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]

BY WALLACE DAVIS, JR.[2]

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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(2) Present address: Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

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oxide yield with temperature indicates that probably the latter is not the case.

Values of Φ_{CO} for experiments 8D–10D should not be considered as valid since recalibration of the photo-cell galvanometer system showed a changed sensitivity.

TABLE I

QUANTUM YIELDS OF CO AND OF C_2 HYDROCARBONS DURING PHOTOCHEMICAL DECOMPOSITION OF DIETHYL KETONE

Run	Temp., °C.	Ketone pressure, mm.	$I_a \times 10^{-13}$ quanta/sec./ccm.	Φ_{CO}	Φ_{C_2}	Analysis of C_2 fraction
1D	28	41	0.22	1.03 ± 0.14		
2D	28	40	.19	0.99 ± .13		
3D	27	37	.17	1.05 ± .14		
4D	27	38	.16	0.93 ± .13		
5D	27	38	.17	0.93 ± .13		
6D	25	34.5	.14	0.99 ± .13		
7D	26	22.0	.084	1.05 ± .14		
8D	86	38.2	.20	0.74 ± .10		
9D	86.4	38.0	.21	0.83 ± .10	0.44	V. P.
10D	86.2	37.9	.24	0.83 ± .10	0.41	V. P.
11D	26	38.0	.15	0.97 ± .13	0.28	V. P.
12D	26	38	(.11)	(1.00)	0.68	
13D	136	36.8	.017	1.05 ± .05	1.48	$C_{2.04}H_{5.92}$
14D	137.5	41.0	.019	1.02 ± .05	1.38	$C_{2.09}H_{6.76}$
15D	136	38	.017	(1.035)[a]	1.47	$C_{2.00}H_{6.02}$ $C_{2.01}H_{5.92}$
16D	26.8	39.6	.014	1.03 ± .05	0.86	$C_{2.02}H_{5.40}$

[a] Φ_{CO} for Run 15D taken as the average of Φ_{CO} from Runs 13D and 14D.

In view of the fact that ethane exceeds ethylene considerably under the conditions of these experiments, these two gases cannot be formed mainly by a disproportionation reaction and the ethane can arise from a reaction of the type

$$C_2H_5 + C_2H_5COC_2H_5 = C_2H_6 + C_2H_4COC_2H_5 \quad (2)$$

This reaction would be analogous to that of methane formation in acetone.[10] One of the main competing reactions for ethyl radicals will certainly be that of butane formation

$$C_2H_5 + C_2H_5 = C_4H_{10}$$

Some ethyl radicals may disappear in forming the compound $C_2H_5COC_4H_9$, but a complete analysis of all products would be necessary before a detailed mechanism could be developed.

From equations (2) and (3) the quantum yields of ethane and of butane formation are found to be given by the following expressions

$$\Phi_{C_2H_6} = k_2(C_2H_5)(C_2H_5COC_2H_5)/I_a \quad (4)$$

$$\Phi_{C_4H_{10}} = k_3(C_2H_5)^2/I_a \quad (5)$$

where the subscripts of the k's correspond to the equation numbers. Hence one may write

$$\Phi^2_{C_2H_6}/\Phi_{C_4H_{10}} = k_2^2(C_2H_5COC_2H_5)^2/k_3I_a \quad (6)$$

If it is assumed that butane is formed by all ethyl radicals which do not form ethane, one can apply equation (6) to the data in Table I. Unfortunately the data are not extensive enough to warrant many conclusions, particularly since the fates of all ethyl radicals are undoubtedly not given by equations (2) and (3) alone. However, equation (6) is at least approximately obeyed.

If one writes $k_2 = a_2\ exp\ (-E_2/RT)$ and $k_3 = a_3\ exp\ (-E_3/RT)$ the data at about 136° and at about 26° may be used to calculate $2E_2 - E_3 =$ 5000 cal. with an uncertainty of about 1500 cal. While an exact value of E_3 is not known, the figure is considered to be small.[11] Thus E_2 may be as little as 2500 cal. and probably is less than 5000 cal.

It is evident that the amount of ethane depends markedly on light intensity, as well as on temperature, and that at high intensities butane should be formed relatively more than at low intensities. If ethylene is formed solely by a disproportionation reaction its yield also would be expected to increase at high intensities. More work is necessary before details of the mechanism can be stated, but complete analysis for all possible products will be difficult.

Summary

1. The quantum yields of CO and of C_2 hydrocarbons during the photochemical decomposition of diethyl ketone have been determined at several temperatures ranging from 26 to 138°.

2. The C_2 hydrocarbons produced during the reaction consist almost solely of C_2H_6.

3. The energy of activation of the reaction $C_2H_5 + C_2H_5COC_2H_5 = C_2H_6 + C_2H_4COC_2H_5$ may be as low as 2500 cal. and is almost certainly below 5000 cal.

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

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

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