[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Methane Formation in the Photolysis of Acetone at 130°[1]

BY WALLACE DAVIS, JR.[2]

The quantum yield of carbon monoxide formation during the photochemical decomposition of acetone has been found to be unity at temperatures slightly above 100°,[3] thus permitting this reaction to be used as an actinometer. Ethane has been reported as the main hydrocarbon produced under the experimental conditions used by most authors, although small amounts of methane have usually been found. The work of Spence and Wild[4] indicates that under certain experimental conditions the amount of methane formed may be quite large. Hence in using the photochemical decomposition of acetone as an actinometer the fraction of the products uncondensed by liquid nitrogen must be analyzed for both carbon monoxide and methane (as well as for traces of ethane) to ensure accurate results.

This paper presents results of a study of methane formation during the photochemical decomposition of acetone at temperatures ranging from 126 to 138°. While certain statements concerning the reaction mechanism are permissible at the present time, details will be left for later presentation after further information is available.

Experimental

The methods of purifying the acetone and of analyzing the reaction products have already been described.[5] The light source and filter solutions used for isolation of the 3130 Å. line of mercury have also been described.[6] The basic equations used for calculation of light absorbed[7] have been expanded[5] and need not be repeated here.

Some of the experiments (6A–18A in Table I) were made using the AH-6 General Electric Company high pressure arc, the beam diameter being 10 mm. The remaining experiments (19A–21A in Table I) were performed with a UA30A2 Hanovia medium pressure arc with a beam diameter of 15 mm.

The values of I_a (the "absorbed intensity") given in Table I have been obtained by dividing the number of quanta absorbed per second by the acetone by the volume of the light beam. Since the cell was 200 mm. in length the latter has the values 15.7 and 35.4 cm.³, respectively, for the two light beams referred to in the preceding paragraph. The light absorbed per unit path length is not constant and moreover the intensity is undoubtedly not uniform over a given cross section of the beam. Nevertheless the quantity given is the average number of quanta absorbed per cc. per second in the light beam and it is believed that this figure represents most nearly the one which should be used in rate equations for those cases in which any activated molecules and free atoms or radicals do not diffuse appreciably out of the light beam.

TABLE I

THE QUANTUM YIELD OF METHANE FORMATION FROM ACETONE

Wave length = 3130 Å.; quantum yield of carbon monoxide formation = 1 (assumed)

Run	Temp., °C.	Acetone pressure, mm.	$I_a \times 10^{-13}$ quanta/sec./cm.³	Φ_{CH_4}
6A	126	194	1.64	0.40
7A	120	205	0.22	.91
8A	120	233	.23	.97
9A	127	152	.24	.60
10A	122	95	.27	.62
11A	126.5	109	.21	.63
12A	138	148.2	.29	.73
13A	137	111.1	.23	.56
14A	134.5	226.0	.21	.96
15A	137	191	.17	1.04
16A	134.5	145.2	.12	0.93
17A	131.5	199.6	.14	0.99
18A	138	184.4	.14	1.06
19A	133	189.6	.042	1.27
20A	136	137.6	.039	1.14
21A	136	101.3	.027	1.15

Results and Discussion

Table I presents the data on quantum yield of methane formation from the photochemical decomposition of acetone at temperatures ranging from 120 to 138°. Since it has been shown previously that the quantum yield of carbon monoxide formation is very close to unity at these temperatures,[3] the values are based on that assumption and should be taken, in reality, as relative values.

Since the carbon monoxide yield is certainly very close to unity, any acetyl radicals produced in the primary process must decompose almost immediately either thermally or due to energy retained from the primary process. Hence for this case of high temperatures one may write

$$CH_3COCH_3 + h\nu = 2CH_3 + CO \qquad (1)$$

Methane is almost certainly produced by the reaction

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3 \qquad (2)$$

Methyl radicals can disappear by reaction (2) as well as by reactions (3) and (4)

$$CH_3 + CH_3 = C_2H_6 \qquad (3)$$

$$CH_3 + CH_2COCH_3 = CH_3CH_2COCH_3\text{[8]} \qquad (4)$$

The acetonyl radicals can also form biacetonyl

$$2CH_2COCH_3 = (CH_2COCH_3)_2 \qquad (5)$$

If reactions (1) to (5), inclusive, are all that can occur and it is assumed that they are all homogeneous gas phase reactions, some kinetic expressions could be derived providing analyses could be

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[4] R. Spence and W. Wild, *J. Chem. Soc.*, 352 (1937).

[5] W. Davis, Jr. and W. A. Noyes, Jr., *ibid.*, **69**, 2153 (1947).

[6] R. E. Hunt and W. Davis, Jr., THIS JOURNAL, **69**, 1415 (1947).

[7] R. E. Hunt and T. L. Hill, *J. Chem. Phys.*, **15**, 111 (1947).

[8] A. O. Allen, THIS JOURNAL, **63**, 708 (1941).

made for all of the products. If C_2H_6, CH_4, and CO were all known certain conclusions would be possible.

The pressures are high enough in the present experiments to ensure that the majority of the bimolecular reactions will occur homogeneously. Consequently the derived expression for the quantum yield becomes so complex that it cannot be applied to the data without making assumptions. It seems best to defer a detailed theoretical treatment until a later date. It may be stated, however, that if the energy of activation for (3) is low,[9] the energy of activation of (2) must also be low.

Summary

1. The quantum yield of methane formation during the photochemical decomposition of acetone in the temperature range 120 to 138° has been determined.

2. In a general way the yield of methane increases with increase in acetone pressure and with decrease in intensity, but a detailed discussion of theory is postponed until a later date.

3. The energy of activation of the reaction $CH_3 + CH_3COCH_3 = CH_4 + CH_3COCH_2$ must be low.

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[9] *Cf.* E. W. R. Steacie, "Atomic and Free Radical Reactions," The Reinhold Publishing Corporation, New York, N. Y., 1946, p. 520.

[10] Original manuscript received September 18, 1947.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photochemical Decomposition of Diethyl Ketone at 3130 Å.[1]

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Previous work[3] has indicated some ethylene and ethane to be produced along with carbon monoxide and butane during the photochemical decomposition of diethyl ketone at wave lengths below 2000 Å. These same products in different proportions have been reported at longer wave lengths.[3,4] Bamford and Norrish[4] suggested that the Type III decomposition directly into ethylene and propionaldehyde proposed by Norrish and Appleyard[5] would account for the ethylene formed, although these authors did not identify propionaldehyde positively. Disproportionation of ethyl radicals to ethylene and ethane has also been suggested.[3]

This paper presents determinations of the quantum yield of various products during the photochemical decomposition of diethyl ketone.

Experimental

The diethyl ketone used in this work was purified by Dr. A. B. F. Duncan for spectroscopic experiments. C. P. diethyl ketone, b. p. range 5°, was washed with potassium carbonate and sodium bisulfite to remove acids and peroxides. After drying over anhydrous calcium chloride the ketone was fractionally distilled in a column, a portion with a boiling range of 0.1° being kept. This product was further fractionated several times at low pressure.

The determination of carbon monoxide was accomplished by removing that portion of the products not condensed by liquid nitrogen. For short runs combustion of this fraction over CuO at 200–240° indicated pure carbon monoxide within experimental error. For longer runs leading to a larger amount of product, duplicate oxygen combustion analyses indicated that as much as 5% of this fraction was a C_2 hydrocarbon.

The C_2 hydrocarbons (C_2H_4 and C_2H_6) were separated from other products, after removal of carbon monoxide by being removed at −165° using a Ward apparatus[6] with a Toepler pump. In some experiments only the quantity of C_2 hydrocarbons was determined; in others this fraction was burned with oxygen on a platinum filament at about 600°. The combustions were all carried out with a trap immersed in dry ice between the filament and any source of mercury vapor to minimize oxidation of the latter.

After removal of the C_2 hydrocarbons, another fraction was removed at about −120°. This fraction was shown to be butane either by vapor pressure measurements or by combustion.

Other experimental details have already been published.[7-9]

Results and Discussion

The quantum yields of carbon monoxide and of C_2 hydrocarbons from diethyl ketone at several temperatures and intensities are presented in Table I. It will be noted that the variation in pressure is small. Experiments 1D–12D were made with a A-H6 General Electric Company high pressure mercury arc, while runs 13D–16D were made with the Hanovia UA30 A2 Uviarc.

It is seen that $\Phi_{CO} = 1.0$ within a 13% experimental error in runs 1D–7D and 11D. For the uviarc runs $\Phi_{CO} = 1.03 \pm 0.05$, assuming a calibration error of not to exceed 1.6%. Therefore the quantum yield of the primary process

$$C_2H_5COC_2H_5 + h\nu = 2C_2H_5 + CO \qquad (1)$$

must be close to unity unless some secondary reaction gives rise to carbon monoxide formation. The absence of any real increase of carbon mon-

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[1] This work was supported by Contract N6-onr-241, Task I with the Office of Naval Research, United States Navy.

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