

experimental results in this direction. There are several possible ways in which catalase can decompose H_2O_2 without causing a detectable O^{18} -enrichment in the oxygen produced. First, the oxygen may be produced through an action of the enzyme on H_2O_2 without breaking the peroxide bond, *e.g.*, by dehydrogenation process. This, however, seems most unlikely, because the peroxide bond is the weakest link in the H_2O_2 molecule. Since catalase is the most efficient of all enzymes, it is very unlikely that such an enzyme would skip the weak peroxide bond and try to break the much stronger O-H bonds. Secondly, one may suggest that the reaction is diffusion-controlled, so that no isotope effect is not detected. But this suggestion contradicts experimental evidence. Chance estimated the activation energy for the catalytic decomposition of H_2O_2 by catalase to be 1400 cal./mole or less,⁵ whereas for a diffusion-controlled reaction in aqueous solution at room temperatures the activation energy should be close to 4.6 kcal./mole. The third possibility is that the splitting of the peroxide bond by catalase is preceded by a slower and hence rate-determining step in which the substrate combines with the enzyme; *i.e.*, once the substrate succeeded in combining with catalase, the peroxide

bond is immediately split irrespective of whether it is $O^{16}-O^{16}$ bond or $O^{16}-O^{18}$ bond. The transition of compound I to compound III in Fig. 1 has some resemblance to this possibility. Finally, the peroxide bond may not be completely broken until fairly stable bonds have been formed between the two O atoms and catalase. The energy consumed in breaking the stronger $O^{16}-O^{18}$ bond is mostly compensated by the energy gained in forming the stronger $Fe^{III}-O^{18}$ bonds, etc.; and if the splitting of the peroxide bond and the formation of the new enzyme-substrate bonds are not isolated events but occur in a more or less continuous transition, this would minimize the activation energy as well as the isotope effect. The mechanisms of most catalytic processes, including the one illustrated in Fig. 1, probably have some feature of this continuous transition from old to new bonds. In general, the efficiency of the catalyst depends largely on the nature of this kind of transition.

Acknowledgment.—In preparing this work, the present author benefited through conversations with Professors H. G. Cassidy, L. Onsager, A. Patterson, S. J. Singer, J. M. Sturtevant, H. H. Wasserman and Dr. E. H. White.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE COMBUSTION BRANCH, U. S. NAVAL ORDNANCE TEST STATION]

The Photolysis and Pyrolysis of Acetone- d_6 in the Presence of Ethane and of Acetone in the Presence of Ethane- d_6

BY JAMES R. MCNESBY AND ALVIN S. GORDON

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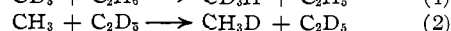
The photolysis and pyrolysis of mixtures of acetone- d_6 and ethane, and of acetone and ethane- d_6 have been studied with particular emphasis on abstraction of H and D and by CD_3 and CH_3 , respectively (reaction 1 and 2). The activation energies found are $E_1 = 11.5$ kcal. and $E_2 = 14.8$ kcal. Changing light intensity and introducing additional surface has no measurable effect on the relative rates of (1) and (3). Small amounts of ethylene- d_4 , HD and D_2 , but no H_2 within the accuracy of the mass spectrometer are found in the products of the photolysis and pyrolysis of the ethane- d_6 -acetone mixture. HD, H_2 but no D_2 were found in the acetone- d_6 -ethane reaction. A fifty-fold increase in surface had no measurable effect upon the HD/ D_2 ratio. Similarly, argon does not appear to affect the ratio measurably. Both the HD/ H_2 and HD/ D_2 ratios increased with temperature. The most reasonable interpretation of the hydrogen analyses appears to be that a H (or D) atom is formed by decomposition of the ethyl radical and the H (or D) atom subsequently either abstracts H or D from acetone or ethane, or recombines with a similar atom.

Introduction

The measurement of activation energies of meta-theoretical reactions of the type $CH_3 + HR \rightarrow CH_4 + R$ has been greatly facilitated in recent years by a technique first introduced by Steacie¹ which involves the use of the CD_3 radical. The rate of formation of CD_3H is compared with the rate of formation of CD_4 in the reaction of CD_3 with acetone- d_6 from which the CD_3 radicals are generated. This comparison is made over a temperature range and the pre-exponential factors and activation energies are obtained relative to those for the reaction of CD_3 with acetone- d_6 . To obtain a meaningful measurement, the amount of CD_3H arising from the incompletely deuterated acetone must represent a very small proportion of the CD_3H produced by the abstraction of hydrogen from the compound under investigation. This requirement demands a

very highly deuterated acetone- d_6 . The acetone- d_6 used by Trotman-Dickenson, Birchard and Steacie¹ in their work on abstractions by CD_3 of hydrogen from hydrocarbons contained some 30% acetone- d_6 . This results in large percentages of the total CD_3H arising from the partially deuterated acetone. We calculate about 80% in the case of C_2H_6 . Recently the reaction between CD_3 and CH_4 ² was studied in this Laboratory. Since methane has only one kind of hydrogen, the significance of these experiments is clear.

In the present investigation the reactions



were studied since they can be interpreted unambiguously by the observation of the CD_3H/CD_4 and CH_4/CH_3D ratios, respectively. Previous work³

(1) J. R. McNesby and A. S. Gordon, *THIS JOURNAL*, **76**, 4196 (1954).

(2) J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 1416 (1954).

(1) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

showed that when acetone and acetone- d_6 reacted with CD_3 , the same activation energy difference (1.7 kcal.) existed as for the reactions with CH_3 . It was of interest to determine whether this activation energy difference is dependent upon the nature of the compound from which H and D are abstracted.

Experimental

Acetone- d_6 was prepared by the method described previously.⁴ Mass spectrometer analysis showed the product to be 97.5% acetone- d_6 and 2.5% acetone- d_3 . The ethane was Phillips research grade material and contained a trace of methane. Acetone was distilled from commercial material. The ethane- d_6 was kindly given to us by Drs. R. E. Varnerin and F. O. Rice. It contained 97.6% ethane- d_6 , 2.2% ethane- d_3 , 0.2% CD_4 and a trace of CD_3H . Two master mixtures were prepared. For the study of the reaction of CD_3 with ethane, the mixture contained ethane and acetone- d_6 in the ratio 2.84, and for the investigation of the reaction of $CH_3 + C_2D_6$, the acetone/ethane- d_6 ratio was 0.53. The light source was a flat spiral Hanovia SC-2537 lamp. The photolyses were carried out in aluminum block furnaces, fitted with double windows, one of fused silica and the other a Corning filter to remove the 1849 mercury line. The fused silica, cylindrical reaction vessels were 4 cm. i.d. \times 4 cm. high. The reaction vessels were protected from mercury vapor with a gold leaf trap. The reaction vessel in one furnace was charged with enough silica rod to increase the surface area sixfold.

The total pressure was 100 mm. for the acetone- d_6 -ethane mixtures, and 80 mm. in the case of acetone-ethane- d_6 mixtures at each of the temperatures at which the mixture was photolyzed.

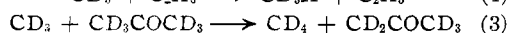
The mixtures were pyrolyzed in Pyrex reaction vessels using the technique described elsewhere.⁴ The vessels were charged at room temperature with about 100 mm. of the master mixture in the case of acetone- d_6 and ethane, and 50 mm. in the case of acetone and ethane- d_6 . In experiments with added surface the reaction vessels were packed with Pyrex wool and the surface area estimated from the weight of the Pyrex wool and the approximate diameter of the fibers.

The analysis for CD_3H and CD_4 in the investigation of reaction (1) has been described previously,⁴ and involves analyzing the fraction of the products volatile at -195° . The analysis for CH_3D and CH_4 in the study of reaction (2) again involved a low temperature fractionation and presented a considerable problem. When a mass spectrometer is in general use, complete removal of mass 18 water vapor from the instrument becomes a virtual impossibility. Since small amounts of CD_4 and CD_3H were present in the initial mixture and some CH_2D_2 was formed in the reaction, the mass 18 peak in the mixture had contributions from a number of compounds. In addition, a large amount of CO is formed which has a considerable contribution at mass 16, while both CH_2D_2 and H_2O have contributions at masses 16 and 17. The Consolidated Engineering mass spectrom-

eter in use in this Laboratory is equipped with a high resolution slit arrangement which facilitates separating the mass 17 due to OH and the mass 16 due to O, from the corresponding 17 and 16 peaks arising from CH_3D , CD_3H , and CH_4 , CD_3 , CH_2D , respectively. The mass spectrum of CH_4 measured on the high resolution instrument compared very well with the cracking pattern in the literature after suitable adjustment of the instrument, and with that previously measured on our instrument without high resolution. It was therefore assumed that the cracking pattern of CD_4 , CD_3H , CD_2H_2 and CH_3D agreed with the literature with the most recent CD_3H pattern being used.³ A typical methane analysis is given in Table I.

Results and Discussion

Two methane producing reactions occur when a mixture of acetone- d_6 and ethane are photolyzed or pyrolyzed.



Mixtures of acetone- d_6 and ethane were photolyzed in the range $246-405^\circ$ and pyrolyzed from $477-524^\circ$. Since the CD_3H/CD_4 ratio for the photolysis and pyrolysis of acetone- d_6 is only about 0.03, no correction in the CD_3H/CD_4 ratios was applied when mixtures were run. The results are given in Table II. No trend with time was observed in the CD_3H/CD_4 ratios since the reactions were stopped after about 1% reaction. A least squares evaluation of the Arrhenius plot gave $E_1 - E_3 = 0.21 \pm 0.04$ kcal. (standard deviation). Since $E_3 = 11.3 \pm 0.2$ kcal.,^{3,4} $E_1 = 11.5 \pm 0.2$ kcal. The Arrhenius plot gives the ratio of pre-exponential factors $A_1/A_3 = 1.21$. It is of interest that the cruder experiments of Trotman-Dickinson and Steacie¹ gave $E_1 - E_3 = 0.1$.

TABLE II
REACTION OF METHYL- d_3 RADICALS WITH ETHANE AND ACETONE- d_6

T, °C.	t, min.	CD_3H/CD_4	k_1/k_3	H_2/HD
246	2	2.82	0.99	
246	4	2.77	0.98	
275	2	2.86	1.01	
275	3	2.85	1.00	
309	1	2.89	1.02	
309	2	2.84	1.00	
309	3	2.86	1.01	
336	1	2.85	1.00	
336	2	2.87	1.01	
405	1	2.93	1.03	7.2
405	2	2.95	1.04	7.1
405	3	2.99	1.05	6.7
477	9	2.97	1.05	6.5
498	12	3.02	1.06	
501	5	3.01	1.06	6.4
524	2	2.98	1.05	5.2
524	4.7	3.00	1.06	
320 ^a	10	2.80	0.99	
320 ^a	15	2.82	0.99	
315 ^b	1	2.85	1.00	
315 ^b	2	2.80	0.99	
315 ^b	3	2.81	0.99	
257 ^b	2	2.78	0.98	
257 ^b	4	2.78	0.98	

^a Light intensity one tenth of other runs. ^b Six \times increase in surface area. Runs at 477° and higher are pyrolyses.

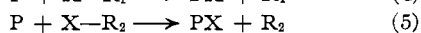
TABLE I

A TYPICAL METHANE ANALYSIS USING HIGH RESOLUTION MASS SPECTROMETRY: PHOTOLYSIS OF ACETONE-ETHANE- d_6 MIXTURE AT 361°

m/e	15	16	17	18	19	20
Peak height	204.9	266.7	42.1	57.0	3.4	59.6
CD_4	...	7.5	0.0	49.5	0.5	59.6
$\Delta 1$	204.9	249.2	42.0	7.5	2.9	..
CD_3H	0.2	0.4	1.5	1.2	2.8	
$\Delta 2$	204.7	258.8	40.5	6.3	0.1	
CH_2D_2	0.6	1.8	3.7	5.9	0.1	
$\Delta 3$	204.1	257.0	36.8	0.4	..	
CH_3D	7.2	26.5	34.3	0.4		
$\Delta 4$	196.6	230.5	2.5	..		
CH_4	198.5	230.5	2.5			

(4) J. R. McNesby, T. W. Davis and A. S. Gordon, THIS JOURNAL, 76, 823 (1954).

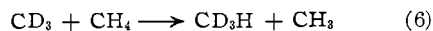
Evans and Polanyi⁵ have developed a theory of relationship between the dissociation energies of the bonds R₁-X and R₂-X and the activation energies for the metathetical reactions



They conclude that, provided certain conditions are fulfilled

$$\frac{1}{2} [D_{R_1-X} - D_{R_2-X}] = E_4 - E_3 \quad (I)$$

Although it is questionable that the theory is applicable to reactions (1) and (6)



it is nevertheless true that equation (I) is obeyed for these two reactions with very high precision. According to the work of Stevenson⁶ $D_{CH_3-H} - D_{C_2H_5-H} = 5.0$ kcal. The Evans-Polanyi theory predicts $E_6 - E_1 = 5.0/2 = 2.5$ kcal. It has been found² that $E_6 - E_3 = 2.7$ kcal. and $E_1 - E_3 = 0.2$ kcal. It follows that $E_6 - E_1 = 2.5$ kcal., in excellent agreement with the prediction of this theory.

As Table II shows, changing the light intensity by a factor of 10 has no appreciable effect on the relative rates of formation of CD₃H and CD₄. A sixfold increase in surface area similarly has no appreciable effect.

TABLE III

REACTION OF CH₃ WITH ACETONE AND ETHANE-*d*₆

The units of CD₄, HD, D₂ are mass spectrometer peak heights. The units of the quantity whose log is given in column 8 are min.^{-1/2}.

T, °C.	t, min.	CD ₄ ^a	CH ₄ / CH ₃ D ^b	k ₁ /k ₂	HD	D ₂	$\frac{\log \frac{[(HD)/t(CD_4)]}{[D_2/t(CD_4)]^{1/2}}}{}$
254	1	..	15.3	28.9
254	2	..	15.8	29.8
254	3	..	12.5	23.6
328	2	439	8.62	16.3	3.0	38.3	-1.79
328	4	431	7.99	15.1	19.5	56.6	-1.21
328	6	440	8.84	16.7	8.8	72.4	-1.71
361	2	419	6.74	12.7	4.6	28.2	-1.51
361	3	470	6.72	12.7	9.1	53.1	-1.47
358 ^c	2	841	3.6	23.0	-1.75
360 ^c	3	673	9.8	35.3	-1.44
406	1	501	4.79	9.05	5.0	19.7	-1.31
406	2	473	4.89	9.23	12.7	35.0	-1.14
406	3	539	5.11	9.65	15.2	56.2	-1.31
451	1	450	3.81	7.20	11.7	22.6	-0.93
451	2	428	3.92	7.40	27.8	44.7	-0.86
507	1	529	3.02	5.70	9.6	5.9	
507	2	479	3.21	6.05	9.2	5.3	
507	3	521	3.19	6.02	15.8	7.8	
507	10	621	38.1	17.6	
507 ^d	2	549	6.1	2.0	
507 ^e	2	501	5.6	1.9	
507 ^f	2	680	5.9	1.9	
507 ^f	3	810	6.0	2.0	

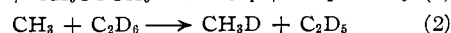
^a This CD₄ is not a reaction product except partly at 507°. It represents that portion of the CD₄ originally in the sample which entered the mass spectrometer in the analysis.

^b Only high resolution runs reported. ^c Surface increased 6 ×. ^d Surface increased 20 ×. ^e Surface increased 50 ×. ^f Argon pressure 3 × mixture pressure.

(5) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

(6) D. P. Stevenson, *Discs. Faraday Soc.*, **35**, (1951).

A mixture of acetone and ethane-*d*₆ was photolyzed and pyrolyzed over the temperature range 254–507°. The results are given in Table III. Since the precision of results at 254° was quite poor, runs at this temperature were not included in the Arrhenius plot shown in Fig. 1, although they do fall within experimental error of the extrapolated line. The filled circles in this plot are data published recently by Rice and Varnerin.⁷ No trend could be observed with time in our data, and each run was given equal weight in the statistical analysis. The two methane forming reactions were



From the Arrhenius plot shown in Fig. 1, $E_2 - E_7 = 5.23 \pm 0.16$ kcal., and $A_7/A_2 = 0.20$. A value for $E_2 - E_7$ of 2.0 kcal. was reported recently by Rice and Varnerin.⁷ This value was obtained from pyrolysis data over a temperature range of only 50°. As Fig. 1 shows, the approximate k_7/k_2 values obtained by Rice and Varnerin are in good agreement with our extrapolated values. It is probable that their measurements were subject to errors at least as large as ours. Their points may fall on our extrapolated Arrhenius plot within experimental error. The comparison of the two sets of data illustrates that either a very large temperature range or a large number of determinations is required to ensure accurate values for the activation energy. The value of E_7 is 9.6 ± 0.1 kcal. and it follows that $E_2 = 14.8 \pm 0.3$.

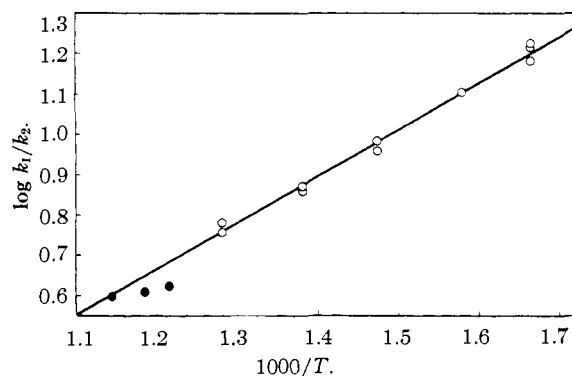


Fig. 1.—The Arrhenius plot for the difference in activation energy between abstraction by CH₃ of H from acetone and D from ethane-*d*₆. The filled circles represent the data of Rice and Varnerin.⁷

It is concluded that $E_2 - E_1 = 3.3 \pm 0.6$ kcal. If it is assumed that CH₃ and CD₃ are confronted by equal activation barriers in the abstraction of hydrogen, this result is surprisingly high. If CH₃ and CD₃ are significantly different when attacking a molecule such as ethane, then the results indicate that ethane presents a higher barrier to CH₃ than to CD₃.

Since a small amount of CD₄ was present in the ethane-*d*₆ it was somewhat difficult to determine whether CD₄ was being formed during the course of the reaction. If CD₄ is not a reaction product, the CH₄/CD₄ ratio should be proportional to the time

(7) F. O. Rice and R. E. Varnerin, *THIS JOURNAL*, **77**, 221 (1955).

of reaction in the early stages since

$$\text{CH}_4/\text{CD}_4 = r_1 t / (r_2 t + [\text{CD}_4]_0) \quad (\text{II})$$

where t is time, $[\text{CD}_4]_0$ is the concentration of CD_4 originally present and r_1 and r_2 are the rates of formation of CH_4 and CD_4 , respectively. If CD_4 is a product, the ratio should be proportional to time at very small times, and as time goes on the ratio should become independent of time. Figure 2 shows that this reasoning leads to the conclusion that CD_4 is not a product in the photolysis but is a product in the pyrolysis at 507° .

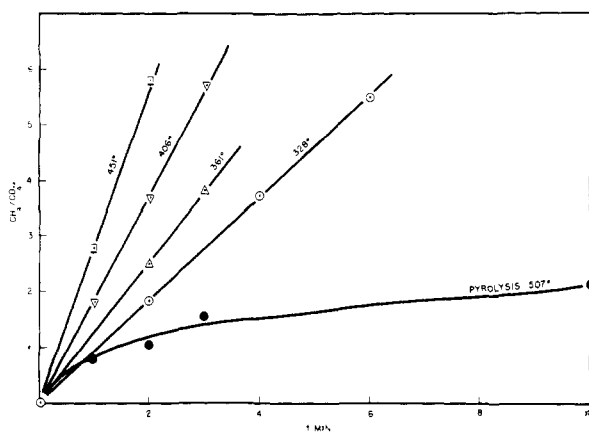
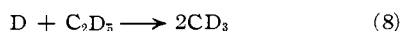
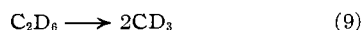


Fig. 2.—The photolysis and pyrolysis of mixtures of acetone and ethane- d_6 . The figure illustrates that CD_4 is formed in the pyrolysis at 507° but not in the photolysis at lower temperatures.

It is possible that the reaction

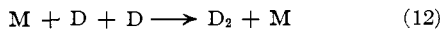
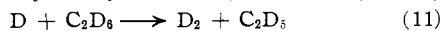


or that the reaction



becomes appreciable in the region of 500° . The two methanes CD_4 and CD_3H can then be formed by abstraction of D and H, respectively, by CD_3 .

Of special interest is the observation that small amounts of HD, D_2 and ethylene- d_4 are formed in both pyrolysis and photolysis of the acetone-ethane- d_6 mixture. Mercury photosensitization can give rise to D atoms in the photolysis if the efficiency of the gold leaf trap is poor. However, HD and D_2 formed in the pyrolysis must arise from a thermal reaction. The fact that the HD/ D_2 ratio increases with temperature in photolysis and pyrolysis suggests that D atoms can react in the following ways



The activation energy for reaction (11) is undoubtedly considerably higher than for reaction (10), so that (11) cannot be important relative to (10). Since E_{12} is about zero, the important hydrogen producing reactions must be (10) and (12). To determine whether M in reaction (12) represents a wall, the surface/volume ratios were increased by factors of 20 and 50 in some pyrolysis experiments. The results in Table III show that the HD/ D_2 ratios were not appreciably affected. If (10) and (12)

are the important reactions, for small percentage conversion

$$(\text{HD}) = k_{10}(\text{A})(\text{D})t$$

$$(\text{D}_2) = k_{12}(\text{M})(\text{D})^2t$$

where t is the time of reaction in minutes. The concentrations (A) and (M) are each proportional to the (CD_4) which is present as an impurity in the C_2D_6 . No CD_4 is formed during the photolysis.

$$(\text{HD}) = k_{10}\beta(\text{CD}_4)(\text{D})t$$

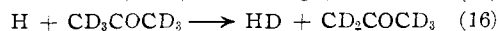
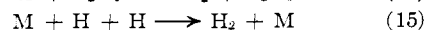
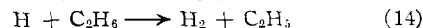
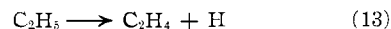
$$(\text{D}_2) = k_{12}\left(\frac{\beta}{\alpha}\right)^2(\text{CD}_4)(\text{D})^2t$$

where β and α are dimensionless, temperature independent, proportionality constants. It follows that

$$\alpha k_{10}/k_{12}^{1/2} = \frac{(\text{HD})}{(\text{CD}_4)t} / \left[\frac{(\text{D}_2)}{(\text{CD}_4)t} \right]^{1/2} \quad (\text{III})$$

The data in Table III indicate that $E_{10} - 1/2 E_{12} \approx 12$ kcal. This value seems rather high when compared with the value of 9 kcal. obtained by Harris and Steacie⁸ for the reaction of a hydrogen atom with acetone but the precision of our data is such that $E_{10} - 1/2 E_{12}$ may be as low as 9 kcal. Table III, column 7, shows that there is no evidence that the D atom recombination is influenced by the wall. The addition of argon may have a slight effect on the D atom recombination, but the effect is not measurable in the present system. The detailed mechanism of D_2 formation cannot be ascertained at this time, but homogeneous D atom recombination is a possible process.

In the case of acetone- d_6 -ethane mixtures, H_2 and HD were formed but D_2 was absent. The H_2 /HD ratio decreased with increasing temperature. These observations are consistent with the following reactions

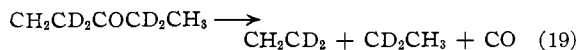
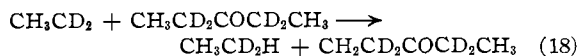
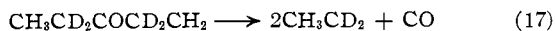


$$\frac{\text{H}_2}{\text{HD}} = \frac{k_{15}(\text{C}_2\text{H}_6) + k_{16}(\text{H})(\text{M})}{k_{17}(\text{CD}_3\text{COCD}_2)} \quad (\text{IV})$$

At high temperatures, the energy of activation difference from the Arrhenius plot of H_2 /HD would tend toward $E_{16} - E_{14}$, which is probably close to zero; at low temperatures a similar plot of $\text{H}_2^{1/2}$ /HD ratios would produce an apparent $E_{16} - 1/2 E_{15}$. The latter activation energy difference would be about 10 kcal. Since both mechanisms are operative in the temperature range studied, the observed energy of activation difference should be roughly 5 kcal. The data in Table II indicate an apparent activation energy difference of about 4 ± 2 kcal. When these results are taken along with the results for acetone-ethane- d_6 case discussed previously, the consistent mechanism of H_2 , HD and D_2 formation represented by reactions 10-16 is in agreement with the results within experimental error. The ethylene produced should be approximately equal to the total hydrogen formed. The data obtained in this work show that this is at least approximately true, so that the only important ethylene producing reaction also produces hydrogen.

(8) C. M. Harris and E. W. R. Steacie, *J. Chem. Phys.*, **13**, 554 (1945).

Wijnen and Steacie⁹ studied the photolysis of α -tetradeuteriodiethyl 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).
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[CONTRIBUTION FROM THE KNOLLS ATOMIC POWER LABORATORY, GENERAL ELECTRIC COMPANY]

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

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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.

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(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).