THE PHOTOLYSIS OF ALKYL ESTERS^{1,2}

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ABSTRACT

An attempt has been made to determine the primary processes in the gas and liquid phase photolysis of simple alkyl esters.

The liquid phase photolysis of methyl, ethyl, n-propyl, and n-butyl formate has been briefly investigated. Besides the dissociation processes, two intramolecular rearrangements were found to occur:

$$\begin{array}{ll} \text{HCOOR} + h\nu = \text{CO} + \text{HOR}, & \text{I} \\ &= \text{HCOOH} + \text{alkene.} & \text{II} \end{array}$$

Process I takes place with approximately the same yield for all the formates studied. Process II occurs only when there is a β -hydrogen in the alkyl group. An investigation of the gas and liquid phase photochemical decomposition of esters other

than formates showed the existence of the following primary processes:

$XCOOY + h\nu = XCOOH + alkene,$	VI
$= CH_3COOY + alkene,$	VII
= XCO + OY,	Х
= X + COOY.	XI

Processes VI and VII require β - and γ -hydrogens, respectively, in the Y and X alkyl groups. It was found that processes I and X occur mostly at short wavelength, while the other processes take place at long wavelengths as well.

EXPERIMENTAL

The liquids were irradiated in a quartz cell of 5 cm. diameter and 0.1 cm. depth. The cell was closed with a break seal which made it possible to attach the cell to the analysis system after each run.

Spectra taken with a Cary spectrophotometer indicated that for a 0.1 cm. path length 100% of the useful radiation was absorbed. Absorption occurred only below 2400 Å. Experiments with a Corning filter 9863, cutting off radiation below 2250 Å, reduced the rates of formation of the products by a factor of approximately 20. Absorption spectra of formates diluted with ethanol showed a maximum around 2150 Å, while the extinction coefficients were appreciably higher than those of ketones and aldehydes.

Irradiation was carried out in a quartz Dewar filled with distilled water. For a few low temperature runs, however, 3-methyl pentane was used.

The gas phase experiments were performed with a cylindrical quartz cell (5 cm. diameter, 10 cm. long) which was completely filled with a nearly parallel light beam. The low temperature runs were performed in a brass cylinder thermostat with double quartz windows. Ethyl alcohol was used as a cooling medium.

Two Hanovia (16A-13) SH type medium pressure lamps were used in the course of this work. Because a slight change in wavelength distribution changes the relative rates of formation of the products, the number of each run is preceded by a letter a or b depending on which lamp was used. Except when stated otherwise, the incident intensity was kept constant for all the runs with lamp a. This allows comparison of the rates of

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The University of Rochester, Rochester, N.Y. ²This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. A F18(600)1528. Reproduction in whole or in part is permitted for any purpose of the United States Government. ³Present address: Department of Chemistry, The University of Rochester, Rochester, N.Y.

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formation of the products from one table to another. All rates are given in cc./min. 10⁺⁴. No absolute quantum yields were determined.

The analysis procedure was the same as described earlier (2).

The esters were obtained from Eastman Kodak Co. (White Label). Ethyl formate, methyl acetate, and methyl propionate were fractionated in a 10 plate column before distillation in the vacuum line. The other compounds were distilled and degassed in vacuum.

PART I. THE PHOTOCHEMICAL DECOMPOSITION OF FORMATES

Results

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The results of runs performed in the liquid phase at constant incident intensity and varying temperatures are given in Table I.

TABLE I LIQUID PHOTOLYSIS OF FORMATES

		Variation of ra	te with te	mperature	_	_	
	Run	Temp., ° C.	R _{co}	R _{H2}	R _{CH4}	$R_{\rm CO_2}$	
Methyl formate	$a1 \\ a2$	$5\\31$	$\begin{array}{c} 82.5\\82.0\end{array}$	8.0 8.0	$\begin{array}{c} 27.5\\ 186 \end{array}$	29.0 160	
	Run	Temp., ° C.	R _{co}	$R_{ m H_2}$	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{\rm CO_2}$
Ethyl formate	$a3\ a4\ a5$	$5 \\ 35 \\ 51$	$\begin{array}{c} 82.0 \\ 80.0 \\ 82.5 \end{array}$	$9.5 \\ 9.0 \\ 10.0$	$171 \\ 184 \\ 205$	$\begin{array}{r}25.8\\120\\214\end{array}$	$27.5 \\ 112 \\ 218$
	Run	Temp., ° C.	R _{co}	R_{H_2}	$R_{C_3H_6}$	$R_{C_{5}H_{8}}$	$R_{\rm CO_2}$
n-Propyl formate	$a6 \\ a7 \\ a8 \\ a9$	$\begin{array}{r} 6\\ 32\\ 50\\ 74\end{array}$	$74.0 \\ 77.0 \\ 77.0 \\ 83.0$	7.07.07.08.0	305 302 295 297	7.0 36.0 70.5 180	$10 \\ 41.5 \\ 84.5 \\ 206$
	Run	Temp., °C.	$R_{\rm co}$	R_{H_2}	R _{C4H8}	R _{C4} H ₁₀	$R_{\rm CO_2}$
<i>n</i> -Butyl formate	$a10\\a11\\a12$	$\begin{array}{c} 6\\ 45\\ 85\end{array}$	67.5 70.0 98.0	7.8 9.0 12.0	$154 \\ 166 \\ 169$	$\begin{array}{r} 4.3\\ 43.0\\ 108\end{array}$	$\begin{array}{r}11.4\\60.0\\116\end{array}$

It can be seen that the rates of formation of hydrogen and of carbon monoxide change very little with temperature for each compound taken separately and show only slight variations from one compound to another.

Formates with a β -hydrogen in the alkyl groups have under these experimental conditions an alkene as most important product. The rates of formation of these alkenes vary only slightly with temperature, but, unlike the rates of formation of carbon monoxide, change considerably from one compound to another.

The only other products analyzed for were carbon dioxide and the hydrocarbons: methane, ethane, propane, butane, formed respectively in the photolysis of methyl, ethyl, propyl, butyl formate.

The results indicate that the rate of formation of carbon dioxide is roughly equal to that of the corresponding hydrocarbon. They both increase appreciably with increase in temperature.

The rates of formation of the recombination products ethane and butane, formed in the photolysis of methyl and ethyl formate, respectively, are not given in Table I because these products were always present in amounts too small to be measured accurately. The amount of ethane formed in experiments 1 and 2 was less than 1% of the carbon dioxide fraction. No attempt was made to determine the rates of formation of hexane and octane in the photolysis of propyl and butyl formate.

The results of a few more liquid phase experiments on ethyl formate are included in Table II. Runs 13, 14, and 15 were performed in order to obtain a rough idea of the effect on the products of a variation in the wavelength distribution. The temperature was

T.	AB.	LE II	
PHOTOLYSIS	OF	ETHYL	FORMATE

A. Liquid phase

Run	Ten ° C	р., 2.	Time, min.	R _{co}	R	H ₂	R _{С2} н.		R _{C2} н ₆	$R_{\rm CO}$	02	$\frac{R_{C_2H_4}}{R_{CO}}$	Irel
Variation of wavelength													
b13 b14* b15† b16* b17*		3 3 3))	$25 \\ 70 \\ 101 \\ 35 \\ 70$	$\begin{array}{r} 42.5 \\ 13.0 \\ 1.1 \\ 14.3 \\ 14.6 \end{array}$	6 1 0 1 1	. 8 . 4 . 18 . 3 . 28	$^{152}_{112}\\^{25.3}_{60.5}_{57.0}$	2 3 1	$ \begin{array}{c} 6.0 \\ 2.5 \\ 8.8 \\ 2.0 \\ 2.0 \\ 2.0 \end{array} $	30.5 35.0 19.0 1.1 1.3)) .0	$3.57 \\ 7.80 \\ 23.0 \\ 4.24 \\ 3.90$	
Variation of intensity													
b18 b19 b20 b21	28 28 28 28	8 8 8 8 	13 88 705 4700	$26.7 \\ 3.15 \\ 0.405 \\ 0.023$	4 0 0 0	. 63 . 68 . 08 . 0036	101 11.9 1.3 0.0	6 1 2 37	$ \begin{array}{r} 2.0 \\ 6.4 \\ 4.68 \\ 0.505 \\ \hline \end{array} $	58.5 15.9 4.5 0.5	5 5 5 12	3.80 3.80 3.25 2.85	$1500 \\ 180 \\ 19 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ $
B. Gas phase													
T Run	Гетр., ° С.	Time, min.	Pres- sure, cm.	R _{co}	R _{H2}	R	2H4	R _{C2} H ₆	$R_{\rm CO_2}$		२ _{сн4}	$R_{C_{3}H_{8}}$	R _{C4H10}
b22 b23 b78§	$\begin{array}{c}0\\29\\27\end{array}$	$45 \\ 35 \\ 20$	$4.1 \\ 4.5 \\ 4.5 \\ 4.5$	62.0 80.0 59.0	$7.7 \\ 8.8 \\ 1.35$	10 10 10	3.6 3.4 3.0	$11.8 \\ 15.8 \\ 0.5$	$22.0 \\ 31.0 \\ 10.6$		2.45 5.75	2.0 3.15	$4.3 \\ 4.0$

*3-Methyl pentane bath.

†Corning filter 9863. §Iodine added 0.035 cm.

kept constant. Run 14 was done with a 3-methyl pentane bath which absorbed most of the radiation below 2150 Å. In order to cut off radiation below 2250 Å, a Corning filter 9863 was used in run 15. It follows from these experiments that a change in the wavelength distribution appreciably affects the ratio C_2H_4/CO . The rates of formation of carbon monoxide and hydrogen decrease appreciably as compared to the rate of formation of ethylene when only the longer wavelengths are absorbed by ethyl formate.

Runs 16 and 17 were done with the same experimental setup and at the same intensity as experiment 14. From the results of these experiments it follows that the rates of formation of carbon monoxide and hydrogen are practically independent of temperature, while the rate of formation of ethylene decreases with decrease in temperature. Runs 3, 4, and 5 of Table I lead to the same observation.

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In the same table results are presented of runs where only the intensity has been varied. It can be seen that the carbon monoxide, hydrogen, and ethylene yields as well as the ratio C_2H_4/CO change only slightly, while the carbon dioxide and ethane yields increase markedly with diminishing intensities.

The results of the gas phase runs given in Table II indicate that addition of iodine does not affect the rate of formation of ethylene to any appreciable extent, while the rates of formation of methane, propane, and butane were reduced to negligible amounts. Increase of the temperature increases the rate of formation of the products with the exception of ethylene.

Discussion

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The results of Tables I and II indicate that the following intramolecular process occurs:

$$HCOOR + h\nu = HOR + CO.$$
 I

The independence with respect to temperature variation of the rate of formation of carbon monoxide over a temperature range from -80° to 13° C. and over a large intensity range is good evidence for the occurrence of this process. The small increase of the hydrogen and carbon monoxide yields at high temperatures and low intensities may be attributed to a thermal decomposition of formyl radicals. The fact that the less stable acetyl radicals formed in the liquid phase photolysis of methyl and ethyl acetate decompose only to a small extent agrees with the proposition that at low temperatures carbon monoxide is formed mostly by process I.

Formates with a β -hydrogen may also decompose by process II:

$$HCOOR + h\nu = HCOOH + alkene.$$

Π

The following facts may be cited as evidence in favor of process II:

(a) the independence of the ethylene yield in the liquid phase photolysis of ethyl formate over a considerable intensity range,

(b) the only slight variation of the rate of formation of the alkenes with temperature,(c) the rate of formation of ethylene which in the gas phase photolysis of ethyl formate

is unchanged upon addition of iodine.

It may be mentioned that pyrolysis studies (5) of several formates by the toluene carrier technique showed that formates with a β -hydrogen decompose by a molecular elimination process analogous to process II. Acetic anhydride may be cited as another example of the same type where photolysis (1) and pyrolysis (8) produce ketene and acetic acid in a direct process.

The ethyl formate results show that process I occurs mostly at wavelengths shorter than are required for process II. This indicates that processes I and II probably occur from different electronic levels.

Besides the intramolecular processes one or more of the following dissociative steps has to occur:

$$HCOOR + h\nu = HCO + OR, \qquad \qquad III$$

$$=$$
 H + COOR, IV

= HCOO + R. V

From our results little can be said about the occurrence of these processes. Analogy with the liquid phase photolysis of the acetates and propionates favors processes III and IV.

Recent studies (6) on the gas phase photolysis of acetone in the presence of methyl formate have shown that methyl radicals only abstract the hydrogen atom from the

acyl group. One carbon dioxide molecule was found for every hydrogen abstracted. In agreement with this, the pronounced increase of the rate of formation of carbon dioxide and the corresponding hydrogen with increase in temperature and diminishing intensities can be explained by the following chain propagating steps:

$$R + HCOOR = RH + COOR,$$

 $COOR = CO_2 + R.$

The initiator may be any of the radicals formed in processes III, IV, and V.

Considering the primary processes mentioned above, hydrogen can at low temperatures only be produced by a reaction of the hydrogen atoms formed in process IV with other radicals present in the system or with formate molecules. It is perhaps surprising that the ratio H_2/CO is approximately the same for all runs done with the same lamp and at the same wavelength distribution.

It may be pointed out that at these wavelengths, hydrogen atoms cannot be formed by a primary process in which a hydrogen atom is split off from the alkyl group. This is substantiated by the fact that no hydrogen was found in the gas or liquid phase photolysis of the esters to be discussed later in this paper.

The methane and propane formed in the gas phase photolysis of ethyl formate indicate that even at room temperature the ethoxy radicals decompose to an appreciable extent into a methyl radical and formaldehyde.

PART II. THE PHOTOLYSIS OF ESTERS OTHER THAN FORMATES

Results

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Liquid Phase

The results of the liquid phase photolysis of a few simple alkyl esters at varying temperatures and intensities have been summarized in Table III.

Only the volatile products have been determined quantitatively. In a few runs however some of the products were present in amounts too small to be measured with any accuracy. Except when stated otherwise, the incident intensity was the same as for the experiments given in Table I. For the runs where the intensity has been changed, the incident intensity is given relative to the constant intensity experiments. All the rates are expressed in cc./min. $\times 10^4$.

A few general features are as follows:

(a) Ethyl acetate and ethyl propionate give ethylene as an important product. The ethylene quantum yields are virtually not affected by a change in intensity.

(b) Propylene is the main volatile product in the photolysis of isopropyl and n-propyl acetate.

(c) In the photolysis of methyl n-butyrate a considerable amount of ethylene has been found.

(d) Some ethylene is also formed in the photolysis of methyl propionate. However, the rate of formation is only 10% of the rate of ethylene production in the photolysis of ethyl propionate.

(e) For most of these compounds a change in temperature produces a slight variation in the yields of the alkenes.

(f) All esters have carbon monoxide and carbon dioxide as products. The rates of formation of both compounds increase with temperature. The acetates produce less carbon monoxide, carbon dioxide, and hydrocarbons than the propionates and the buty-rates.

	Run	Temp., °C.	Time, min.	Rc	o	R _{cO2}	R_{CH_4}	ŀ	R _{C2H6}
Methyl acetate	$a24 \\ a25$	$5 \\ 29$	85 55	7 11	3.8	2.47 7.80	$\begin{array}{c} 8.80\\ 12.0\end{array}$	-	1.4 2 1.80
	Run	Temp., ° C.	Time, min.	R _{co}	$R_{\rm CO_2}$ R	сн ₄ R _{C2} н	6 R _{C2H4}	R _{C3H8}	R _{C4} H ₁₀
Methyl propionate	$a26 \\ a27 \\ a28 \\ a29$	5 31 50 70	8 7 6 5	$\begin{array}{r} 6.10 \\ 12.8 \\ 26.6 \\ 57.5 \end{array}$	$\begin{array}{cccc} 38.6 & 2 \\ 154 & 10 \\ 245 & 21 \\ 292 & 25 \end{array}$	$\begin{array}{cccc} 7.0 & 135 \\ 5 & 248 \\ 6 & 278 \\ 8 & 328 \end{array}$	$20.5 \\ 6.4 \\ 5.10 \\ 4.30$	$5.20 \\ 8.35 \\ 8.60 \\ 4.30$	$22.5 \\ 14.3 \\ 7.80 \\ 3.50$
	Relativ <i>a</i> 30 <i>a</i> 31 <i>a</i> 32 <i>a</i> 33	ve intensity 5 30 50 70	$0.125 \\ 35 \\ 35 \\ 30 \\ 30 \\ 30$	$\begin{array}{c} 0.75 \\ 1.50 \\ 4.45 \\ 8.80 \end{array}$	$\begin{array}{c} 7.45 \\ 21.0 \\ 36.5 \\ 34.0 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{ccc} 7 & 2.30 \\ 2 & 1.70 \\ 8 \\ 0 & \\ \end{array} $		
	Run	Temp., °C.	Time, min.	R _{co}	$R_{\rm CO_2}$	$R_{ m CH4}$	R _{C3H8}	R _{C3H6}	$R_{C_2H_4}$
Methyl <i>n</i> -butyrate	a = a = a = a = a = a = a = a = a = a =	5 36 85	8 8 7	$2.90 \\ 9.53 \\ 66.0$	$9.50 \\ 45.0 \\ 155$	$\begin{array}{r} 6.55 \\ 38.4 \\ 140 \end{array}$	30.5 100 192	$3.05 \\ 4.20$	$203 \\ 176 \\ 101$
	Run	Temp., °C.	Time, min.	R _{co}	$R_{\rm CO_2}$	R_{CH_4}	R_{C_2}	1 ₆	$R_{C_2H_4}$
Ethyl acetate	a37 a38 a39	3 30 70	5 4 4	$\begin{array}{c}1.1\\4.3\\20.5\end{array}$	3.8 25.5	1.0 4.0 14.0	- 15.	0	$255 \\ 260 \\ 238$
	Relative in	ntensity 0.2 3 26 52 74	$1 \\ 122 \\ 37 \\ 41 \\ 20 \\ -$	$0.34 \\ 1.10 \\ 2.80 \\ 4.75$	$0.90 \\ 2.25 \\ 3.15 \\ 5.40 $	$\begin{array}{c} 0.3 \\ 0.8 \\ 2.0 \\ 4.4 \end{array}$	$ \begin{array}{c} 0 \\ 0 \\ 5 \\ 0 \\ 4 \end{array} $	70 00	$\begin{array}{c} 46.0 \\ 55.8 \\ 58.0 \\ 47.0 \end{array}$
	Run	Temp., °C.	Time, min.	R _{co}	$R_{\rm CO_2}$	 R _{C2H6}	 R ₀₂ н4		R _{C4H10}
Ethyl propionate	a44a45a46a47a48a49	$ \begin{array}{r} 4 \\ 30 \\ 30 \\ 50 \\ 70 \\ 90 \\ 90 \end{array} $		$\begin{array}{r} 8.40 \\ 20.5 \\ 19.0 \\ 36.0 \\ 59.2 \\ 83.5 \end{array}$	$\begin{array}{r} 33.2\\85.0\\87.0\\155\\186\\198\end{array}$	71.0 130 135 227 315 384	200 176 181 168 155 136		$\begin{array}{r} 34.4 \\ 25.0 \\ 22.0 \\ 19.5 \\ 16.0 \\ 10.0 \end{array}$
	Relative i	$\begin{array}{c} \text{elative intensity } 0.12\\ a50 & 3\\ a51 & 30\\ a52 & 61\\ a53 & 90 \end{array}$		$0.81 \\ 2.80 \\ 7.80 \\ 13.0$	$5.90 \\ 12.8 \\ 21.3 \\ 23.5$	12.6 23.7 42.0 51.0	22. 19. 18. 18. 18.	0 0 0 0	$\begin{array}{c} 0.60\\ 0.80 \end{array}$
]	Relative i a54	ntensity 0.0 30	023 1035	0.06	0.223	7 0.4	1 9 0.	315	
	Run	Temp., °C.	Time, min.	R _{co}	$R_{\rm CO_2}$	R _{CH}	R _C	H8	R _{C3H6}
Isopropyl acetate	$a55 \\ a56 \\ a57$	7 31 77	$\begin{array}{c} 6\\ 6\\ 6\end{array}$	$\begin{array}{r} 0.40 \\ 1.40 \\ 16.0 \end{array}$	15.0	0.5 2.6 18.0	50 50 50 18	.5	$370 \\ 319 \\ 255$
n-Propyl acetate	$a58\ a59$	28 75	6 6	$\begin{array}{c} 2.70 \\ 26.5 \end{array}$	20.0	1.5 16.0	54) 21	.2	180 198

TABLE III

LIQUID PHASE PHOTOLYSIS OF ESTERS

(g) In the photolysis of methyl and ethyl propionate, the rates of formation of carbon dioxide, methane, and ethane approach constant values at high temperatures. A decrease in intensity results in an increase of the yields of these three products. The results of the methyl propionate experiments indicate that at low intensities the rates of formation of carbon dioxide and methane are equal, while at high intensities the rate of formation of methane is somewhat less than that of carbon dioxide.

(h) Ethers were found to be present in the liquid phase photolysis of all the esters but their rates of formation were too small to be measured with any accuracy.

Gas Phase

Table IV represents the results of a few gas phase experiments. The incident intensity

				Gas pi	HASE PH	OTOLYSI	S OF ES	TERS				
		Run	Temp., °C.	Pres- sure, cm.	Time min.	, Rco	$R_{\rm CO_2}$	R _{CH}	RC2H6			
Methyl aceta	te	$a60 \\ a61 \\ a62$	$27 \\ 120 \\ 177$	$\begin{array}{c} 6.4 \\ 8.35 \\ 9.50 \end{array}$	$35 \\ 25 \\ 25 \\ 25$	13.8 73.2 74.8	$\begin{array}{cccc} 8 & 8.30 \\ 2 & 16.7 \\ 3 & 16.1 \end{array}$	$\begin{array}{ccc} 0 & 1.93 \\ & 7.00 \\ 17.3 \end{array}$	$\begin{array}{c} 3 & 5.50 \\ 0 & 33.8 \\ & 26.2 \end{array}$			
		Run	Temp., °C.	Pres- sure, cm.	Time min.	, $R_{\rm co}$	$R_{\rm CO_2}$	Ron	4 R _{C2H6}	$R_{C_2H_4}$	R _{C3H8}	R _{C4} H ₁₀
Methyl propie	onate	$a63 \\ a64 \\ a65 \\ a66 \\ a67$	$34\\124\\196\\1\\37$	7.1 9.1 8.8 1.8 2.05	$30 \\ 25 \\ 25 \\ 40 \\ 25$	50.8 59.0 56.8 19.2 45.0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{r} 1.8\\ 3.9\\ 8.1\\ 0 \\ 0.7\\ 1.1\end{array} $	$\begin{array}{cccc} 0 & 8.4 \\ 5 & 11.0 \\ 2 & 21.1 \\ 9 & 4.02 \\ 3 & 8.50 \end{array}$	$\begin{array}{c} 3.69 \\ 4.10 \\ 3.42 \\ 1.80 \\ 3.75 \end{array}$	$\begin{array}{c} 6.73 \\ 8.40 \\ 3.95 \\ 2.86 \\ 6.70 \end{array}$	$\begin{array}{r} 13.82 \\ 12.40 \\ 7.03 \\ 7.10 \\ 15.2 \end{array}$
		Run	Temp., °C.	Pres- sure, cm.	Time min.	, Rco	, R _{co}	₂ R _{CH}	4 R _{C2} н6	$R_{\mathrm{C_{2}H_{4}}}$	<i>R</i> _{С3} н ₆	R _{C3H8}
Methyl <i>n</i> -but	yrate	$b68 \\ a69^{*}$	29 29	$egin{array}{c} 2.85\ 3.0 \end{array}$	$\begin{array}{c} 25 \\ 800 \end{array}$	55.0 0) 15.3 3 0.4	$1.4 \\ 15 0.0$	$\begin{array}{ccc} 0 & 1.7 \\ 43 & 0.05 \end{array}$	$\begin{array}{c} 4.65\\ 0.13 \end{array}$	$\begin{array}{c} 3.25\\ 0.029 \end{array}$	9.10 0.089
	Run	Temp °C.	Pres- D., sure, cm.	Time, min.	R _{co}	$R_{\rm CO_2}$	R _{CH4}	$R_{C_2H_6}$	R _{C2H4}	<i>R</i> _{С3} н ₈	R _{C4} H ₁₀	$\frac{R_{\rm C_2H_4}}{R_{\rm CO_2}}$
Ethyl acetate	b70 b71 a72 a73 a74	$-23 \\ 0 \\ 34 \\ 124 \\ 195$	$\begin{array}{c} 0.45 \\ 1.95 \\ 5.8 \\ 7.5 \\ 8.8 \end{array}$	60 43 20 15 15	$\begin{array}{c} 0.34 \\ 4.1 \\ 9.60 \\ 45.0 \\ 54.5 \end{array}$	$\begin{array}{c} 0.80 \\ 7.90 \\ 8.95 \\ 16.5 \\ 18.0 \end{array}$	$\begin{array}{c} 0.076 \\ 0.82 \\ 1.06 \\ 8.55 \\ 35.4 \end{array}$	$\begin{array}{c} 0.17\\ 2.80\\ 3.26\\ 23.0\\ 13.8 \end{array}$	$\begin{array}{r} 3.00 \\ 12.6 \\ 9.80 \\ 11.2 \\ 12.6 \end{array}$	$\begin{array}{c} 0.20 \\ 1.65 \\ 2.49 \\ 14.8 \\ 7.2 \end{array}$	${\begin{array}{c} 0.1 \\ 0.6 \\ 0.54 \\ 0.57 \end{array}}$	$\begin{array}{r} 3.75 \\ 1.60 \\ 1.10 \\ 0.68 \\ 0.70 \end{array}$
Ethyl propionate	a75 b76† b77*	$34 \\ 30 \\ 30$	$\begin{array}{c} 3.8\\ 3.3\\ 3.3\end{array}$	$35 \\ 1340 \\ 1140$	$\begin{array}{c} 25.0\\ 2.1\\ 0.59 \end{array}$	$8.75 \\ 0.76 \\ 0.445$	$\begin{array}{c} 0.30 \\ 0.015 \\ 0.01 \end{array}$	$5.80 \\ 0.312 \\ 0.14$	$7.05 \\ 0.573 \\ 0.325$	${}^{1.26}_{0.055}_{0.032}$	$12.8 \\ 0.775 \\ 0.42$	0.81 0.755 0.73
		lodin preser	e nt	$R_{\rm CO}$	$R_{ m CO_2}$	R _C	14 K	C_{2H_6}	$R_{\mathrm{C_{2}H_{4}}}$	Rc	_{зна} 1	R _{C4H10}
Ester-iodine 1	nixtur	es.—Te	mperatu	-e: 28° (C. Ester	pressur	e: 2.7 ci	n. lodin	e pressur	e: 0.03	5 cm.	
C ₂ H ₅ COOC	CH 3	No Yes]	30 46 5	$34.0 \\ 32.5$	5.2	2	22.5	9.60	18	.0	36.5
C ₂ H ₅ COOC	$^{2}H_{5}$	No		90.0	33.7	0.6	5 1	17.3	29.2	3.	2	41.3
CH ₃ COOC	₂ H 5	No	5	$\frac{23.0}{34.0}$ 10.0	$ \begin{array}{r} 33.4 \\ 29.0 \\ 24.0 \end{array} $	3.3		11.0	20.4 37.0 35.0	8	- 5 -	2.1

TABLE IV								
Gas	PHASE	PHOTOL	YSIS	OF	ESTERS			

*Experiments carried out with Corning filter 9863.

 $\dagger Experiment \ carried \ out \ at \ I_{rel} = 0.084.$

was kept the same for all experiments done with mercury arc *a*. Except for runs 69, 76, and 77, the incident intensity has been kept constant for the runs performed with lamp *b*.

It can be seen that at high temperatures and for unfiltered light, carbon monoxide is the main product for all the esters studied. Under these experimental conditions CO/CO_2 was found to be larger than 3. However, a Corning filter 9863 used in the photolysis of ethyl propionate and methyl *n*-butyrate brings this ratio close to unity, while the C_2H_4/CO_2 ratio stays practically unchanged.

The results indicate that the rates of formation of carbon monoxide and carbon dioxide decrease appreciably with decrease in temperature. In the photolysis of ethyl acetate C_2H_4/CO_2 increases gradually with diminishing temperature. At -23° C. ethylene accounts for about 70% of the volatile products.

Addition of iodine to ethyl acetate and ethyl propionate causes only a slight decrease of the ethylene yield, while all the other hydrocarbons are reduced to trace amounts. In the photolysis of the methyl propionate – iodine mixture, the ethylene yield amounted to about 10% of the ethylene yield found in the photolysis of ethyl acetate and ethyl propionate. No other hydrocarbons were formed.

Except for the iodine mixtures, ethers were found in all runs but were not determined quantitatively.

Discussion

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The results given in Tables III and IV indicate that the following intramolecular processes occur:

$$XCOOY + h\nu = XCOOH + alkene,$$
 VI

$$= CH_3COOY + alkene.$$
 VII

Y and X represent alkyl groups with respectively β - and γ -hydrogens.

In favor of process VI the following facts may be mentioned:

(a) At low temperatures ethylene is practically the only volatile product formed in both the gas and liquid phase photolysis of ethyl acetate. The other esters with a β -hydrogen in the alkoxy group have an alkene as major product. There is only slight variation with temperature of the rate of formation of the alkenes in the photolysis of these esters.

(b) In the liquid phase photolysis of ethyl acetate and ethyl propionate, the ethylene yields are independent of intensity.

(c) In the photolysis of the ethyl propionate – iodine mixture, ethylene is a major product. The decrease of the ethylene yield is probably due to the elimination of the following disproportionation reactions:

$$C_2H_5 + C_2H_5 = C_2H_4 + C_2H_6, \qquad [1]$$

$$C_{2}H_{5} + C_{2}H_{5}O = C_{2}H_{4} + C_{2}H_{5}OH.$$
[2]

The existence of process VII is substantiated by the presence of ethylene as an important product in both the gas and liquid phase photolysis of methyl *n*-butyrate. This process is analogous to the intramolecular rearrangement which was found to occur in the photolysis of ketones and aldehydes with γ -hydrogens in the alkyl groups (7).

The small ethylene and propylene yields in the liquid phase photolysis of methyl propionate and methyl *n*-butyrate indicate that process VIII does not occur to any appreciable extent,

$$XCOOY + h\nu = HCOOY + alkene.$$
 VIII

Also, a considerable fraction of the ethylene and propylene may be expected to be formed in disproportionation reactions between ethyl radicals and other radicals present.

However, the small amount of ethylene found in the gas phase photolysis of the methyl propionate – iodine mixture seems to indicate that process VIII might occur to some extent. In analogy with this, recent work (4) on the gas phase photolysis of propionaldehyde and *n*-butyraldehyde showed that at 2380 and 1870 Å, these two compounds decompose to some extent into formaldehyde and the corresponding alkene. It should be pointed out, however, that the iodine runs given in Table IV were performed with unfiltered light. This may have led to the formation of ethylene by a disproportionation between ethyl radicals and iodine atoms.

The low carbon monoxide yields in the low temperature gas and liquid phase photolysis of the acetates, the very small ether yields in the liquid phase photolysis of all the compounds studied, and the absence of ethers in the iodine experiments indicate that process IX does not occur,

$$XCOOY + h\nu = XOY + CO.$$
 IX

Dissociation Processes

The following primary processes will be considered briefly:

$$XCOOY + h\nu = XCO + OY,$$
 X

$$= X + COOY.$$
 XI

$$= XCOO + Y.$$
 XII

The fact that for unfiltered light, carbon monoxide is the main product in the high temperature gas phase photolysis of all the esters indicates that under these experimental conditions process X is the most important one. It can be seen that the carbon monoxide yield for the high temperature gas phase runs is practically the same for all compounds and does not show any appreciable variation with temperature.

The decrease of the rate of formation of carbon monoxide with diminishing temperatures in both gas and liquid phase photolysis proves that only a small fraction of the XCO radicals decompose by the excess energy carried over from the primary process. In the iodine runs the CO yields are fairly high. However, it is possible that at these low iodine pressures a fraction of the XCO radicals decompose before reacting with iodine.

It is not possible to decide from the gas phase runs if the CO_2 comes from the decomposition of COOY, XCOO, or from both radicals:

$$COOY = CO_2 + Y, \qquad a$$

$$XCOO = CO_2 + X. \qquad b$$

Both radicals are considered to be fairly unstable at room temperature. However, at low temperatures the CO_2 yield decreases appreciably in both the gas and liquid phase photolysis. Although no conclusive evidence can be given, the following facts indicate that reaction b and consequently process XI is the most likely one to occur:

1. The rates of formation of methane and carbon dioxide in the liquid phase photolysis of methyl propionate are equal at low intensities and at all temperatures. Recombination of methyl radicals with other radicals present in the system explains the somewhat lower methane yields in the high intensity runs. The results of the liquid phase photolysis of methyl *n*-butyrate lead to the same conclusion.

2. At low temperatures $(C_2H_6+2 C_4H_{10}+C_3H_8)/(CO+CO_2)$ is much larger than unity in the liquid phase photolysis of methyl propionate, while $C_3H_8 > (CO_2+CO)$ in the photolysis of methyl *n*-butyrate. This proves that there are COOY radicals formed which react with other species instead of decomposing.

However, the fact that the carbon dioxide yields are considerably lower for the acetates than for the propionates and butyrates remains unexplained. On the assumption that the CH_3CO_2 radicals are more stable than the $C_2H_5CO_2$ or $C_3H_7CO_2$ radicals, this observation would rather tend to favor process XII.

Cutting off short wavelengths in the gas phase photolysis of ethyl propionate and methyl *n*-butyrate reduces considerably the carbon monoxide yield as compared to the ethylene and carbon dioxide yields. This proves that process X occurs at shorter wavelengths than processes VI, VII, and XI.

After subtracting the amounts of ethylene formed in reaction [1], values of 0.66, 0.64, and 0.63 can be obtained for the ratio C_2H_4/CO_2 in the gas phase ethyl propionate runs a75, b76, and b77. The ethyl propionate – iodine run indicates that the contribution of reaction [2] is small. In the gas phase photolysis of methyl n-butyrate, values of 0.304 and 0.303 were obtained for the ratio C_2H_4/CO_2 in experiments b68 and b69. From the independence of the C_2H_4/CO_2 rates with change in wavelength, it may be concluded that processes VI and XI on the one side, and processes VII and XI on the other side, probably result from the same electronic level.

It can be seen that the value for the C_2H_4/CO_2 ratio in the liquid phase photolysis of ethyl propionate at 90° C. and low intensity, under which conditions the CO₂ yield attained a constant value, does not differ very much from the one found in the gas phase photolysis of this compound.

Summarizing the results, it may be concluded that processes I and X take place at short wavelengths, while the other intramolecular and dissociation processes occur at long wavelengths as well. In a later publication (3) it will be shown that addition of certain solvents leaves processes I and X unaffected, while the others are strongly suppressed.

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