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The Gas Phase Radiolysis of 2-Butyne

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S. Zakanycz

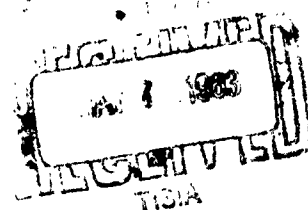D. Hale

D. Dunbar

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ORGANIC CHEMISTRY
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2ND ANALYST _____   DATE 5/16/63

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ALKYL

Code	Card		Name
21Q.1	01	0	ALKANES
3015.25		1	1C
1663.25		2	2C
3885.25		3	3C
0745.25		4	4C
3561.25		5	5C
2288.25		6	6C
2285.25		7	7C
3392.25		8	8C
3311.25		9	9C
1245.5		11	10C
0210.11	01	12	10+C
0210.14	02	0	TERMINAL
0210.12		1	NONTERMINAL
0210.13		2	POLY USAGE

ALKENES

Code	Card		Name
0210.15		3	ALKENES
3015.5		4	=CH?
1663.75		5	C=C
3885.75		6	3C
0745.75		7	4C
3561.75		8	5C
2288.75		9	6C
2285.75		11	7C
3392.75	02	12	8C
3311.75	03	0	9C
1247.5		1	10C
0210.16		2	10+C
0210.20		3	TERMINAL
0210.17		4	NONTERMINAL
0210.18		5	POLY =
0210.19		6	POLY USAGE

ALKYNYL

Code	Card		Name
0211.2		7	ALKYNES
3015.75		8	≡C
0022.5		9	C≡C
3906.5		11	3C
0747.5	03	12	4C
3565.5	04	0	5C
0211.3			6+C
0211.7			TERMINAL
0211.4			NONTERMINAL
0211.5		4	POLY ≡
0211.6		5	POLY USAGE

ARYL

Code	Card		Name
0570.10		6	BENZENE
0570.15		7	MONOSUB
0570.11		8	DISUB
0570.21		9	TRISUB
0570.16		11	ORTHO
0570.14	04	12	META
0570.17	05	0	PARA
0570.20		1	SYM-TRISUB
0570.19		2	POLYSUB
0570.13		3	IND
0570.12		4	FUSED
0570.18		5	POLY USAGE

CYCLOALKANES

Code	Card		Name
1225.10		6	CYCLOALKANES
1225.11		7	3,4M
1225.12		8	5M
1225.13		9	6M
1225.14		11	7+M
1225.19	05	12	SAT
1225.21	06	0	UNSAT
1225.15		1	BICYCLO
1225.17		2	IND
1225.16		3	FUSED
1225.20		4	SPIRO
1225.18		5	POLY USAGE

HALOGENS

Code	Card		Name
2214		6	HALOGENS
1883.2		7	F
0921.5		8	Cl
0724.5		9	Br
2596.5		11	I
0421	06	12	At
2214.5		0	POLY USAGE

CARBONYL

Code	Card		Name
0803.7		1	CARBONYL
0803.2		2	C=O
1915.5		3	HC=O
5091.6		4	C=S
5091.30		5	HC=S
3468.25		6	O=(RING)
5090.11		7	S=(RING)
2982.5		8	MET.CARBONYLS
3461.5		9	-C-C- (O O)
0803.5		11	POLY USAGE
0803.4	07	12	MISC.

COOR

Code	Card		Name
0804.3	08	0	COOR
0804.1		1	-COO-ESTER
0804.2		2	COOH
0804.7		3	CARBOXY HALIDES
0804.6		4	F-C=O
0804.5		5	Cl-C=O
0804.4		6	Br-C=O
0804.8		7	I-C=O
0804.9		8	OCOO
0182.5		9	-C-O-C-
0805.25		11	METAL SALT
0805.75	08	12	POLY USAGE
0805.5	09	0	MISC.

S-COOR

Code	Card		Name
5090.15		1	S-COOR
5090.12		2	THIO ACIDS (CXXH)
5091.5		3	S=C-O
5091.4		4	O=C-S
5090.22		5	-S-COOH
5090.20		6	S=C-HALOGEN
5090.17		7	S=C-Br
5090.15		8	S=C-Cl
5090.19		9	S=C-F
5090.21		11	S=C-I
5090.14		12	POLY USAGE
5090.13	10	0	MISC.

S – HETERO

Code	Card		Name
4863.10		1	S-HETERO
4863.14		2	3, 4M
4863.15		3	5M
4863.16		4	6M
4863.17		5	7+M
4863.21		6	O-CONT.
4863.20		7	N-CONT.
4863.22		8	OTHER-CONT.
4863.11		9	IS
4863.12		11	2S
4863.12	10	12	3+S
4863.19	11	0	IND
4863.18		1	FUSED
4863.24		2	SPIRO
4863.23		3	POLY USAGE

N – HETERO

Code	Card		Name
3298.10		4	N-HETERO
3298.14		5	3, 4M
3298.15		6	5M
3298.16		7	6M
3298.17		8	7+M
3298.20		9	O-CONT.
3298.23		11	S-CONT.
3298.21	11	12	OTHER-CONT.
3298.11	12	0	IN
3298.12		1	2N
3298.13		2	3+N
3298.24		3	SALT
3298.19		4	IND
3298.18		5	FUSED
3298.25		6	SPIRO
3298.22		7	POLY USAGE

O – HETERO

Code	Card		Name
3475.10		8	O-HETERO
3475.13		9	3, 4M
3475.14		11	5M
3475.15	12	12	6M
3475.16	13	0	7+M
3475.19		1	N-CONT.
3475.22		2	S-CONT.
3475.20		3	OTHER-CONT.
3475.11		4	I-O
3475.12		5	2+O
3475.18		6	IND
3475.17		7	FUSED
3475.23		8	SPIRO
3475.21		9	POLY USAGE

N, C, S

Code	Card		Name
3297.5		11	N,C,S
5090.16	13	12	=N-C=S
1398.75	14	0	-N-C(=S)-S
5091.7		1	=N-C(=S)-N=
5091.20		2	-S-CN
2618.5		3	-N=C=S
3297.7		4	POLY USAGE
3297.6		5	MISC.

N, C, O

Code	Card		Name
3297.2		6	N,C,O
4462.5		7	NC(=O)-N-N-
0785.25		8	-N-C(=O)-O-
5361.5		9	=N-C(=O)-N=
0785.75	14	12	-C(=O)-N-
2613.25	15	0	-N=C=O
1222.5			-O-CN
3297.4		1	POLY USAGE
3297.3		2	MISC.

C, N

Code	Card		Name
0797.25		3	C,N
1223.5		4	CN
2613.75		5	-N=C
0239.2		6	-N-C=N
2150.5		7	-N-C(=N)-N-
0787.5		8	-N=C=N-
0797.75		9	POLY USAGE
0797.5		11	MISC.

OH, SH

Code	Card		Name
2391.6	15	12	OH, SH
2391.4	16	0	OH
2968.25		1	SH
2391.8		2	POLY USAGE

N, O, (S)

Code	Card		Name
3298.27		3	N,O (S)
2391.2		4	=N-OH
2968.75		5	=N-SH
3295.5		6	-NO2
3299.75		7	-N=O
3299.25		8	-N-N=O
3289.5		9	N-NO2
3298.29		11	POLY USAGE
3298.27	16	12	MISC.

S, O, (N)

Code	Card		Name
4863.25	17	0	S, O (N)
4860.75		1	O=S=O
4860.25		2	SO3H
4859.5		3	S=O
4860.5		4	SO2-N
4863.27		5	POLY USAGE
4863.26		6	MISC.

O, S

Code	Card		Name
3475.26		7	O,S
3468.75		8	-O-
3587.5		9	-O-O-
5090.10		11	-S-
1398.25	17	12	-S-S-
5257.5	18	0	-S-S-S-
3475.28		1	POLY USAGE
3475.27		2	MISC.

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DATE 5/16/63

S – HETERO

4863.10	1	S-HETERO
4863.14	2	3, 4M
4863.15	3	5M
4863.16	4	6M
4863.17	5	7+M
4863.21	6	O-CONT.
4863.20	7	N-CONT.
4863.22	8	OTHER-CONT.
4863.11	9	IS
4863.12	II	2S
4863.12	10 12	3+S
4863.19	11 0	IND
4863.18	I	FUSED
4863.24	2	SPIRO
4863.23	3	POLY USAGE

N – HETERO

3298.10	4	N-HETERO
3298.14	5	3, 4M
3298.15	6	5M
3298.16	7	6M
3298.17	8	7+M
3298.20	9	O-CONT.
3298.23	II	S-CONT.
3298.21	11 12	OTHER-CONT.
3298.11	12 0	IN
3298.12	I	2N
3298.13	2	3+N
3298.24	3	SALT
3298.19	4	IND
3298.18	5	FUSED
3298.25	6	SPIRO
3298.22	7	POLY USAGE

O-HETERO

3475.10	8	O-HETERO
3475.13	9	3, 4M
3475.14	II	5M
3475.15	12 12	6M
3475.16	13 0	7+M
3475.19	I	N-CONT.
3475.22	2	S-CONT.
3475.20	3	OTHER-CONT.
3475.11	4	I-O
3475.12	5	2+O
3475.18	6	IND
3475.17	7	FUSED
3475.23	8	SPIRO
3475.21	9	POLY USAGE

N, C, S

3297.5	II	N,C,S
5090.16	13 12	=N-C=S
1398.75	14 0	-N-C(=S)-S
5091.7	I	=N-C(=S)-N=
5091.20	2	-S-CN
2618.5	3	-N=C=S
3297.7	4	POLY USAGE
3297.6	5	MISC.

N, C, O

3297.2	6	N,C,O
4462.5	7	NC(=O)-N-N-
0785.25	8	-N-C(=O)-O-
5361.5	9	=N-C(=O)-N=
0785.75	II	-C(=O)-N-
2613.25	14 12	-N=C=O
1222.5	15 0	-O-CN
3297.4	I	POLY USAGE
3297.3	2	MISC.

C, N

0797.25	3	C,N
1223.5	4	CN
2613.75	5	-N=C
0239.2	6	-N-C=N
2150.5	7	-N-C(=N)-N-
0787.0	8	-N=C=N-
0797.75	9	POLY USAGE
0797.5	II	MISC.

OH, SH

2391.6	15 12	OH, SH
2391.4	16 0	OH
2968.25	I	SH
2391.8	2	POLY USAGE

N, O, (S)

3298.27	3	N,O (S)
2391.2	4	=N-OH
2968.75	5	=N-SH
3295.5	6	-NO2
3299.75	7	-N=O
3299.25	8	-N-N=O
3289.5	9	N-NO2
3298.29	II	POLY USAGE
3298.27	16 12	MISC.

S, O, (N)

4863.25	17 0	S, O (N)
4860.75	I	O=S=O
4860.25	2	SO3H
4859.5	3	S=O
4860.5	4	SO2-N
4863.27	5	POLY USAGE
4863.26	6	MISC.

O, S

3475.26	7	O,S
3468.75	8	-O-
3587.5	9	-O-O-
5090.10	II	-S-
1398.25	17 12	-S-S-
5257.5	18 0	-S-S-S-
3475.28	I	POLY USAGE
3475.27	2	MISC.

AMINES

0239.5	3	AMINES
3852.5	4	NH2- (PRI)
4442.5	5	-NH- (SEC)
5036.5	6	-N= (TER)
3984.5	7	-N≡ (QUAT)
2442.5	8	=N
0503.5	9	-N=N-
1329.5	II	N≡N (N≡N=)
2359.5	18 12	-N-N-
5251.5	19 0	N-N=N-
0501.5	I	N, N≡N
1883.4	2	FLUOROAMINES
1883.8	3	-NF2
1883.6	4	-NF
1884.5	5	F2N-NF-
0239.4	6	SALT (NON-QUAT)
0239.9	7	POLY USAGE
0239.7	8	MISC.

PHOSPHORUS

3634.2	9	PHOSPHORUS RAD.
3634.16	II	P=O,S,O
3634.18	19 12	P=S,2O
3634.17	20 0	P=O, S, 2O
3634.19	I	S=PO3
3634.15	2	S=P-F
3634.14	3	S-P-F
3634.11	4	O=P(N) (O)--F
3634.10	5	O=P, (F), 2N
3634.13	6	O=P(F) O2
3634.12	7	O-P-F
3634.23	8	P,S-(I TO 3S)
3634.24	9	P,S-(4S)
1224.75	II	CYCLIC P
3632.25	20 12	P(+3)
3632.75	21 0	P(+5)
3617.5	I	PO4
3634.21	2	P-MISC.
3634.25	3	P,S-MISC.
3634.22	4	POLY USAGE

BORANES

0687	5	BORANES

SILANES

4530	6	SILANES

MISCELLANEOUS

22	23
0	0
I	I
2	2
3	3
4	4
5	5
6	6
7	7
8	8
9	9
II	II
12	12

METALS AND METALLOIDS

2140	24 0	GROUP I
0205	I	ALKALI
0877	2	Cs
1925	3	Fr
2787	4	Li
3806	5	K
4592	6	Na
4365	7	Rb
1134	8	Cu
2102	9	Au
4542	II	Ag
2141	24 12	GROUP II
0208	25 0	ALKALINE
0536	I	Ba
0573	2	Be
0760	3	Ca
2845	4	Mg
4110	5	Ra
4821	6	Sr
0755	7	Cd
0970	8	Hg
5585	9	Zn
2142	II	GROUP III
0043	25 12	Ac
0232	26 0	Al
1996	I	Ga
2467	2	In
2707	3	La
4410	4	Sc
5055	5	Tl
5583	6	Y
2143	7	GROUP IV
2072	8	Ge
2201	9	Hf
2719	II	Pb
5128	26 12	Sn
5139	27 0	Ti
5590	I	Zr
2144	2	GROUP V
0330	3	Sb
0610	4	Bi
3287	5	Nb
	6	P
4956	7	Ta
5381	8	V
2145	9	GROUP VI
0883	II	CHALCOGENS
3781	27 12	Po
4457	28 0	Se
0935	I	Cr
3122	2	Mo
5277	3	W
2146	4	GROUP VII
5223	5	TRANS. ELEM.
0992	6	Co
2604	7	Ir
2607	8	Fe
3276	9	Ni
3456	II	Os
3492	28 12	Pd
3744	29 0	Pt
4277	I	Rh
4373	2	Ru

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FOREWORD

This report was prepared by the Radiation Studies Section of the Radiation Branch. The work was initiated under Project No. 7367, "Research on Characterization and Properties of Materials," Task No. 736701, "Fundamental Interactions of Nuclear Radiations with Matter," and administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division. Mr. Roger E. Rondeau was the project engineer.

This report covers work conducted from March to December 1962.

ABSTRACT

Pyrex ampoules of gaseous 2-butyne (dimethylacetylene) were exposed to cobalt-60 gamma rays, and the hundred electron-volt yields of the lower molecular weight products are given. The radiation induced products were studied as a function of sample pressure and total dose. The products, which include hydrogen, methane, acetylene, propene, propyne, cis- and trans- 2-butene, butane, 1,2-butadiene, and vinylacetylene, are explained on the basis of ion-molecule and free radical reactions. Some mechanisms of product formation which are consistent with product distribution and magnitude of the yields are discussed.

This technical documentary report has been reviewed and is approved.

RICHARD J. VOSSLER, Capt, USAF
Chief, Radiation Branch
Physics Laboratory
Directorate of Materials and Processes

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INTRODUCTION

The radiation polymerization of acetylene to form cuprene and benzene is one of the earliest hydrocarbon reactions studies (refs 1,2,3). However, except for acetylene, little or no data can be found in the literature relating to the radiolysis of triple-bonded compounds. The stability or sensitivity of the heavier members of the acetylenic series has yet to be established (refs 4,5); even related data on the radiolysis of double-bonded compounds is largely confined to polymerization. The lack of knowledge of the radiation chemistry of this important class of compounds constitutes a serious deficiency in our ability to predict the radiation behavior of potentially useful materials.

This study is the first in a series of investigations of radiation chemistry of triple bonds. Some of the compounds to be examined include the alkyl cyanides, 1-alkynes, 2-alkynes, and some alkadiynes; see figure 1. These compounds permit convenient variation of molecular structure and a detailed study of each should yield valuable information concerning the extent of the influence of the triple bond along the hydrocarbon chain. Also, in each of the above compounds, the triple bond should readily undergo observable reactions and should serve as an indicator for the radiation sensitivity of the molecule.

At least three compounds from each homologous series will be studied in the gas phase and where possible in the liquid phase. The nitrile group includes aceto-, propio-, and butyronitrile; the 1-alkyne group takes in propyne, 1-butyne and 1-pentyne; while 2-butyne, 2-pentyne, and 2-hexyne make up the 2-alkynes.

In this investigation, the radiation induced products of gaseous 2-butyne are studied as a function of sample pressure and total dose. This particular compound was selected as a starting point for several reasons: the material is liquid between -32° and 27°C, and hence can be easily handled in a vacuum system; the symmetry of the molecule tends to keep the number of products down to a practical number; while, the internal location of the unsaturation in the molecule militates against the formation of free radical polymerization.

The main disadvantage of working with these particular systems is that no information can be drawn from existing literature data and therefore intercomparison of our results or extension of any theoretical treatment cannot be performed. Nevertheless, the results from all this work should give a clear picture of the radiation behavior of two heretofore ignored, but very important classes of compounds.

EXPERIMENTAL PROCEDURES

Materials

The 2-butyne was obtained from Farchan Research Laboratories and was purified further by vacuum distillation through a cooled (-95°C) silica gel column. The resulting material contained a maximum impurity level of 0.01 mole percent.

Target Preparation

The purified 2-butyne was vacuum distilled into cylindrical glass ampoules equipped with break-seals whose volumes had been previously determined. The sample pressure was varied between 25 and 200 mm of mercury. When the ampoules were filled to the desired pressure, they were cooled with liquid nitrogen, degassed, and sealed under a vacuum of less than 10^{-4} Torr (mm Hg).

Irradiations

The gases were irradiated for periods of 16 to 72 hours in a 1500 curie cobalt-60 source of gamma rays. The source is pictured in figure 2. All radiations were made at room temperature. At these exposure times the total conversion was kept below 0.5 percent, thereby minimizing complicating product irradiation effects.

Dosimetry

The energy absorbed in the 2-butyne was determined through the use of an acetylene dosimeter. It has been shown (ref 6) that in the radiolysis of acetylene gas, polymerization to cuprene and cyclization to benzene account for all the reacted acetylene. The rate of consumption of acetylene has been measured at 0.72 molecules per electron volt of energy absorbed and is linear over a wide range of total dose and pressure. This reaction has been used to measure the energy absorbed in the 2-butyne.

The acetylene was purified by trap to trap vacuum distillations using a toluene/liquid nitrogen (-95°C) slush bath at each trap. The purification step was immediately followed by liquid nitrogen pumping into the pyrex ampoule. The gas pressure and geometry used in the dosimeter experiments were identical to those used in the radiolysis experiments. The decrease of acetylene pressure after exposure was determined by attaching the ampoule to a vacuum line and measuring the acetylene pressure and ampoule volume.

Having found the dose rate in electron-volts per gram of acetylene per hour, the dose rate in 2-butyne was obtained from the following equation:

$$D_{C_4H_6} / D_{C_2H_2} = E_{C_4H_6} / E_{C_2H_2}$$

where E is the electron density of the material in electrons per molecule. For 2-butyne E = 0.555, while $E_{C_2H_2}$ = 0.538. Since $D_{C_2H_2}$ was determined to be 1.60 ev/g - hr, then

$$D_{C_4H_6} = \frac{0.555}{0.538} \times 1.60 = 1.65 \text{ ev/g-hr}$$

ANALYSIS

The irradiated ampoule was attached to a calibrated trap which in turn was attached to the inlet system of a time of flight mass spectrometer. After evacuating the entire system and cooling the trap with liquid nitrogen, the ampoule break seal was opened and a portion of the gas sample was admitted into the mass spectrometer. Hydrogen and methane were analyzed with this portion of the sample. The remaining gas sample was collected in the trap, and subsequently introduced into a gas chromatograph equipped with a six-foot column of di-n-butyl maleate. The remaining products were measured quantitatively in this way. The unknown products were identified by connecting the exhaust line of the chromatograph to the mass spectrometer.

RESULTS AND INTERPRETATION

The products formed from the gamma radiolysis of 2-butyne gas are shown in table 1. The yields are expressed in terms of "G" values or the number of molecules formed per one hundred electron-volts absorbed. All yields were extrapolated to zero dose to eliminate the effects of secondary processes. Figure 3 is a plot showing the linearity of product yield with dose over the doses used in this study.

To interpret the results of these experiments in terms of the radiolysis mechanisms leading to the formation of these observed products, let us review the elementary processes to be expected in the system under consideration.

If the reasonable assumption is made that the effective radiation in the glass ampoule consists primarily of secondary electrons ejected from the walls of the ampoule, which is certainly true at the lower gas pressures used, then it can be shown that these electrons are rapidly degraded in energy by collision with target molecules and finally captured either by the walls of the ampoule or by positive ions produced during a high energy collision. The reactive, excited species, formed by high energy electron impact, react with unchanged target molecules, other excited species, and low energy electrons to form the final products. If this sequence of events truly represents the radiolysis process, then the final products may be deduced by considering the excited or ionic species observed in the electron impact mass spectra of 2-butyne. Since the electrons ejected from the ampoule wall may have energies as high as 1.2 Mev and through collision may be degraded to the order of 1 volt before capture, an average energy mass spectrum should be used to evaluate the primary radiolysis. For this purpose, the mass spectra at 30 and 3000 ev were examined to indicate the most probable species formed. At both bombarding electron energies, mass peaks at 54, 53, and 39 mass units were highest in intensity indicating the following most prevalent reactions:

$$CH_3 - C \equiv C - CH_3 \longrightarrow C_4H_6^{*+} + e$$

$$CH_3 - C \equiv C - CH_3 \longrightarrow C_4H_5^+ + H + e$$

$$CH_3 - C \equiv C - CH_3 \longrightarrow C_3H_3^+ + CH_3 + e$$

3

Reactions of minor importance include:

$$CH_3 - C \equiv C - CH_3 \longrightarrow C_2H_3^+ + (C_2H_3) + e$$

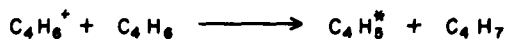$$CH_3 - C \equiv C - CH_3 \longrightarrow C_4H_4^+ + (H_2 \text{ or } H + H^+) + e$$
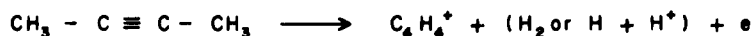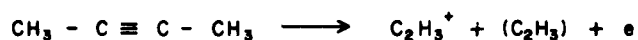
Some of the ions formed by electron impact will have considerable excess energy which may be dissipated by further fragmentations, by radiation, or by collision. The time scale of these various events is important in predicting their occurrence. Fragmentation will occur during the time of a single molecular vibration which for a carbon hydrogen bond is about 10^{-14} seconds, a carbon carbon triple bond, 1.5×10^{-14} seconds, a carbon carbon double bond, 2×10^{-14} seconds, and a carbon carbon single bond, 3×10^{-14} seconds. The time required for a radiative transition is about 10^{-8} seconds and for collision (in the pressure range studied) between 10^{-9} seconds and 10^{-8} seconds. Reduction in energy will then take place by fragmentation to an energy level below which no further fragmentation can occur. Ions and radicals which have internal energies from their ground states to the energy of dissociation will continue the reactions. The energetically possible reactions of ionic species in the γ-radiolysis of 2-butyne gas are summarized in tables 2 and 3. Table 4 summarizes the free radical reactions, and table 5 lists the final products to be expected along with the observations or absence of the postulated products.

In those tables, certain reactions are labelled improbable and would not be expected to occur with high yields in the gas phase. These are reactions of the type: $A + B \rightarrow C$. If a collision occurred between two reactive species A and B and a bond were formed, the excess energy contained in the complex AB^* would be at least the energy required to cause scission of the bond formed between A and B. For most such reactions there would be, in addition, the kinetic energy of impact. For AB^* to remain in existence, this energy must be dissipated before a dissociation could take place (in the order of 10^{-14} to 10^{-13} second). This excess energy may be dissipated by collision with another molecule or by collision with the walls of the container. If the mean time between collisions is much greater than the lifetime of AB^* for dissociation, then the reaction $A + B \rightarrow AB^* \rightarrow C$ becomes highly improbable. In some cases, such reactions can occur if no other possibility for reaction is present. Methane, for instance, in our system is a product of such a reaction. It is likely that the methane, produced from methyl radical hydrogen atom combination, occurs at the vessel walls where the energy may be quickly dissipated as heat to the wall. In other reactions where two or more possibilities exist, such as the following:

$$(1) \quad C_4H_7 + C_4H_7 \longrightarrow C_8H_{14}$$

$$(2) \quad C_4H_7 + C_4H_7 \longrightarrow C_4H_6 + C_4H_8$$
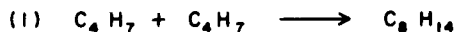
the disproportionation reaction (ref 2) will be favored in the gas phase. With the exception of ethylene, the observed products coincide with those products considered most probable in this analysis (table 5). The ethylene may be present but may not be observed in our analytical scheme because other products may interfere.

The large amount of 2-butene observed in the radiolysis is believed to arise through the following series of reactions:

$$C_4H_6^+ + C_4H_6 \longrightarrow C_4H_5^* + C_4H_7$$

$$C_4H_7^+ + C_4H_6 \longrightarrow C_4H_8 + C_4H_5^+$$

$$C_4H_5^+ + C_4H_6 \longrightarrow C_4H_7^+ + C_4H_4$$
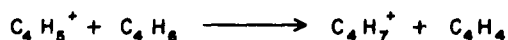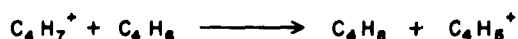
The last three reactions represent a chain of events which can be summarized in one reaction:

$$2C_4H_6 \longrightarrow C_4H_8 + C_4H_4$$
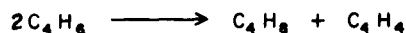
Figure 4 is a pictorial representation of this chain reaction. If we apply the usual steady state approximation to the above reaction, we arrive at the following expressions for dependence of butene and vinyl acetylene yields on solvent pressure:

$$P_{C_4H_8} = KP^2_{C_4H_6}$$

$$P_{C_4H_4} = KP^2_{C_4H_4}$$

These expressions are consistent with experimental observations.

CONCLUSIONS

This investigation has demonstrated that the room temperature gamma radiolysis of 2-butyne gas can be satisfactorily explained primarily through an ion-molecule reaction scheme and with some simple calculations that are consistent with accepted concepts of mass spectrometry and reaction kinetics. The experiment has also shown that this particular compound is relatively radiation stable and that the polymerization produced is through a secondary process.

The results emphasize the need to explore low conversion phenomena to obtain a true picture of the primary processes of the gamma radiolysis. A surprising result is that the C-C single bonds are not readily ruptured. Table 1 shows that the high yield products are the C_4 compounds, thereby indicating that they have skeletal stability.

Although further work is required to firmly establish the radiation behavior of the -C ≡C- linkage it is apparent from this study that the inclusion of the acetylenic linkage in a synthetic material will improve its radiation stability. Furthermore, it may be possible to protect materials having other desirable properties, but lacking stability towards ionizing radiations, by synthesizing the analogous compounds with acetylenic bonds at the sensitive positions.

This experiment has served as an orientation study which points towards a more detailed study of 2-butyne and other compounds in the triple-bond class.

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TABLE I

ONE HUNDRED ELECTRON-VOLT YIELDS FROM γ-RADIOLYSIS OF 2-BUTYNE

	25 mm	100 mm	200 mm
H_2	—	0.85	1.36
CH_4	0.4	0.59	0.35
C_2H_2	0.463	0.36	0.43
C_3H_6	nil	0.02	0.02
C_3H_4	0.295	0.26	0.27
C_4H_{10}	nil	—	0.03
$t-C_4H_8$	1.64	1.67	1.98
$c-C_4H_8$	0.98	1.00	1.29
$1,2-C_4H_6$	nil	0.22	0.53
C_4H_4	nil	0.19	0.36

TABLE 2

PRIMARY REACTION WITH HIGH ENERGY ELECTRONS
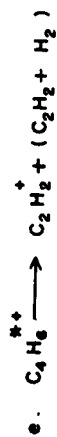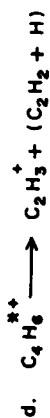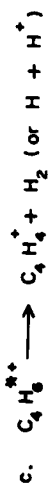
$$C_4H_6 \xrightarrow{\sim\!\sim\!\sim} C_4H_6^* \longrightarrow C_4H_6^{*+} + e$$

EXCITED MOLECULE ION – SOLVENT REACTIONS:

a. $C_4H_6^{*+} + C_4H_6 \longrightarrow C_4H_5 + C_4H_7^+$

b. $C_4H_6^{*+} + C_4H_6 \longrightarrow C_4H_4^+ + C_4H_8$

c. $C_4H_6^* + C_4H_6 \longrightarrow 2C_4H_6$ – possible rearrangement

DISSOCIATIONS:

a. $C_4H_6^{*+} \longrightarrow C_4H_5^+ \pm H$

b. $C_4H_6^{*+} \longrightarrow C_3H_3^+ + CH_3$

c. $C_4H_6^{*+} \longrightarrow C_4H_4^+ + H_2$ (or $H + H^+$)

d. $C_4H_6^{*+} \longrightarrow C_2H_3^+ + (C_2H_2 + H)$

e. $C_4H_6^{*+} \longrightarrow C_2H_2^+ + (C_2H_2 + H_2)$

f. $C_4H_6^* \longrightarrow C_4H_5 + H$

g. $C_4H_6^* \longrightarrow C_3H_3 + CH_3$
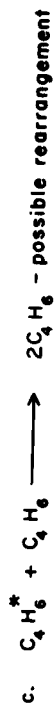
TABLE 3

ION-MOLECULE REACTIONS

SECONDARY ION MOLECULE (SOLVENT) REACTIONS:

a. $C_4H_7^+ + C_4H_6 \longrightarrow C_4H_8 + C_4H_5^+$ cis & trans

b. $C_4H_5^+ + C_4H_6 \longrightarrow C_4H_4 + C_4H_7^+$

c. $C_3H_3^+ + C_4H_6 \longrightarrow C_3H_4 + C_4H_5^+$

ION NEUTRALIZATION

a. $C_4H_7^+ + e \longrightarrow C_4H_7$ Improbable (except at walls)

b. $C_4H_7^+ + e \longrightarrow C_2H_5 + C_2H_2$

c. $C_4H_7^+ + e \longrightarrow CH_4 + C_3H_3$

d. $C_4H_5^+ + e \longrightarrow C_4H_5$ Improbable (except at walls)

e. $C_4H_5^+ + e \longrightarrow 2C_2H_2 + H$

f. $C_4H_5^+ + e \longrightarrow C_2H_3 + C_2H_2$

g. $C_4H_4^+ + e \longrightarrow 2C_2H_2$

TABLE 4

FREE RADICAL REACTIONS

a. $2C_4H_7 \rightarrow C_8H_{14}$ improbable

b. $C_4H_7 + H \rightarrow C_4H_8$ improbable

c. $C_4H_7 + CH_3 \rightarrow C_5H_{10}$ improbable

d. $C_4H_7 + C_3H_3 \rightarrow C_7H_{10}$ improbable

e. $2C_4H_7 \rightarrow C_4H_6 + C_4H_8$

f. $C_3H_3 + H \rightarrow C_3H_4$ improbable

g. $C_3H_3 + CH_3 \rightarrow C_4H_6$ improbable

h. $C_3H_3 + C_4H_6 \rightarrow C_3H_4 + C_4H_5$

i. $2C_3H_3 \rightarrow C_6H_6$ improbable

j. $C_2H_5 + H \rightarrow C_2H_6$ improbable

k. $C_2H_5 + CH_3 \rightarrow C_3H_8$ improbable

l. $2C_2H_5 \rightarrow C_4H_{10}$ improbable

m. $2C_2H_5 \rightarrow C_2H_4 + C_2H_6$

n. $C_4H_5 + H \rightarrow C_4H_6$ improbable

o. $C_4H_5 + CH_3 \rightarrow C_5H_8$ improbable

p. $2C_4H_5 \rightarrow C_4H_4 + C_4H_6$

q. $2C_4H_5 \rightarrow C_8H_{10}$ improbable

r. $CH_3 + H \rightarrow CH_4$

s. $CH_3 + CH_3 \rightarrow C_2H_6$

t. $H + H \rightarrow H_2$

TABLE 5

FINAL PRODUCTS OF RADIOLYSIS

H_2 – Observed

CH_4 – Observed

C_4H_8 – cis + trans 2 Butenes – Observed

C_4H_6 1,2 Butadiene – Observed; 1 Butyne – Observed; 2 Butyne – Observed; 1,3 Butadiene – Not Observed

C_4H_4 – Vinyl Acetylene – Observed

C_3H_4 – Propyne – Allene – Observed

C_2H_2 – Observed

C_2H_4 – Not Observed

C_2H_6 – Observed (Low Pressures)

C_4H_{10} – Observed

C_3H_8 – Not Observed

C_6H_6 – 2,4 Hexadiyne – Not Observed

C_8H_{10} – 2,6 Octadiyne – Not Observed

C_8H_{10} – 2,6 Octadiyne – Not Observed

C_5H_8 – 2,–Pentyne – Not Observed

C_7H_{10} – 2,5 Heptadiyne – Not Observed

C_5H_{10} – 2-Pentyne – Not Observed

C_8H_{14} – 2,6 Octadiene – Not Observed

C_3H_6 – Observed

Nitrile}
Series}
$$HC - C \equiv N$$
Acetonitrile

$$HC - C - C \equiv N$$
Propionitrile

$$HC - C - C - C \equiv N$$
Butyronitrile

1-Alkyne}
Series}
$$HC - C \equiv CH$$
Propyne

$$HC - C - C \equiv CH$$
1-Butyne

$$HC - C - C - C \equiv CH$$
1-Pentyne

2-Alkyne}
Series}
$$HC - C \equiv C - CH$$
2-Butyne

$$HC - C - C \equiv C - CH$$
2-Pentyne

$$HC - C - C - C \equiv C - C - H$$
2-Hexyne

Alkyl Diyne}
Series}
$$HC \equiv C - C - C - C \equiv CH$$
1,5 Hexadiyne

$$HC \equiv C - C - C - C - C \equiv CH$$
1,6 Heptadiyne
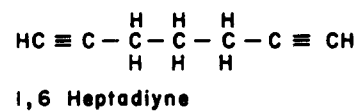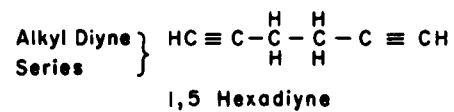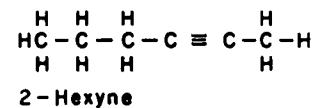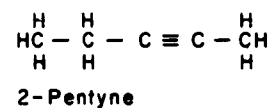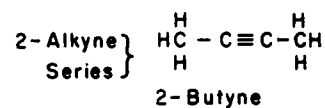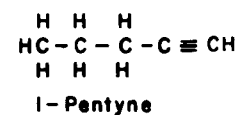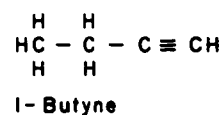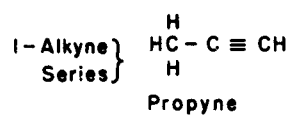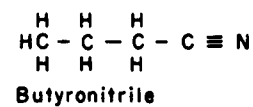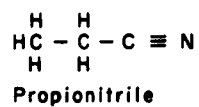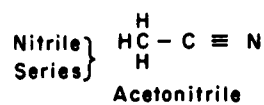
Figure 1. Molecule Dictionary
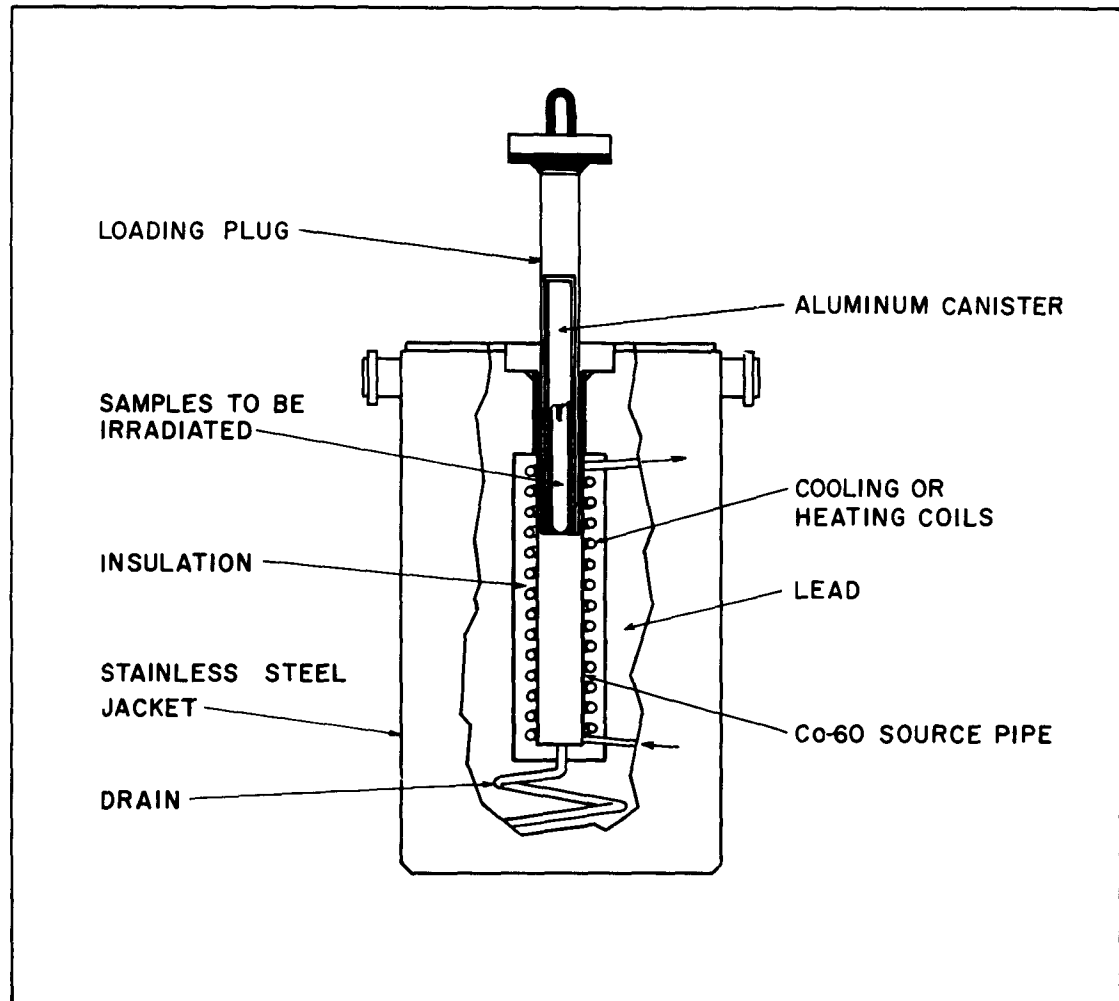
Figure 2. Sectional View of a Cobalt-60 "Pig"
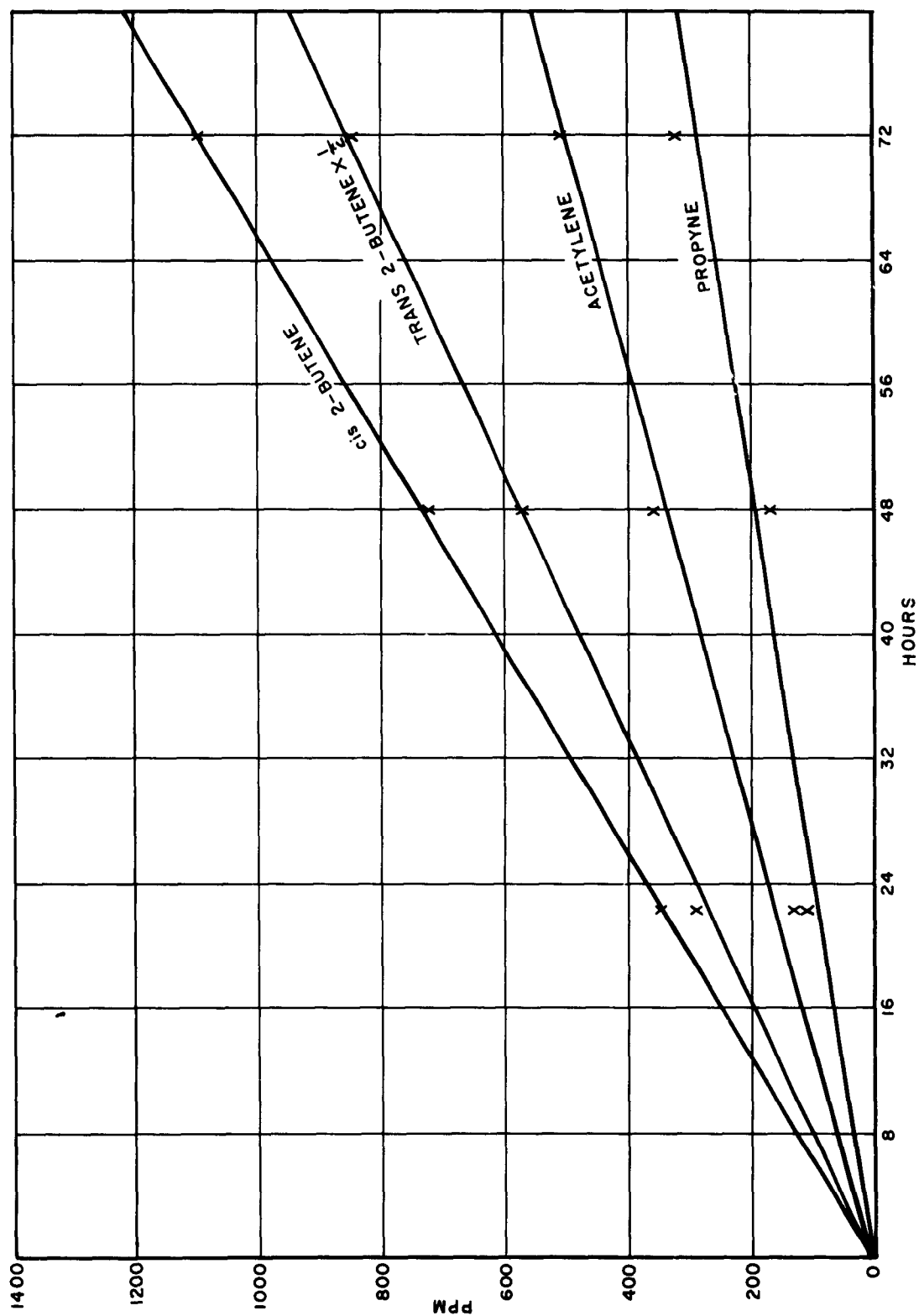
Figure 3. Product Formation versus Irradiation Time

$$C_4H_6^+ \quad \underline{\text{Solvent}} \quad \begin{cases} \longrightarrow C_4H_7^+ \\ \longrightarrow C_4H_8^+ \end{cases}$$
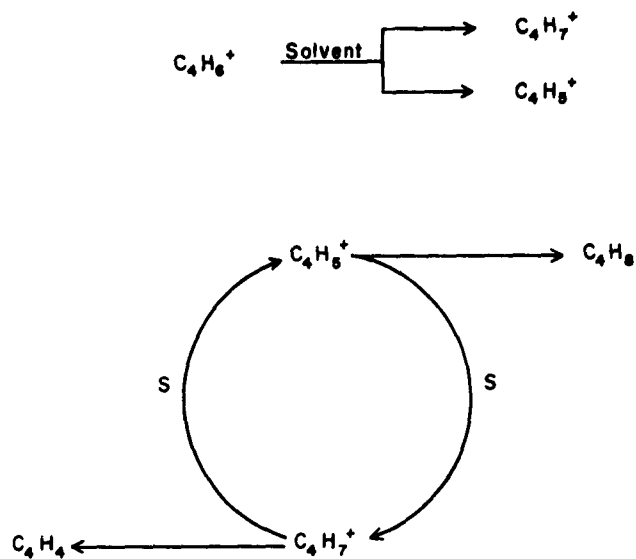
Figure 4. Production of Vinyl Acetylene and 2-Butene Via a Chain Reaction

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Aeronautical Systems Division, Dir/Materials
and Processes, Physics Lab,
Wright-Patterson AFB, Ohio.
Rpt No. ASD-TDR-63-65. THE GAS PHASE
RADIOLYSIS OF 2-BUTYNE. Final report, Feb.
63, 14 pp. incl illus., tables, 7 refs.
Unclassified Report

Fyrex ampoules of gaseous 2-butyne (dimethyl-
acetylene) were exposed to cobalt-60 gamma
rays, and the hundred electron-volt yields
of the lower molecular weight products are
given. The radiation induced products were
studied as a function of sample pressure and
total dose. The products, which include
hydrogen, methane, acetylene, propene,
(over)

propyne, cis- and trans- 2-butene, butane,
1,2-butadiene, and vinylacetylene, are
explained on the basis of ion-molecule and
free radical reactions. Some mechanisms
of product formation which are consistent
with product distribution and magnitude of
the yields are discussed.

1. 2-Butyne
2. Gas phase radioly-
   sis
3. Cobalt-60 radiation
I. AFSC Project 7367,
   Task 736701
II. R. E. Rondeau et al
III. Avail fr OTS
IV. In ASTIA collec-
    tion