THE LIQUID PHASE PHOTOLYSIS OF DIETHYL KETONE AND METHYL ETHYL KETONE[1,2]

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ABSTRACT

The liquid phase photolysis of diethyl ketone has been studied in the temperature range from −35° to 95° C. The CO quantum yield at 95° C. was found to be close to unity. At 28° C. decrease in intensity and addition of heptane led to a substantial increase of the CO and the ethane yields.

The methyl ethyl ketone liquid phase photolysis at temperatures between 5° and 75° C. led to the same observations. Arrhenius plots of $R_E/R_B^{1/2}[K]$ gave for both compounds a value of 5 kcal./ mole.

Gas phase studies in the temperature range of 0° to 60° C. confirmed the low CO quantum yield reported previously and showed evidence for disproportionation and recombination reactions between ethyl and propionyl radicals.

EXPERIMENTAL

Eastman Kodak Company methyl ethyl ketone and diethyl ketone (white label) were distilled through 10 theoretical plates with rejection of large head and tail fractions. Air was removed by bulb-to-bulb distillation in the vacuum line.

Gas phase experiments were performed with a Hanovia (16A-13) SH type medium pressure lamp. The cylindrical quartz cell (5 cm. diameter, 10 cm. long) was completely filled with a nearly parallel light beam.

The liquids were irradiated in a quartz cell of 5 cm. diameter and 0.05 cm. depth. The cell was provided with two outlets, one of which was sealed after filling, while the other was closed by a break seal which made it possible to attach the cell to the analysis system after each experiment. Between runs the cell was washed out with diethyl ketone and dried at about 150° C. The irradiation was carried out in a thermostat consisting of a brass cylinder with evacuated double walls and double quartz windows. For experiments above room temperature an electric immersion heater was brought into distilled water, while for the low temperature experiments the thermostat was filled with methanol cooled by dry ice. In this way it was possible to maintain the temperature constant within half a degree.

At 3130 Å about 98% of the incident radiation is absorbed by the undiluted ketone. In order to compensate for this sharp absorption decrease throughout the cell, two Hanovia lamps were placed opposite each other with the cell fixed in the center of the nearly parallel light beam.

Except for experiments 1 and 2 Corning filters (9-53) were used to cut off wavelengths below 2800 Å. The incident intensity was varied by means of copper gratings.

After irradiation of the liquid the cell was attached to the analysis system, consisting of three traps and one modified Ward still. The CO–CH_4 fraction was removed at solid nitrogen temperature and was analyzed by combustion over hot CuO. The C_2H_6–C_2H_4 fraction was taken off at −160° C. C_2H_4 was determined by hydrogenation over a Ni

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catalyst (16). The C_4H_{10} fraction was separated at about −120° C. In view of the high C_2H_6/C_4H_{10} ratio, which in some experiments was higher than 100, great care was taken that no ethane was left over from the previous distillation.

RESULTS

Gas Phase

Table I represents the data of experiments performed at approximately constant diethyl ketone concentration. Runs 1 and 2 were done with an unfiltered light beam and at constant intensity. The other runs were performed with a Corning filter 9-53 and constant incident light intensity.

TABLE I

GAS PHASE PHOTOLYSIS OF DIETHYL KETONE

Run	Temp., ° C.	Time, min.	Pressure, molec./cc.10^{-17}	R_{CO}	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{C_4H_{10}}$	C_2H_4/C_4H_{10}	C_2H_6/C_4H_{10}	M.B.
				molec./cc./sec.10^{-11}						
				Unfiltered light						
1	0	10	2.45	51.0	11.2	11.4	72.3	0.155	0.157	1.64
2	57	10	2.45	220.0	23.4	26.5	194.0	0.120	0.136	1.00
				Corning filter 9–53						
3	0	8	2.42	13.05	2.97	3.15	17.9	0.166	0.176	1.60
4	13	12	2.48	27.0	4.27	4.60	28.5	0.149	0.162	1.22
5	25	12	2.46	43.8	5.29	5.95	41.2	0.128	0.144	1.07
6	60	12	2.45	54.8	5.50	6.98	46.4	0.119	0.150	0.96
7*	25	12	2.43	2.12	<0.1	<0.1	0.1			

**Iodine added.*

It can be seen that in both series of experiments the rates of formation of all the products decrease with temperature. In the last column M.B. stands for the material balance $[\frac{1}{2}(C_2H_4+C_2H_6)+C_4H_{10}]/CO$. This ratio increases appreciably with decrease in temperature.

Liquid Phase

All experiments given in Tables II and IV and runs 36, 39, 40, 44, 45 of Table V were conducted at the same incident intensity.

Table II shows the results of experiments done in a temperature range from −35°

TABLE II

LIQUID PHASE PHOTOLYSIS OF DIETHYL KETONE

Variation of rate with temperature

Run	Temp., ° C.	Time, min.	R_{CO}	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{C_4H_{10}}$	$R_E/R_B^{\frac{1}{2}}.10^{-8}$
			molec./cc./sec.10^{-15}				
8	−35	8	0.20	1.05	4.30	0.54	1.86
9	−14	8	0.58	1.40	11.6	0.75	4.25
10	5	6	1.26	1.62	26.0	1.02	8.20
11	28	4	4.10	3.40	70.0	2.21	14.9
12	51	4	22.0	2.73	111	1.80	26.0
13	72	2	52.0	2.07	145	1.26	40.8
14	84	2	63.0	1.91	146	0.90	48.5
15	86	2	64.2	1.58	149	0.82	52.0
16	94	2	70.0	1.25	152	0.55	65.0

Acetone at 28° C.: R_{CO}, *0.15;* R_{CH_4}, *3.20;* $R_{C_2H_6}$, *0.078.*

to 94° C. It can be seen that the rates of formation of carbon monoxide and ethane both increase with temperature. At higher temperatures they approach constant values.

A rough measure of the quantum yield was obtained by comparing the rate of formation of carbon monoxide from the gas phase photolysis of diethyl ketone at 95° C. with the rate of formation from the liquid phase photolysis at the same temperature. The measurements were done with Corning filter 9-53 and cells of respectively 5 and 0.05 cm. depth. On the assumption that the quantum yield for CO in the vapor phase was unity, it was found that approximately 8×10^{16} quanta per second were absorbed by the liquid. This led to $\phi(\mathrm{CO}) \sim 0.87$ at 95° C.

The rates of formation of ethylene and butane show a pronounced increase with temperature up to 28° C. followed by a gradual decrease.

In the same table are included the results of one acetone liquid phase experiment, performed at 28° C. and under the same experimental conditions as the previous runs. Comparison with the diethyl ketone results leads to a CO quantum yield roughly equal to 2×10^{-3}. This figure is somewhat higher than previous estimates (11, 15).

In Table III the results of experiments carried out at 5°, 28°, and 84° C. and at various intensities are shown. I_{rel} represents the incident intensity relative to the highest intensity run. Values of $R_{\mathrm{C_2H_6}}/I_{\mathrm{rel}}$ given in the last column show an increase with decrease in intensity. It can be seen from the data that this trend is even more pronounced for $R_{\mathrm{CO}}/I_{\mathrm{rel}}$. These results indicate clearly that the CO and ethane yields increase with diminishing intensity. However, this increase is much smaller at 84° C. where the quantum yield is already close to unity.

TABLE III

Liquid phase photolysis of diethyl ketone
Variation of rate with intensity

Run	I_{rel}	Time, min.	R_{CO}	$R_{\mathrm{C_2H_4}}$	$R_{\mathrm{C_2H_6}}$	$R_{\mathrm{C_4H_{10}}}$	$R_{\mathrm{E}}/R_{\mathrm{B}}^{\frac{1}{2}}.10^{-8}$	$R_{\mathrm{E}}/I_{\mathrm{rel}}$
			molec./cc./sec.10^{-15}					
				At 28° C.				
17	1	6	3.87	3.15	70.1	2.25	14.8	70.1
18	0.410	10	2.11	1.15	35.5	0.59	14.6	86.5
19	0.354	15	1.66	0.80	28.1	0.435	13.5	79.8
20	0.354	15	1.72	0.79	28.0	0.42	13.6	79.5
21	0.125	35	0.82	0.21	11.7	0.090	12.3	93.5
22	0.044	100	0.49	0.045	4.25	0.014	11.2	96.5
23	0.0055	800	0.19	0.003	0.75	~0.0009	~ 8.00	136.0
				At 5° C.				
24	1	10	1.24	1.59	26.1	1.06	8.00	26.1
25	0.354	30	0.39	0.54	11.9	0.235	7.80	33.7
26	0.125	90	0.20	0.225	6.52	0.09	6.80	52.2
				At 84° C.				
46	1	4	62.2	1.85	147.0	—	—	147
47	0.0067	504	0.0512	0.18×10^{-3}	0.103	—	—	154

In Table IV are given results of experiments made at 28° C. with *n*-heptane and *n*-octane as solvents. In the second column the percentage of light absorbed by the liquid has been given. Absorption measurements were made with a Cary absorption spectrophotometer. From the data it follows that the ratios $R_{\mathrm{C_2H_6}}/I_{\mathrm{abs}}$ and $R_{\mathrm{CO}}/I_{\mathrm{abs}}$ increase with dilution.

TABLE IV

LIQUID PHASE PHOTOLYSIS OF DIETHYL KETONE HYDROCARBON MIXTURES AT 28° C.

Run	I_{abs}	Time, min.	Heptane	DK	R_{CO}	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{C_4H_{10}}$	$R_E/R_B^{\frac{1}{2}}.10^{-8}$
			molec./cc. 10^{-21}		molec./cc./sec. 10^{-15}				
27	95%	6	1.36	3.85	5.75	4.95	67.5	3.37	11.6
28		6	2.03	2.84	5.20	5.10	53.0	3.72	8.70
29		6	3.05	1.42	5.27	3.15	32.2	2.40	6.60
30		6	3.25	1.14	4.85	2.80	25.3	2.14	5.50
31	22%	6	3.55	0.71	4.36	2.70	19.0	2.00	4.25
32		6	3.70	0.515	3.60	2.22	14.8	1.70	3.60
33	8.5%	6	3.88	0.27	2.82	1.96	10.8	1.04	3.35
34		6	2.67*	1.14	4.40	4.00	32.5	2.76	6.18
35		6	3.25*	0.515	3.43	3.82	18.9	2.75	3.60

*Octane.

In Table V are given the results of the liquid phase photochemical decomposition of methyl ethyl ketone. The experiments were done in the temperature range from 5° to 70° C. and at varying intensities. The rates of formation of carbon monoxide, methane, ethylene, ethane, and butane have been measured. Although propane was present, it could not be determined with any accuracy because it was present in an amount less than 1% of the ethane fraction.

TABLE V

LIQUID PHASE PHOTOLYSIS OF METHYL ETHYL KETONE

Variation of rate with temperature and intensity

Run	I_{rel}	Time, min.	Temp., ° C.	R_{CO}	R_{CH_4}	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{C_4H_{10}}$	$R_E/R_B^{\frac{1}{2}}.10^{-8}$
				molec./cc./sec.10^{-15}					
36	1	10	6	0.54	0.88	1.70	17.2	1.12	5.15
37	0.354	30	6	0.18	0.215	0.310	7.70	0.225	5.15
38	0.125	80	6	0.028	0.036	0.076	3.20	0.039	5.10
39	1	10	23	1.66	2.05	1.93	34.0	1.46	9.22
40	1	10	26	1.76	2.42	2.17	38.2	1.65	9.40
41	0.354	30	26	0.50	0.85	0.62	17.2	0.35	9.20
42	0.125	80	26	0.10	0.15	0.115	6.30	0.070	7.50
43	0.125	80	26	0.089	0.122	0.080	5.95	0.050	8.40
44	1	10	45	3.20	4.05	1.56	49.5	1.14	14.6
45	1	8	70	7.00	7.60	1.01	59.2	0.56	24.8

Comparison of the runs at constant intensity at varying temperatures shows that the rates of formation of carbon monoxide, methane, and ethane increase with temperature. However, the increase of the rate of formation of ethane is less pronounced at higher temperatures, where it reaches a value close to one half the value found in the liquid phase photolysis of diethyl ketone under the same experimental conditions.

The ratios C_2H_4/C_4H_{10} do not differ very much from those found in the diethyl ketone photolysis. The rates of formation of ethane and butane both go through a maximum around 28° C. Decrease of intensity leads to a substantial decrease in the CO, C_2H_4, and C_4H_{10} yields, while the C_2H_6 yields increase slightly.

DISCUSSION

Diethyl Ketone

(*a*) *Gas Phase*

The gas phase photolysis of diethyl ketone has been extensively investigated in the past (8, 9, 10, 13).

In the course of this work a few runs were performed at low temperatures in order to obtain additional information about the primary process and reactions involving the propionyl radical.

The results given in Table I indicate that at relatively high intensities, the quantum yield of the CO production drops appreciably at temperatures below 60° C. A value of 0.23 can be estimated for the CO quantum yield at 0° C., if at 60° C. the quantum yield is assumed to be 1. These results are in agreement with earlier work (13), where at 25° C. and comparable intensities a value of 0.6 was found for the quantum yield of the CO formation.

The low CO quantum yield suggests as main primary process:

$$C_2H_5COC_2H_5 + h\nu = C_2H_5CO + C_2H_5, \tag{I}$$

in which the propionyl radical may eventually decompose by excess energy carried over from the primary process or by thermal reaction:

$$C_2H_5CO = C_2H_5 + CO. \tag{1}$$

Assuming that no collisional deactivation of the excited diethyl ketone molecules occurs, run 7 as well as recent work on the photooxidation of diethyl ketone (12) suggests that at most 5% of the propionyl radicals decompose as a result of the primary process.

Besides decomposing, the propionyl radical may react with other species. Several combination and disproportionation reactions involving the propionyl radical may occur:

$$\begin{aligned}
C_2H_5CO + C_2H_5 &= C_2H_5COC_2H_5, &&[2]\\
&= C_2H_6 + CH_3CH{=}CO, &&[3]\\
&= C_2H_4 + C_2H_5CHO; &&[4]\\
C_2H_5CO + C_2H_5CO &= C_2H_5COCOC_2H_5, &&[5]\\
&= C_2H_5CHO + CH_3CH{=}CO; &&[6]\\
C_2H_5CO + C_2H_5COC_2H_4 &= C_2H_5COC_2H_4COC_2H_5, &&[7]\\
&= C_2H_5CHO + C_2H_5COCH{=}CH_2, &&[8]\\
&= CH_3CH{=}CO + C_2H_5COC_2H_5. &&[9]
\end{aligned}$$

The increase of the C_2H_4/C_4H_{10} and C_2H_6/C_4H_{10} ratios with diminishing temperatures may be considered as good evidence for the occurrence of the reactions [3] and [4], while the fact that $(C_4H_{10}+\frac{1}{2}C_2H_4+\frac{1}{2}C_2H_6)/CO$ becomes larger than unity at low temperatures substantiates reaction [5] and perhaps also reaction [6]. Although there is no direct evidence for reactions [7], [8], and [9], it is quite likely, in view of their exothermicity, that these reactions occur.

Ethyl radicals disappear mainly by reactions [2], [3], [4], or by one of the following reactions:

$$\begin{aligned}
C_2H_5 + C_2H_5COC_2H_5 &= C_2H_6 + C_2H_5COC_2H_4; &&[10]\\
C_2H_5 + C_2H_5 &= C_4H_{10}, &&[11]\\
&= C_2H_4 + C_2H_6; &&[12]
\end{aligned}$$

$$C_2H_5 + C_2H_5COC_2H_4 = C_2H_5COC_4H_9, \quad [13]$$

$$= C_2H_4 + C_2H_5COC_2H_5, \quad [14]$$

$$= C_2H_6 + C_2H_5COCH{=}CH_2. \quad [15]$$

Gas phase studies led to a value of 0.12±0.01 for k_{12}/k_{11} (2, 8, 13), while $E_{10}-\frac{1}{2}E_{11}$ was found to vary from 7.5 to 9 kcal./mole depending on the temperature range (3, 8, 13).

At the temperatures used in this work the pentanonyl radical does not decompose to any appreciable extent and will eventually disappear by a radical reaction such as [7], [8], [9], [13], [14], [15] or by one of the following reactions:

$$C_2H_5COC_2H_4 + C_2H_5COC_2H_4 = C_2H_5COC_2H_5 + C_2H_5COCH{=}CH_2, \quad [16]$$

$$= (C_2H_5COC_2H_4)_2. \quad [17]$$

(*b*) *Liquid Phase*

Primary process

From the results given in Table II it follows that the carbon monoxide and ethane yields approach constant values at high temperatures, which correspond to a primary quantum yield close to unity.

The fact that at room temperature the carbon monoxide yield increases appreciably with diminishing intensity and increasing dilution may be considered as evidence for a competition between reaction [1] and the radical reactions involving the propionyl radical. It is likely that infinite dilution at these temperatures may lead to a primary quantum yield equal to one.

The quantum yield determination at 95° C. is not accurate enough to decide whether any primary or secondary diffusive recombination occurs. If any recombination takes place between original partners, disproportionation ought to occur as well. From the results given in Table I, a rough estimate of 0.02 can be obtained for the ratio of the rate of the disproportionation reaction [4] to the rate of the recombination reaction [2].† From this estimate and from the amount of ethylene formed in the lowest intensity runs (Table III), it follows that under these conditions less than 20% of the ethyl radicals recombine with propionyl radicals. In view of the fact that ethylene may also be formed in several other reactions, recombination between original partners may be considered negligible.

Recent work (15) on the liquid phase photolysis of mixtures of light and heavy acetone showed that deactivation is a more likely explanation for the low quantum yield than primary or secondary diffusive recombination. In earlier work (7) diacetone alcohol was determined in the liquid phase photolysis of undiluted acetone. It was also found that addition of hydrocarbons led to a decrease of the quantum yield of the volatile products (15) and the formation of an alcohol (6, 11). These results indicate that, besides dissociation and normal deactivation by collision, the following processes involving excited acetone molecules have to be considered:

$$CH_3COCH_3^* + CH_3COCH_3 = (CH_3)_2COHCH_2COCH_3, \quad a$$

$$CH_3COCH_3^* + RH = (CH_3)_2COHR. \quad b$$

When RH is a hydrocarbon like hexane or heptane, process *b* is faster than *a*. It may be mentioned that processes of type *b* have also been found to occur in the liquid phase photolysis of esters (1).

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†*In order to obtain this value the assumption was made that the* CO *quantum yield was one at 60° C., and a value of 0.12 was used for the ratio of the rate of reaction [12] to the rate of reaction [11].*

The fact that at 28° C. addition of normal heptane to diethyl ketone increases the quantum yield of the volatile products to a value close to unity indicates that at these temperatures the process analogous to process *b* does not occur. A shorter lifetime of the excited diethyl ketone molecules may explain the difference in quantum yield between the liquid phase photolysis of acetone and diethyl ketone.

In analogy with the acetone photolysis, where a decrease of the quantum yield with temperature was found in both gas (14) and liquid (15) phase, it is quite possible that the low quantum yield at temperatures below 28° C. (Table II) is partly due to deactivating processes.

It has been suggested previously (5) that, in view of the relatively high ethylene yield, the following primary process occurs:

$$C_2H_5COC_2H_5 + h\nu = C_2H_5CHO + C_2H_4.$$

The fact, however, that the ethylene yield drops appreciably with intensity means that this compound is formed mainly in a radical–radical reaction. The iodine experiments (run 7) and the lowest intensity run of Table III indicate that the quantum yield of this process has to be lower than 5×10^{-3}.

Secondary reactions

Although their relative importance may change, the same secondary reactions can be expected to occur in both gas and liquid phase photolysis. In order to explain the liquid phase results, it has to be visualized that, owing to the higher ketone concentration, alkyl radicals will react mostly with diethyl ketone itself. Consequently, reactions of the ethyl radical with other radicals will be of less importance. Indeed, it can be seen from the data of Tables II and III that ethane is the main product. The fact that at higher temperatures the amount of CO formed is about half the amount of ethane proves that at these temperatures practically all of the propionyl radicals are decomposed.

As mentioned before, the decrease of the rate of formation of ethylene and butane with intensity points to the formation of these products in a radical–radical reaction. The data of Table II show that both compounds go through maxima around 28° C. This can be explained by a competition between an increase of the ethyl radical concentration caused by a substantial increase of the quantum yield up to 28° C. and the increase in rate of the hydrogen abstraction reaction [4] which tends to decrease the stationary radical concentration.

The C_2H_4/C_4H_{10} ratio is under all conditions considerably higher than the value of 0.12 generally accepted for k_{11}/k_{12}. Because no third body is required for processes [11] and [12] (8), the ratio for the two rate constants should be the same in both gas and liquid phase. It is probable that the excess ethylene is formed in a radical–radical reaction such as [4] and [14]. Reaction [4] may be expected to be of importance at low temperatures, while reaction [14] will occur mainly in the high temperature region.

If ethane and butane are produced only by reactions [10] and [11], the following relationship exists:

$$R_E/R_B^{1/2}[K] = k_{10}/k_{11}^{1/2} = A_{10}/A_{11}^{1/2}e^{-(E_{10}-\frac{1}{2}E_{11})/RT};$$

[K], R_E, and R_B represent respectively the concentration of diethyl ketone and the rates of formation of ethane and butane.

If this relation holds, $R_E/R_B^{1/2}$ should be independent of the absorbed intensity.

The results given in Table III indicate that this ratio varies only slightly over a considerable intensity range. From this it may be concluded that ethane and butane are formed in normal kinetic processes.

In Fig. 1, log $R_E/R_B^{1/2}[K]$ calculated from the data of Table II has been plotted as a function of $1/T$. It can be seen that a good straight line is obtained which corresponds to an activation energy of 5 kcal./mole. This value may be ascribed to the activation difference $E_{10}-\frac{1}{2}E_{11}$. Gas phase studies in a temperature range from 25° to 150° C. lead to a value of 7.5 kcal./mole. The lower value obtained in the liquid phase photolysis may at least be partly due to the fact that, in a liquid, recombination of radicals may require an activation energy. In order to account for the difference between the gas and liquid phase photolysis results, a value of 5 kcal./mole has to be ascribed to the activation energy of the diffusion process.

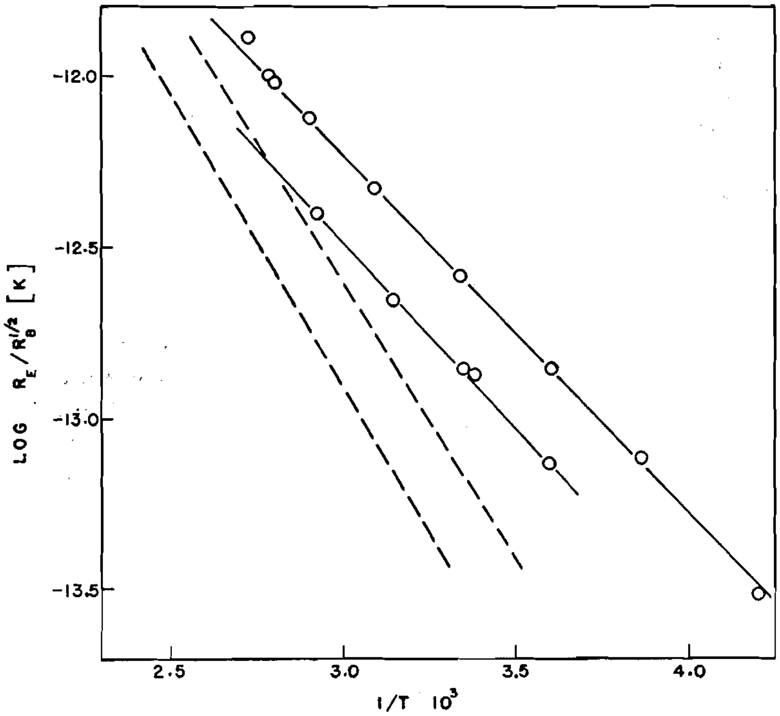

FIG. 1. Plot of log $R_E/R_B^{\frac{1}{2}}[K]$ against $1/T$ for the photolysis of diethyl ketone and methyl ethyl ketone:
——— liquid phase photolysis: upper curve—diethyl ketone,
lower curve—methyl ethyl ketone;
— — — gas phase photolysis: upper curve—diethyl ketone,
lower curve—methyl ethyl ketone.

In the above treatment, the ethane formed by reactions [3], [12], and [15] has not been taken into account. The low amount of butane formed shows reaction [12] to be unimportant. Assuming that reactions [14] and [15] on one side and [3] and [4] on the other side have comparable rates, it can be deduced from the low ethylene yield that the amount of ethane formed by reactions [3] and [15] is small compared to the amount formed by the abstraction reaction [10].

Addition of n-heptane and n-octane to diethyl ketone leads to a substantial decrease of the ratio $R_E/R_B^{1/2}$. Increasing dilution apparently leads to a limiting constant value for this ratio which is about 22% of the one found for the undiluted diethyl ketone. These results point to an appreciably lower rate for the abstraction of a hydrogen atom from heptane and octane than from diethyl ketone itself. In agreement with this, a few gas phase photolysis experiments of equal diethyl ketone heptane mixtures at 95° C. (1) indicated that at least 80% of the ethyl radicals abstract a hydrogen atom from the diethyl ketone molecules.

Methyl Ethyl Ketone

Primary Process

Gas phase studies (17) have shown that two primary processes have to be considered:

$$CH_3COC_2H_5 + h\nu = CH_3CO + C_2H_5, \qquad \text{II}$$

$$= CH_3 + C_2H_5CO. \qquad \text{III}$$

At 3130 Å process II was found to occur about 10 times more often than process III.

The data given in Table V show that at higher temperatures, the methane and CO yields are approximately equal and appreciably lower than the ethane yields. From this it follows that in the liquid phase photolysis too, process II is the most important. The fact that at higher temperatures the ethane yield is approaching a constant value, which is approximately half that obtained in the liquid phase photolysis of diethyl ketone, indicates that in this temperature range the primary quantum yield is approximately the same for both compounds.

As in the liquid phase photolysis of diethyl ketone, the ethane yield increases slightly with decrease in intensity. From this it may be concluded that the low ethane yield at the lower temperatures is at least partly due to the disappearance of the ethyl radicals by normal radical recombination processes. However at low temperatures, diminishing intensities led to a decrease in the carbon monoxide and methane yields; this is contradictory to what was found in the liquid phase photolysis of diethyl ketone. It may be pointed out that liquid phase photolysis studies of several compounds where acetyl radicals are formed in the primary process led to the same observation (1). At high temperatures where normal thermal decomposition of acetyl radicals becomes important, an increase of the CO yield with decrease in intensity was found for all the compounds studied. Although no conclusive interpretation can be given, it is likely that at low temperatures CO and methane result from a radical–radical process.

The decrease in ethylene yield with diminishing intensity indicates that, as in the diethyl ketone photolysis, ethylene is produced mainly in a radical–radical process, instead of being formed in a primary process.

Secondary Reactions

Essentially the same reactions may be expected to occur as those described in an earlier paper on the gas phase photochemical decomposition of methyl ethyl ketone (4).

Only the following two reactions will be considered:

$$C_2H_5 + CH_3COC_2H_5 = C_2H_6 + CH_6COC_2H_4, \qquad [18]$$

$$C_2H_5 + C_2H_5 = C_4H_{10}. \qquad [11]$$

Then

$$R_E/R_B^{1/2}[K] = k_{18}/k_{11}^{1/2} = A_{18}/A_{11}^{1/2}e^{-(E_{18}-\frac{1}{2}E_{11})/RT}.$$

The data of Table V indicate that the ratio $R_E/R_B^{1/2}$ is practically independent of intensity, which substantiates the above relationship.

In Fig. 1, log $R_E/R_B^{1/2}$[K] has been plotted against $1/T$. It can be seen that this Arrhenius curve corresponds to an activation energy which is about the same as the one found for diethyl ketone. The two plots are separated by approximately 0.3 logarithmic units. The dashed lines which represent the gas phase results for the hydrogen abstraction reaction from diethyl ketone (3) and methyl ethyl ketone (4) show clearly that these plots are also approximately parallel and show the same separation as the liquid phase Arrhenius curves. These results can be explained by assuming that mainly secondary hydrogen atoms are abstracted from the ketones.

As mentioned earlier, the lower values found for the activation energy differences $E_{12}-\frac{1}{2}E_{11}$ and $E_{18}-\frac{1}{2}E_{11}$ in the liquid phase experiments may be due to the fact that diffusion of radicals in a liquid requires an activation energy. However, solvation of the reactants and activated complexes may also influence the rate of the abstraction and recombination reactions.

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