which are capable of oxidizing nitric oxide to nitrogen dioxide. For each molecule of nitric oxide oxidized to nitrogen dioxide by a non-ozone species, a molecule of ozone accumulates in the atmosphere. At high hydrocarbon and nitrogen oxide concentrations representative of urban atmospheres, the concentration of hydrocarbons is more influential than that of nitrogen oxides in dictating the resulting ozone concentration. At lower hydrocarbon and nitrogen oxide concentrations representative of nonurban atmospheres, the ozone concentration is thought to be influenced more strongly by the nitrogen oxide concentration. Thus, injection of nitrogen oxides into nonurban air may enhance the ozone generative potential of the air mass. It should be noted, however, that under conditions where the concentration of nitrogen oxides is in substantial excess of the concentration of hydrocarbons, oxidant formation is inhibited and any ozone that may enter such an atmosphere is quickly destroyed by its reaction with the nitrogen oxides.

Since explosives plants are sources of both organic and nitrogen-containing compounds, the setting of the facility as well as the magnitude of the emissions relative to the local emissions will determine the impact on both the local and downwind oxidant levels. The data in Table 6A-20 show that the emission rate of nitrogen oxides is at least four times that of any other EPA criteria pollutant and that the mass ratio of the emission rates of nitrogen oxides to nonmethane hydrocarbons is approximately 22. The dominant impact of this ratio in the immediate vicinity of the RDX facility will be to destroy any ozone which may enter the plume and inhibit its formation until atmospheric processes facilitate attainment of a more favorable nitrogen

oxide-hydrocarbon ratio. Thus, the concentration of ozone in the plume should be less than that in the surrounding air parcels. In the atmosphere downwind from HAAP, the ratio may be more favorable to ozone production. However, it is difficult to ascertain the contribution of a single source to rural oxidant levels at long distances downwind because the ozone precursors may be emitted by many sources within the region.

Non-EPA Criteria Pollutants

Other emissions associated with the manufacture of RDX include such compounds as methane, toluene, alcohols (methanol, propanol, and butanol), phenol, aldehydes (formaldehyde and acetaldehyde), ketones (acetone, methyl ethyl ketone, and cyclohexanone), organic acids (formic and acetic acids), esters (methyl formate, methyl acetate, propyl formate, propyl acetate, and isobutyl acetate), acetic anhydride, ammonia, amines (methyl- and dimethyl-amine), nitric acid, nitromethane, and methyl nitrate. Emission rates for some of these compounds can be found in Table 6A-20 and a discussion of their potential atmospheric chemistry in the previous sections. The maximum ground level concentration at the boundary of HAAP can be found in Table 6A-25. The total ambient concentration of organics was found to be 1.90 ppm (carbon).

As previously mentioned, hydrocarbons (organic compounds) and nitrogen oxides are ozone precursors.[9] The organic non-EPA criteria pollutants will also generate ozone in the atmosphere (see Known or Potential Secondary Reactions). However, among these pollutants, differences exist in structure and reactivity. To assess their reactivity in the atmosphere, the rate of nitrogen dioxide formation (ppm/min), the maximum concentration of ozone produced (ppm), and the total amount of ozone produced within a given time period (ppm-min) have been measured from experiments conducted in smog chambers. The reactivities of selected organic compounds were obtained from several studies, and their reactivities relative to toluene are summarized in Table 6A-26.[133,135]

TABLE 6A-26. SUMMARY OF SMOG CHAMBER RESULTS FOR SELECTED ORGANIC SOLVENTS (RELATIVE TO TOLUENE).

Compound	Relative Reaction Rate with NO_2 ppm/min	O_3 Max ppm	O_3 Dosage ppm/min
Toluene	1.00	1.00	1.00
Ethyl alcohol	0.50[a]	1.00	---
Isopropyl alcohol	0.45[a]	0.65	--
	0.61[b]	0.20	0.15
n-butyl alcohol	1.00[a]	1.40	---
Formaldehyde	1.58[c]	0.42	0.34
Acetaldehyde	2.66[c]	1.98	1.97
Acrolein	1.70[c]	1.70	1.58
Benzaldehyde	0.30[c]	0.08	0.05
Acetone	0.30[a]	0.07	---
	0.24[b]	0.0	0.0
Methyl ethyl ketone	0.55[a]	0.90	---
	0.90[b]	0.64	0.54
Cyclohexanone	0.80[a]	0.60	---
	0.82[b]	0.23	0.36
Ethyl acetate	0.5[a]	0.80	---
n-butyl acetate	0.70[a]	0.85	---
Isobutyl acetate	0.90[a]	1.00	---
	0.58[b]	0.18	0.07

[a]See Reference 122. Initial conditions: 1.5 ppm (by volume) organic solvent, 0.6 ppm NO_x (0.57 ppm NO and 0.03 ppm NO_2), relative humidity 20%, temperature 22°C to 32°C, and irradiation time 5 hrs. No actual data are reported for Toluene.

[b]See Reference 133. Initial conditions: 4 ppm organic solvent, 2 ppm NO, and irradiation time 6 hrs. Toluene data: NO_2 rate 10.4 ppb/min, O_3 Max 0.44 ppm, and O_3 Dosage 67 ppm-min.

[c]See Reference 135. Initial conditions: 1 ppm organic solvent and 0.5 ppm NO_x. Toluene data: NO_2 rate 4.4 ppb/min, O_3 Max 0.355 ppm, and O_3 Dosage 72 ppm-min.

If the data from these studies are comparable, then the reactivities of these selected organic compounds can be assessed. From the data in Table 6A-26, it appears that acetaldehyde and acrolein have the greatest reactivity with nitric oxide and produce the greatest concentration of ozone. At the other extreme, benzaldehyde and acetone appear to be the least reactive and produce the smallest concentration of ozone.

Atmospheric Chemistry

In the atmosphere, the lifetime of an air contaminant is largely determined by the propensity of the compound to photodissociate and by its reactivity with species such as ozone and hydroxyl radicals. A compilation of half-lives ($t_{1/2}$) has been assembled in Table 6A-27 for selected air contaminants associated with RDX installations. These half-lives consider each pathway to be independent of the others and do not consider secondary or competitive pathways. The photolytic half-life assumes a first order reaction with the light intensity equivalent to that with the sun at a zenith angle of 40° (z = 40°).[59,68] The half-life in the presence of ozone assumes a constant ozone concentration equal to the NAAQS, $[O_3]$ = 0.08 ppm (see Table 6A-23). A range of half-lives is presented for the compound in the presence of hydroxyl radicals because the mean ambient hydroxyl radical concentration is not currently well established. Since it is believed to lie between 0.5 and 5.0 x 10^{-7} ppm ($0.5 \times 10^{-7} < [OH] < 5 \times 10^{-7}$ ppm),[135] these two values were chosen to bound the disappearance rate due to hydroxyl radical attack.

Nitric oxide and nitrogen dioxide are the most reactive species in this atmosphere. Half of the nitric oxide may react within minutes with ozone to form nitrogen dioxide and within hours with hydroxyl radicals to form nitrous acid. In the atmosphere, half of the nitrogen dioxide may photodissociate into nitric oxide and atomic oxygen within one minute. The nitrogen dioxide may also react with ozone or hydroxyl radicals within hours. In contrast, nitrous oxide is one of the least reactive species; the half-life of its reaction with hydroxyl radicals is great ($t_{1/2}$ = 1.72 -17.2 x 10^4 days).

Both nitrous acid, a secondary pollutant, and nitromethane rapidly photolyze. Within minutes, the atmospheric concentrations of these compounds

TABLE 6A-27. HALF-LIVES OF SELECTED AIR CONTAMINANTS ASSOCIATED WITH THE MANUFACTURE OF RDX[a,b]

Compound (A)	A + hν → $t_{1/2}$	A + O_3 → $t_{1/2}$	A + OH → $t_{1/2}$
Methane	---	9.4×10^5 days	87-870 days
Toluene	---	330 days	2.1-21 hr
Carbon Monoxide	---	1.0×10^7 days	4.6-46 days
Methanol	---	?	16.5-165 hr
n-propanol	---	?	4.1-41 hr
n-butanol	---	6.3×10^3 days	2.3-23 hr
Phenol	?	?	~29.5-295 min[c]
Formaldehyde	99 min	1.9×10^6 days	1.1-11 hr
Acetaldehyde	12 hr[d]	120 days	46.2-462 min
Acetone	14 hr	?	~12-120 hr[e]
Methyl Ethyl Ketone	14 hr	2.2×10^6 days	4.7-47 hr
Cyclohexanone	?	4.3×10^5 days	2.5-25 hr
Formic Acid	---	?	2.8-28 days
Acetic Acid	---	2.4×10^4 days	20.5-205 days
Methyl Formate	---	?	?
Methyl Acetate	---	?	?
n-propyl formate	---	?	?
n-propyl acetate	---	?	?
Isobutyl Acetate	---	?	?
Acetic Anhydride[f]	---	?	?
Ammonia	---	?	4.0-40 days
Methylamine	---	?	42.6-426 min
Dimethylamine	---	?	<42-420 min
Nitric Oxide	---	0.33 min	2.8-28 hr
Nitrogen Dioxide	1.1 min	3.0 hr	3.5-35 hr

TABLE 6A-27. (cont'd)

Compound (A)	$A + h\nu \rightarrow$ $t_{1/2}$	$A + O_3 \rightarrow$ $t_{1/2}$	$A + OH \rightarrow$ $t_{1/2}$
Nitrous Oxide	---	---	$(1.72\text{-}17.2) \times 10^4$ days
Nitrous Acid	5.8 min	---	7.0-70 hr
Nitric Acid	55 hr	---	6.9-69 days
Nitromethane	4.3 hr	?	16.5-165 hr
Methyl Nitrate	92 hr	---	?
Sulfur Dioxide	120 hr	6×10^4 days	26-260 hr

[a]The half-life of a reaction is defined by the equation, $t_{1/2} = 0.693/k$. Except for the photolyses of nitrous acid and sulfur dioxide, the rate constants are those reported in the preceding sections. The rate constant for the photolysis of nitrous acid is from Reference 59 and that for the photolysis of sulfur dioxide from Reference 68.

[b]A blank space (---) designates that the reaction between a particular species and light, ozone, or hydroxyl radical is unimportant in the atmsophere. A question mark (?) indicates that the rate constant for the reaction between a species and light, ozone, or hydroxyl radical was unavailable.

[c]The half-life of the addition reaction between o-cresol and hydroxyl radical.

[d]The rate constant used to determine this half-life is the rate constant for the photolysis of acetaldehyde at a solar zenith angle of 0° ($z = 0°$).

[e]The rate constant between acetone and hydroxyl radicals was estimated, see Reference 95.

[f]The half-life for the hydrolysis of acetic anhydride is 4.3 min.

are cut by half. Nitric acid, on the other hand, photodissociates at a negligible rate relative to nitrous acid and nitromethane; it has a half-life of fifty-five hours. Like its analogue nitric acid, methyl nitrate also photodissociates slowly ($t_{1/2}$ = 92 hr).

None of the organic compounds emitted from HAAP react with ozone at an appreciable rate; all reactions with ozone have half-lives of days. However,

the alcohols, aromatics, aldehydes, ketones, and amines are oxidized by hydroxyl radicals within hours. The higher molecular weight alcohols, aldehydes, and ketones react faster than those of lower molecular weight (i.e., butanol reacts faster than methanol, acetaldehyde faster than formaldehyde, and methyl ethyl ketone faster than acetone). The reaction between dimethylamine and hydroxyl radical is believed to be more rapid than that between methylamine and hydroxyl radical.[101]

In addition to their reactions with hydroxyl radicals, the aldehydes and ketones may photodissociate. Formaldehyde, acetaldehyde, acetone, and methyl ethyl ketone are known to photolyze within hours. It is believed that cyclohexanone also will photolyze within approximately the same amount of time.

To determine the total effect of the emissions from HAAP on the atmosphere, the secondary pollutants must also be considered. Two of the chief secondary pollutants in this atmosphere are ozone and nitrous acid. The formation and chemistry of ozone and the potential effects of explosives emissions on its formation and destruction were both discussed earlier. Nitrous acid, a secondary pollutant, is formed in an equilibrium reaction involving nitric oxide, nitrogen dioxide, and water and also in the reaction between nitric oxide and hydroxyl radicals. Nitrous acid in the presence of secondary amines can lead to the formation of carcinogenic nitrosamines either in ambient air or in the work place. Since the secondary amine, dimethylamine, is emitted from HAAP, nitrosamine formation is anticipated. No data or estimates of the quantity of this carcinogenic substance were obtained. Limited chemical modeling of the reactivity of dimethylamine is recommended to provide such estimates.

Toxicity (See also Appendix 2)

Most of the compounds emitted from HAAP are known to irritate the eyes and/or mucous membranes of the upper respiratory tract. Besides being irritants, methanol, acetaldehyde, acetone, methyl ethyl ketone, propyl formate, methyl acetate, propyl acetate, and methyl nitrate are also narcotics. In addition, formaldehyde is a suspected carcinogen of the lung and dimethylamine is known to react with nitrous acid in the atmosphere to form N-nitroso dimethylamine, a known carcinogen.[4] Permissible threshold level values for the compounds emitted from HAAP are presented in Table 6A-28.

TABLE 6A-28. PERMISSIBLE THRESHOLD LEVEL VALUES OF EMISSIONS FROM HAAP[4]

Compound	TLV[a]
Methane	---
Ethane	---
Toluene	100
Carbon Monoxide	50
Methanol[b]	200
n-propanol[b]	200
n-butanol	---
Phenol[b]	5
Formaldehyde	2
Acetaldehyde	100
Acetone	1,000
Methyl Ethyl Ketone	200
Cyclohexanone	50
Ketene	0.5
Diketene[c]	---
Formic Acid	5
Acetic Acid	10
Methyl Formate	100
n-propyl formate	---
Methyl Acetate	200
n-propyl acetate	200
Isobutyl Acetate	150
Acetic Anhydride	5
Ammonia	25
Methylamine	10
Dimethylamine	10

TABLE 6A-28. (cont'd)

Compound	TLV[a]
Hexamine	---
Nitric Oxide	25
Nitrogen Dioxide	5
Nitrous Oxide	---
Nitromethane	100
Nitric Acid	2
Methyl Nitrate	---
Cyclonite	---
Sulfur Dioxide	1 mg/m^3

[a]Unless otherwise stated, the units of the threshold level values are ppm.

[b]Threshold level values for this compound refers to the recommended upper limit in concentration which should contact the skin.

[c]Less toxic than ketene, see Reference 136.

6.A.2.5 Recommendations

In the present study, the emissions from HAAP were identified to the extent available data permitted and their emission rates were estimated. With this information in hand, a literature review was conducted to determine the known or potential atmospheric chemistry of these emissions and a meteorological dispersion analysis was performed to estimate their ambient air concentrations. If the identified emissions and the estimated rates are comprehensive and reflect reality, then the literature review of the atmospheric chemistry and the dispersion analysis will also reflect reality. From the available data, it appears that the emission rates of air pollutants, especially of the nitrogen oxides, from HAAP are of sufficient magnitude to have a significant impact on the local environment. Therefore, it is recommended that action be taken along several lines.

It is clear from the emission inventory portion of this investigation that definitive data are lacking in several instances. In particular, the nitrogen oxide emission rate from HAAP is excessive. A sizeable quantity of the reported NO_x emission may actually consist of nitrous oxide, a relatively unreactive species. It is recommended that a source sampling program be initiated to define the emission rate of each nitrogen oxide species (NO, NO_2, and N_2O) from the ammonia oxidation, nitric acid concentrators, RDX/HMX manufacturing, and steam generation processes.

Dispersion modeling analysis was employed to elucidate the impact of the identified species on the local air quality. However, this is only an initial step. Further modeling studies which couple both meteorology and chemistry are necessary to assess the hundreds of potential reactions occurring over a diurnal cycle.

To rank reactions on the basis of importance is difficult in such an interactive, dynamic system. For example, the photolytic reactions which are significant during the daylight hours are unimportant at night. Furthermore, secondary reactions involving products of photolytic reactions assume roles of various importance at night. Even within a daylight or nighttime period, different reactions may assume roles of different importance depending on the reaction time or "state of progression" for the reacting matrix.

For computer modeling to serve as a valid approach, it is necessary that the relevant individual reactions be identified in terms of both reactants and products and that the rate expressions include known rate constants. The present review of atmospheric chemistry of emissions from RDX installations revealed several cases in which this information was lacking and the literature provided little guidance in estimating the desired information. In spite of these shortcomings, computer modeling is nevertheless recognized as a valid approach for bounding atmospheric chemistry problems. Computerized models of atmospheric chemistry should be adapted to the explosives plants atmosphere and employed to identify the significant reactions under various scenarios (mobilization, non-mobilization, day, night). This is a first priority need.

Laboratory experiments should be conducted in those cases where the atmospheric chemistry of emitted species is lacking. Unfortunately, there are many compounds which fall into this catagory. Therefore, the compounds which

have the greatest concentration in the atmosphere should be given precedence. Organic compounds with estimated plant boundary concentrations greater than 10 percent of the NAAQS (0.024 ppm carbon) include acetone, cyclohexanone, acetic acid, propyl acetate, and methyl nitrate.* These compounds occur in sufficient concentration to warrant further investigation. Experiments can be conducted in large reaction vessels designed to simulate ambient conditions and define the reaction mechanisms needed for accurate simulation of the plant atmosphere.

Based on air quality data from monitors and modeling, realistic experimental conditions can be established. Reactivity parameters such as nitric oxide oxidation rate and maximum ozone concentration generated can be measured for each species. In addition, measurement programs employing such sophisticated instrumentation as GC-MS can be designed to identify and quantify reaction products. This should resolve many of the uncertainties about the identity of reaction products that were raised in the current study.

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*Acetic anhydride also falls into this category; however, it is believed by the authors that this compound will quickly hydrolyze to form acetic acid.

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APPENDIX 4

PLANT BOUNDARY CONCENTRATIONS, HAAP

Pollutant concentrations at the boundaries of HAAP were calculated using a combination of actual and estimated conditions to give what is considered to be a realistic approximation.

From the engineering analyses of the several steps in the production processes at HAAP, emissions of each pollutant were determined for each building. Due to the lack of detail available for the physical arrangements of exhaust stacks and vents, all emission points from each building were assumed to have a common location. The relative locations of the pollutant emission points in Area A and in Area B were determined from scale maps whereas the location of Area A was translated to place it directly upwind of Area B at a distance equivalent to the true separation measured not in a straight line, but along the floor of the Holston River Valley. This adjustment was made to permit the application of existing atmospheric dispersion equations and is considered not unrealistic since under drainage winds the valley would channel flow from Area A to Area B much as though the two areas were aligned along the axis of flow of the wind.

Meteorological conditions assumed to represent the worst case (resulting in high concentration of pollutants at points on the Area B boundary) were: a down valley wind from 115° (measured from North) of 1 meter sec^{-1}, and a thermodynamically stable layer above 100 meters above ground level. Between the ground level and the base of the stable layer at 100 meters, the atmospheric stability was varied through the six classes A through F.[173]

Figure 4-1 shows the locations of the receptor points for which calculations of concentrations were made. Calculations were carried out using the IBM 370 PTMTP model by Turner.[173] Maximum concentrations at the downwind boundary of Area B, resulting from emissions from Area A, Area B, and A and B combined, irrespective of boundary location and of stability class, were given in Table 6A-25 of the text.

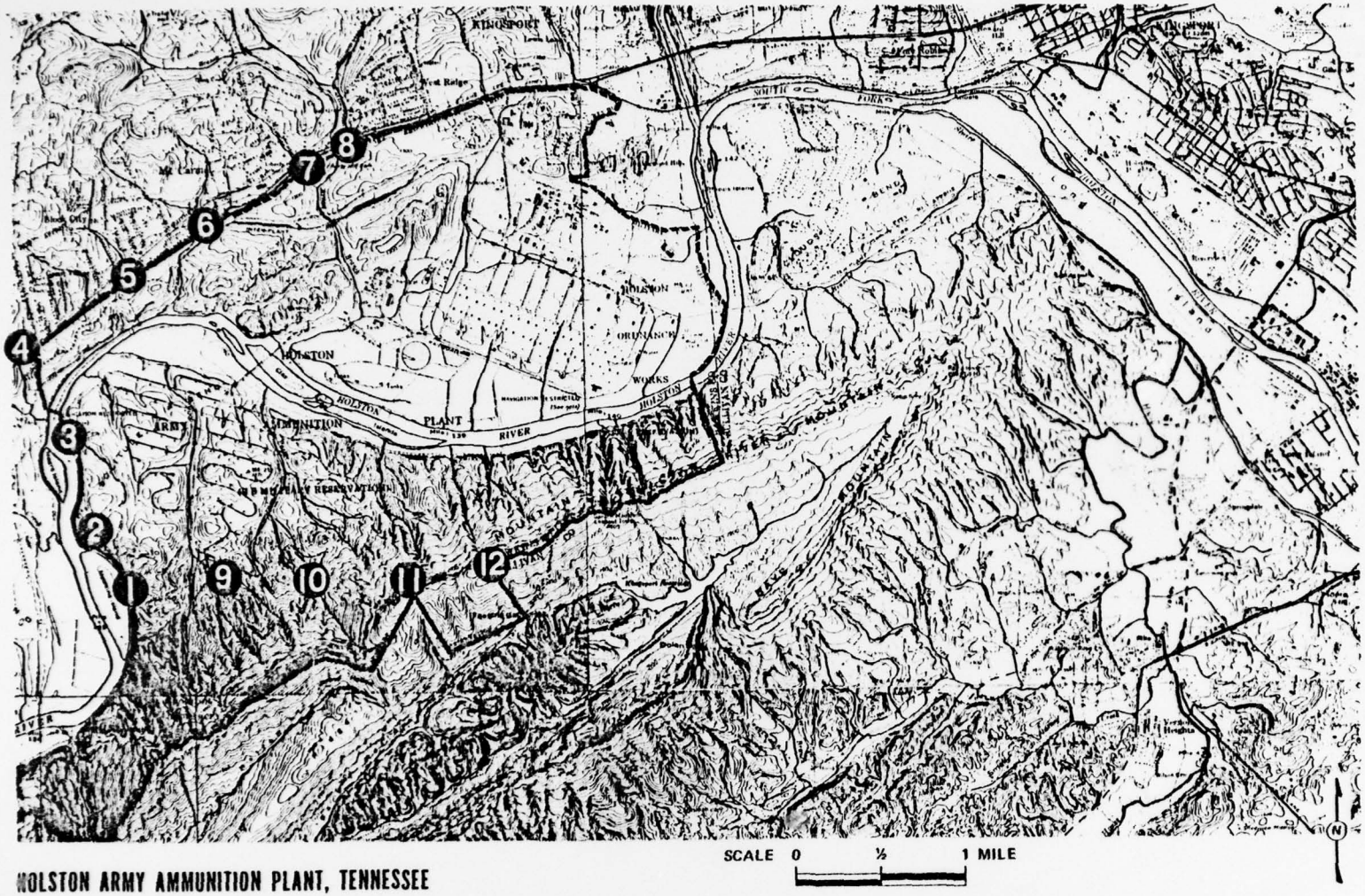

Figure 4-1. Area B receptors. (Furnished by the Ecological Research Office, Chemical Systems Lab, Aberdeen Proving Ground, MD 21010.)