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

The Effect of Solvents on the Liquid Phase Photolysis of Alkyl Esters[1]

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The liquid phase photochemical decomposition of several alkyl esters has been studied in the presence of neopentane, *n*-heptane, methyl alcohol, ethyl alcohol and ethyl ether. An investigation of the effects of intensity, temperature and concentration indicated that several of the primary processes were strongly suppressed while others remained unaffected. A reaction between the electronically excited ester molecule and the solvent molecule is suggested to occur.

Earlier investigations[2-4] on the liquid phase photolysis of acetone indicated that addition of *n*-hexane and *n*-heptane led to the formation of alcohols and a decrease of the quantum yields of the volatile products. It was thought[5] that these results could be explained by a reaction between electronically excited acetone and the solvent.

This work was undertaken in connection with a recent study[6] of the gas and liquid phase photolysis of alkyl esters. In view of the existence of several primary processes occurring from different electronic levels, these compounds seemed favorable for a study of reactions between electronically excited molecules and solvent molecules.

Experimental

The liquids were irradiated in a quartz cell of 5 cm. diameter and 0.1 cm. in depth. The cell was provided with two outlets, one of which was sealed after filling while the other was closed by a break seal.

The experiments were performed with a Hanovia (16A-13) SH type medium pressure mercury arc, no filters for monochromatic illumination were used. The light intensity was varied by gratings. Irradiation was carried out in a quartz dewar. For runs above room temperature an electric immersion heater was brought into distilled water, while for the low temperature experiments the thermostat was filled with ethyl alcohol cooled by a liquid nitrogen or Dry Ice cold finger.

After irradiation the cell was attached to the analysis system, consisting of two traps, a modified Ward still and a toepler pump. The H_2, CO, CH_4 fraction was removed at liquid nitrogen temperature and was analyzed by combustion over hot CuO. The C_2 fraction was taken at $-160°$. C_2H_4 was determined by hydrogenation over a Ni catalyst.[7] CO_2, C_2H_6 and C_3H_8 were separated at $-130°$ and analyzed with a mass spectrometer. The C_4 fraction which consisted mainly of butane was too small to be measured with any accuracy.

The esters were obtained from the Eastman Kodak Co. (White Label) and were fractionated with rejection of large head and tail fractions before distillation in the vacuum line. Neopentane was a National Bureau of Standards sample. *n*-Heptane, which was a Phillips Pure Grade hydrocarbon, and the alcohols have been treated with sulfuric acid. Ultraviolet absorption spectra showed negligible absorption in the wave length region 2000-2500 Å.

Results

Only the volatile products which could be easily distilled from the irradiated mixtures were measured quantitatively.

Ultraviolet absorption spectra indicated that practically all the useful radiation was absorbed by mixtures containing up to 90% of the solvent by volume. From this it follows that the rates divided by the incident intensity are proportional to actual quantum yields.

Except when stated otherwise the incident intensity was kept constant within 5% for all experiments presented in this paper. Rates are given in cc./min. 10^4 and solvent concentrations in mole per cent. Rates were calculated using the cell volume.

Formates.—Table I presents the rates of formation of the volatile products as functions of the

TABLE I

THE EFFECT OF SOLVENTS ON THE PHOTOLYSIS OF ETHYL AND *n*-PROPYL FORMATE, $T = 5°$

Solvent mole %	Time, min.	Rates, cc./min. × 10^4					C_2H_4/CO
		CO	H_2	C_2H_4	C_2H_6	CO_2	
				ETHYL FORMATE			
0	35	48.0	6.80	137	18.8	19.9	2.87
				Neopentane			
47	30	47.6	7.02	104	25.7	17.6	2.18
				n-Heptane			
15.4	30	45.6	7.25	109	22.5	15.6	2.38
35.4	30	48.0	9.3	57.0	25.8	14.7	1.19
35.4	27	47.5	9.0	57.3	24.0	12.5	1.18
62	25	45.6	8.2	41.0	21.3	11.3	0.92
73	30	45.0	8.8	25.2	18.2	9.65	.56
91.5	20	40.5	10.0	13.6	10.0	9.9	.335
				Methyl alcohol			
66.3	37	44.5	8.7	41.7	28.1	11.3	0.94
				Ethyl alcohol			
4	25	48.0	6.7	104	25.4	17.4	2.17
11.8	30	45.4	7.4	79.0	34.6	17.1	1.74
31	30	42.1	7.9	51.5	42.5	15.4	1.22
57.3	30	43.5	8.4	27.0	37.5	8.7	0.62
77	25	45.6	8.9	20.3	32.4	8.9	.445
87	30	44.5	8.8	17.2	32.3	8.2	.386
96.5	20	34.5	8.8	8.65	20.5	6.1	.25
				Ethyl ether			
7.25	31	44.8	6.45	42.2	19.9	4.85	0.94
61.0	30	53.0	8.70	9.15	22.1	3.7	0.172
				C_3H_6	C_3H_8		C_3H_6/CO
				n-PROPYL FORMATE			
0	25	50.5	5.2	230	4.75	6.8	4.6
				n-Heptane			
66.5	40	50.0	6.2	132	9.80	4.2	2.64
93.5	26	55.7	7.7	78.0	16.2	3.4	1.4

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF18(600)1528. Reproduction in whole or in part is permitted for any purpose by the United States Government.

[2] E. J. Bowen and A. T. Horton, *J. Chem. Soc.*, 1685 (1936).

[3] P. E. Frankenburg and W. A. Noyes, Jr., THIS JOURNAL, **75**, 2847 (1953).

[4] R. Pieck and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1304 (1955).

[5] P. Ausloos, *ibid.*, in press.

[6] P. Ausloos, *ibid.*, in press.

[7] A. Shepp and K. O. Kutschke, *ibid.*, **32**, 1112 (1954).

per cent. solvent added to ethyl and *n*-propyl formate at 5° and constant incident intensity.

It is seen that the CO yield is not affected to any appreciable extent by addition of solvents. The small decrease in the rates of formation of CO at high dilution is largely due to a decrease in absorption. The rates of formation of the alkenes however decrease markedly with increasing dilution. It can be deduced from the data that the efficiencies in reducing the alkene rates are related as follows: ethyl ether > ethyl alcohol > *n*-heptane > methyl alcohol > neopentane.

The rates of formation of carbon dioxide decrease with increasing dilution, while the rates of formation of ethane and propane increase upon addition of solvents. The decrease of the rate of formation of ethane at high dilution may be partly due to a decrease in absorption.

Table II gives data on the photolysis of *n*-heptane–ethyl formate mixtures containing 68.5% *n*-heptane. The intensity has been varied over a range of about 100.

TABLE II

THE EFFECT OF INTENSITY ON THE PHOTOLYSIS OF ETHYL FORMATE–*n*-HEPTANE MIXTURES

$T = 25°$, *n*-heptane = 68.5%

I_{rel}	Time, min.	Rates, cc./min. × 10^4					C_2H_4/CO
		CO	H_2	C_2H_4	C_2H_6	CO_2	
1	20	47.9	10.2	30.2	33.8	11.0	0.63
0.32	55	15.7	3.90	9.75	14.5	9.60	.62
.036	252	1.79	0.45	1.10	3.75	2.20	.615
.009	1100	0.46	0.11	0.264	1.90	0.99	.58

It can be seen that CO/I_{rel} and C_2H_4/I_{rel} stay practically unchanged while C_2H_4/CO shows only a very slight decrease with decreasing intensities. The carbon dioxide and ethane yields increase appreciably with diminishing intensities.

Esters other than Formates.—The photolyses of methyl *n*-butyrate and ethyl acetate have been investigated in presence of solvents. The results given in Table III indicate clearly that the ethylene yields for both compounds decrease sharply upon addition of solvents. The same efficiency sequence exists as for the formates.

The rate of formation of methane increases strongly upon addition of solvents to methyl *n*-butyrate. For the ethyl alcohol–methyl *n*-butyrate mixtures the rate of formation of methane reaches a constant value at high dilution.

The rates of formation of propane and carbon dioxide decrease with increasing dilution. A decrease in temperature from 5 to −40° results in a drastic decrease of the rate of formation of all products except ethylene. Addition of ethyl alcohol to ethyl acetate produces an increase in the ethane yield.

A few experiments were carried out in order to study the effect of temperature and intensity on the photolysis of methyl propionate–ethyl alcohol mixtures. The data of Table IV indicate that the rates of formation of all products except propane increase with increase in temperature. The methane yield however reaches a constant value at high temperatures. Comparison with a run in which the undiluted ester was irradiated at 70° shows that the ethane and carbon dioxide yields are, respectively, 3 and 7 times higher for the undiluted liquid than for solutions, while the carbon monoxide yields are practically unchanged.

TABLE III

THE EFFECT OF SOLVENTS ON THE PHOTOLYSIS OF METHYL *n*-BUTYRATE AND ETHYL ACETATE

Temp., °C.	Solvent, mole %	Time, min.	Rates, cc./min. × 10^4					
			CO	CH_4	C_2H_4	C_2H_6	C_3H_8	CO_2
METHYL *n*-BUTYRATE								
5	0	25	2.6	5.0	168	3.6	26.5	6.4
Ethyl alcohol								
5	17.5	35	3.0	20.6	123	3.5	17.7	5.9
5	39.0	35	2.4	56.0	79.0	2.0	14.2	4.25
5	65.8	35	2.5	75.0	58.5	1.6	11.2	3.8
5	88.5	30	2.1	76.0	36.8	1.4	10.0	3.5
5	95.0	25	2.1	76.0	29.0	1.1	6.2	3.1
−40	88.5	28	0.56	3.7	31.0		2.1	
n-Heptane								
5	76.0	30	3.3	24.6	88.5	3.0	16.0	5.0
Methyl alcohol								
5	91.5	36	3.2	42.8	59.2	2.0	11.1	5.1
Ethyl ether								
5	52.5	30	2.1	60.0	32.0		3.2	2.3
ETHYL ACETATE								
5	0	25	1	1	210	1		2.5
Ethyl alcohol								
5	87	30	0.8	1.3	27.5	36.7		2.0

A decrease in intensity at 70° does not affect the yields to any appreciable extent. At 5°, however, a lowering in intensity produces an increase in the yields of all products except propane.

Discussion

Formates.—Previous work[5] on the liquid phase photochemical decomposition of formates indicated that the following molecular rearrangement occurs

$$HCOOY + h\nu = CO + HOY \qquad (I)$$

Formates with a β-hydrogen also were found to rearrange into an alkene and formic acid

$$HCOOY + h\nu = \text{alkene} + HCOOH \qquad (II)$$

The fact that the ratio CO/alkene diminishes considerably by cutting off short wave lengths, was considered as evidence for process I occurring at shorter wave lengths and probably from a different electronic excitation level than process II.

In view of this the results of Table I can easily be explained by assuming that the primary process II is strongly suppressed by addition of solvents, while process I is unaffected. In agreement with this it is seen from the data of Table II that the ratio CO/C_2H_4 is independent of intensity.

Esters other than Formates.—A previous investigation[5] of the gas and liquid phase photolyses of several esters gave evidence for the existence of the primary processes

$$\begin{aligned} XCOOY + h\nu &= \text{alkene} + XCOOH &\quad (III)\\ &= \text{alkene} + CH_3COOY &\quad (IV)\\ &= X + COOY &\quad (V)\\ &= XCO + OY &\quad (VI) \end{aligned}$$

Processes III and IV were found to occur when there were β- and γ-hydrogens, respectively, in the Y and X alkyl groups. The ratio alkene/CO_2, CO_2 coming from the decomposition of COOY, was not affected by a change in wave length distribution, while CO/CO_2 diminished markedly by cutting off short wave lengths. These observations were interpreted by assuming that processes III, IV and V result from the same electronic excitation level, while process VI just like process I in the case of the formates, takes place at shorter wave lengths and from a different electronic level than the other processes.

It can be seen that the results of Tables III and IV can be interpreted in accordance with this general picture. The decrease of the ethylene yields in the photolyses of ethyl acetate and methyl *n*-butyrate upon addition of solvents points to a suppression of processes III and IV. In support of this it may be mentioned that in the photolysis of methyl *n*-butyrate–ethyl alcohol mixtures, a decrease in temperature from 5 to −40° did not affect the ethylene yield to any appreciable extent, while the rates of formation of all other products decreased considerably.

Table IV

Photolysis of Methyl Propionate in the Presence of Ethyl Alcohol

Temp., °C.	I_{re}	Alcohol, mole %	Time, min.	Rates, cc./min. × 10^4					
				CH_4	C_2H_4	C_2H_6	C_3H	CO	CO_2
−50	1	87	40	1.0					
5	1	87	30	77.0	1.84	10.0	1.3	2.68	2.70
35	1	87	30	123	1.40	32.5	1.2	10.3	11.6
55	1	87	25	138	1.2	59.0	1.1	23.5	23.4
70	1	87	21	136	1.3	80.5	1.5	38.0	34.7
70	1	0	15	217	5.3	243	5.8	40.7	234
5	0.115	87	155	15.0		2.1	0.15	0.41	0.51
71	0.115	87	112	16.0		10.2	0.10	4.10	3.95

If, as mentioned above, processes IV and V result from the same electronic excitation level, a suppression of process IV by addition of solvents may be expected to be accompanied by a quenching of process V. Due to the rather low CO_2 yields in the photolysis of methyl *n*-butyrate and ethyl acetate, the results of Table III are not conclusive. However, it has been shown previously[5] that in the liquid phase photolyses of ethyl propionate and methyl propionate, the rate of formation of CO_2 is much higher than for the acetates and reaches a constant value at temperatures around 70°. From the data of Table IV it can be seen that at 70° the CO_2 yield is much lower for the methyl propionate–ethyl alcohol mixture than for the undiluted ester. The CO yield, however, stays practically unchanged. These observations are in agreement with the supposition that the dissociative process V is suppressed by addition of solvents, while process VI is not affected.

The results of Table I indicate that addition of solvents to formates produces also a decrease of the CO_2 yields. This may eventually be explained by a quenching of a process analogous to V. It must be pointed out, however, that the interpretation is more complex for the formates in view of the occurrence of a chain reaction

$$R + HCOOR = HR + COOR$$
$$COOR = CO_2 + R$$

The increase of the carbon dioxide yield with decrease in intensity in the photolysis of ethyl formate–heptane mixtures is evidence for the occurrence of this chain reaction.

Summarizing the results given in this paper, it may be concluded, that the short wave length processes I and VI are not affected by addition of solvents while processes II, III, IV and V which occur mainly at long wave lengths are strongly suppressed.

The data do not provide a clear picture on how the interaction between the solvent molecules and the excited ester molecules takes place. However, two observations may help in understanding the process by which some of the primary processes are suppressed:

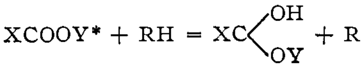
1. The sequence: ethyl ether > ethyl alcohol > *n*-heptane > methyl alcohol > neopentane which represents the efficiencies in reducing the alkene yields for both the ethyl formate and the methyl *n*-butyrate photolyses is about the same as that for the ease of the abstraction of a hydrogen atom by methyl radicals.

2. Addition of solvents led to a pronounced increase of the hydrocarbons YH which is not accompanied by an increase of the CO_2 or XH yields. It can be seen that, as may be expected from the occurrence of processes V and VI, the rate of formation of ethane in the photolyses of methyl propionate–ethyl alcohol mixtures is roughly equal to the sum of the rates of formation of carbon monoxide and carbon dioxide. The methane yield, which in the photolysis of the pure ester at high intensities is always somewhat less than the carbon dioxide yield, is for the diluted ester at 35° about ten times higher than the carbon dioxide yield. As mentioned above, the results of Table IV show that at high intensities the methane yield is constant at temperatures above 35°. Also, in the photolysis of methyl *n*-butyrate in presence of solvents, the methane yield is approximately 15 times higher at high dilution than for the pure ester. The efficiency of solvents in increasing methane yields is related to that of reducing the alkene yields.

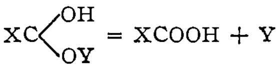
These facts may perhaps be explained by a reaction between the electronically excited ester molecule responsible for the processes III, IV and V and the solvent molecule

$$XCOOY^* + RH = XCOOH + R + Y \qquad (VII)$$

It is conceivable that this process might occur in two steps



$$\mathrm{XCOOY^* + RH = XC}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OY}\end{matrix}\right. + \mathrm{R}$$



$$\mathrm{XC}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OY}\end{matrix}\right. = \mathrm{XCOOH + Y}$$

Such a mechanism may be expected to depend on the ease of abstraction of a hydrogen atom from the solvent molecule and would also account for the increase of the YH yields with increase of solvent concentration and increase in temperature. If every Y radical abstracts a hydrogen atom from the surrounding molecules, one YH molecule may be expected to be formed for every excited ester molecule reacting by process VII. The data of Tables I, II, III and IV indicate, however, that the YH yield is always too small compared with the number of molecules deactivated by the solvent. The occurrence of a recombination process such as

$$\mathrm{Y + R = YR}$$

may account for this discrepancy. In the photolysis of methyl *n*-butyrate–ethyl alcohol mixtures, the CH_4 yield does not change at high dilution while the C_2H_4 yield is still decreasing. The explanation of these points is not obvious.

In connection with this work it may be mentioned that in the photolysis acetone–hydrocarbon mixtures an alcohol was formed,[2,3] while the quantum yield of the volatile products was less than for the undiluted ketone.[4] A process analogous to VII may account for these results

$$\mathrm{CH_3COCH_3^* + RH = (CH_3)_2COH + R} \quad \text{(VIII)}$$

followed by

$$\mathrm{(CH_3)_2COH + R = (CH_3)_2COHR}$$

It is likely that processes VII and VIII also occur in the gas phase at high pressures and intensities.[8]

Acknowledgment.—The author is indebted to Professor W. A. Noyes, Jr., for advice and encouragement.

(8) Added in proof.—Recently G. K. Osler and R. A. Marcus, *J. Chem. Phys.*, **27**, 472 (1957), suggested a process such as VIII in the flash photolysis of acetone in the presence of butane.

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[Contribution from the McPherson Chemical Laboratory, The Ohio State University]

A Kinetic Study of the Thermodynamic Properties of the Acetyl Free Radical[1]

By Jack G. Calvert and Jerry T. Gruver

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Azomethane is photolyzed at 3660 Å. in the presence of acetaldehyde or carbon monoxide in gas phase experiments at several temperatures and reactant concentrations. Product rate data lead to estimates of the rate constants for the acetyl free radical decomposition reaction, $CH_3CO \rightarrow CH_3 + CO$ (1), and the formation reaction, $CH_3 + CO \rightarrow CH_3CO$ (2). From these data the approximate thermodynamic functions of reaction (1) are estimated. These results and suitable published enthalpy values give the heat of formation of the acetyl free radical $\cong -3.0$ kcal./mole, and the bond dissociation energies, $D_{\mathrm{CH_3CO-CH_3}} \cong 82$, $D_{\mathrm{CH_3CO-H}} \cong 89$, $D_{\mathrm{CH_3CO-COCH_3}} \cong 72$ kcal./mole.

Quantitative information is needed concerning the acetyl free radical reactions of decomposition (1) and formation (2)

$$\mathrm{CH_3CO \longrightarrow CH_3 + CO} \quad (1)$$

$$\mathrm{CH_3 + CO \longrightarrow CH_3CO} \quad (2)$$

to establish the thermodynamic properties of the acetyl free radical and to obtain realistic estimates of the bond strengths in the ketones and aldehydes. Published information related to (1) and (2) is very limited and of questionable reliability. The data pertinent to reaction 1 have been re-evaluated recently.[2] It was concluded that the majority of the information favored a "low" activation energy ($E_1 \cong 12 \pm 2$ kcal./mole), but a clear choice between this and an alternative "high" value ($E_1 \cong 17 \pm 1$ kcal./mole) was not possible.

The available information concerning reaction 2 is even less satisfactory. Faltings[3] has given indirect evidence that this reaction may occur at room temperature. He reports that acetone was detected among the products of the Schumann ultraviolet photodecomposition of ethane in the presence of added carbon monoxide. However, Porter and Benson[4] were unable to detect the occurrence of (2) at 150°; C^{14}-containing acetone was not found in the products of di-*t*-butyl peroxide thermal decomposition in the presence of $C^{14}O$. They concluded that $k_2 \leqslant 3 \times 10^9$ cc./mole-sec. at 150°.

In the work reported here the rate constants for the reactions 1 and 2 are estimated from rate data derived in azomethane photolyses in the presence of added acetaldehyde and carbon monoxide.

Experimental

Apparatus.—The photolysis system consisted of a cylindrical quartz photolysis cell (420-cc. volume), a quartz spiral manometer, an all glass in-line circulating pump and a trap. This system was isolated by modified Veeco metal valves. In most of the experiments the photolysis cell was suspended in a large aluminum block oven regulated to ±1°. In three experiments at 0° the oven was removed and the cell was surrounded with an ice-bath. A collimated beam of filtered 3660 Å. light almost completely filled the cell; it was generated from a Hanovia Type A (S-500) burner operated on a regulated a.c. power supply, and filtered with a Corning 5840 filter in combination with a 0.8 cm. thickness of plate glass. The relative energies of the various wave lengths present in the "3660 Å." filtered beam were: 4045 Å., 0.23; 3906 Å., 0.53; 3660 Å., 100.00; 3340 Å., 1.04; 3130 Å., 0.05.

Materials.—Azomethane was prepared and purified by

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[1] This study was aided by a research grant from the Department of Health, Education, and Welfare, Public Health Service, National Institutes of Health, Bethesda 14, Md.

[2] J. G. Calvert, *J. Phys. Chem.*, **61**, 1206 (1957).

[3] K. Faltings, *Ber.*, **72B**, 1207 (1939).

[4] G. B. Porter and S. W. Benson, This Journal, **75**, 2773 (1953).