Table II. Density Data for Three Binary Solutions

Temperature, ° C.	Density, G./Ml., for Hydrazine, Mass Fraction		
	0.3024	0.5615	0.7804
30.00	0.9064	0.9419	0.9679
35.00	0.9016	0.9371	0.9634
40.00	0.8969	0.9322	0.9589
45.00	0.8921	0.9274	0.9544
55.00	0.8827	0.9179	0.9455
60.00	0.8779	0.9131	0.9411
70.00	0.8682	0.9036	0.9322
80.00	0.8584	0.8936	0.9231
90.00	0.8480	0.8838	0.9135

the validity of this expression for the hydrazine used in these measurements exhibited agreement within the reported experimental error. Calculated values were based on the mass fraction of pure components. The average absolute deviation between observed and predicted values was 0.18% of the observed density. The largest deviation, among 27 experimental points, was −0.25%. The authors concluded that calculated, mass average densities are acceptable predictors exhibiting a uniform low deviation from measured data over the entire composition range and a range of temperatures from 30° to 90° C.

SAFETY

Hydrazine and methylhydrazine are highly toxic materials. They can be absorbed through the skin and can cause blindness on very short contact with the eye. Every effort should be made to avoid oral ingestion, breathing, or skin contact. In this work, good ventilation, safety glasses, and rubber gloves were mandatory.

Compounds of the hydrazine family undergo violent autodecomposition at high temperatures. They also decompose readily in the presence of inorganic catalysts and common laboratory residues. Clean glassware and stainless steel equipment are necessary safety precautions. Excessive heating—i.e., above 200° C.—is to be avoided. Unnecessary confinement under pressure and/or in metal containers is hazardous.

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LITERATURE CITED

(1) Ahlert, R. C., Bauerle, G. L., Lecce, J. V., J. CHEM. ENG. DATA 7, 158–60 (1962).
(2) Barger, J. N., "Application of Alkylhydrazines to Rocket Power Plants," Aeroject-General Corp., Azusa, Calif., May 1958.
(3) Ohm, G. E., "Properties of Selected Rocket Propellants, Vol. II," p. 267, The Boeing Co., Seattle, Wash., 1964.

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Mass Spectral Data of Substituted Acetylenes

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The Time-of-Flight mass spectra of 12 alkynes were obtained at a bombardment energy of 30 electron volts. All of the alkynes studies were unbranched disubstituted acetylenes ranging in length from four to 10 carbon atoms. The fragmentation patterns were normalized to a total ionization of 100 units and analyzed in terms of the relative occurrence of α, β, and γ carbon-carbon scissions. In the 2-alkyne series, β scission predominated in the C_4 to C_8 compounds. As the chain length increases, the γ scission products increase until they eventually predominate at C_9 and C_{10}. β Scission products were the most abundant in all of the 3-alkynes studied. In the 4-alkynes, α bond rupture prevailed with only a slight tendency toward α bond scission.

ALTHOUGH several acetylenic compounds have been studied through electron impact phenomena (*2*), no systematic study has every been done on the fragmentation patterns of disubstituted acetylenes. Because of a separate study (*5*) on the radiation chemistry of acetylenic compounds, the authors have undertaken this mass spectrometric study of alkynes to aid in the interpretation of the degradation of these compounds. This approach is based on the assumption that the mass spectrum of a particular compound gives a distribution of ionic species which reasonably resembles that created when the compound is exposed to a highly energetic radiation field (*3*).

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EXPERIMENTAL

The spectra were obtained with a Bendix Model 14 Time-of-Flight mass spectrometer (*4*) operated in the pulsed electron beam mode with an electron beam energy of 30 e.v. and electron beam current of 0.125 μamp. This particular beam energy was chosen as typical of the secondary electron mean energy in equilibrium during radiolysis so that direct comparison with radiation chemistry would be meaningful. Analyses which are usually conducted at a beam energy of 70 e.v. can be easily performed at the lower energy. Also, the lower energy may, because of the complex mixtures of energetic species often encountered in radiation chemical systems, be of considerable advantage in mass spectrometric analyses (*1*).

Each alkyne was obtained from Farchan Research Laboratories, purified by vacuum distilling, and admitted to the Bendix 922 inlet system as a liquid. The source pressure

Table I. Fragmentation Pattern of 2-, 3-, and 4-Alkynes[a]

m/e	2-Butyne	2-Pentyne	2-Hexyne	2-Octyne	2-Nonyne	2-Decyne	3-Hexyne	3-Octyne	3-Nonyne	3-Decyne	4-Octyne	4-Nonyne
15	0.038	0.20	0.04	T[b]	T	0.028	0.23	0.10	T	0.01	0.04	T
26	0.46	0.13	0.04	T	T	T	0.07	T	T	...	0.02	T
27	10.31	4.57	2.38	1.22	0.76	0.57	1.76	1.16	0.54	0.36	0.80	0.82
28	7.35	1.08	1.20	0.63	0.43	0.40	0.99	0.46	0.74	0.49	0.40	0.67
29	0.20	0.87	1.71	5.29	1.95	1.35	1.12	1.21	2.89	1.32	1.34	1.06
30	...	...	0.06	0.11	0.08	T	T	0.05	0.08	0.06	0.04	T
37	0.02	...	...	...	...	...					...	...
38	0.67	0.14	0.04	...	...	...	0.07	T	...	...	T	...
39	11.5	4.44	4.94	1.81	1.03	0.57	4.86	1.16	0.58	0.36	0.85	0.53
40	0.42	6.19	1.39	0.57	0.43	0.28	2.07	1.55	0.74	0.57	0.67	0.38
41	0.03	8.08	8.65	7.47	4.92	3.73	13.5	6.96	6.20	4.43	5.94	4.9
42	...	4.03	2.95	1.76	1.94	1.19	4.05	1.50	1.45	1.29	1.07	0.77
43	...	0.30	0.59	0.77	7.84	7.51	0.70	2.99	1.07	5.09	0.98	2.31
44	...	...	T	T	0.32	0.23	T	0.13	T	0.18	0.04	0.14
49	T	...	...	...	...	...	...	...	...	...		
50	0.95	0.30	0.13	...	...	...	0.14	T	T	T	T	T
51	3.11	1.27	0.57	0.18	0.16	0.06	0.68	0.13	0.04	0.05	0.18	0.07
52	3.48	2.00	1.65	0.32	0.22	0.14	0.79	0.33	0.21	0.10	0.49	0.31
53	17.0	18.9	10.75	3.70	2.59	1.70	6.62	4.63	2.68	1.80	4.91	2.79
54	42.4	1.19	8.87	9.55	7.24	6.05	6.71	1.86	1.53	1.50	3.75	8.17
55	2.08	0.18	1.48	6.69	5.51	6.38	1.85	3.35	4.21	4.73	4.64	4.47
56	T	T	0.30	1.92	1.08	1.86	0.50	1.03	1.49	0.90	0.67	0.72
57	...	...		1.85	0.22	0.96	T	0.21	1.90	0.30	0.18	1.44
58	...	...		0.09	T	0.11	...	0.05	0.08	T	T	...
63		0.11	0.04	...	...	...	0.09	T	...	...	...	...
64		0.07	T	...	...	...	0.04	T	...	...		
65		1.97	1.52	0.54	0.35	0.23	3.29	0.82	0.58	0.36	0.85	0.48
66		1.51	0.76	0.59	0.46	0.51	1.26	0.93	0.70	0.60	1.03	0.48
67		11.0	18.6	6.51	7.03	7.97	24.3	14.43	14.9	15.3	14.7	20.1
68		30.0	1.22	8.69	9.30	9.27	1.58	14.43	12.4	12.0	7.8	4.23
69		1.92	0.21	2.40	3.78	2.26	0.09	2.22	3.14	4.50	1.2	1.05
70		0.09	T	0.45	1.03	0.51	...	0.26	0.66	0.54	0.09	0.19
71		...	...	...	T	0.05	...	...	T	0.21	T	T
72											T	T
77			0.44	0.18	0.22	0.14	0.63	0.51	0.33	0.21	0.67	0.48
78			0.11	0.05	T	T	0.95	0.09	T	0.03	0.11	0.05
79			1.43	1.22	0.97	0.79	1.71	1.85	1.16	1.0	3.12	1.63
80			0.68	0.59	0.49	0.57	0.27	0.44	0.62	0.3	0.67	0.77
81			3.16	13.55	7.68	8.47	4.32	12.1	7.0	5.75	12.9	9.85
82			21.7	2.26	2.38	2.43	24.8	2.58	3.8	4.58	2.54	3.37
83			1.65	0.14	0.76	1.36	1.94	0.16	0.83	0.60	0.11	0.67
84			T	...	0.11	0.37	T	...	T	0.15		
85			...	...	...	0.14						
91				0.14	0.14	0.06		0.13	0.08	0.11	0.11	0.19
92				T	...	T		...	T	0.03	T	T
93				0.38	0.43	0.42		0.36	0.58	0.45	0.35	0.53
94				0.04	0.38	0.42		T	T	0.21	T	0.14
95				9.73	18.65	15.2		6.7	14.5	7.49	5.05	8.17
96				0.91	2.16	4.63		0.46	1.49	1.56	0.45	1.10
97				...	0.11	0.68		...	T	0.3	0.11	T
107				...	0.08	T		T	0.12	0.18	0.04	T
108				...	T	T		T	0.04	...	T	T
109				0.50	2.05	6.10		0.31	2.48	12.6	0.22	1.73
110				9.95	0.57	0.85		11.3	0.33	1.41	14.3	0.24
111				0.70	0.06	T		1.03	...	0.3	0.14	T
122					...				...	...		
123					...	0.54			...	0.39		
124					3.51	0.48			6.86	0.25		9.85
125					0.27	T			0.54	0.03		1.06
126					...	...			...	...		T
138					...	2.37				4.58		
139					...	0.28				0.51		

[a] Based on total ionization of 100 units, excluding H^+. [b] T = trace.

was adjusted to an indicated pressure of 200 microns before introduction to the spectrometer.

The mass spectrum of each of the 12 alkynes analyzed was recorded in triplicate from a mass to charge ratio (m/e) of 12 to the m/e of the parent ion. The peak heights at each m/e in the spectra were averaged numerically and the averaged spectra were normalized by setting the total ionization at 100 (excluding H^+, Table I).

RESULTS AND DISTRIBUTION

Bond scission can occur in the mass spectrometer by several processes. With the alkynes, certain of these processes involving excitation and bond scission will probably be important in their radiation chemistry. The mass spectra of these hydrocarbons should be useful as guides in the interpretation of their radiation chemical behavior and certain generalizations based on these mass spectra regarding routes of bond scission are possible.

It is not possible to deduce complete radiation chemical behavior from these data owing to the atypically low pressures prevailing in the mass spectrometer. Nevertheless, the data contained here regarding the relative effects of different scission or rearrangement reactions in these acetylenic molecules can be used to predict the initial "cage free" scission processes and their relative importance in bond-breaking environments. In many instances, the exact nature of the scission process is not directly evidenced by the mass-to-charge ratios, and two or more similar processes can give rise to species having the same mass-to-charge ratios. Since these cannot be distinguished, the simplest or least energetic process should be assumed in comparing the spectrum with supposed radiation chemical behavior. Carbon-carbon bond scissions taking place at different positions in these unbranched hydrocarbons can be distinguished by mass-to-charge ratios of the products. However, C—H bond scissions are indistinguishable, and no attempt should be made to relate the carbon-hydrogen bond scission to radiation chemistry except by inference from the carbon-carbon bond scission processes. Table II summarizes the carbon-carbon bond scission as observed from mass spectra and is based upon the sum of fragments associated with α, β, or γ scission for a total ionization of 100 units.

β scission appears to be the dominant process in the short chain members of the 2-alkynes studied. Both α and γ scissions do occur and with only slightly reduced probability. As the chain length increases, the yield of γ scission increases and both the α and β scission decrease. At C_9 (2-nonyne), the γ scission process predominates and α scission is reduced fivefold from its maximum value.

Table II. Abundance of Scission Products

(Based on total ionization of 100 units, excluding H^+)

	α	β	γ
2-Alkynes			
2-Butyne	11.95		...
2-Pentyne	(20)[a]	10	...
2-Hexyne	(16)	22.6	(10)
2-Oxtyne	(13.02)	17.07	15.20
2-Nonyne	4.08	9.83	16.33
2-Decyne	1.87	7.75	17.24
3-Alkynes			
3-Hexyne	13.33	25.88	...
3-Octyne	(11.5)	(34)	14.68
3-Nonyne	20.2[b]	30.11[b]	10.8
3-Decyne	17.31[b]	27.94[b]	10.33
4-Alkynes			
4-Octyne	22.5	15.44	5.50
4-Nonyne	(30)	(13)	(6)

[a] Values in parentheses are derived from mass spectra where more than one type of scission are involved. [b] Probably interferred with by rearrangement processes.

β scission predominated for all of the 3-alkynes studied, but there is indication of an increased tendency for α scission in the higher homologs.

In the two 4-alkynes studied, α bond scission predominates with only a small tendency toward γ bond scission. β bond scission still occurs more strongly than γ scission.

In alkynes with asymmetric alkyl substitution, α, β, and γ scission can, in general, occur in two ways, and Table II was calculated by summing the ions for both possibilities (where both can occur).

LITERATURE CITED

(1) Dunbar, D. J., Harrah, L. A., *Air Force Materials Lab., Tech. Rept.* **64-381** (Febuary 1965).
(2) Franklin, J. L., Field, R. H., *J. Am. Chem. Soc.* **76**, 1994 (1954).
(3) Futrell, J. H., *J. Chem. Phys.* **35**, 353 (1961).
(4) Harrington, D. B., "Time-of-Flight Mass Spectrometry," Encyclopedia of Spectroscopy, p. 628, C. F. Clark, Ed., Reinhold, New York, 1960.
(5) Rondeau, R. E., Harrah, L. A., Nevitt, T. D., Barber, H. H., Jr., *Air Force Materials Lab., Tech. Rept.* **65-236** (July 1965).

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