[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Formation of Methylketene in the Photolysis of Diethyl Ketone

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(1) Methylketene and hydrogen are reported for the first time as products of the high temperature photolysis of diethyl ketone in a flow system. (2) Four competing reactions based on a free radical mechanism are presented to explain the products. Ratios of products to substrate calculated on the basis of this mechanism agree well with the observed values. (3) Weightings of these four reactions show little temperature dependence and these irregularities are assumed due to differences in contact time and light intensities.

High temperature photolyses of diethyl ketone have been carried out in a manner similar to that used for previous investigations[2] of acetone in this Laboratory. Hurd[3] found both ketene and methylketene as products of the pyrolytic decomposition of diethyl ketone and suggested that ketene itself was formed as a secondary product, the methylketene being a primary product. Neither ketene has been reported as a product of the photolysis of diethyl ketone. Methylketene was formed during runs with our flow system at contact times of about eight seconds and less, but our initial efforts using longer contact times had failed to give this product in detectable amounts.

Previous reports of the products formed in the photochemical decomposition of diethyl ketone differ. Berthelot and Gaudechon[4] obtained a gaseous mixture that consisted of about fifty per cent. carbon monoxide and the rest hydrocarbons having the composition of ethane but from which both methane and butane were isolated. Ells and Noyes[5] found carbon monoxide, butane and smaller—approximately equivalent—amounts of ethane and ethylene in runs at 25°. Davis[6] found appreciably greater quantities of ethane than ethylene in the C_2 hydrocarbons from runs at temperatures varying from 26 to 136°.

Experimental

A diagram and description of the apparatus used for the photolysis of diethyl ketone is given in the report on acetone by Ferris and Haynes.[2] Condensable products were trapped and the gases analyzed as described therein. A modification in procedure was introduced with respect to the analysis for methylketene. It was considered sufficient to place excess aniline in the first two traps initially to react with the small amounts of the ketene that condensed in them. As before, the gases were bubbled through aniline only in the third trap. The condensed ketone was distilled from the combined condensates of the first two traps at reduced pressures with an aspirator. The residue was combined with the solution from the third trap and aniline distilled off at pressures of about 0.1 mm. to leave a crystalline residue.

The residue, formed by reaction with aniline, had a melting point of 98–103°. The crude residues from the high and low temperature runs were mixed and recrystallized from 1:1 ethyl acetate and petroleum ether (30–60°). The purified crystals thus obtained were colorless and melted at 104–105°. After mixing with an authentic sample of propionanilide, the melting point was not depressed. This was excellent evidence that methylketene was formed during the runs and that ketene itself was absent or possibly produced in negligibly small quantities lost during the careful recrystallization process.

The possibility of some pyrolysis at higher temperatures must be considered. A blank run on diethyl ketone for one hour at 450° produced only 56 ml. of air-free permanent gas, compared to 2050 ml. with the ultraviolet light.

The General Electric A-H6 lamps have been used because of the need for a high intensity source, but their lives have not approached the average value of 75 hours claimed for them and their intensities drop noticeably after an hour or two of use. There also seems to be considerable variation between lamps as indicated by the different adjustments of our temperature controller necessary to keep the temperature of our reaction chamber at a given value for different runs. The lamp used for runs 4, 5 and 7 broke after the last of these runs and a new lamp was used in runs 10, 11 and 12. There was definite carbonization on the end of the reaction chamber nearest the lamp in the first three of these runs but none appeared in the last three. This seemed at least partially due to differences of light intensity although the position of the lamp relative to the reaction chamber also affected carbonization.

Our diethyl ketone, obtained from the Eastman Kodak Company, was their best grade. It was redistilled and dried over anhydrous sodium sulfate. The aniline was redistilled at about 0.1 mm. and used immediately.

Results

In all the experimental runs the pressure was maintained at 77 (± 2) mm. and diethyl ketone vapors were passed through the flow system for a period of one hour. The other experimental conditions, amount of decomposition, and moles of products formed in each run per mole of ketone decomposed are given in Table I. The number of moles of ketone decomposed was calculated as the sum of the weights of the products, this seeming more accurate than using less precise differences of large weights. The volumes of permanent gases are reported on an air-free basis, and the weights of methylketene are obtained by conversion from the weights of propionanilide isolated.

TABLE I

Run	Temp., °C.	Contact time, sec.	Diethyl ketone, mole		Substrate decomposed, mole %	Vol. of permanent gases, ml.	Methylketene formed, g.	Moles of product per mole diethyl ketone decomposed					
			Passed	Decomposed				CO	C_4H_{10}	C_2H_6	C_2H_4	H_2	CH_3CHCO
4	450	2.6	0.423	0.0244	5.8	2050	0.169	0.94	0.03	0.79	0.96	0.14	0.12
7	400	8.1	.150	.0281	18.7	2610	.101	1.00	.00	.74	1.12	.32	.06
10	350	4.2	.314	.0277	8.8	2030	.094	0.99	.41	.54	0.52	.05	.06
11	300	3.1	.465	.0195	4.2	1450	.041	1.02	.41	.60	.48	.05	.04
12	280	6.5	.220	.0173	7.9	1330	.094	1.06	.30	.47	.67	.13	.10
5	190	7.3	.246	.0155	6.3	1330	.083	1.00	.13	.57	.98	.27	.10

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[1] This paper is based on part of the research work to be submitted by Pete D. Gardner as a partial fulfillment of the degree of Doctor of Philosophy at the University of Utah.

[2] R. C. Ferris and W. S. Haynes, THIS JOURNAL, **72**, 893 (1950).

[3] C. D. Hurd, *ibid.*, **45**, 3095 (1923).

[4] D. Berthelot and H. Gaudechon, *Compt. rend.*, **151**, 478 (1910).

[5] V. R. Ells and W. A. Noyes, THIS JOURNAL, **61**, 2492 (1939).

[6] W. Davis, *ibid.*, **70**, 1868 (1948).

In each run the total number of gram atoms of carbon in the products, per mole of substrate decomposed, should be five, that of hydrogen should be ten, and that of oxygen, one. For runs 4, 7, 10, 11, 12 and 5, the total gram atoms of carbon in the products are 4.95, 4.91, 4.95, 4.93, 4.84 and 4.91, respectively. Those of hydrogen are 9.70, 9.80, 9.80, 9.87, 9.17 and 9.57, respectively, and of oxygen are 1.06, 1.07, 1.05, 1.05, 1.16 and 1.10, respectively. In only one of these—the oxygen balance for run 12—is there an error in the experimental total greater than ten per cent. The other balances for run 12 are also the poorest, indicating that the analysis of its products is not as accurate as that of the other runs.

Equations and Mechanisms Proposed for Reactions Occurring Simultaneously

There is abundant experimental evidence[7-11] that the primary photochemical decomposition of diethyl ketone gives ethyl radicals. It is proposed that a free radical mechanism of the type suggested by Rice and Herzfeld[12] accounts for the products found in our work in a semi-quantiative manner. The radicals formed after absorption of the ultraviolet by the substrate molecules may react with other diethyl ketone molecules or with one another. By using sets of reactions similar to those proposed for the thermal decomposition of diethyl ketone by Rice and Rice[13] one is able to derive the equations which are submitted here to account for our products.

$$C_2H_5COC_2H_5 = C_2H_6 + CH_3CH{=}CO \quad (1)$$

$$C_2H_5COC_2H_5 = C_2H_6 + C_2H_4 + CO \quad (2)$$

$$C_2H_5COC_2H_5 = 2C_2H_4 + H_2 + CO \quad (3)$$

$$C_2H_5COC_2H_5 = C_4H_{10} + CO \quad (4)$$

Equation 1 assumes that the ethyl radical, formed by an initial splitting of a substrate molecule, removes a hydrogen atom from an alpha carbon of another diethyl ketone molecule. If the resulting pentanonyl radical then decomposes into methylketene and another ethyl radical a chain is propagated. On the other hand, if an ethyl radical removes hydrogen from a beta carbon of the substrate the resulting pentanonyl radical could decompose to form ethylene, carbon monoxide, and a new ethyl radical, producing another chain for which the products are shown in equation 2. The products of reaction 3 could be formed if the latter pentanonyl radical decomposed into two ethylenes, carbon monoxide and a hydrogen atom. The chain-breaking step of most importance undoubtedly involves the union of two ethyl radicals and accounts for reaction 4.

In using the above equations to account for the quantities of products obtained, the weight of reaction 1 was taken as unity and the relative weights of reactions 2, 3 and 4 were calculated for each run in a manner analogous to that described previously.[2] The ratios of the moles of each product per mole of diethyl ketone decomposed, calculated on the basis of these reaction weightings, are in close agreement with the ratios observed experimentally and reported in Table I. Of the thirty-six pairs of ratios so obtained, only two differ by more than ten per cent. This is considered strong supporting evidence for the use of these equations to describe the behavior of diethyl ketone when exposed to ultraviolet radiation under our experimental conditions.

Discussion

Our results show that at higher temperatures and under proper conditions of contact time, etc., the photochemical decomposition of diethyl ketone yields methylketene and hydrogen, not reported previously. The formation of hydrogen may be due to absorption of shorter wave length ultraviolet inasmuch as no filters were used.

Because of the formation of methylketene none of the experimental ratios for CO/substrate can actually be as great as 1.00. It is undoubtedly more accurate to get these by subtracting the CH_3CHCO/substrate ratios from 1.00. If this is done, the agreement with the corresponding ratios calculated from the weighted equations is better than two per cent. in all such cases.

A small portion of the hydrocarbons undoubtedly dissolved in the condensed substrate and avoided detection. This is indicated by the somewhat high oxygen but low carbon and hydrogen balances. The fact that our ratios for ethylene calculated from the weighted equations were consistently higher than those observed suggests that it mainly is the deficient hydrocarbon, and it seems reasonable that it should be the most soluble in diethyl ketone.

In most of the runs the quantities of ethane and ethylene differ appreciably from one another, the amount of the latter being greater in four of them. Thus, it is clear that at least not all of these two products is formed by disproportionation of ethyl radicals. Davis[6] came to the same conclusion upon finding larger amounts of ethane than ethylene in lower temperature photodecompositions of diethyl ketone.

In our gas analyses we have assumed that the saturated hydrocarbons were composed of ethane and butane only. Methane was reported as a product only by Berthelot and Gaudechon[4] and by Bamford and Norrish,[8] who found little more than traces. The obvious chain mechanism in which methane would be a product of importance would also yield ketene, the absence of which has already been mentioned.

Conceivably some of the methylketene formed during our runs might have been pyrolyzed but unfortunately there is no report of the products formed in such a reaction. In previous work on the photolysis of acetone[2] an equation for the pyrolysis of the ketene formed was needed to check the results with a group of weighted equations. Reaction 2 may take care of this eventuality. On the other hand, decomposition of methylketene

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(7) T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, 1151 (1935).

(8) C. H. Bamford and R. G. W. Norrish, *ibid.*, 1531 (1938).

(9) M. S. Matheson and J. W. Zabor, *J. Chem. Phys.*, **7**, 536 (1939).

(10) C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A179**, 169 (1941).

(11) L. M. Dorfman and Z. D. Sheldon, *J. Chem. Phys.*, **17**, 511 (1949).

(12) F. O. Rice and K. F. Herzfeld, This Journal, **56**, 284 (1934).

(13) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, p. 111.

may not occur under conditions in which ketene itself decomposes because of stabilization by resonance of the radical formed after loss of a methyl hydrogen from methylketene.

The ratios of products to ketone decomposed of Table I show distinctly different results for runs 4, 7 and 5 compared to those of the other three runs. In the first three, the ethylene and hydrogen yields are definitely higher but butane yields are lower. It is suspected that the use of different A-H6 lights for these sets of three runs is largely responsible for these differences although variations in contact time and temperature must also have a bearing on the matter, too. The weightings of the four competing reactions do not show the temperature dependence that one would expect had other variables such as light intensities and contact times been kept constant.

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Synthetic and Degradative Investigations of the Structure of Folinic Acid-SF

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Mechanisms of synthesis of folinic acid-SF from folic acid and a mechanism of degradation of folinic acid-SF to folic acid have been investigated with regard to the structure of this synthetic member of the folinic acid group. Folinic acid-SF is readily degraded to folic acid under relatively mild conditions similar to those used in the isolation of folic acid from liver.

A group of factors, termed the folinic acid group, has been reported to be more effective than folic acid in preventing the toxicity of x-methylfolic acid for *Lactobacillus casei*[3] and in promoting the growth of *Leuconostoc citrovorum* 8081.[4ab] Several members of the folinic acid group have been prepared recently by formylation of members of the folic acid group, reduction of the formyl derivatives and heating the reduced products.[5] One member of this group of factors, folinic acid-SF which is synthesized by this procedure from folic acid, has been recently described.[6] The barium salt of a factor apparently identical with folinic acid-SF has been obtained from a reaction mixture resulting from reduction of either folic acid or formylfolic acid in formic acid.[7]

Paper chromatography and development of bioautographs of liver digest have indicated that the natural factor, folinic acid, and a slower moving factor not identical with folic acid constitute the major part of the principles of liver which promote the growth of *Lactobacillus casei* in place of folic acid.[8] By paper chromatography of mixtures of varying concentrations of folic acid with the digests of liver, it was shown that the supplemented folic acid could be detected in such small amounts that the original digests could not have contained appreciable amounts of folic acid relative to the concentration of these other factors.[8] Consequently, since folic acid has been isolated in relatively good yields from such liver digests,[9a,b] it appears likely that folinic acid and related factors may have been converted into folic acid during the isolation process.

In the present work, mechanisms of synthesis of folinic acid-SF from folic acid and reconversion of folinic acid-SF to folic acid have been studied in order to elucidate the structure of folinic acid-SF and in order to demonstrate that folinic acid-SF can be converted into folic acid by the relatively mild conditions employed in the isolation procedures whereby folic acid is obtained from liver.[9a,b]

The elementary analysis of folinic acid-SF corresponds closely to $C_{20}H_{23}N_7O_7$.[6] The factor is formed by heating the reduction product of N^{10}-formylfolic acid, and can be reconverted to N^{10}-formylfolic acid as subsequently demonstrated. Thus, folinic acid-SF appears to be a tetrahydrofolic acid combined with a formyl group. This is adequately demonstrated by the direct formation of folinic acid-SF by treatment of tetrahydrofolic acid in acetic acid solution with formic acid at room temperature. Tetrahydrofolic acid is prepared by hydrogenation of folic acid in acetic acid solution in the presence of a platinum catalyst.[10] Because of the ease of reduction of pyrazines in comparison to pyrimidines, it has been generally assumed that the structure of this reduction product is 5,6,7,8-tetrahydrofolic acid,[10] but no direct proof has been presented.

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[1] Eli Lilly and Co. Post-doctoral fellow.

[2] A portion of this investigation is from a thesis presented by Frank Lynn Barger in partial fulfillment of the requirement for Master of Arts degree, University of Texas, Jan., 1951.

[3] T. J. Bond, T. J. Bardos, M. Sibley and W. Shive, THIS JOURNAL, **71**, 3852 (1949).

[4] (a) T. J. Bardos, T. J. Bond, J. Humphreys and W. Shive, *ibid.*, **71**, 3852 (1949); (b) H. E. Sauberlich and C. A. Baumann, *J. Biol. Chem.*, **176**, 165 (1948).

[5] W. Shive, T. J. Bardos, T. J. Bond and L. L. Rogers, THIS JOURNAL, **72**, 2817 (1950).

[6] E. H. Flynn, T. J. Bond, T. J. Bardos and W. Shive, *ibid.*, **73**, 1979 (1951).

[7] J. A. Brockman, B. Roth, H. P. Broquist, M. E. Hultquist, J. M. Smith, M. J. Fahrenbach, D. B. Cosulich, R. P. Parker, E. L. R. Stokstad and T. H. Jukes, *ibid.*, **72**, 4326 (1950).

[8] W. Shive, Paper presented at 117th Meeting, American Chemical Society, Houston, March, 1950.

[9] (a) J. J. Pfiffner, S. B. Binkley, E. S. Bloom and B. L. O'Dell, THIS JOURNAL, **69**, 1476 (1947); (b) E. L. R. Stokstad, B. L. Hutchings and Y. SubbaRow, *ibid.*, **70**, 3 (1948).

[10] B. L. O'Dell, J. M. Vandenbelt, E. S. Bloom and J. J. Pfiffner, *ibid.*, **69**, 250 (1947).