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SUBSTITUTED HYDRAZINE CHEMISTRY AND CHEMILUMINESCENCE IN HIGH ALTITUDE PLUMES

Ralph H. Kummler, et al

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Ralph H. Kummler
Edward R. Fisher
Frederick P. Boynton

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$$O + N_2H_4 \rightarrow N_2H_2 + H_2O^\dagger$$

or

$$O + H_2N_2HCH_3 \rightarrow N_2HCH_3 + H_2O^\dagger$$

is capable of initiating the emission of infrared radiation. A specific set of reactions and energy transfer processes which characterize this potential emission are presented and an extensive review of the current literature related to amine oxidation is included.

A flow field calculation directed toward testing the importance of chemiexcitation in amine afterburning is presented. The results of this calculation show that enhancement in the expected infrared signature above that due to V-V and V-T processes could approach an order of magnitude due to the above afterburning reactions.

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Dr. Alva T. Stair/(617)-861-4911

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Hydrazine and amine based fuels are shown to undergo highly exothermic oxidation reactions which can be a major source of infrared energy under conditions appropriate to high altitude plume afterburning. In low pressure, high oxygen atom environments, a single step, highly exothermic mechanism

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INTRODUCTION

Hydrazine and substituted amines form an important class of rocket fuels because they can be used with storable oxidizers such as N_2O_4 or fuming nitric acid. When the products of these amine fuels interact with the atmosphere at high altitudes, measurable infrared radiation results. Although the products of substituted amine combustion (CO_2, H_2O, CO) can undergo energy transfer processes leading to infrared signatures, chemiluminescent reactions initiated by O atom attack can appreciably augment the available energy for infrared radiation. These chemiluminescent reactions occur when fuel which has passed through the main rocket engine or through auxiliary systems encounters O atoms as the exhaust gases mix with the atmosphere above about 100 km. Reactions of O atoms with hydrazine or its derivatives are strongly exothermic. Much of the energy released in such reactions is expected to form vibrationally excited reaction products and thereby be available for conversion to infrared radiation. Minor quantities of radiation (in terms of available energy) are also expected to be observable in the vacuum ultraviolet spectral region. Either wavelength region provides diagnostic information, but the value of the diagnostic depends upon our quantitative knowledge and understanding of the radiation mechanism.

Predictions of the radiation associated with chemiluminescent processes require knowledge of the concentration of reactive species, rate constants for the important reactions, and the fraction of the energy liberated by the reaction which ends up in a given internal mode. Although little is known directly about unreacted fuel concentrations in rocket engine exhausts, there is some evidence that levels of a few percent may exist and that such levels affect engine performance only slightly. Preliminary measurements of photon yields from some of these reactions are now under way at Wayne State University. In this report, we review what is known about the chemical kinetics of hydrazine and substituted amines. We include a review of the pertinent rate constant literature which supplements older but more exhaustive reviews (Bahn, 1968; Kondratiev, 1972). Finally, we postulate a zeroth order mechanism and use this mechanism in a flow field calculation to assess the production of infrared emission levels from hydrazine-MMH fueled vehicles.

SUBSTITUTED HYDRAZINE CHEMISTRY

An analogous review of reactions of hydrocarbons and partially oxidized hydrocarbons in high-altitude plumes has been issued previously [Kummler, Fisher, and Boynton (1972)]. The chemistry of RHNNR′R″ compounds is expected to be quite different from the hydrogen and hydrocarbon chemistry because of the characteristic strong NN bonding. In addition, the different chemical behavior of unsymmetrical dimethyl hydrazine (UDMH),

$$H_2NN(CH_3)_2 \quad ,$$

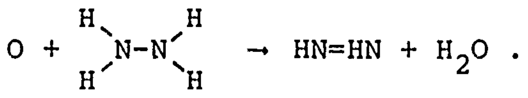
and hydrazine or monomethyl hydrazine (MMH),

$$H_2NNHCH_3 \quad ,$$

precludes some of the simplicity of the generalizations inherent in the lumped parameter approach to the hydrocarbon oxidation. However, major radiating steps in this system appear to be associated with the initial attack of O atoms on the fuel-like species, rather than the secondary reactions of products of the initial attack as in hydrocarbon oxidation.

The results of incomplete combustion at relatively low temperatures could provide a small but important mass fraction of unburned amines to the plume. Saad, et al (1972) have analyzed the products of the nitrogen tetroxide oxidation of hydrazine under nonignition conditions, attempting to simulate low pressure reaction. Mass spectroscopy, gas chromatography, and infrared absorption spectroscopy were employed to identify the stable products of the reaction system. Oxidation products which were found by Saad, et al are given in Table I. Such products are thought to be characteristic of amine-fueled engines during space ignition. For steady burn, formation of large quantities of the more complicated partially oxidized species appears unlikely, although such species may be present in the exhausts of very fuel-rich turbine gases. Thus, the oxidation products plus some fraction of unburned fuel might provide the initial conditions for chemi-excitation calculations.

In the plume, oxidation by atom attack is the chain initiation step. Oxygen atom attack on hydrazine has been studied using high intensity crossed molecular beams [Gehring, et al, (1970)]; Foner and Hudson, (1970)] to obviate the complex kinetics of a high pressure system. The approach permits identification of reaction products even when the product is highly reactive. The products of the reaction have been found to be N_2H_2 + H_2O, via the elementary reaction:

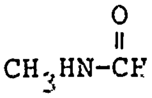
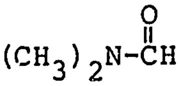


$$O + H_2N\text{-}NH_2 \rightarrow HN{=}NH + H_2O \ .$$

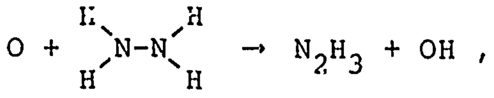
This reaction is highly exothermic (90 kcal) and forms a completely new water molecule by simultaneously abstracting two

TABLE I.

LOW TEMPERATURE OXIDATION PRODUCTS OF UDMH AND MMH WITH N_2O_4; ROUGH ESTIMATES, mole (%)

	MMH	UDMH
Methylamine $(CH_3)NH_2$	25	1
Methanol CH_3OH	20	1
Dimethylamine $(CH_3)_2NH$	20	9
Monomethylnitrosamine $CH_3HNN{=}O$	20	--
Dimethylnitrosamine $(CH_3)_2HH{=}O$	5	80
N-methylformamide  $CH_3HN{-}\overset{\overset{O}{\|}}{C}H$	2	--
Dimethylformamide  $(CH_3)_2N{-}\overset{\overset{O}{\|}}{C}H$	--	9
Other small compounds	8	--

hydrogen atoms. The expected (from, for example, the analogous O attack on ethylene) atom transfer reaction,



$$O + H_2N\text{-}NH_2 \rightarrow N_2H_3 + OH\ ,$$

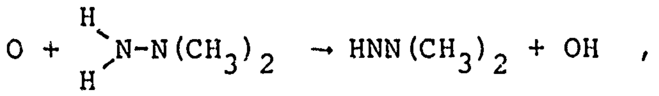
which is 26 kcal exothermic, is about 1/25 as probable (Foner and Hudson, 1970). The identification of the N_2H_2 product as HNNH rather than $:NNH_2$ is established through the ionization potentials as well as the lack of an equivalent reaction between oxygen atoms and unsymmetrical dimethyl hydrazine. In this latter case, removal of the only two hydrogens would give

$$:NN(CH_3)_2\ ,$$

and even if methyl rearrangement took place, azomethane

$$CH_3NNCH_3$$

would be formed. The actual reaction, however, is



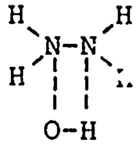
$$O + H_2N\text{-}N(CH_3)_2 \rightarrow HNN(CH_3)_2 + OH\ ,$$

so Foner and Hudson (1970) concluded that in the case of hydrazine, the hydrogens are removed from opposite ends of the molecule. Moreover, it can be anticipated that oxygen atom attack on UDMH will be much slower than O atom attack on hydrazine or MMH, which has at least one hydrogen available on each N. The absolute rate constants for these processes are not well established, but the faster double abstraction reactions probably are about a tenth of gas kinetic [Gehring, et al (1969)].

Once significant quantities of OH become available through the chain reaction sequence, additional processes are possible. Again, high intensity molecular beams [Gehring, et al (1970)] have been used to identify the products of the reaction:

$$OH + N_2H_4 \rightarrow NH_3 + NH_2O \ ,$$

which is the key reaction in severing the N-N bond. Less is known about the details of this process, but it is likely that a transition state like



forms so that no H migration is necessary. The structure of H_2NO is not known, nor are its subsequent reactions. It can be assumed in this case that UDMH and MMH undergo analogous reactions:

$$OH + H_2NN(CH_3)_2 \rightarrow H_2NO + HN(CH_3)_2$$

$$OH + H_2NNHCH_3 \rightarrow H_2NO + H_2N(CH_3) \ .$$

Thus, hydroxyl radical attack on any of the hydrazine based fuels will lead to severing of the NN bond and presumably to the formation of a substituted amine as a major intermediate. This is, however, of most critical importance for UDMH which does not have a rapid initial attack by O. It is important to note that methylamine, CH_3NH_2, is found to be an important decomposition product in MMH oxidation by N_2O_4 as well (Table I). Hence, partially oxidized fuel may be an important input to the plume. The likely mechanism for oxidation of substituted hydrazine compounds is illustrated schematically in Figure 1, and the subsequent reactions for one product (NH_3) are given in Figure 2. The reaction rate constants for the principal reactions are given in Table II. A more complete literature review of pertinent reactions is given in Appendix I.

Ultimately, complete combustion produces primarily H_2O, N_2, and CO_2 as illustrated in Table III.

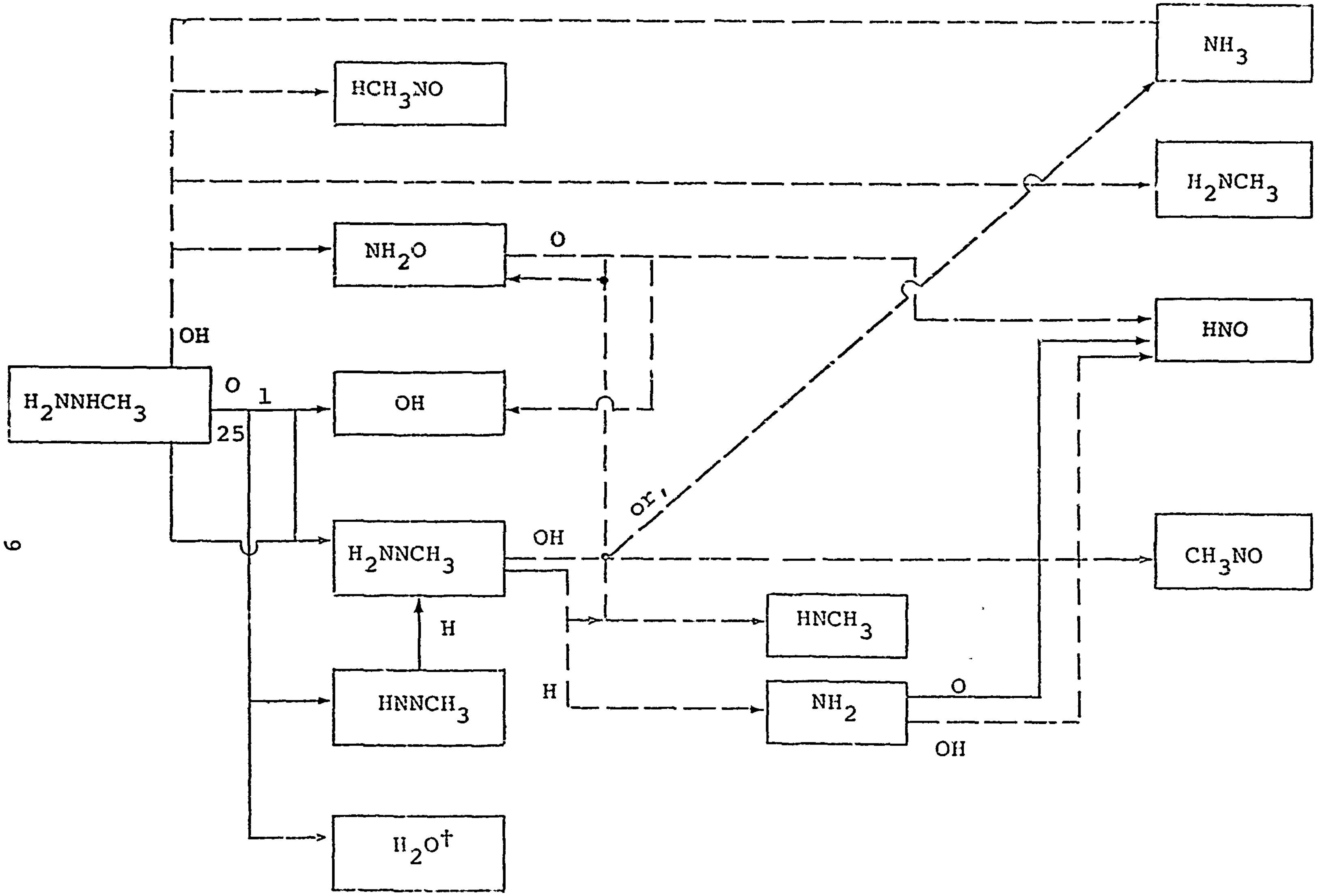


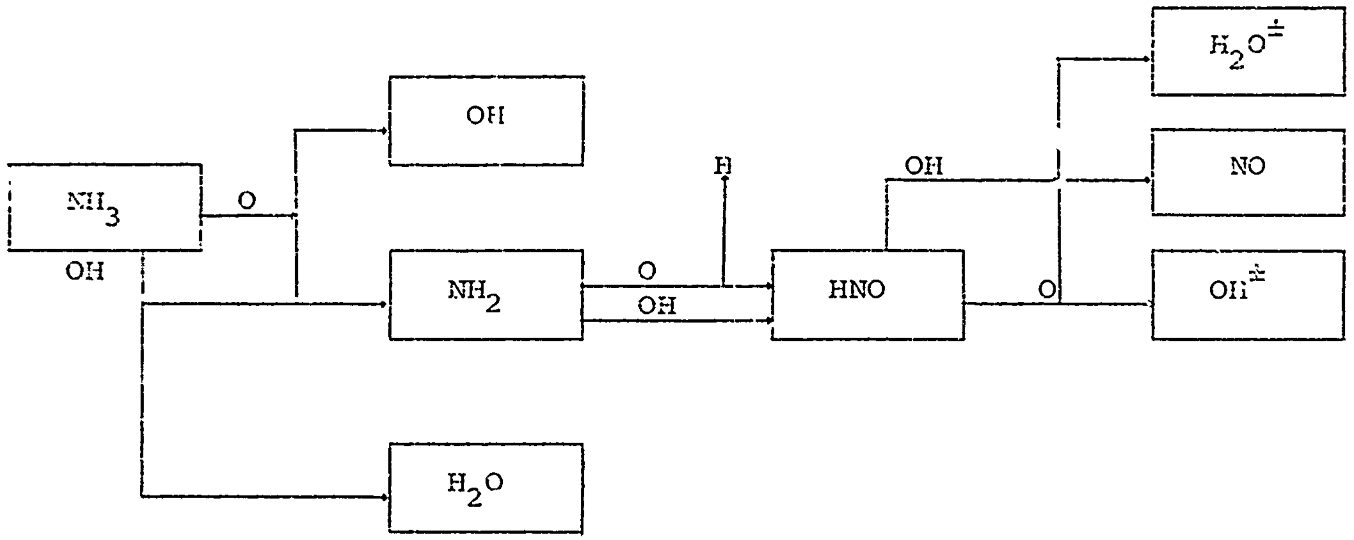
FIGURE 1. Simplified O atom oxidation mechanism for MMH (UDMH and N_2H_4 are similar) illustrating the stable species which can form in this system as intermediates. The dotted lines represent reactions which are probable, but which have not yet been experimentally observed.

TABLE II

RECOMMENDED RATE CONSTANTS FOR

$O + H_2NNR'R''$ SYSTEM

Reaction	Rate Constant, cc/sec	ΔH^R_{298}	Reference
$O + H_2NN(CH_3)_2 \rightarrow HN_2(CH_3)_2 + OH$	1×10^{-12}		Analogy with N_2H_4
$O + H_2NNHCH_3 \rightarrow HNNCH_3 + H_2O$	2×10^{-11}	-102.5	Foner and Hudson (1970) and analogy with N_2H_4
$O + N_2H_4 \rightarrow N_2H_2 + H_2O$	1.8×10^{-11}	-90	Gehring, *et al* (1969)
$OH + N_2H_4 \rightarrow NH_3 + NH_2O$	2×10^{-11}		Estimate. Product identification by Gehring, *et al* (1970).
$H + N_2H_4 \rightarrow N_2H_3 + H_2$	$2.2 \times 10^{-11}\ e^{-1260/T}$		Gehring, *et al* (1971)
$H + N_2H_3 \rightarrow 2NH_2$	2.7×10^{-12}		Gehring, *et al* (1971)
$H + N_2H_2 \rightarrow N_2H_3$	10^{-10}		Estimated [Bahn (1968)]
$O + NH_3 \rightarrow NH_2 + OH$	$2.5 \times 10^{-12}\ e^{-3000/T}$	2.7	Albers, *et al* (1969)
$OH + NH_3 \rightarrow NH_2 + H_2O$	$6.6 \times 10^{-14}\ T^{0.68}\ e^{-560/T}$	-14	Kondratiev (1972)
$O + NH_2 \rightarrow HNO + H$	10^{-11}	-15.7	Albers, *et al* (1969)
$OH + HNO \rightarrow H_2O + NO$	3×10^{-11}	-69.3	Sawyer and Glassman (1967)



$\xrightarrow{O}$ NO+O Glow

$\xrightarrow{H}$ NO+H Glow

H atom attack on
NH_3 slow

FIGURE 2. Ammonia Oxidation.

TABLE III

FINAL COMBUSTION PRODUCTS

FUEL: Unsymmetrical UDMH (50% by weight)
Hydrazine (50% by weight)

EXHAUST (mole percent):

H_2	3%
H_2O	50
N_2	35
CO	3
CO_2	10

MODEL SYSTEM

As we have discussed, oxidation of hydrazine based fuel systems leads to considerable water formation accompanied by release of considerable energy. In order to assess the potential magnitude of the resulting infrared emission, we have taken the mechanism of Figure 1 and reduced it to the simplest form consistent with the production and loss of vibrationally excited H_2O. We have also included a number of V-T and V-V excitation and deexcitation reactions for H_2O in order to have a basis for comparing calculations with and without chemi-excitation and to provide for quenching of excited species produced by reaction. The mechanism is presented in Table IV; rate data for the H_2O V-V and V-T processes are the same as we have used in calculations on the Apollo system [Boynton (1973)] and follow the recommendations of the Plume Chemistry Workshop held at Physical Dynamics, Berkeley, in January 1973 [Fisher (1973)].

The rate equations for the above mechanism were integrated through a flow field simulating the mixing layer of a Titan II exhause plume at 120 km. Details of the flow field calculation will be presented in a separate report, but a brief outline is presented here. The exit plane conditions are taken from an unpublished nozzle flow calculation by D. Thomas (Aerospace Corp.) who included finite-rate chemistry and film cooling effects.

TABLE IV

INFRARED HYDRAZINE MODEL A

FUEL CHEMI-EXCITATION REACTIONS

Reaction	Forward Rate Constant cc/sec	Reaction Energy kcal/gmole
$O + MMH \rightarrow HN_2CH_3 + H_2O$ (001) (100) H_2O (020) (010)	2×10^{-11}	-102
$O + N_2H_4 \rightarrow N_2H_2 + H_2O$ (001) (100) H_2O (020) (010)	1.8×10^{-11}	-90
$O + UDMH \rightarrow HN_2(CH_3)_2 + OH$	1×10^{-12}	-25
$OH + N_2H_4 \rightarrow NH_3 + NH_2O$	2×10^{-11}	

TABLE IV
(cont'd)

REACTIONS OF OH AND H_2O

Reaction	Rate Constant cc/molecule-sec
$O + OH \rightarrow O_2 + H$	4.0×10^{-11}
$H_2 + O \rightarrow OH + H$	$2.9 \times 10^{-11}\ e^{-4725/T}$
$OH + H \rightarrow H_2 + O$	$1.22 \times 10^{-11}\ e^{-3650/T}$
$H_2^* + O \rightarrow OH + H$	0.65×10^{-10}
$OH + H \rightarrow H_2^* + O$	$2.75 \times 10^{-11}\ e^{-4925/T}$
$H_2^* + O \rightarrow OH^* + H$	0.65×10^{-10}
$OH^* + H \rightarrow H_2^* + O$	$2.75 \times 10^{-11}\ e^{215/T}$
$OH + H_2 \rightarrow H_2O + H$	$3.8 \times 10^{-11}\ e^{-2600/T}$
$H_2O + H \rightarrow OH + H_2$	$1.5 \times 10^{-10}\ e^{-10075/T}$
$OH + H_2^* \rightarrow H_2O^* + H$	1.5×10^{-10}
$H_2O^* + H \rightarrow OH + H_2^*$	$5.8 \times 10^{-10}\ e^{-13475/T}$
$OH^* + H \rightarrow OH + H_2$	1.5×10^{-11}
$H_2O^* + H \rightarrow OH^* + H_2$	$5.8 \times 10^{-11}\ e^{-12475/T}$
$OH + OH \rightarrow H_2O + O$	$9.6 \times 10^{-12}\ e^{-390/T}$
$H_2O + O \rightarrow OH + OH$	$9.5 \times 10^{-11}\ e^{-9000/T}$
$O + OH \rightarrow O_2 + H$	4×10^{-11}
$O_2 + H \rightarrow OH + O$	$6.9 \times 10^{-10}\ e^{-8400/T}$
$O + OH^* \rightarrow O_2 + H$	4×10^{-11}
$O_2 + H \rightarrow O + OH^*$	$6.9 \times 10^{-10}\ e^{-13400/T}$

TABLE IV
(cont'd)

RELAXATION PROCESSES OF OH AND H_2O

Reaction		Forward Rate Constant (cc/molecule-sec)
$OH^* + M \rightleftarrows OH + M$	$M = H$	3×10^{-11}
"	$M = O$	3×10^{-11}
"	$M = H_2$	1×10^{-11}
"	$M = H_2O$	3×10^{-12}
$H_2O(010) + M \rightleftarrows H_2O(000) + M$	$M = H$	2×10^{-10}
"	$M = O$	1×10^{-11}
"	$M = H_2$	1×10^{-11}
"	$M = H_2O$	1×10^{-11}
$H_2O(100) + M \rightarrow H_2O + M$	$M = H$	1×10^{-11}
"	$M = O$	1×10^{-11}
"	$M = H_2$	2×10^{-13}
"	$M = H_2O$	1×10^{-12}
$H_2O(001) + M \rightarrow H_2O + M$	$M = H$	1×10^{-11}
"	$M = O$	1×10^{-11}
"	$M = H_2$	2×10^{-13}
"	$M = H_2O$	1×10^{-12}

TABLE IV
(cont'd)

$H_2O(001) + M \rightarrow H_2O(020) + M$	$M = H$	1×10^{-11}
"	$M = O$	1×10^{-11}
"	$M = H_2$	1×10^{-11}
"	$M = H_2O$	1×10^{-11}
$H_2O(100) + M \rightarrow H_2O(020) + M$	$M = H$	1×10^{-11}
"	$M = O$	1×10^{-11}
"	$M = H_2$	1×10^{-11}
"	$M = H_2O$	1×10^{-11}
$H_2O(010) + H_2O(010) \rightarrow H_2O(020) + H_2O$		$1 \times 10^{-12}\sqrt{T}$
$H_2O(020) + M \rightarrow H_2O(010) + M$	$M = H$	2×10^{-10}
"	$M = O$	1×10^{-11}
"	$M = H_2$	1×10^{-11}
"	$M = H_2O$	1×10^{-11}
$H + N_2H_4 \rightarrow N_2H_3 + H_2$		$2.2 \times 10^{-11}\ e^{-1260/T}$
$H + N_2H_3 \rightarrow 2NH_2$		
$H + N_2H_2 \rightarrow N_2H_3$		1×10^{-10}
$O + NH_3 \rightarrow NH_2 + OH$		$2.5 \times 10^{-12}\ e^{-3000/T}$
$OH + NH_3 \rightarrow NH_2 + H_2O^{(*)}$		$6.6 \times 10^{-14}\ e^{-560/T}(T)^{.68}$

TABLE IV
(cont'd)

$O + NH_2 \rightarrow HNO + H$		1×10^{-11}
$OH + HNO \rightarrow H_2O^{(*)} + NO$		3×10^{-11}
$H_2^* + M \rightarrow H_2 + M$	$M = H$	$3.2 \times 10^{-11}\ e^{-1400/T}$
"	$M = O$	$4.4 \times 10^{-13}\ \sqrt{T}$
"	$M = H_2$	$1.5 \times 10^{-7}\ e^{-139/T^{1/3}}$
"	$M = H_2O$	$1.5 \times 10^{-7}\ e^{-139}/T^{1/3}$
$N_2^* + M \rightarrow N_2 + M$	$M = H$	$6.7 \times 10^{-9}\ e^{-208/T^{1/3}}$
"	$M = O$	$1.2 \times 10^{-13}\ e^{-23/T^{1/3}}$
"	$M = H_2$	$3.9 \times 10^{-8}\ e^{-164/T^{1/3}}$
"	$M = H_2O$	$3.9 \times 10^{-8}\ e^{-164/T^{1/3}}$
$H_2^* + H_2O \rightarrow H_2 + H_2O(100)$		$2.5 \times 10^{-14}\ T^{5/6}\ e^{-30.1/T^{1/3}}$
$H_2^* + H_2O \rightarrow H_2 + H_2O(001)$		$2.5 \times 10^{-14}\ T^{5/6}\ e^{-30.1/T^{1/3}}$
$H_2^* + OH \rightarrow H_2 + OH^*$		1×10^{-12}
$N_2^* + H_2O(010) \rightarrow N_2 + H_2O(100)$		3×10^{-13}
$N_2^* + H_2O(010) \rightarrow N_2 + H_2O(001)$		3×10^{-13}
$N_2^* + H_2O \rightarrow N_2 + H_2O(010)$		$9.4 \times 10^{-11}\ e^{-64/T^{1/3}}$

TABLE IV
(cont'd)

$O + NH_2 \rightarrow HNO + H$		1×10^{-11}
$OH + HNO \rightarrow H_2O^{(*)} + NO$		3×10^{-11}
$H_2^* + M \rightarrow H_2 + M$	$M = H$	$3.2 \times 10^{-11}\ e^{-1400/T}$
"	$M = O$	$4.4 \times 10^{-13}\ \sqrt{T}$
"	$M = H_2$	$1.5 \times 10^{-7}\ e^{-139/T^{1/3}}$
"	$M = H_2O$	$1.5 \times 10^{-7}\ e^{-139/T^{1/3}}$
$N_2^* + M \rightarrow N_2 + M$	$M = H$	$6.7 \times 10^{-9}\ e^{-208/T^{1/3}}$
"	$M = O$	$1.2 \times 10^{-13}\ e^{-23/T^{1/3}}$
"	$M = H_2$	$3.9 \times 10^{-8}\ e^{-164/T^{1/3}}$
"	$M = H_2O$	$3.9 \times 10^{-8}\ e^{-164/T^{1/3}}$
$H_2^* + H_2O \rightarrow H_2 + H_2O(100)$		$2.5 \times 10^{-14}\ T^{5/6}\ e^{-30.1/T^{1/3}}$
$H_2^* + H_2O \rightarrow H_2 + H_2O(001)$		$2.5 \times 10^{-14}\ T^{5/6}\ e^{-30.1/T^{1/3}}$
$H_2^* + OH \rightarrow H_2 + OH^*$		1×10^{-12}
$N_2^* + H_2O(010) \rightarrow N_2 + H_2O(100)$		3×10^{-13}
$N_2^* + H_2O(010) \rightarrow N_2 + H_2O(001)$		3×10^{-13}
$N_2^* + H_2O \rightarrow N_2 + H_2O(010)$		$9.4 \times 10^{-11}\ e^{-64/T^{1/3}}$

TABLE IV
(cont'd)

$CO^* + M \rightarrow CO + M$	$M = H$	$6.7 \times 10^{-8}\ e^{-208/T^{1/3}}$
"	$M = O$	$1 \times 10^{-8}\ e^{-96/T^{1/3}}$
"	$M = H_2$	$9 \times 10^{-9}\ e^{-119/T^{1/3}}$
"	$M = H_2O$	$1 \times 10^{-8}\ e^{-96/T^{1/3}}$
$CO_2(010) + M \rightarrow CO_2 + M$	$M = H$	$3.8 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = O$	$2.3 \times 10^{-9}\ e^{-77/T^{1/3}}$
"	$M = H_2$	$7.6 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = H_2O$	1×10^{-11}
"	$M = CO_2$	$4.6 \times 10^{-9}\ e^{-77/T^{1/3}}$
$CO_2(001) + M \rightarrow CO_2 + M$	$M = H$	$6.7 \times 10^{-8}\ e^{-208/T^{1/3}}$
"	$M = O$	$1 \times 10^{-8}\ e^{-96/T^{1/3}}$
"	$M = H_2$	$9 \times 10^{-9}\ e^{-119/T^{1/3}}$
"	$M = H_2O$	$9 \times 10^{-9}\ e^{-119/T^{1/3}}$

TABLE IV
(cont'd)

$CO_2(001) + M \rightarrow CO_2(030) + M$	$M = H$	$2.13 \times 10^{17}\, T^{-6.34} \exp(-3013/T - 378.7/T^{1/3} + 1416/T^{2/3})$
"	$M = O$	$4.6 \times 10^{24}\, T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
"	$M = H_2$	$4.27 \times 10^{17}\, T^{-6.34} \exp(-3013/T - 378.7/T^{1/3} + 1416/T^{2/3})$
"	$M = H_2O$	$4.71 \times 10^{-40}\, T^{4.54} \exp(2081/T + 454/T^{1/3} - 1729/T^{2/3})$
"	$M = CO_2$	$9.16 \times 10^{23}\, T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
"	$M = CO$	$6.87 \times 10^{23}\, T^{-5.89} \exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$
"	$M = N_2$	$6.87 \times 10^{23}\, T^{-5.89} \exp(-4223/T - 672.7/t^{1/3} + 2683/T^{2/3})$
$CO_2(001) + H_2O \rightarrow CO_2(010) + H_2O(010)$		1×10^{-13}
$N_2{}^* + CO_2 \rightarrow N_2 + CO_2(001)$		$\left\{\begin{array}{l} 1.72 \times 10^{-6}\, e^{-175/T^{1/3}} \\ 6 \times 10^{-14}\, e^{15.3/T^{1/3}} \end{array}\right\}$ largest

TABLE IV
(cont'd)

$N_2^* + CO \rightarrow N_2 + CO^*$		$\left\{\begin{matrix} 1.78\times 10^{-6}\ e^{-210/T^{1/3}} \\ 7\times 10^{-13}\ e^{-25.6/T^{1/3}} \end{matrix}\right\}$ largest
$CO_2(001) + CO \rightarrow CO_2 + CO^*$		$1.57\times 10^{-11}\ e^{-30.1/T^{1/3}}$
$CO_2(101) + H_2O \rightarrow CO_2 + H_2O(100)$		$2\times 10^{-13}\ \sqrt{T}$
$CO_2(101) + H_2O \rightarrow CO_2 + H_2O(001)$		$2\times 10^{-13}\ \sqrt{T}$
$CO_2(021) + H_2O \rightarrow CO_2 + H_2O(100)$		$2\times 10^{-13}\ \sqrt{T}$
$CO_2(021) + H_2O \rightarrow CO_2 + H_2O(001)$		$2\times 10^{-13}\ \sqrt{T}$
$CO_2(101) + CO_2 \rightarrow CO_2(001) + CO_2(100)$		$2\times 10^{-11}\ \sqrt{T}$
$CO_2(020) + CO_2 \rightarrow CO_2(010) + CO_2(010)$		$2\times 10^{-13}\ \sqrt{T}$
$CO_2(100) + M \rightarrow CO_2 + M$	$M = H$	$3.8\times 10^{-12}\ e^{-17.6/T^{1/3}}$
"	$M = O$	$2.3\times 10^{-9}\ e^{-194/T^{1/3}}$
"	$M = H_2$	$7.6\times 10^{-12}\ e^{-17.6/T^{1/3}}$
"	$M = H_2O$	3×10^{-13}
$CO_2(101) + M \rightarrow CO_2(100) + M$	$M = H$	$6.7\times 10^{-8}\ e^{-208/T^{1/3}}$
"	$M = O$	$1.0\times 10^{-8}\ e^{-96/T^{1/3}}$
"	$M = H_2$	$9.0\times 10^{-9}\ e^{-119/T^{1/3}}$
"	$M = H_2O$	$9.0\times 10^{-9}\ e^{-119/T^{1/3}}$

TABLE IV
(cont'd)

$CO_2(101) + M \rightarrow CO_2(001) + M$	$M = H$	$3.8 \times 10^{-12}\ e^{-17.6/T^{1/3}}$
"	$M = O$	$2.3 \times 10^{-9}\ e^{-194/T^{1/3}}$
"	$M = H_2$	$4.6 \times 10^{-9}\ e^{-194/T^{1/3}}$
"	$M = H_2O$	3×10^{-13}
$CO_2(020) + M \rightarrow CO_2(010) + M$	$M = H$	$3.8 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = O$	$2.3 \times 10^{-9}\ e^{-77/T^{1/3}}$
"	$M = H_2$	$7.6 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = H_2O$	1.0×10^{-11}
"	$M = CO_2$	$4.6 \times 10^{-9}\ e^{-77/T^{1/3}}$
$CO_2(021) + M \rightarrow CO_2(011) + M$	$M = H$	$3.8 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = O$	$2.3 \times 10^{-9}\ e^{-77/T^{1/3}}$
"	$M = H_2$	$7.6 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = H_2O$	1.0×10^{-11}
"	$M = CO_2$	$4.6 \times 10^{-9}\ e^{-77/T^{1/3}}$

TABLE IV
(cont'd)

$CO_2(011) + M \rightarrow CO_2(001) + M$	$M = H$	$3.8 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = O$	$2.3 \times 10^{-9}\ e^{-77/T^{1/3}}$
"	$M = H_2$	$7.6 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = H_2O$	1.0×10^{-11}
"	$M = CO_2$	$4.6 \times 10^{-9}\ e^{-77/T^{1/3}}$
$CO_2(021) + M \rightarrow CO_2(020) + M$	$M = H$	$6.7 \times 10^{-8}\ e^{-208/T^{1/3}}$
"	$M = O$	$1.0 \times 10^{-8}\ e^{-96/T^{1/3}}$
"	$M = H_2$	$9.0 \times 10^{-9}\ e^{-119/T^{1/3}}$
"	$M = H_2O$	$9.0 \times 10^{-9}\ e^{-119/T^{1/3}}$
$CO_2(030) + M \rightarrow CO_2(020) + M$	$M = H$	$3.8 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = O$	$2.3 \times 10^{-9}\ e^{-77/T^{1/3}}$
"	$M = H_2$	$7.6 \times 10^{-11}\ e^{-7/T^{1/3}}$
"	$M = H_2O$	1.0×10^{-11}

External flow calculations were performed with the MULTITUBE and BOW codes [Boynton (1971)]. Unburned fuel concentrations of 5% in the film cooling layer and 1% in the interior exhaust gases were assumed; reactions of N_2H_4 and UDMH with O were included in the flow field calculation, so that depletion of these species would be properly accounted for in a subsequent (overlay) chemistry calculation. The rate equations were then integrated along mean flow streamlines in the mixing layer using a separate chemistry (NONEQ) which accepts the taped output of the flow field calculation.

Results of these exploratory calculations are shown in Figure 3. We show cumulative radiant intensity as a function of distance behind the vehicle for the sum of the H_2O ν_1 and ν_3 bands and the OH band (which is negligible in this calculation because important because important formation mechanisms such as $H_2 + O \rightarrow OH + H$ have not been included). The lower curve is for the H_2O excitation processes alone, and the upper curve includes the effects of the simplified chemi-excitation mechanism. The assumed production of excited H_2O by $O + N_2H_4$ is as follows:

$$O + N_2H_4 \rightarrow \left\{ \begin{matrix} 2H_2O \ (001) \\ 2H_2O \ (100) \\ 2H_2O \ (020) \\ 2H_2O \ (010) \end{matrix} \right\} + N_2H_2$$

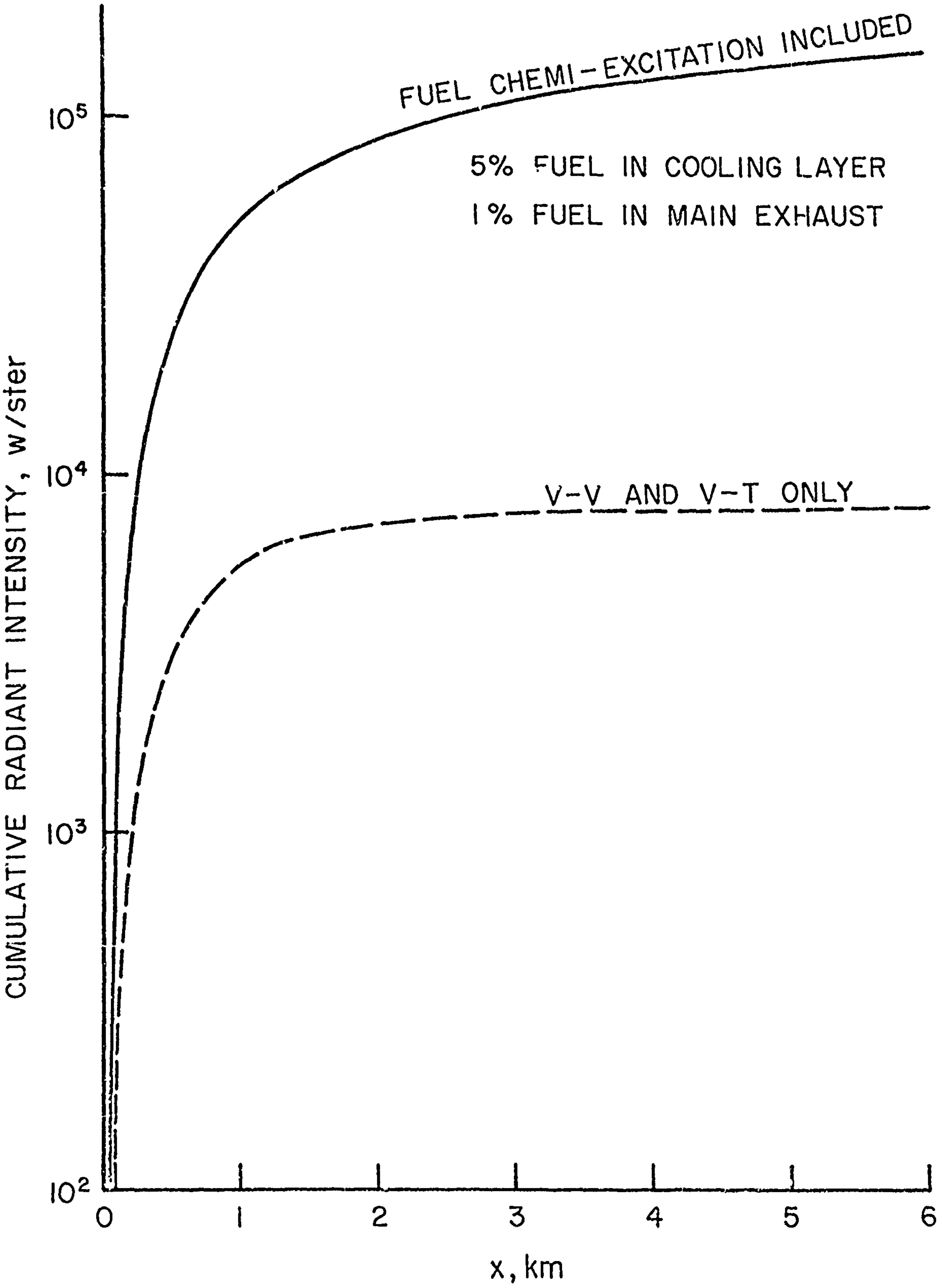


FIGURE 3. The effect of chemi-excitation on predicted cumulative radiant intensity.

This puts about 40% of the reaction energy into the stretching modes of product H_2O. (For purposes of computational convenience, we have treated a molecule excited to the second level as two singly-excited molecules; the quenching is thus somewhat more efficient than it should be.) With this assumption of product energy distribution, together with those about initial fuel concentrations, there is a substantial difference in calculated radiant intensity with and without chemiluminescent reaction.

These calculations may overestimate the contribution of chemiluminescence to the plume signature for any or all of the following reasons:

1) The exhaust-gas concentrations of N_2H_4 and UDMH may be too high. In that connection, note that N_2H_4 (the major reacting species in this system) is a good monopropellant and decomposes spontaneously at elevated temperatures to give less reactive NH_3, N_2, and H_2. The amoung of external reaction may depend on the extent of such decomposition as well as the overall unburned fuel level. This should not be the case with MMH, which is more stable.
2) The photon yields may be optimistic, although a rather drastic decrease would still allow substantial chemiexcitation relative to V-T and V-V excitation.
3) Unburned fuel could be ejected from the engine or turbine exhaust in the form of droplets which would have

> to be vaporized in the plume before reacting. [Webber, et al (1972), using a detailed combustion code to evaluate the external surface contamination potential due to unburned propellants from two small engines, calculate that essentially all unburned propellant leaving these engines is in the form of small droplets.]

However, even with these qualifications, it is evident that there is a distinct possibility that external chemiluminescence of unburned fuel species comprises a substantial fraction of amine-fueled missile plume signatures. This possibility should not be ignored in studies aimed at elucidating plume emission mechanisms.

APPENDIX I

REACTIONS OF HYDRAZINE AND AMINE COMPOUNDS WITH O AND OH

A. Reactions of Methyl Hydrazines

Reaction	Rate Constant	ΔH_{298}	Reference
$O + H_2NN(CH_3)_2 \rightarrow HNN(CH_3)_2 + OH$	(Fast)		Foner and Hudson (1970)
$\rightarrow CH_3NNCH_3 + H_2O$	(Slow)		Foner and Hudson (1970)
$\rightarrow NN(CH_3)_2 + H_2O$	(Slow)		Foner and Hudson (1970)
$O + H_2NNHCH_3 \rightarrow HN_2CH_3 + H_2O$		-102.5	Foner and Hudson (1970)
$H + H_2N_2(CH_3)_2 \rightarrow HN_2(CH_3)_2 + H_2$			Foner and Hudson (1970)

B. Reactions of Hydrazine and Derivatives

Reaction	Rate Constant	ΔH_{298}	Reference
$N_2H_4 + O \rightarrow N_2H_2 + H_2O$	$1.1 \times 10^{-10}\ e^{-600/T}$		Gehring, *et al* (1969)*
	1.8×10^{-11} (300°K)		Gehring, *et al* (1969)
$N_2H_4 + O \rightarrow$ products	$(3 \pm 1.5) \times 10^{-12}$		Shane and Brennen (1971)
a. $N_2H_4 + O \rightarrow N_2H_2 + H_2O$	product identification	-90	Foner and Hudson (1970)
b. $N_2H_4 + O \rightarrow N_2H_3 + OH$	$k_b = \frac{1}{25} k_a$	-26	Foner and Hudson (1970)
$N_2H_4 + OH \rightarrow N_2H_3 + H_2O$			Sawyer and Glassman (1967)
$N_2H_4 + OH \rightarrow NH_3 + NH_2O$	product identification		Gehring, *et al* (1970)
$N_2H_4 + NH_2 \rightarrow N_2H_3 + NH_3$			Sawyer and Glassman (1967)
$N_2H_4 + NH_2 \rightarrow NH_3 + N_2H_3$	5.2×10^{-13} (300°K)		Gehring, *et al* (1971)
$N_2H_4 + H \rightarrow N_2H_3 + H_2$	$2.2 \times 10^{-11}\ e^{-1260/T}$ (213-473°K)		Gehring, *et al* (1971)
$N_2H_4 + D \rightarrow N_2H_3 + HD$	6×10^{-13} (251-315°K)		Gehring, *et al* (1969)
$N_2H_4 + N \rightarrow$ products	1.4×10^{-13} (293°K)		Gehring, *et al* (1969)

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* Note there is a 30% error in the rate constant reported in the original reference (corrected by the authors in a private communication).

$N_2H_3 + OH \rightarrow N_2H_2 + H_2O$			Sawyer and Glassman (1967)
$N_2H_3 + H \rightarrow 2NH_2$	2.7×10^{-12} (300°K)		Gehring, <u>et</u> <u>al</u> (1971)
$N_2H_3 + O_2 \rightarrow NH_2NO + OH$			Sawyer and Glassman (1967)
$N_2H_2 + O \rightarrow N_2^* + H_2O$		-169	Becker and Bayes (1967)
$N_2H_2 + H \rightarrow N_2H_3$	$2.3^{-9}\ T^{0.5}$ (?)		Bahn (1968)
$N_2H_2 + NO \rightarrow NH_2 + N_2O$			Gehring, <u>et</u> <u>al</u> (1971)

C. Reactions of N and NH Compounds

Reaction	Rate Constant	ΔH_{298}	Reference
$N + N \rightarrow N_2(a^1\Pi_g)(J > 13)(v' = 6)$			Golde and Thrush (1972a)
$N + OH \rightarrow H + NO$	$> 10^{-11}$		Garvin and Broida (1963)
	6×10^{-11}		Miller and Permagent (1965)
	5.8×10^{-11} (320°K)		Wilson (1972) Rec.
$N + HO_2 \rightarrow NH + O_2$	$> 1.7 \times 10^{-13}$		Kretschmer and Peterson (1963)
$NH_3 + O \rightarrow NH_2 + OH$			
(main channel)	$2.5 \times 10^{-12}\ e^{-3000/T}$	$+2.7 \pm 3$	Albers, et al (1969)
	$1.7 \times 10^{-13}\ e^{-2450/T}$		Wong and Potter (1965, 1963)
	2×10^{-14} (360-460°K)*		Avramenko, et al (1962)
$NH_3 + OD$	$\sim 1^{-13}$ Exp. Est. at 500°K		Albers, et al (1969)
$NH_3 + OH \rightarrow NH_2 + H_2O$			Maclean and Wagner (1967)
	$6.6 \times 10^{-14}\ T^{0.68}\ e^{-560/T}$	-14	Kondratiev (Ref. 1288) (1972)
	$3.3 \times 10^{-9}\ e^{-19200/T}$ (1760-2037°K)*		Fenimore and Jones (1961)

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* Probably wrong or applicable only at high temperatures.

$NH_3 + H \rightarrow NH_2 + H_2$	$< 2 \times 10^{-17}$ 500°K)		Albers, et al (1969)
	$< 2 \times 10^{-16}$ (800°K)		
$NH_2 + O_2 \rightarrow HNO + OH$		-9	Sawyer and Glassman (1967)
$NH_2 + O \rightarrow HNO + H$	$\geq 10^{-11}$ (320°K)	-15.7	Albers, et al (1969)
$\rightarrow NH + OH$?	2.6×10^{-11}	-11.0	Bahn (1968)
$NH_2 + OH \rightarrow HNO + H_2$		-25.7	Bahn (1968)
$NH + O \rightarrow N + OH$	$1.7 \times 10^{-12}\ T^{1/2}\ e^{-50/T}$	-16.5	Mayer and Schieler (1966)
$\rightarrow H + NO$	E = 5000 kcal		
$NH + OH \rightarrow NO + H_2$	$2.7 \times 10^{-12}\ T^{0.56}\ e^{-760/T}$		Mayer, Schieler and Johnston (1966)

D. Reactions of H-N-O Systems

Reaction	Rate Constant	ΔH_{298}	Reference
$NO_2 + H \rightarrow OH + NO$	4.8×10^{-11} (298°K)	$E_{act} < 2$ kcal	NBS CIAP Eval.
$NO_2 + O \rightarrow NO + O_2$	7.5×10^{-11} (± 3)		Cvetanovic (1972)
	$9.1 \times 10^{-12}\ e^{-0/T}$		Davis (1972)
	4×10^{-12}		Stuhl and Niki (1970)
$OH + NO_2 \xrightarrow{\text{(wall?)}} HNO_3$	3.3×10^{-13}		Mulcahy and Smith (1971)
$NO_2 + O + M \rightarrow NO_3 + M$	5.8×10^{-32}		NBS CIAP Eval.
$NO_2 + O_3 \rightarrow NO_3 + O_2$	6.1×10^{-17}	-25 ± 5	NBS CIAP Eval.
$NO + O_3 \rightarrow NO_2 + O_2$	$9 \times 10^{-13}\ e^{-1200/T}$	-47.7	NBS CIAP Eval.
$HNO_2 + H \rightarrow N_2O + NO$		-69.3	
$HNO_2 + H \rightarrow H_2 + HO_2$		-25.2	
$HNO_2 + O \rightarrow OH + NO_2$		-23.5	
$HNO_2 + OH \rightarrow H_2O + NO_2$	$1^{-12}\ e^{-1000/T}$	-40.2	Est.- NBS CIAP Eval.
$HNO_3 + O \rightarrow OH + NO_3$	$\leq 1.5 \times 10^{-14}$		NBS CIAP Eval.

$HNO_3 + H \rightarrow$ products	$< 1 \times 10^{-13}$		Morris and Niki (1971)
$OH + HNO_2$		-29.5	
$H_2 + NO_3$		-3 ± 5	
$H_2O + NO_2$		-69.7	
$HNO_3 + OH \rightarrow H_2O + NO_3$	$1.4 \times 10^{-12}\ e^{-1000/T}$	-18 ± 5	Est. - NBS CIAP Eval.
$HNO + H \rightarrow H_2 + NO$	$> 5 \times 10^{-14}$	-53.3	NBS CIAP Eval.
$HNO + O \rightarrow OH + NO$	$8 \times 10^{-13}\ T^{1/2}$	-53	Kondratiev (1972)
$HNO + OH \rightarrow H_2O + NO$	1.5×10^{-10}	-69.4	NBS CIAP Eval.
$HNO + H \rightarrow H_2 + NO$	10^{-11} (1600-2000°K)		Bulewicz and Sugden (1964)
	5×10^{-14} (300°K)		Thrush (1965)
	$2 \times 10^{-13} - 2 \times 10^{-14}$ (300°K)		Kohout and Lampe (1967)
$HNO + OH \rightarrow H_2O + NO$	$\sim 3 \times 10^{-11}$	-69.3	Sawyer and Glassman (1967)
	1.5×10^{-10} (1600-2000°K)		Bulewicz and Sugden (1964)

E. Energy Transfer and Energy Pooling

Reaction	Reference
$N_2(a^1\Pi_g) + CO \rightarrow N_2 + CO(A^1\Pi,\ v' \leq 8)$ by level	Golde and Thrush (1971) Golde and Thrush (1972a) Golde and Thrush (1972b)
$N_2(a^1\Pi_g) + CO \rightarrow N_2 + CO(\text{Triplet})$	Golde and Thrush (1972b)
$N_2^* + NO^* \rightarrow N_2^{**} + NO$	Fontijn, et al (1970)
$N_2^{**} + CO(X) \rightarrow N_2(X) + CO(A)$	Fontijn and Ellison (1971)
$\left.\begin{array}{l} NO^* \\ N_2^* \end{array}\right\} + CO^* \rightarrow \begin{array}{l} NO + CO(A) \\ N_2 \end{array}$	Fontijn, et al (1970) Fontijn and Ellison (1971)

F. Radiative Lifetimes

Reaction	Radiative Lifetime, sec	Reference
$CO(A^1\Pi) \rightarrow CO(X^1\Sigma^+) + h\nu$ (Fourth Positive)	10^{-8}	Hesser (1968)
$CO(a^3\Pi) \rightarrow CO(X^1\Sigma) + h\nu$ (Cameron System)	$(4.4 \pm 1.1) \times 10^{-3}$	Slanger and Black (1971)
$N_2(a^1\Pi_g) \rightarrow N_2X + h\nu$	1.4×10^{-4}	Shemansky (1969)

G. Nitrogen Chemistry: Quenching

$N(^4S) + N_2(B^3\Pi_g) \rightarrow N(^4S) + N_2(a^1\Pi_g)$	3.3×10^{-11}	Golde and Thrush (1971)

APPENDIX II

THERMODYNAMIC PROPERTIES

HEATS OF FORMATION EMPLOYED BY BAHN (1968)

Wherever available, JANAF Thermochemical Tables have been used. The values are in kcal/mole.

H_2	0.
H	52.102
OH	9.432
HO_2	5.
H_2O	-57.798
H_2O_2	-32.53
O_2	0.
O	59.559
O_3	34.1
N_2	0.
N	112.965
NH	79.2
NH_2	40.07
NH_3	-10.79
N_2H_2	50.9
N_2H_3	36.8
N_2H_4	22.79
NO	21.58
NO_2	7.91
NO_3	17.
N_2O	19.61
N_2O_3	19.8
N_2O_4	2.17
N_2O_5	2.7
HNO	23.8
HNO_2	-18.34 & -18.84
HNO_3	-32.1

FONER AND HUDSON (1970)
HEATS OF FORMATION, kcal/mole

N_2H_2	48.7 ± 5	Foner and Hudson (1958)
$HNNCH_3$	37.4 ± 3	Foner and Hudson (1970)
H_2NNHCH_3	22.55	Foner and Hudson (1970)
CH_3NNCH_3	43.2 ± 2	Page, et al (1953)

Bond Dissociation

$H\text{-}HN_2(CH_3)_2$	85 ± 5	Foner and Hudson (1970)
$H\text{-}HN_2HCH_3$	66 ± 5	Foner and Hudson (1970)
$H\text{-}N_2H_3$	76 ± 5	Foner and Hudson (1970)
$H\text{-}HN_2H$	54 ± 7	Foner and Hudson (1970)
$H\text{-}(CH_3)N_2H$	53 ± 6	Foner and Hudson (1970)

MMH Vapor Pressure $\ell og_{10} P = -7.88 \, \ell og_{10} T - \frac{3.146}{T} + 31.746$ Aston, et al (1951)

APPENDIX III
OBSERVED CHEMILUMINESCENCE

Spectra Observed

Transition / Reaction	NH_2 (4000 A)	NH 3360-3370 $^3\Pi - ^3\Sigma$	OH 3066	$A^3\Sigma - X^2\Pi$ NO γ Band 225-2850	HNO 7600	Reference
$O + NH_3$					M	Kreiger and Kummler, unpublished work
$O + N_2H_4$	S	S	S	S		Becker and Bayes (1967) Hall and Wolfhard (1956)
$H + NH_3$	-	-	-	-		Moore, *et al* (1956)
$H + N_2H_4$	M	W				Moore, *et al* (1956) Becker and Bayes (1967)

W = Weak

M = Moderate

S = Strong

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