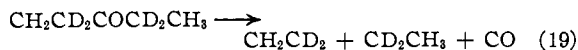
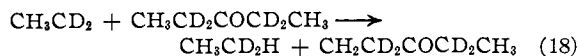
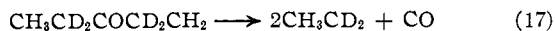


Wijnen and Steacie⁹ studied the photolysis of α -tetradeuterodiethyl ketone in an effort to investigate the reactions of ethyl radicals. At temperatures above 200° they concluded that the ethylene produced was not the result of disproportionation, but was largely due to the decomposition of the pentanonyl radical.



However, it was evident that some other ethylene producing reaction was taking place, since $\text{C}_2\text{D}_2\text{H}_2$ was formed considerably faster than the $\text{C}_2\text{D}_2\text{H}_4$

(9) M. H. J. Wijnen and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1092 (1951).

at temperatures of 300° and above. The authors apparently did not analyze for hydrogen in this work. Our work supports the thesis that the ethyl radical can decompose to give ethylene and a hydrogen atom in the region of 300°. It is probable that it is this decomposition of the CH_3CD_2 radical which caused the elevation of the $\text{C}_2\text{D}_2\text{H}_2/\text{C}_2\text{D}_2\text{H}_4$ ratio in the work of Wijnen and Steacie.⁹ If the decomposition of the ethyl radical is an important reaction above 300°, hydrogen must appear in the products. In a later paper, Kutschke, Wijnen and Steacie¹⁰ found no hydrogen in the products of the photolysis of the diethyl ketone, but all of their experiments were done at temperatures below 300°, where none would be expected.

(10) K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, *THIS JOURNAL*, **74**, 714 (1952).

CHINA LAKE, CALIF.

[CONTRIBUTION FROM THE KNOLLS ATOMIC POWER LABORATORY, GENERAL ELECTRIC COMPANY]

The β -Particle Radiolysis of Acetylene^{1,2}

BY LEON M. DORFMAN³ AND F. J. SHIPKO

RECEIVED APRIL 26, 1955

The β -particle radiolysis of acetylene has been investigated at room temperature for the system tritium-acetylene. The 100 e.v. yields for the over-all rate of disappearance of acetylene to form cuprene and benzene, the only volatile product, and of benzene formation are: $-G_{\text{C}_2\text{H}_2} = 71.9$ and $G_{\text{C}_6\text{H}_6} = 5.1$. The fraction of the acetylene going to form benzene is independent of acetylene pressure and radiation intensity, and has an average value of 0.21. Since the ratio of the rates of cyclization and polymerization is independent of acetylene pressure, the two processes are not competitive for the same trimer intermediate. A mechanism is suggested in which the reaction paths are determined by the formation of different excited states of acetylene. Cyclization is initiated by an excited molecule, in a triplet state, which may have a bent configuration. Such a state has been characterized in a recent analysis of the acetylene ultraviolet spectrum by Ingold and King. Experiments with deuterioacetylene show that exchange occurs between the isotopic acetylene molecules, indicating that carbon-hydrogen bond rupture does occur in the radiolysis.

Introduction

The radiation polymerization of acetylene to form cuprene is one of the earliest hydrocarbon radiolyses studied,^{4,5} and the over-all yield for the reaction has been quite accurately established.⁶ The reaction has been investigated from many points of view, and in recent years attention has been directed chiefly to the question of transfer mechanisms occurring in the primary process when mixtures are irradiated. One aspect of the reaction, which may be of particular importance in understanding the role of excited electronic states has been largely neglected. This concerns the formation of benzene. Benzene has been identified⁷ as a product, and the significance of its formation has been pointed out.⁸ No kinetic analysis has yet been carried out in which both the rate of cyclization to form benzene and the over-all reaction rate have been determined over any variation of condi-

tions, such as pressure and intensity. A knowledge of the relationship between these rates is essential to an understanding of the mechanism of the radiolysis.

In the present investigation, the rate of the acetylene polymerization, initiated by tritium β -particles, has been determined at room temperature for the system $\text{T}_2\text{-C}_2\text{H}_2$. The tritium serves as a highly intense source of β -radiation. The incident intensity is readily determinable from mass spectrometric analysis of the starting tritium along with the known nuclear properties of this isotope. In some of the runs, mixtures of acetylene and deuterioacetylene were used to determine whether dissociation occurs during the course of the reaction.

Experimental

The acetylene reactant and the tritium were purified as follows. Technical grade acetylene was degassed at -140° , then purified by bulb-to-bulb distillation at -95° . Routine mass spectrometric analysis of the acetylene, carried out before each run, failed to disclose the presence of any impurity, so that impurity, if any, amounted to certainly less than 0.1% of the reactant acetylene. Partially deuterated acetylene, used in three of the runs, was made by passing deuterium oxide over calcium carbide which had been previously degassed. The deuterioacetylene was then subjected to a similar distillation purification. The tritium gas was stored on a uranium bed and degassed and desorbed as required for each run. The tritium contained varying amounts of hydrogen, with the purest gas consisting of about 85% tritium.

(1) The Knolls Atomic Power Laboratory is operated for the United States Atomic Energy Commission by the General Electric Co., Contract No. W-31-109 Eng. 52.

(2) Presented before the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955.

(3) General Electric Research Laboratory, Schenectady, N. Y.

(4) S. C. Lind and D. C. Bardwell, *Science*, **62**, 423 (1925).

(5) W. D. Coolidge, *ibid.*, **62**, 441 (1925).

(6) S. C. Lind, D. C. Bardwell and J. H. Perry, *THIS JOURNAL*, **48**, 1556 (1926).

(7) W. Mund and C. Rosenblum, *J. Phys. Chem.*, **41**, 469 (1937).

(8) C. Rosenblum, *ibid.*, **52**, 474 (1948).

TABLE I

Run no.	H ₂	Reactant pressures (mm.)		$\Delta P_{C_2H_2}$ (mm.)	Reaction yields (molec./100 e.v.)		$\frac{3P_{C_6H_6}}{\Delta P_{C_2H_2}}$	$\frac{\Delta P + P_{C_6H_6}}{\Delta P_{C_2H_2}}$
		T ₂	C ₂ H ₂		-GC ₂ H ₂	GC ₂ H ₂		
1	48.3	60.8	101.8	18.0	72.7	5.9	0.24	0.93
2	8.1	12.2	115.5	17.9	72.4	5.3	.22	1.00
9 ^a	3.2	19.5	116.0	24.3	66.8	5.6	.25	0.97
8 ^b	3.5	15.3	143.0	19.8	65.5	3.5	.17	..
10 ^b	2.7	16.0	147.6	20.4	67.1	4.8	.21	..
7 ^a	3.0	17.3	159.3	35.5	63.5	3.2	.15	1.01
5	22.3	11.4	178.9	25.3	67.4	5.2	.22	1.04
4 ^a	34.2	39.2	204.1	21.8	70.3	6.1	.26	1.02
3	6.6	3.2	220.6	12.0	80.3	5.8	.22	1.04
14	3.9	16.3	370.2	38.5	78.0	6.1	.24	1.06
12	3.0	14.4	469.8	53.8	78.7	5.5	.21	1.04
11	3.5	27.2	515.1	33.7	76.8	4.5	.18	0.97
13	5.6	23.6	547.2	74.6	66.1	5.2	.23	1.04
6	40.5	17.7	554.9	44.1	81.6	4.5	.16	1.07
				Mean	71.9	5.1	.21	

^a Contain deuterioacetylene. ^b Cold finger maintained at -78° during run. For runs 1, 2 and 9, $98 \pm 1\%$ of the β -energy is absorbed. This has been taken into account in calculating the yields.

The runs were all carried out at room temperature ($26 \pm 2^\circ$) in a 100-cc. spherical Pyrex bulb closed off by a mercury cut-off. The cut-off also served as a manometer. A clean reaction bulb was used for each run since cuprene polymer is deposited at the bottom of the reaction bulb during the run. The acetylene was introduced first, frozen down at liquid nitrogen temperature, and degassed. The tritium was then added and the whole reaction cell brought to room temperature to start the run. The run times ranged from 5 to 66 hours. For most of the runs, a pressure-time curve was determined.

The analyses were carried out on a General Electric analytical mass spectrometer. Previous calibrations⁹ had shown that the mass spectrometric sensitivities for hydrogen and tritium are equal.

At the end of each run, the non-condensable fraction consisting of tritium was removed at -195° , sampled and taken up on the uranium bed. The residual pressure was then read at room temperature. The acetylene fraction was then distilled off at -95 to -90° , with the exception of a few mm. which was intentionally left behind with the benzene product. This was done to bring the pressure of the last fraction to an easily readable level, since the benzene itself usually amounted to less than 5 mm. and in most runs was less than 2 mm. All three fractions were analyzed in the mass spectrometer.

In runs no. 8 and 10 a small cold finger, attached directly to the reaction cell, was maintained at a temperature of -78° throughout the run. The purpose of this arrangement was to condense out the benzene product as it was formed and thus remove it from the radiation field. The path length from the reaction bulb to the cold zone was only 2 to 3 cm., and material balance measurements indicated that the benzene was frozen out.

Three of the runs contain deuterioacetylene. The acetylene in run no. 4 was 83.5% deuterated. The acetylene used in runs no. 7 and 9 was, respectively, 66.9 and 52.3% deuterated. These latter two mixtures were made up by adding normal acetylene to deuterioacetylene to ensure that the isotopic molecules represented a non-equilibrium system.

In all the runs only a fraction of the acetylene reactant was polymerized. This amount ranged from 5 to 20% of the initial acetylene, so that the residual acetylene was always at least 50 times as high as the amount of benzene formed.

Results and Discussion

The experimental conditions and results obtained in a series of fourteen runs, all carried out at $26 \pm 2^\circ$, are shown in Table I. The acetylene pressure has been varied 5-fold. The tritium pressure, proportional to the incident intensity of β -radiation, has been varied 20-fold.

(9) H. C. Matraw, C. F. Pachucki and L. M. Dorfman, *J. Chem. Phys.*, **20**, 926 (1952).

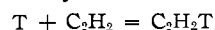
The absolute intensity of incident β -radiation is accurately determinable from the pressure of tritium and the known values of the nuclear constants for this isotope: half-life¹⁰ 12.4 years, average energy¹¹ 5.69 kev. From a recent determination¹² of the absorption curves for tritium β -particles in various gases, as well as from the value for the range¹³ of these betas, 0.7 mg./cm.², it can be shown that the absorption of β -energy is complete for most of these runs. For runs no. 1, 2 and 9, at the lowest acetylene pressures the absorption is $98 \pm 1\%$ complete.

The pressure of acetylene used up in each run is shown in col. 5 of Table I. The over-all yield for the reaction $-GC_2H_2$, in terms of molecules of acetylene disappearing per 100 e.v., is shown in the next column. The benzene yield, GC_6H_6 , is shown in col. 7, and the fraction of the acetylene going to form benzene in col. 8. The material balance, given by $(\Delta P + P_{C_6H_6})/(\Delta P_{C_2H_2})$, where ΔP is the observed pressure drop, is shown in the last column.

In addition to the results shown in Table I, a number of observations were made which will not be described in detail, but which are of general significance. Firstly, no disappearance of tritium or exchange of tritium between the hydrogen isotopes and the acetylene was observed in the mass spectrometric analyses. Recovery of the initial tritium was always complete within the accuracy (*ca.* 1-2%) of the analyses. This indicates that there was no significant dissociation of the hydrogen isotope molecules, since the reaction



would almost certainly be followed by



with a resulting loss of tritium from the non-condensable fraction, as well as exchange between the hydrogen and acetylene, since exchange does occur between the isotopic acetylene molecules. It would

(10) G. H. Jenks, F. N. Sweeton and J. A. Ghormley, *Phys. Rev.*, **80**, 990 (1950).

(11) G. H. Jenks, J. A. Ghormley and F. N. Sweeton, *ibid.*, **75**, 701 (1949).

(12) L. M. Dorfman, *ibid.*, **95**, 393 (1954).

(13) L. E. Glendenin, *Nucleonics*, **2** (No. 1), 12 (1948).

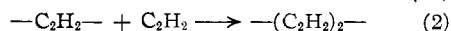
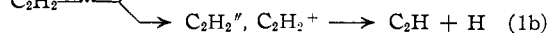
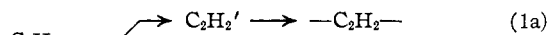
seem, therefore, that there is efficient transfer of charge (and probably of excitation energy) from the hydrogen to the acetylene. This requirement is consistent with the values for the ionization potentials of these molecules, that of acetylene being considerably lower than for hydrogen. The first excited state of acetylene also occurs at a lower energy level than that of hydrogen. Secondly, it is of interest that the pressure-time curves obtained in the polymerization are quite linear. It is thus understandable that the over-all yield is independent of the degree of conversion of the acetylene. And finally, in the runs with deuterioacetylene, no deuterium appears in the non-condensable fraction.

Since investigations at different intensities have resulted in similar values for the over-all yield, it is to be expected that the over-all yield is independent of intensity. This has been checked under the present conditions and, as may be seen from the data in Table I, the yield for acetylene disappearance is independent of the intensity of β -radiation over a 20-fold range. This yield is also independent of acetylene pressure, and has the average value $-G_{C_2H_2} = 71.9$ molecules/100 e.v., with an average deviation of 7%. The energy requirement per ion-pair in acetylene is indicated¹⁴ to be about 27 e.v. per ion-pair. On the basis of this value, the over-all yield obtained in the present work is within experimental agreement with the yield of 21 ± 2 obtained by Rosenblum⁸ for α -particles, and in very close agreement with the value of 19.8 obtained by Lind, *et al.*,⁶ for radon α -particles.

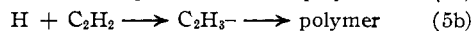
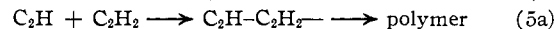
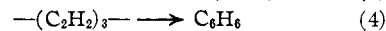
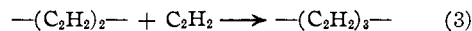
The yields for the formation of benzene, which is the only volatile product found, have an average value of $G_{C_6H_6} = 5.1$. There is some scatter in the values, but it is clear that the benzene yield shows no trend with increase in acetylene pressure. The fraction of the acetylene going to form benzene is similarly independent of acetylene pressure and radiation intensity and has the average value 0.21. This is in excellent agreement with the value reported by Rosenblum⁸ for the initial formation of benzene.

The suggestion has been made⁸ that the mechanism of this radiation reaction involves the formation of an excited acetylene molecule, which on successive addition to acetylene forms the trimer $(C_2H_2)_3^*$, which was presumed linear, and that this transitory intermediate leads either to benzene by cyclization or to cuprene by a continuation of the addition polymerization. It is apparent, however, from the fact that the benzene yield is independent of the acetylene pressure, that the secondary reactions leading to the two different products are not competitive for the same trimer intermediate.

Rather, it is suggested that the different reaction paths are determined by the formation of different species in the primary excitation and ionization. One of these, an excited electronic state, can lead to cyclization, the other to dissociation and hence the initiation of polymerization and exchange.



(14) W. P. Jesse and J. Sadauskis, *Phys. Rev.*, **97**, 1668 (1955).



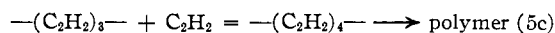
The excited electronic state formed in reaction (1a) is the precursor of the cyclic trimer which always forms benzene. This mechanism leads to the following rate equation for benzene formation

$$R_{C_6H_6} = \phi_1 I_a \quad (1)$$

where $R_{C_6H_6}$ is the rate of formation of benzene, ϕ_1 is a fractional constant, and I_a is the absorbed radiation intensity. The rate of formation of benzene is thus independent of pressure, and the benzene yield is independent of pressure and intensity

$$G_{C_6H_6} = \phi_1 \times 100 \quad (II)$$

If the same trimer intermediate leads also to polymerization



the mechanism then leads to

$$R_{C_6H_6} = \frac{k_4 \phi_1 I_a}{k_4 - k_{5c}(C_2H_2)} \quad (III)$$

which is contrary to the experimental result.

The particular excited state which leads to cyclization may be a triplet state and will then have the characteristics of a biradical. Ingold and King¹⁵ have recently characterized the first excited electronic state of acetylene from the ultraviolet absorption spectrum. It is a *trans*-bent state, not a linear state, with bond angles, bond lengths, and other molecular constants almost identical with those in normal benzene. The CCH bond angle is 120.2° and the C-C bond length is 1.385 Å. The electronic and geometric configuration of the acetylene molecule in this excited state is such that it would be expected to participate readily in the formation of the benzene ring, with the exception perhaps that it is *trans*-bent rather than *cis*-bent. The carbon-carbon bond is a three-electron bond and the other three electrons are shared between these carbon atoms in two *trans*-orbitals, so that the molecule has the characteristics of a biradical.

In the cyclization mechanism suggested, the bent excited molecule can add to an acetylene molecule in the ground state to form a dimer with a bent configuration. If the dimer has been formed from a *trans*-bent molecule, a further vibrational rearrangement is necessary in order to form the cyclic trimer, because of coulomb repulsion of the hydrogen atoms at the ends. This rearrangement probably involves small energies, on the order of 1 to 2 kcal./mole. If the initial addition involves the *cis*-bent form, trimer formation and hence cyclization can occur without further rearrangement.

Polymerization may be initiated by the monoradicals and atoms formed in reaction (1b). However, the nature of the polymerization termination step cannot be elucidated on the basis of the present or earlier rate data, since no information is available about the structure or molecular weight of the polymer.

It is known¹⁶ that polymerization in acetylene

(15) C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702 (1953).

(16) D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, **12**, 369 (1944).

can be initiated by hydrogen atoms. And it is significant to point out that rupture of the carbon-hydrogen bond in acetylene does occur in the radiation reaction. This is evidenced by the occurrence of exchange between the isotopic acetylene molecules in those runs containing deuterioacetylene. The data for three runs are shown in Table II.

TABLE II

Run no.		Initial acetylene	Final acetylene	Mole fraction D in benzene
7	C ₂ H ₂	0.220	0.135	0.669
	C ₂ HD	.223	.392	
	C ₂ D ₂	.557	.473	
9	C ₂ H ₂	.386	.291	...
	C ₂ HD	.179	.377	
	C ₂ D ₂	.435	.332	
4	C ₂ H ₂	.033	.023	.831
	C ₂ HD	.272	.276	
	C ₂ D ₂	.695	.701	

The occurrence of the exchange



is clear in the two runs in which normal acetylene has been added to the prepared deuterioacetylene. No HD appears in the non-condensable fraction. The mechanism of the exchange is not clear, and the data are not extensive enough to warrant discussion. The over-all reaction rate for polymerization is apparently the same for the deuterated and normal acetylene. This observation was made some years ago by Lind, *et al.*¹⁷

Acknowledgment.—The authors are indebted to Mr. C. F. Pachucki who performed the mass spectrometric analyses, and to Dr. N. J. Hawkins for many discussions concerning the excited states.

(17) S. C. Lind, J. C. Jungers and C. H. Schiffert, *THIS JOURNAL*, **57**, 1032 (1935).

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

The Stability of Aqueous Chloramine Solutions

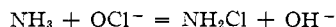
BY L. F. AUDRIETH AND R. A. ROWE¹

RECEIVED MAY 25, 1955

The decomposition of chloramine prepared from ammonia and hypochlorite has been studied in alkaline solutions at 0°. The mole ratio of ammonia to hypochlorite was varied from 1:1 to 3:1. The concentration of hydroxide ion present initially ranged from 0.36 to 1 *M*. The reaction of sodium hypochlorite with excess ammonia will produce a solution which is initially higher in its chloramine content. However, such solutions decompose more rapidly than those prepared from stoichiometric quantities of ammonia and hypochlorite. The stability and initial concentration of monochloramine decrease with increasing concentrations of hydroxide ion. Reactions of chloramine in alkaline solution can be divided into three categories: (a) those reactions in which no decomposition takes place and in which chloramine acts as an aminating agent to produce hydrazine, *N*-substituted hydrazines, hydroxylamine and *O*-substituted hydroxylamines by interaction with NH₃, RNH₂, H₂O and ROH; (b) those reactions in which hydrolysis takes place, entailing conversion of chloramine into hypochlorite or chlorate; and (c) reactions of self oxidation-reduction, in which chloramine as an imide carrier undergoes disproportionation into nitrogen and ammonia.

Introduction

In previous publications^{2,3} we have discussed in some detail the various factors which govern the yields of *N*-substituted hydrazines obtainable by the amine-chloramine reaction. Yields have been based upon the analyzed chloramine content of solutions prepared from hypochlorite and ammonia.



Qualitative studies have shown that such solutions undergo rapid decomposition, especially if the hydroxide ion concentration is increased beyond that which is formed as a result of the reaction given above. Thus, McCoy⁴ has reported that "a solution initially 6²/₃ *M* in NaOH and 0.0515 *M* in NH₂Cl lost 32% of its oxidizing power in five minutes, but in 41 minutes, only 38%," and "that the addition of ammonia . . . to chloramine solutions markedly depressed the rate of decomposition by hydroxide." A more detailed study was therefore undertaken to evaluate specifically the effects of

both hydroxide ion and ammonia concentrations upon the stability of chloramine solutions prepared from hypochlorite and ammonia.

The experimental work which is presented in this paper demonstrates that the stability of chloramine decreases with increasing concentrations of both ammonia and hydroxide ion. It is significant, however, that the addition of ammonia to hypochlorite in mole ratios greater than 1 does yield initially solutions which contain a higher concentration of chloramine than those employing only stoichiometric quantities of the two reagents. We have applied these findings to improve the yields of *N*-disubstituted hydrazines obtainable by the reaction between chloramine and secondary amines.⁵

Experimental

Preparation of Material and Analytical Procedures.—Sodium hypochlorite solutions were prepared as described by Coleman and Johnson⁶ using an excess of sodium hydroxide. Such solutions also contain an amount of NaCl equimolar to the hypochlorite content. Deionized water was used in all experiments.

The hypochlorite content was determined by addition of potassium iodide to a measured volume of the hypochlo-

(1) Abstracted from the doctoral dissertation submitted to the faculty of the Graduate College of the University of Illinois.

(2) L. F. Audrieth and L. H. Diamond, *THIS JOURNAL*, **76**, 4869 (1954).

(3) L. H. Diamond and L. F. Audrieth, *ibid.*, **77**, 3131 (1955).

(4) R. E. McCoy, *ibid.*, **76**, 1447 (1954).

(5) R. A. Rowe and L. F. Audrieth, unpublished observations.

(6) G. H. Coleman and H. L. Johnson, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 59.