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FINAL REPORT

THE RADIATION CHEMISTRY OF ACETYLENIC COMPOUNDS

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THE AMERICAN OIL COMPANY

TECHNICAL REPORT NO. AFML-TR-65-236
JULY, 1965

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NOTICES

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Air Force Materials Laboratory
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FOREWORD

This report was prepared by the American Oil Company of Whiting, Indiana, under USAF Contract No. AF 33(616)-8247. This contract was initiated under Project No. 7360, "The Chemistry and Physics of Materials", Task No. 736003, "Atomic and Molecular Interactions". The work was administered under the direction of the Materials Physics Division, Air Force Materials Laboratory, Research and Technology Division, with Mr. R. E. Rondeau acting as Project Engineer.

This report covers work from 1 December 1961 to 1 May 1965. This work was done jointly by the American Oil Company and the High Energy Physics Branch, Materials Physics Division, Air Force Materials Laboratory.

Major contributions to the work were made by R. E. Rondeau and L. A. Harrah of the High Energy Physics Branch, and T. D. Nevitt, J. Maniotes, R. Schaffer, and H. H. Barber, Jr., of the American Oil Company.

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This technical report has been reviewed and is approved.

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ABSTRACT

G-values for radiolysis products were determined for propyne and butyne-1 in the vapor phase and for butyne-1, butyne-2, pentyne-1, pentyne-2, hexyne-3, acetonitrile and propionitrile in the liquid phase.

The rupture of a C-H bond probably from a carbon β to the triple bond results in H_2, coupling products, and H atom addition. H atom addition leads to mono and poly olefins. The rupture of a C-C bond results in fragmentation in the vapor phase but recombination to form 1,2-diolefins in liquid phase. Both α and β C-C bond rupture occur. Alkyl benzene--alkyne trimers--form, probably by excitation. Analogous C_3N_3 ring compounds may form but were not detected. Gas chromatography techniques for alkyne and nitrile analyses are described.

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I. INTRODUCTION

The purpose of this contract is to study the effects of radiation on hydrocarbons that contain a triple bond. The ultimate objective is to determine reaction mechanisms so that detailed analysis of these few compounds can be used to predict the radiation chemistry of the broad class of triple bond compounds. Our approach involves submitting selected compounds to controlled doses of radiation and then separating and analyzing the products of the reaction. Thus, an important part of the work was the development of reliable analytical techniques, particularly gas chromatography.

Acetonitrile and propionitrile, compounds representative of the nitriles, were studied first. However, as reported earlier (1), their products were too complex for reliable identification with our available analytical methods. Consequently, we directed our attention toward the acetylenes, a class of compounds that should permit more accurate analyses and thus yield information that should also be of value in interpreting the results obtained with the nitriles. Butyne-2 was the first acetylene chosen for detailed study. (1) Butyne-1, pentyne-1, pentyne-2 and hexyne-3 were then studied to show the effect of structure change. Finally, radiolysis of propyne and butyne-1 in the gas phase were examined and compared with liquid phase work. (2)

II. EXPERIMENTAL PROCEDURES

Sample preparation and irradiation were usually carried out at the Air Force Materials Laboratory. Separation of products and analysis by gas chromatography were usually done by The American Oil Company.

Sample Preparation and Irradiation

Acetonitrile (Eastman) was purified by distillation on a Todd column, 5 mm I.D., at a reflux ratio of 50 to 1. The middle cut was collected and treated with KOH to remove traces of HCN. Degassing was accomplished by the Newton technique (3). The liquid was transferred to a flask containing P_2O_5 and a Teflon encased stirring magnet. The flask was equipped with a reflux dewar and attached to a high vacuum system. The dewar was filled with a chlorobenzene-liquid nitrogen slush bath (-45°C), the rotating magnet was turned on, and the apparatus was opened to the pumping system through a liquid nitrogen cold trap. After refluxing for several minutes, the refrigerant was removed from the reflux dewar, and the degassed liquid was distilled into irradiation ampoules and sealed off at a pressure of 1 micron.

Propyne, butyne-1, butyne-2, pentyne-1, pentyne-2, and hexyne-3, obtained from various sources, were also purified by distillation. Butyne-1 proved particularly difficult to purify and could be obtained sufficiently pure only by preparative-scale gas chromatography. Sample preparation of the acetylenes was the same as that used for the nitriles.

The irradiation vessels for liquid samples were pyrex glass tubes, 13 x 90 mm., fitted with break seals. For gas samples, glass tubes, 35 x 250 mm, fitted with break seals were used. Irradiation was by a 1500-curie cobalt 60 gamma-ray source of Brookhaven design for successive 24-hour periods to a maximum of 120 hours (4). Doses ranged from 2 x 10^{20} to 10^{21} ev/g. Dose rate was usually obtained through the use of ferrous sulfate, where the ferric ion concentration was determined by measuring the ultraviolet absorption at 304 millimicrons with a Carey recording spectrophotometer (5). These results were cross-checked with plastic dosimeters using the same instruments. In some of the later work ceric sulfate dosimetry was also used. Electron density factors were employed to compensate for density differences between the dosimeters and systems under investigation (6). Product yields are reported as G-values, the number of molecules per 100 electron volts of radiation absorbed in the system.

Separation of Products

After irradiation, the sample was opened on the vacuum line, total hydrogen and methane separated and the gas volume measured. The ratio of hydrogen to methane was determined by mass spectrography. Hydrocarbons, used as internal standards for gas chromatography, were added to the remaining sample and the resulting mixture was removed from the line. The weight of the sample could be obtained by weighing the sealed sample tube at this time and after the liquid sample had been removed. Samples were cooled and analyzed immediately after opening by gas chromatography. Some material was saved from each run for future analysis by placing it in indium capillary tubing and sealed by pinching the ends of the tubing. Samples have been kept intact for several years by this method.

Vacuum Line Operations--The vacuum line used in this work is shown in Figure 1. Glass sample tubes containing radiated gases were attached to the line at point A; those containing radiated liquids were sealed at point B. Prior to opening the samples, the vacuum line was evacuated to less than 1 micron, as indicated by the McLeod gauge C.

The gaseous sample was placed at point A; opened by dropping an iron slug on the break-off-ski; and total gas in the irradiated sample was measured in a calibrated volume D. Samples were then cooled in liquid nitrogen; the non-condensible gases consisting mainly of hydrogen and methane were transferred by Toepler pump E via valve F, cold trap G, and valve H into a calibrated measuring tube I. (Operation of this pump is described at the end of this section.) Initial handling of liquid samples was similar except that the samples were first cooled in liquid nitrogen, then opened and the non-condensibles Toepler pumped over into tube I.

When the transfer of non-condensibles appeared complete, valve H was closed and the liquid nitrogen at G removed to allow any condensibles to thaw out and re-enter the sample tube; the liquid nitrogen was replaced at G but removed from the sample to free any trapped non-condensibles in the condensed phase. After the condensibles thawed out, the sample was again cooled with liquid nitrogen, valve H opened, and the pumping operation resumed.

After all non-condensibles were pumped into tube I and measured, they were transferred by Toepler pump J via valves K, L, M into gas bulb N. The condensibles were transferred into tube O by removing the liquid nitrogen from the sample tube and cold trap G and placing it at O.

Internal standards (for gas chromatographic analysis) were a added to the condensibles either from bulbs P or Q, and measured in calibrated volume R by manometer S. The glass tubes containing condensible and non-condensible phases were removed from the line and analyzed by gas chromatography and mass spectrometry, respectively.

Toepler Pump Operation--An apparatus designed for measuring small amounts of non-condensibles is shown in Figure 2. A compact Toepler pump is used to compress the non-condensibles into a modified McLeod gauge. As now assembled, measurements of non-condensibles ranging from less than 0.02 ml. to more than 1 ml. can be obtained with an accuracy of better than 1%.

The Toepler pump was obtained from H. S. Martin (No. M-40155). The float valve assembly E, from Delmar Scientific Laboratories (No. DS-6010), was modified by removing one of the float valves. The manometer C was constructed of 3/8-inch gauge glass and 2 mm. capillary tubing. The measuring tube B was made from 3/8-inch gauge and calibrated with mercury prior to assembly of the apparatus.

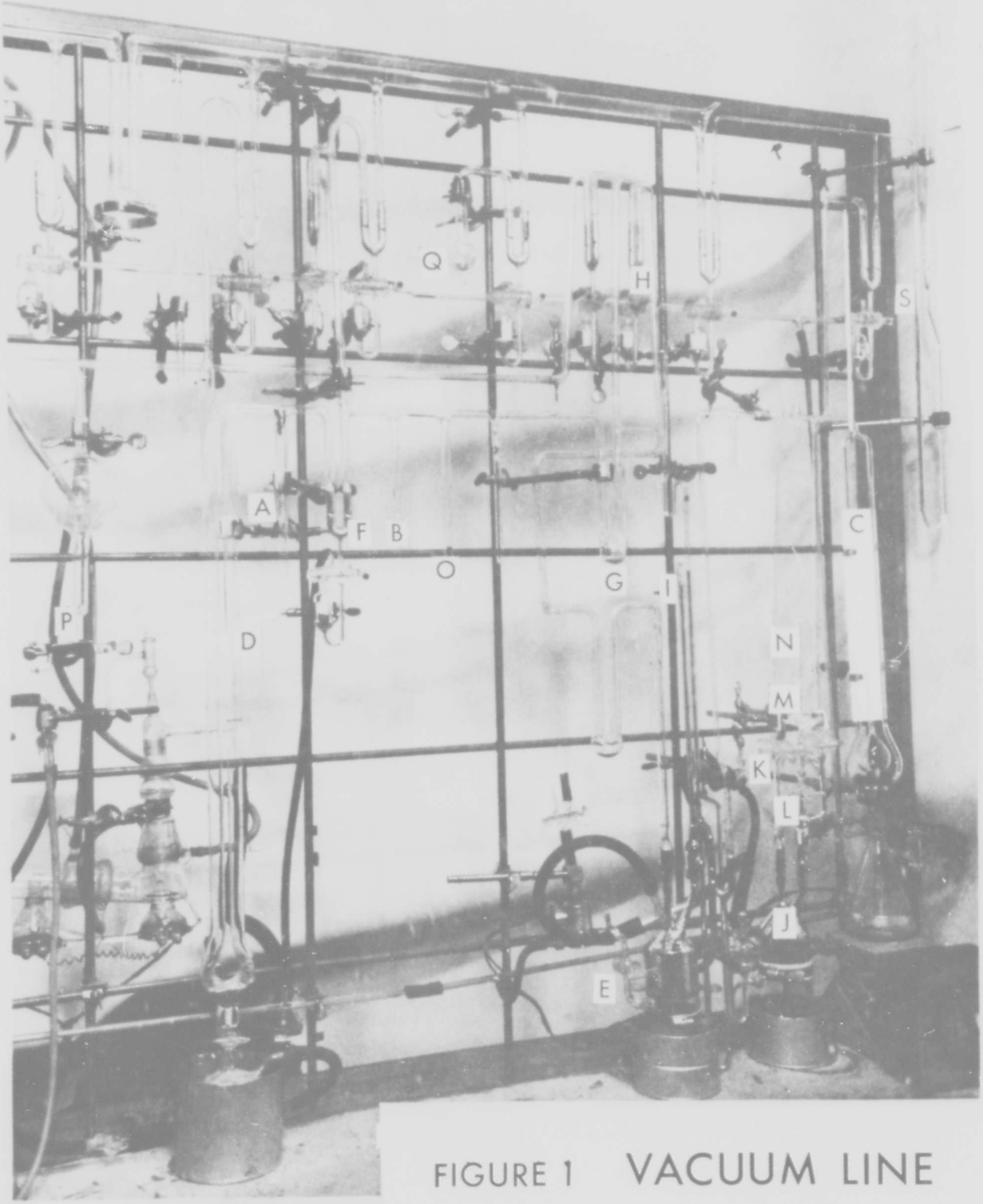


FIGURE 1 VACUUM LINE

With float valve E open and the Toepler pump in operation, the system is thoroughly evacuated, as shown in Figure 2. Float valve E is closed and the non-condensible gases are introduced via tube A, as shown in Figure 2. The Toepler pump is operated until no more gas appears to be forced into the measuring tube B.

The Toepler pump is then shut off and mercury is allowed to fill manometer C and measuring tube B; Figure 2. The amount of non-condensibles is computed by measuring the mercury levels with a cathetometer. A check on the completeness of gas removal from tube A can be made by resuming the operation of the Toepler pump, followed by a redetermination of the mercury levels.

Gas Chromatography of the Nitriles

Considerable time was spent in a search for a gas chromatographic columns, detector evaluation, analysis of pilot samples, and establishment of limits of detection. Chromatographic columns were needed that would separate products having widely differing boiling ranges as well as products boiling close to acetonitrile. Because the products were highly polar, stationary phase supports were prepared with a very low adsorption level. Three methods were used to reduce column adsorption: high concentrations of stationary phases, caustic-treated supports, and Teflon supports. All columns had to be conditioned by nitrogen purging for hours or even days at temperatures at least 50°C. above the projected column temperature. Columns developed for nitrile analysis are shown in Table 1.

TABLE 1

CHROMATOGRAPHIC COLUMNS FOR NITRILE ANALYSIS

	Materials Separated
10% LAC 2R-446 on Fluoropak 80 2' x 1/4" column, 155°C.	Malononitrile Unknown 5 Succinonitrile
20% ET-540 on 4% KOH & 96% Chromosorb W 12' x 1/4" column, 65°C.	Dimethylamine Ethylamine Unknown 1
Same, 107°C.	Acetonitrile Propionitrile Butyronitrile Unknown 3 Unknown 4
8% OF-6-7009 on Fluoropak 80 12' x 3/16" column, 45°C.	HCN H_2O Acetonitrile Propionitrile
2% β,β-thiodipropionitrile on 28% Carbowax 400	Light hydrocarbons
30-60 mesh Chromosorb W 12' x 1/4" column 82°C	Unknown 2

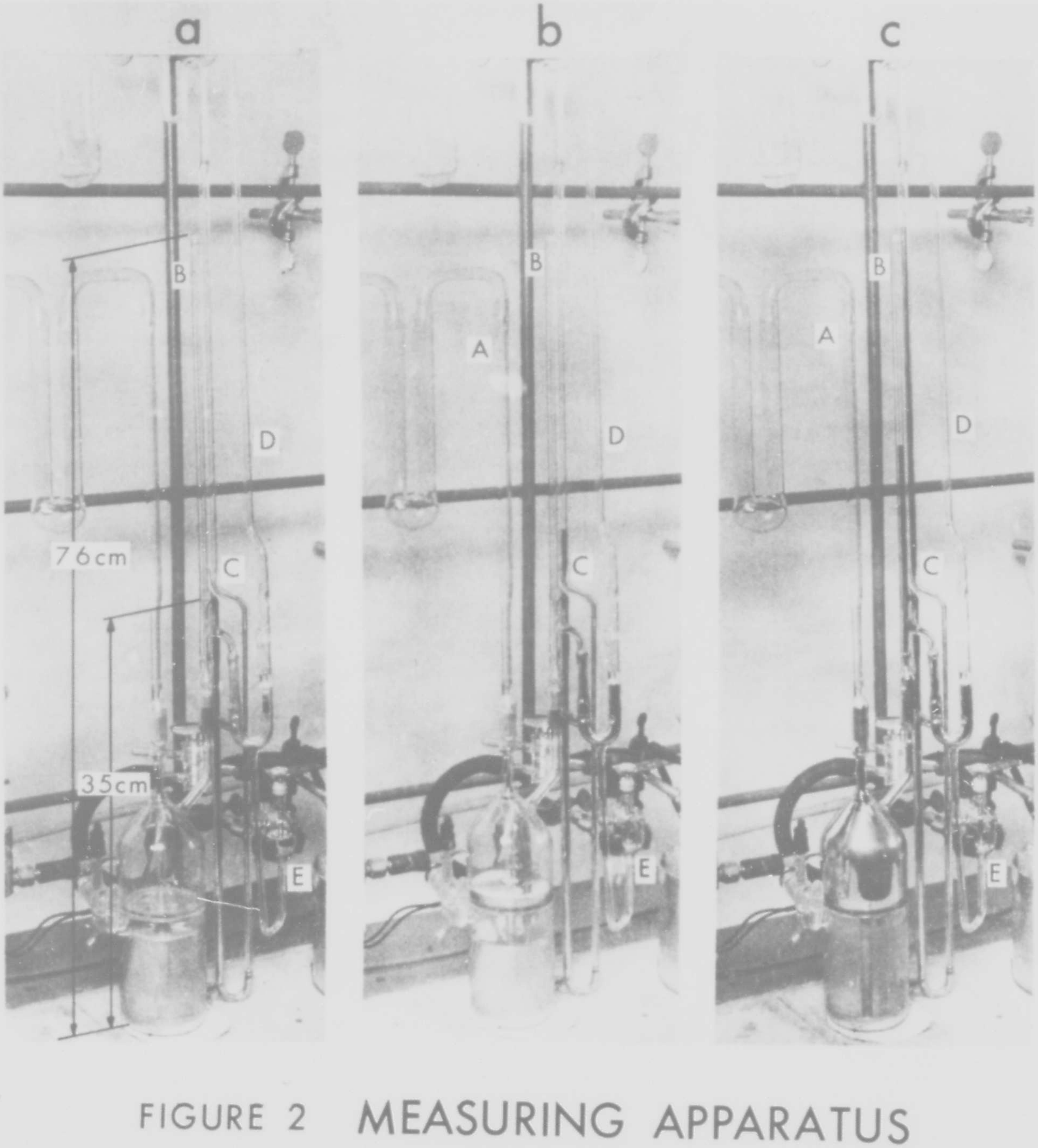


FIGURE 2 MEASURING APPARATUS

Both thermal conductivity and hydrogen flame ionization were evaluated for sensitivity to hydrogen cyanide and nitriles. The factors are given relative to acetonitrile, CH_3CN, defined as 1.00 when measured by thermal conductivity. Sensitivity factors are given in Table 2.. Hydrogen cyanide sensitivity was four times higher with thermal conductivity than with hydrogen flame ionization. Except for hydrogen cyanide and cyanogen, the sensitivity of other components was much higher by hydrogen flame detection.

TABLE 2

GAS CHROMATOGRAPHY DETECTOR SENSITIVITY FACTOR

Thermal Conductivity		Hydrogen Flame Ionization	
HCN	0.79	Propane	3.00
CH_3CN	1.00	Toluene	6.91
C_2H_5CN	1.06	HCN	0.11
		C_2N_2	0.12
		CH_3CN	1.30
		C_2H_5CN	2.37
		$(CH_2CN)_2$	1.22

Analysis of Low Molecular Weight Hydrocarbons

Unusually selective and sensitive methods of hydrocarbon analysis were required for acetylene analysis. These requirements stemmed from the complexity and low concentration of products. Low molecular weight products were alkanes, olefins, diolefins, acetylenes, and vinyl acetylene; high molecular weight products were a complex mixture of polyunsaturates. Total products from irradiations were less than 0.4%.

The gas chromatographic equipment consists of sample injection ports, a four-way Teflon-plug valve, a silver-nitrate absorber, a chromatographic column, a hydrogen flame ionization detector, an electrometer, and a recording potentiometer, Figure 3. A Teflon-plug valve provides a convenient means for inserting or removing the silver nitrate absorber between the chromatographic column and the detector. Needle valves, positioned in front of capillary tubing restrictors, regulate the flow of nitrogen carrier gas through the chromatographic column and the flow of hydrogen to the detector.

Columns used for hydrocarbon analysis are shown in Table 3. The C_1 through C_5 light hydrocarbons are analyzed on the itaconate column. Use of the silver nitrate absorber for removal of 1-alkynes is limited to separations on the itaconate column and is further limited to operating temperatures of 25 to 50°C.

Impurities and products which elute from the itaconate column near the irradiated alkyne are analyzed on the polyphenyl ether column.

Analysis of Polymeric Hydrocarbons

Both packed and capillary columns are used for the analysis of polymeric products. Pressure-programmed analyses on the capillary column give the highest resolution of polymeric products (7). This technique, followed by temperature programming after a pressure of 70 psi is attained, has permitted elution of products through tripropylbenzenes.

Temperature-programmed gas chromatography on the packed Polyox columns permits elution of some C_{20} products. Although resolution on the packed column is less than that obtained on the capillary column, the capacity of the packed column is much greater. After separation on packed columns, fractions were concentrated twenty-fold and examined further by mass spectrometry. Reduced-pressure distillation eliminates most of the unreacted alkyne, while most of the dimers and higher-boiling products are retained.

Silver nitrate absorbers which quantitatively absorb 1-alkynes without removing other classes of hydrocarbons have been developed for subtractive gas chromatography. The absorbers were prepared by adding saturated solutions of silver nitrate in glycerol dropwise, to Chromosorb W which was stirred continuously to effect uniform dispersion. After adding 35% by weight of the saturated solution of silver nitrate, the absorbent was placed in an oven at 45° for two hours and then packed into a 10" section of 1/4" aluminum tubing. Initially, a chromatogram of all the light hydrocarbons in a sample containing alkynes is obtained without the absorber. A second chromatogram of the same sample is obtained with the silver nitrate absorber. Disappearance of a particular peak means the 1-alkyne was the only hydrocarbon present which eluted at that relative retention time. If the area of the peak is reduced, another class of hydrocarbon in addition to the alkyne is present. An analysis of butyne-2 products given in Table 4 shows how this technique is used.

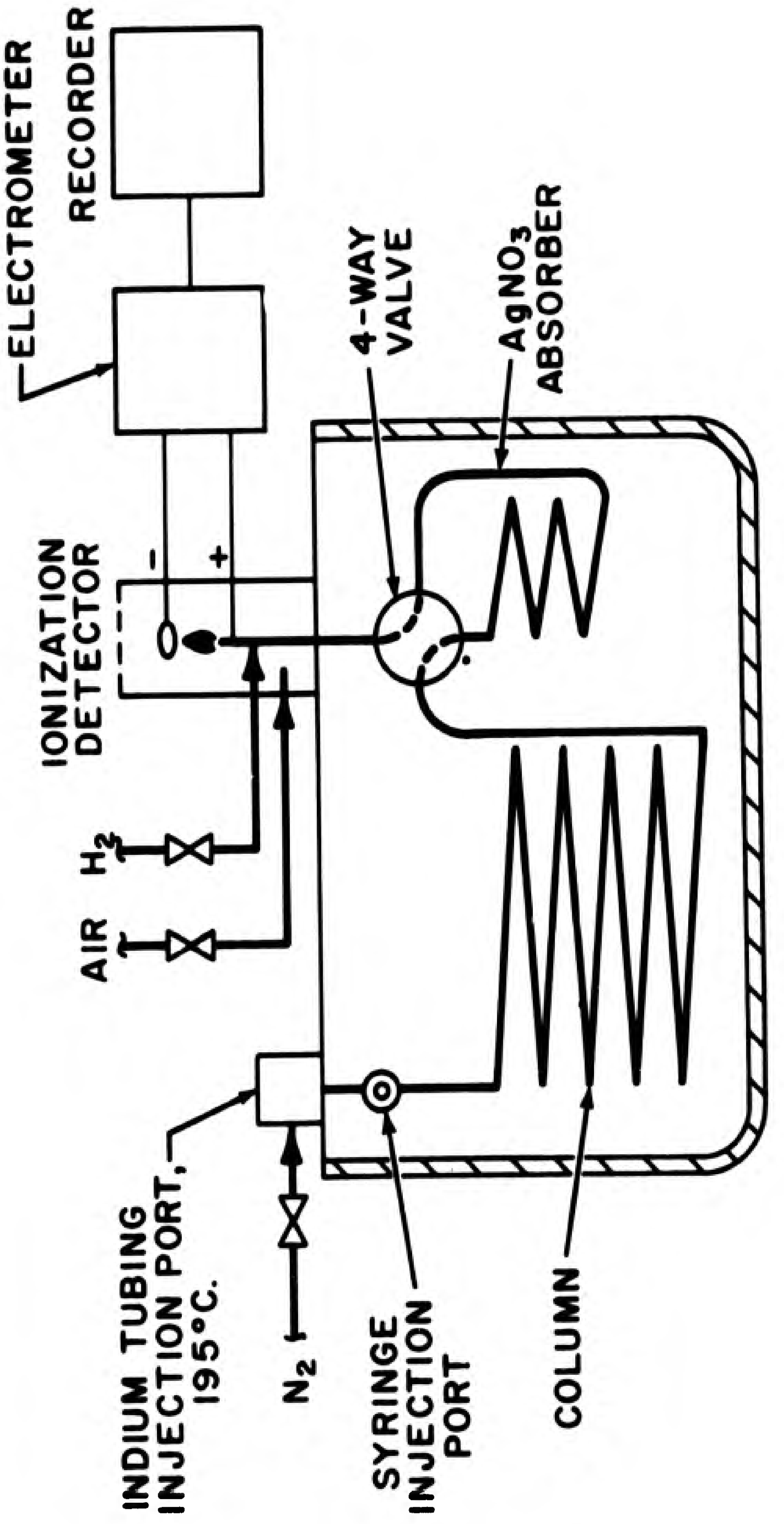


FIGURE 3 DOUBLE CHROMATOGRAM APPARATUS

TABLE 3

CHROMATOGRAPHIC COLUMNS FOR HYDROCARBON ANALYSES

			Dual	
Column Dimensions	35' x 1/4"	17' x 3/16"	15' x 3/16"	400' x 0.01"
Column Temp., °C.	35	88	30 200	Init 100
Stationary Phase	di-n-butyl itaconate	ET-540	Polyox WSR-301	CW1540 LAC737
% St. Phase	10	20	10	7 in methyl ethyl ketone 3 in acetone
Sample Size, microliters	5-15	5-15	5-50	0.6 - 1.2
Carrier Gas	N_2	He	He	N_2
Flow, ml/min.	22.5	25	24	1.3
Flash Temp., °C.	None	None	180	240
Splitter Ratio	None	None	None	11 to 1
Prog. Pressure	None	None	None	10 → 70 psi 0.67 psi/min.
Prog. Temp.	None	None	4°C./min.	100° → 155° 12°/min.

TABLE 4

DOUBLE CHROMATOGRAM METHOD OF ALKYNE ANALYSIS

	Mole % x 10^4	
	No Absorber	Absorber
Ethane	10	9
Acetylene or propane	30	0
Propyne	85	0
t-butene-2	1070	1060
c-butene-2	795	800
1,2-butadiene	295	275
Butyne-1	61	0
Vinylacetylene or 2-methylbutene-2	68	31

In the first analysis, the acetylene and propane peak in the chromatogram is due entirely to acetylene; the vinylacetylene and 2-methylbutene peak however is due to both compounds; note that peaks for propyne and butyne-1 are absent from the second analysis.

III. ACETONITRILE AND PROPIONITRILE

Acetonitrile and propionitrile were irradiated at varying doses to about 11 x 10^{20} ev/g. with cobalt-60 gamma radiation. Products were separated by gas chromatography and attempts were made to characterize them. Separation of the highly polar products was difficult even with advanced gas chromatographic techniques. Identification of most of the products was impossible within the limitations of the time available. Yields of H_2 and CH_4 were obtained; succinonitrile was found as a major product of acetonitrile and a minor product of propionitrile. Cyanogen and acetonitrile were found among the products of propionitrile. Mass spectra and NMR data were obtained on unidentified products isolated by trapping out material separated by gas chromatography. All this data taken together, is enough to show the general pattern of radiation decomposition of the triple bond compounds.

Gas Yields

Table 5 shows gas yields from acetonitrile and propionitrile. In acetonitrile, hydrogen and methane were formed in equal yields. In contrast, more than four times as much methane as hydrogen is formed during the radiolysis of propionitrile. The yields of hydrogen and methane are dependent on the lability of bonds during radiation, as well as the ratio amount of addition to abstraction reaction for each radical. The effect of the triple bond on β bond cleavage should act to accentuate methane radical production from propionitrile and hydrogen radical from acetonitrile. Judging from results obtained with acetylenes, most methyl radicals abstract hydrogen to form methane (rather than add to the triple bond.) Thus the methane yields are a measure of methyl radical. Hydrogen yields, however, may not reflect hydrogen atom yield because unless hydrogen radical is formed with excess kinetic energy, hydrogen may add to the triple bond rather than abstract hydrogen. Further, the proportion of hydrogen addition and abstraction is likely to be different for acetonitrile and propionitrile. Thus, there is danger in placing great significance in hydrogen yield differences. However, the large differences in hydrogen yield observed, together with the small difference in methane yield indicate that compared with acetonitrile significantly less hydrogen radical and significantly more methyl radical is produced from propionitrile.

TABLE 5

NITRILE GAS YIELDS

Dose Rate=10^{19} ev/gr/hr

	Acetonitrile	Propionitrile
Hydrogen	0.74	0.175
Methane	0.74	0.86
Hydrogen Cyanide	Not found	Not found
Cyanogen	Not found	0.028

Both hydrogen cyanide and cyanogen were expected to form as radiation products:

$$\begin{aligned} RCN &\rightarrow R + CN \\ 2\ CN &\rightarrow (CN)_2 \\ CN + RH &\rightarrow HCN + R \end{aligned}$$

Only with propionitrile and only cyanogen was found. This is particularly puzzling, especially because of the readily measured amounts of methane formed from acetonitrile. The fate of the nitrile radical from acetonitrile could not be determined. It may add to acetonitrile rather than dimerize and abstract hydrogen, or it may not have been detected by our analysis.

Acetonitrile Liquid Products

The liquid products resulting from the radiolysis of acetonitrile are shown in Table 6. Identification of compounds "A" and "B" was not possible. Compound "A" appeared on the chromatograms immediately before elution of acetonitrile; compound "B", several minutes after the acetonitrile peak. Also, compound "C" appeared in the chromatograms immediately after elution of compound "B". Compound "C" was about 10% of the concentration of compound "B", but an exact measurement could not be made because of the spread of the peak on the chromatogram.

Compound "A" appeared sensitive to water or air or both. After the irradiated sample was opened to air, successive chromatograms showed a steady decrease in the concentration of "A" until, in 2-3 hours, it decreased beyond the limit of detection. Irradiated samples were placed in indium tubing <u>in vacuo</u> prior to exposing the irradiated sample to the air in an attempt to obtain reliable analyses. However, flash evaporation of the indium tubing (200°C.) to liberate the sample in the chromatography apparatus evidently destroys the material because chromatograms obtained in this way showed no compound "A". Isolation of this compound by gas chromatographic trap-outs was attempted. At least two compounds appeared to be present as evidenced by mass spectra. Molecular weights of 43, 57, and 71 were indicated, but these may result from reaction products of this unstable compound.

Compound "B" had a retention time identical with propionitrile. Unfortunately, excessive tailing by acetonitrile on the gas chromatogram precluded trapping-out a sample for mass spectrometry analysis.

Succinonitrile, an expected product, was found in high yield. A small peak, compound "D", accompanied succinonitrile, but no other gas chromatography peaks could be ascribed to dinitriles.

TABLE 6

ACETONITRILE LIQUID PRODUCTS

Dose Rate, 10^{19} ev/g/hr

	G-value	ppm/10^{20} ev/g
Succinonitrile	0.52	6.3
Compound "A"	-	~1
Compound "B"	-	5

Polymeric products were given only a brief examination, and mass spectra of polymeric material obtained by simple evaporation of acetonitrile was uninterpretable. Further examination of the polymer was postponed when it was found that compound "B" was polymerizing after termination of the radiolysis.

In devising a chromatographic column for analysis of the radiolysis mixture, retention times were obtained for several compounds that might be products of the radiolysis. The following compounds were found separable by gas chromatography and were <u>absent</u> from the radiolysis products of acetonitrile:

HCN
CH_3CH_3
CH_3NC
$NCCN$
CH_3NH_2
CH_3CH_2CN
$NCCH_2CN$
$(CH_3CN)_2$*
$CH_3CH_2CH_2N = CH_2$

* $2\ CH_3CN \xrightarrow{Na} (CH_3CN)_2$

TABLE 7

PROPIONITRILE LIGHT LIQUID PRODUCTS

Product	$G(-C_3H_5N)$
Acetonitrile	0.06
Unknown	0.03
Unknown	0.6
Unknown	0.6
Unknown	0.2
Succinonitrile	0.08

TABLE 8

PROPIONITRILE, HEAVY LIQUID PRODUCTS

Product	$G(-C_3H_5N)$
1	0.02
2	0.23
3	0.04
4	0.02
5	0.02
6	0.36
7	0.36
8	0.02
9	0.02
10	0.15
11	0.13
12	0.05

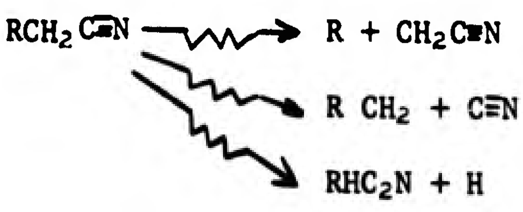
Propionitrile Liquid Products

Two separate analyses of propionitrile radiation products are shown in Table 7 and in Table 8. Table 7 gives the yields of light liquid products from the separation of compounds eluted from the chromatograph up to succinonitrile. In all, six major peaks were separated. Only acetonitrile and succinonitrile were identified. Isolation of the other four peaks and subsequent analysis by mass spectrometry gave uninterpretable results. Decomposition of products on the chromatography columns or in the inlet of the mass spectrometer may have occurred. It was determined that dihydropropionitrile, CH_3CH_2CHNH, was not one of the four peaks.

From the first analysis, there appeared to be high boiling material that had not been separated. A second analysis by a temperature programmed chromatography column separated additional heavy compounds and these are shown in Table 7. Unfortunately, we did not establish the relationship between compounds in Table 7 and Table 8. The later set of compounds are higher boiling or at least take a longer time and a higher temperature to elute from the chromatography column. These compounds were examined by both NMR and mass spectrography. No positive identification of individual compounds could be made. However, a review of all this data shows that no evidence could be found for compounds having the structure $R_2C = NH$. The structure $R_2C = NR$ also did not appear to be present but evidence for its absence was not as strong. In most fractions the triple-bond of the nitrile group remained intact, and the reactions appeared to take place on the alkyl chain. For example, the compound  $N\equiv C\underset{CH_3}{CH}-\underset{CH_3}{CH}C\equiv N$, appears to be a major product. However, as with acetonitrile, decomposition in the gas chromatograph or polymerization to high boiling material may explain why compounds containing $C=N$ groups could not be detected.

Radiation Decomposition of Nitriles

Although it is not possible to write a formal mechanism for radiolytic decomposition of the nitriles some general comments can be made. At least three primary radical forming processes are possible and all seem to occur.



$$RCH_2C\equiv N \rightsquigarrow R + CH_2C\equiv N \qquad (1)$$

$$\rightsquigarrow R\,CH_2 + C\equiv N \qquad (2)$$

$$\rightsquigarrow RHC_2N + H \qquad (3)$$

Reaction (1) represents β-bond cleavage yielding hydrogen radical from acetonitrile and methyl radical from propionitrile. The differences in H_2 and CH_2 yields between acetonitrile and propionitrile probably result from reaction (1) but the effect is partially masked by abstraction reactions (see earlier discussion). The fate of some of the CH_2CN radicals formed by β-bond cleavage is the succinonitrile product shown in Table 7.

Reaction (2) results from α-bond cleavage. Although not usually noted in thermal or photolytic reactions α-bond cleavage apparently assumes some importance in radiation decomposition. This is shown by the high yield of methane from acetonitrile and cyanogen from propionitrile. Peculiarly, direct evidence for the other radical in each case, CN from acetonitrile and C_2H_5 from not propionitrile, was not found. An alternative way of forming CH_3 and CN by some metathetical reaction seems unlikely.

Reaction (3) represents cleavage of hydrogen-carbon bonds. Except for scission of the hydrogen bond from carbon-3 in propionitrile, this is the same reaction as β-bond cleavage.

Products result from secondary reactions. Hydrogen and methyl radicals formed in the primary process appear to react primarily to abstract hydrogen atom to form H_2 and CH_4. No positive evidence for H• or CH_3 addition could be found, but some must occur. The remainder of the products found and examined with NMR or mass spectrometry were compatible with the dimerization of the open carbon atom valencies of the akyl nitrile radicals. This stability was unexpected in view of the reactivity of the corresponding $C{\equiv}CH$ radicals.

Although the outlines of the radiation catalyzed decomposition have been determined, much remains to be learned. A major task remaining is the identification of the unknown compounds. During the course of this work attempts were made to prepare some of these unknown products H atoms were generated from the radiation of cyclohexane and CH_3 and CN radicals were generated by the photolysis and thermolysis of acetone and acetylnitrile (CH_3COCN). The radicals were generated in acetonitrile. Unfortunately, except for succinonitrile, compounds formed in this way did not match the unknown radiation produced compounds. Probably the best approach to determining the identity of the products is to separate gram amounts for study by preparative gas chromatography. This will be a formidable and lengthy task.

IV. ACETYLENES

Butyne-2, butyne-1, pentyne-2 and hexyne-3 were irradiated in the liquid phase at varying doses up to about 20 x 10^{20} ev/g with cobalt-60 gamma radiation. Propyne and butyne-1 were irradiated as gases. Products were separated and analyzed by gas chromatography, Tables 9 and 10. Low molecular products were identified. Except for the alkyl benzene trimers of the acetylenes, higher products were generally not identified. Reaction product did not undergo secondary reactions because the rate of product formation did not increase or decrease with time. Also, reactive impurities present at low levels were unchanged during radiolysis.

Liquid Phase Radiation

Butyne-2 The product from butyne-2 were previously discussed (1).

Most of the products can be explained by cleavage of a carbon hydrogen bond as the initiation step leading to what are postulated to be consequent radical reactions:

$$CH_3C\ CCH_3 \longrightarrow C_4H_5 + H_2$$

The H atom can abstract an hydrogen

$$H^\cdot + CH_3C\ CCH_3 \rightarrow C_4H_5 + H_2 \qquad G = .79$$

or add (8),

$$H^\cdot + CH_3C{\equiv}CCH_3 \rightarrow CH_3CH{=}CCH_3$$

This vinyl radical is reactive and abstracts H atom to form butene-2.

$$CH_3CH{=}CCH_3 + CH_3C{\equiv}CCH_3 \rightarrow C_4H_5{+}CH_3CH{=}CHCH_3 \qquad G = 1.7$$

The C_4H_5 species, nominally a butynyl radical, reacts to form dimers, trimers, etc. The C_4H_5 radical might also undergo an "identity reaction" to form butadiene-1,2

$$CH_3C{=}C{=}CH_2 + CH_3C{\equiv}CCH_3 \longrightarrow CH_3C{\equiv}CCH_2 + CH_3CH{=}C{=}CH_2$$

TABLE 9

ALKYNE PRODUCTS LIQUID PHASE

	G(-butyne-2)	G(-butyne-1)	G(-pentyne-2)	G(-pentyne-1)	G(-hexyne-3)
Hydrogen	0.79	0.42	0.62	.49	0.57
Methane	0.14	0.12	0.16	.17	0.13
Acetylene	0.04	0.05	-	-	-
Ethane	+	+	0.15	0.15	0.05
Ethylene	+	+	0.05		
Propane	-	-	-	0.14	-
Propylene	-	-	-	0.06	-
Propadiene	+	+	-	+	-
Propyne	0.09	0.13	-	+	-
Butene-2	1.7	-	-	-	-
Butene-1	-	1.0	-	-	-
Butadiene 1,2	0.23	0.45	+	-	-
Butyne-2	-	-	0.14	-	-
Pentenes	0.01	0.06	2.0	0.9	-
Pentadienes	-	-	0.4	?	-
Hexenes	-	-	0.7	+	1.9
Dimers	0.7	1.2	2.8	1.2	3.1
Alkyl benzene	0.5	2.3	0.20	0.7	0.16
Other trimer	+	0.4_5	0.4	0.9	0.4
Tetramer	0.4_5	0.7	-	-	-

TABLE 10

ALKYNE PRODUCTS GAS PHASE

Gas yields as moles relative to hydrogen from butyne-1 = 100

	butyne-1	propyne		
Pressure, mm	200	100	200	400
Hydrogen	100	85	76	57
Methane	140	15	14	10
Ethane	10			
Ethylene	50			
Acetylene	+	+	+	+
Propane	3	-	-	-
Propylene	12	4	6	8
Propyne	+	-	-	-
Propadiene	14	+	+	+
Butane	7	-	-	-
Butene-1	105	?	?	4
Butadiene-1,2	6	1	2	2
Butyne-2	±	-	-	-
Pentenes	15	-	-	-

Although, as will be discussed, butadiene is probably formed by a recombination reaction.

Methane and propyne are minor products that occur by carbon-carbon cleavage. Loss of methyl leads to methylpropargyl radical, C_4H_5.

$$CH_3C{\equiv}CCH_3 \longrightarrow C_3H_3 + CH_3$$

$$CH_3 + CH_3C{\equiv}CCH_3 \longrightarrow C_4H_5 + CH_4 \qquad G = 0.14$$

The C_3H_3 radical (9) abstracts hydrogen to form propyne.

$$C_3H_3 + CH_3C{\equiv}CCH_3 \longrightarrow C_4H_5 + CH_3C{\equiv}CH \qquad G = 0.09$$

Propadiene is also detected as a very low level product of C_3H_3.

$$C_3H_3 + CH_3C{\equiv}CCH_3 \longrightarrow C_4H_5 + CH_2{=}C{=}CH_2 \qquad G = 0.02$$

A material balance on CH_3 and CH_4 shows that methyl radical is largely accounted for by the products, Table 11.

TABLE 11

	G	CH_3 Equivalent
Methane	0.14	0.14
Acetylene	0.04	-0.08
Propyne	0.09	-0.09
2-methylbutene-2	0.01	0.01
Methyl Deficiency		0.02

Ethane, which was detected as a low level product but not measured, could account for this small deficiency.

An approximate material balance for hydrogen (considering only the major products) sets a lower limit on polymer formation.

TABLE 12

	G	H_2 Equivalent
Hydrogen	0.79	0.79
Butene-2	1.73	1.73
Octadiyne-2,6	1.09	-0.55
Hydrogen Deficiency		~2

Hence, $G\left[-C_4H_5 \longrightarrow (C_4H_5)_n\right]$ must be about 4 for polymer formation. This agrees with $G(-C_4H_5) = 4$ to 6 found by weighing the residue after butyne-2 was evaporated from a heavily irradiated sample. Although the mass spectra of the residue extended out beyond mass 300, dimers, trimers and tetramers constituted almost all the residue. As shown by the weight balance in Table 13 less than 10% of the product is larger than tetramer.

The distribution of the C_8 to C_{16} products is shown in Table 14 and in the chromatogram of heavy products shown in Figure 4. Octadiene-2,6 and hexamethyl benzene are probably formed by reactions not typical of the other products and are 44% of the total products. Of the 56% left, 22% is dimer, 3.6% is trimer and 27% tetramer. The significance of this distribution, particularly the large amount of tetramer is not known. Even including hexamethyl benzene, more tetramer is formed than trimer.

TABLE 13

BUTYNE-2: MATERIAL BALANCE OF POLYMER PRODUCTS

	Weight % of Residue
Total C_8-C_{16} product	75±5
Butyne-2 in residue	22±2%
Undetected polymer	1 to 10%

TABLE 14

BUTYNE-2: C_8-C_{16} PRODUCT DISTRIBUTION

	Product	Weight %
14	Hexamethylbenzene	17.0
6	Octadiyne-2,6	27.0
1	Dimer (M.W. 108)	3
2	Dimer	1.6
3	Dimer	1.8
4	Dimer	8.5
5	Dimer	10.0
7	Trimer (M.W. 160)	3.6
8	Trimer (M.W. 162)	
9	Tetramer	5.0
10	Tetramer	4.0
11	Tetramer (M.W. 216)	
12	Tetramer (M.W. 214, 11%)	18.0
13	Tetramer	
	Total	100.0

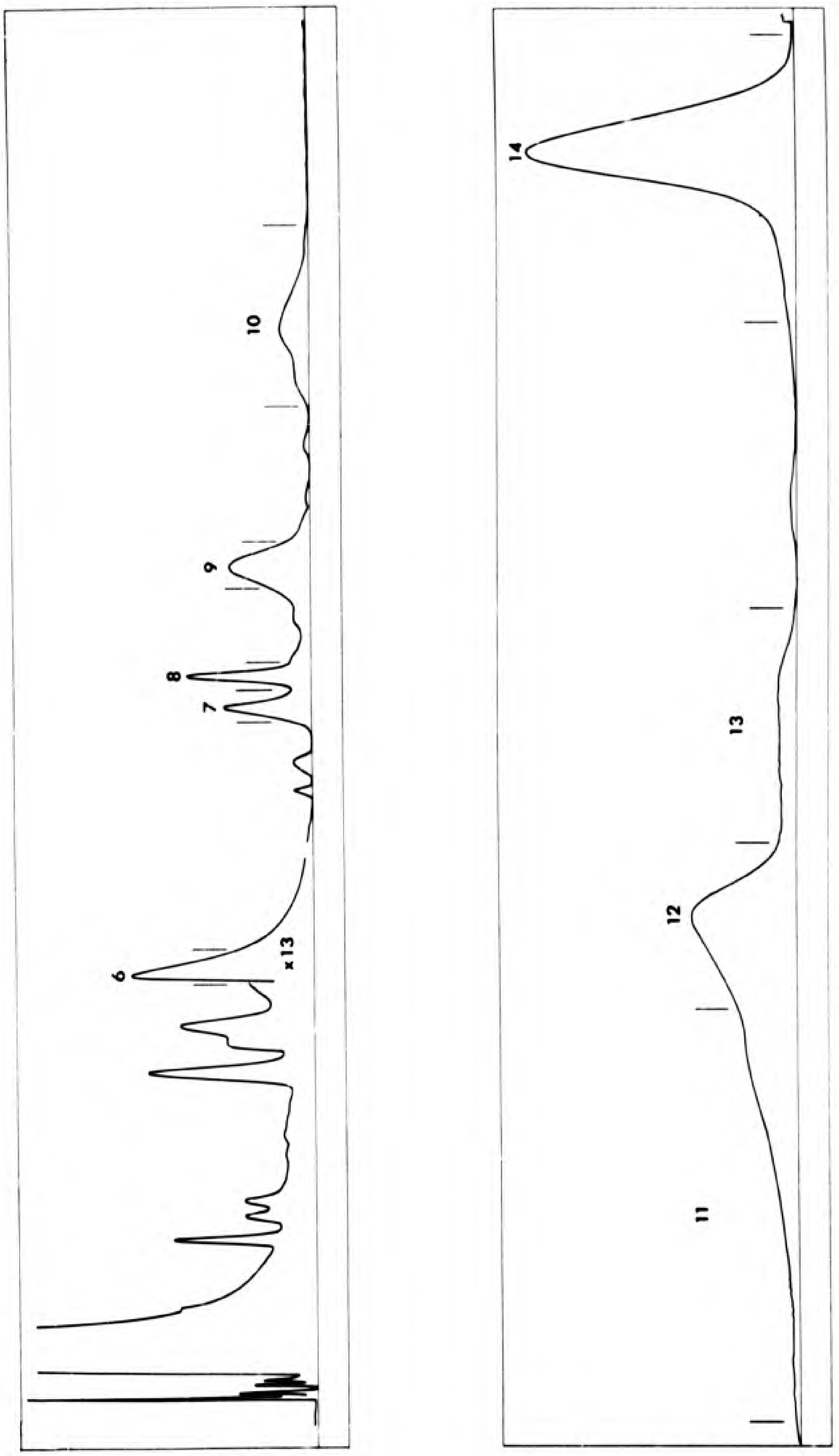


FIGURE 4 CHROMATOGRAM OF C_8-C_{16} PRODUCTS

Butyne-1 and Pentyne-1 Products from the radiolysis of butyne-1 and pentyne-1 contrast sharply with those obtained from butyne-2. Both G(H_2) and G(olefin) are less with 1-alkynes. With butyne-1 the butadiene-1,2 and alkylbenzene yields are higher. Difference in the dimer, trimer and tetramer yield is also marked, but these represent smears of products on the chromatographs and less reliance can be placed on these data.

Carbon-carbon bond cleavage is again a minor process, and the G values do not differ significantly from G values from butyne-2. Again traces of propadiene were formed.

Pentyne-2 and Hexyne-3 The products from pentyne-2 and hexyne-3 were remarkably similar. Hydrogen yields were somewhat lower than with butyne-2 and reflect additional degrees of freedom within these molecules that dissipate energy without CH bond scission. A large proportion of the products result from addition of hydrogen across the triple bond to form olefin and the formation of dimer products. Hydrogen addition is of the same magnitude as was found with butyne-2; the amount of dimerization however is 2 to 4 times greater.

Pentyne-2 gave ethane and ethylene in much larger amounts than the other acetylenes. Butyne-2 was found as a fragmentation product of pentyne-2; pentyne-2 was not detected as a product of hexyne-3 although it may have been present. Also, a product concluded to be pentadiene was found as product of pentyne-2; analytical shortcomings probably precluded the detection of a diene from hexyne-3.

Overall, the chromatographs of pentyne-2 and hexyne-3 are fairly clear-cut. That is, the myriad of trace components found among the products of the butynes was absent.

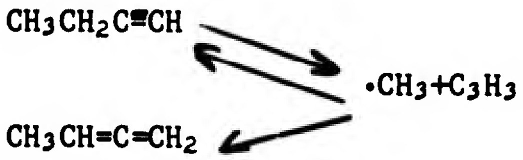
Gas Phase Radiation

Although we are primarily interested in the effect of radiation in condensed phases, a study of radiation of propyne and butyne-1 in the gas phase helped to define the liquid phase mechanism. Products resulting from irradiation of butyne-1 at 200 mm and propyne at 100 mm, 200 mm, and 400 mm, are shown in Table 10. The G values shown are averages and, particularly the case of butyne-1, selected as best values rather than chance averages.

Propyne With propyne the major reaction is CH bond scission and fragmentation products are formed in low concentration. Differences of product yields with pressure are probably due to bremsstrahlung from the walls of the container. Major products are dimers, trimers, etc. The trimers, 1,3,5-and 1,2,4-trimethylbenzene were identified as products but were not measured. The formation of trialkylbenzenes eliminates consideration of solvent cage mechanisms in their formation in the liquid phase.

<u>Butyne-1</u> In contrast to propyne, with butyne-1 carbon-carbon scission is an important reaction. More methane is formed than hydrogen; ethylene is a major product In contrast to liquid phase butyne-1, in the gas phase, methane is formed in much larger quantities. This is due to the cage effect that promotes recombination in the liquid phase.

The absence of butadiene-1,2 in the gas phase suggests that butadiene 1,2 results primarily from recombination in the liquid phase:



Mechanism of Acetylene Decomposition

The objective of this work is to formulate a mechanism for the radiation decomposition of triple bond compounds. The following mechanism for acetylenes is in agreement with our data and should help predict the effects of radiation on other triple bond compounds.

Three primary steps are involved in the radiation induced reactions of acetylenes. Once these occur, all other products are determined by chemical considerations. The primary step of most importance is loss of hydrogen

$$AH^* \longrightarrow A \pm H$$

Hydrogen is probably lost most readily from carbon atom β to the triple bond. The hydrogen yields from the acetylenes studied substantiate this. Although other factors also enter in the hydrogen yields increase with the number of β hydrogens:

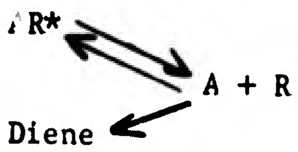
	β-Hydrogen	$G(H_2)$
butyne-1	2	.42
pentyne-1	2	.48
hexyne-3	4	.57
pentyne-2	5	.62
butyne-2	6	.79

If β hydrogens are lost, the radical, A, left behind is stable and will tend to react as a chain stopper by coupling:

$$A^{\cdot} + R^{\cdot} \longrightarrow AR$$

Thus, the reaction most likely to occur in liquid phase radiolysis is loss of hydrogen and the hydrogen most apt to be lost is one on a carbon atom β to a triple bond.

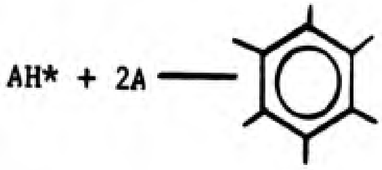
Another primary step is carbon-carbon bond breaking. This reaction is held in check in the liquid phase by the cage effect and the resulting recombination reaction. Thus qualitatively, the wide difference in the radiation products of liquid and gas phase butyne-1 show this. The relatively large amounts of 1,2-diene products formed are best explained by this recombination. Again carbon-carbon bond breaking at β carbon should be the preferred reaction. The reaction sequence can be summarized.



The formation of CH_3 from butyne-2 and the large amounts of ethane from pentyne-2, and propane from pentyne-1 appear to result from α-bond fragmentation during a primary step. This α-bond cleavage is peculiar to radiation chemistry and not usual in thermal systems.

Thus, carbon-carbon bond splitting is a primary process. Although cleavage of bond β to the unsaturation should be preferred, α-bond cleavage is also important.

A third primary process is formation of alkyl benzenes



There is no direct evidence for this reaction, but because alkyl benzenes form equally well in both the liquid and gas phase, these appear to form directly from an excited acetylene. Isomers appear to form in about statistical proportion also indicating a concerted reaction via an excited state rather than a step-wise reaction subject to steric control (10).

Products form by conventional radical reactions. The important chain initiating reaction results from hydrogen addition to acetylene

$$AH + H \longrightarrow AH_2$$

This vinyl radical adds to an acetylene

$$AH_2 + AH \longrightarrow A_2H_3$$

$$A_2H_3 + AH \longrightarrow A_3H_4 \qquad \text{etc.}$$

Chains also may be started by addition of alkyl radicals resulting from carbon-carbon bond breaking

$$AH + R \longrightarrow AHR$$

$$ARH + AH \longrightarrow A_2RH_2 \quad \text{etc.}$$

The important chain stopping reaction is hydrogen abstraction to form a propargyl radical

$$AH_2 + AH \longrightarrow AH_3 + A$$

or

$$R + AH \longrightarrow RH + A$$

and subsequent dimerization of the stable propargyl radical

$$A + A \longrightarrow A_2$$

V. CONCLUSIONS

These conclusions on the radiation chemistry of triple bond compounds are based primarily on our study of alkynes, but are compatible with our less comprehensive data on the nitriles.

1. G(-triple bond compound) is in the range of 6 to 10. Therefore, at the dose levels studied there is no marked radiation protection nor does much polymerization occur.

2. In the liquid phase the major primary reaction is rupture of a C-H bond on a carbon β to the triple bond.

3. More of the hydrogen formed adds than abstracts hydrogen and this ratio increases with increasing molecular weight. Perhaps less "hot" H atom is formed from the more complex molecules.

4. The cage effect reduces carbon-carbon bond rupture in the liquid phase to a minor process.

5. Recombination due to the cage effect results in 1,2-diene formation.

6. Both α and β carbon-carbon bond cleavage occur. The α-bond cleavage results from some radiation process and occurs with more facility than in thermal systems.

7. Alkyl benzene, an alkyne trimer, probably forms by the interaction of a excited alkyne with two additional alkyne molecules. Although the analogous C_3N_3 aromatic ring system was not found in the nitrile system a further search for it should be made.

8. Alkyl benzene formation should give radiation protection to alkyne systems at high doses.

9. Toxic products are formed on radiation of nitriles.

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13. ABSTRACT

G-values for radiolysis products were determined for propyne and butyne-1 in the vapor phase and for butyne-1, butyne-2 pentyne-1, pentyne-2, hexyne-3, acetonitrile and propionitrile in the liquid phase.

The rupture of a C-H bond probably from a carbon β to the triple bond results in H_2, coupling products, and H atom addition. H atom addition leads to mono and poly olefins. The rupture of a C-C bond results in fragmentation in the vapor phase but recombination to form 1,2-diolefins in liquid phase. Both α and β C-C bond rupture occur. Alkyl benzene--alkyne trimers--forms, probably by excitation. Analogous C_3N_3 ring compounds may form but were not detected. Gas chromatography techniques for alkyne and nitrile analyses are described.

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