THE GAS PHASE PHOTOLYSIS OF ACETIC AND PROPIONIC ANHYDRIDE[1]

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ABSTRACT

The photolysis of acetic anhydride has been reinvestigated in the temperature region from 30 to 195° C. Two primary processes occur with about equal probability:

$$(CH_3CO)_2O + h\nu = CH_3COO + CH_3CO,$$

$$(CH_3CO)_2O + h\nu = CH_2CO + CH_3COOH.$$

Analogous primary processes have been proposed for the photochemical decomposition of propionic anhydride.

The abstraction reaction:

$$CH_3 + (CH_3CO)_2O = CH_4 + CH_3COCOOCH_2$$

is of importance, and the results indicate that it has an activation energy of about 9.6 kcal./mole.

EXPERIMENTAL

Acetic and propionic anhydride were obtained from the Eastman Kodak Company (White Label) and thoroughly outgassed in the vacuum line.

The light source used in all experiments was a Hanovia (16A-13) SH type medium pressure lamp. The intensity was varied by means of gratings; no other filters were used in this work.

The gas phase photolysis was carried out in a cylindrical quartz cell about 10 cm. long (180 cm.^{3}). Pressures were measured by means of a U-tube mercury manometer which also served to isolate the cell from the remainder of the apparatus. Since the vapor pressure of acetic anhydride was only about 0.6 cm. at 25° C., the external parts of the reaction system were electrically heated.

The analysis system consisted of three traps, a low temperature fractionating column, McLeod gauge, Toepler pump, and gas burette.

In the course of an analysis the CO–CH_4 fraction was removed at liquid nitrogen temperature and passed over hot (240° C.) copper oxide. The C_2 fraction was taken off at -170° C. C_2H_4 was determined by hydrogenation over a Ni catalyst (8). A fraction coming over at -140° C. was on a few occasions analyzed by a mass spectrometer and consisted mainly of CO_2 and CH_2CO. It was found possible to determine ketene by bringing the fraction over a Ni catalyst (150° C.) in the presence of hydrogen. While carbon dioxide did not react, ketene broke down to methane, carbon monoxide, and small quantities of ethane. The amount of carbon dioxide originally present could be determined by bringing the whole mixture over ascarite. CH_3CHCO was determined by bringing the C_4H_{10}–CH_3CHCO fraction, removed at -110° C., over ascarite. The amount of conversion of acetic and propionic anhydride was kept below 5%.

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RESULTS AND DISCUSSION

Acetic Anhydride

Table I includes the results of runs conducted in the gas phase at temperatures ranging from 30 to 195° C. The rates quoted are in the units cc. at NTP per min. Experiments 1 to 5 were performed at approximately constant incident light intensity and constant pressure. In the first three runs, the methane concentration was too small to be measured accurately. Although there is some scattering of the results, it can be seen that the ketene and carbon dioxide concentrations are independent of temperature, while the rate of the carbon monoxide and ethane production decreases sharply in the lower temperature region. These results can be accounted for by postulating that two primary processes occur with about equal probability:

TABLE I

GAS PHASE PHOTOLYSIS OF ACETIC ANHYDRIDE

Run	Temp., ° C.	Pressure, cm.	Rate, cc./min. × 10^4					$R_M/R_E^{1/2} \times 10^{13}$, cm.$^{3/2}$ molecule$^{-1/2}$ sec.$^{-1/2}$	$(C_2H_6+\frac{1}{2}CH_4)/CO$
			CO	CO_2	CH_2CO	C_2H_6	CH_4		
1	30	0.68	5.30	21.0	19.2	7.80			
2	63	0.67	10.3	22.3	22.0	11.0			
3	93	0.72	14.0	21.6	21.4	15.1			
4	139	0.75	21.8	22.0	21.3	22.2	0.76		
5	165	0.73	23.0	24.5	22.1	18.6	1.40		
6	107	3.75	58.0	60.0	55.0	57.0	2.30	1.54	1.001
7	125	4.20	64.0	66.0	63.0	62.5	4.55	2.80	1.02
8	126	4.20	9.50	9.45	8.95	7.61	1.74	3.05	0.89
9	143	4.25	70.5	71.0	68.2	64.0	7.80	4.87	0.96
10	165	4.30	92.0	97.0	96.5	85.0	13.8	7.82	0.995
11	166	4.30	11.2	12.0	11.0	7.05	4.08	8.00	0.812
12	165	4.30	1.51	1.40	1.20	0.51	1.11	8.15	0.71
13	196	5.00	97.5	96.8	280.0	48.7	24.6	17.1	0.626

$$(CH_3CO)_2O + h\nu = CH_3COO + CH_3CO, \qquad [Ia]$$

$$(CH_3CO)_2O + h\nu = CH_2CO + CH_3COOH. \qquad [IIa]$$

It is known (2, 7) that in the gas phase, for comparable systems, the CH_3COO radicals decompose easily at low temperature. This explains the constancy of the CO_2 concentration over the whole temperature region. The decrease of the CO concentration with decrease in temperature is due to the higher stability of CH_3CO at low temperatures. The fact that at these temperatures the C_2H_6 concentration is larger than the CO concentration indicates that some biacetyl is formed by the recombination of two acetyl radicals. At higher temperatures the CO concentration is equal to the CO_2 concentration as it should be if [I*a*] and [II*a*] were the only two primary processes occurring.

From these results it is not possible to decide if the process

$$(CH_3CO)_2O + h\nu = CH_3COCOO + CH_3 \qquad [III]$$

followed by the thermal decomposition of CH_3COCOO into CH_3CO and CO_2 is of any importance. Analogy with the photochemical decomposition of simple alkyl esters (2) favors, however, process [I*a*].

In a recent publication (4) on the photochemical decomposition of acetic anhydride, no ketene was observed. Instead, a value of about two was found for the ratio CO_2/CO. This can be explained by the fact that the CH_2CO–CO_2 fraction was brought over ascarite, which absorbs both compounds. This procedure led the authors to the erroneous conclusion that the fraction consisted entirely of CO_2.

Incidentally, it may be mentioned that runs done at high conversion (results not included in this paper) always lead to much higher values for the CO/CH_2CO ratio, while at the same time increasing amounts of ethylene are found in the C_2 fraction. This can be accounted for by the photochemical decomposition of ketene, which is of importance at higher conversions.

For runs performed at temperatures above 170° C. large quantities of ketene were detected. Run 13 at 196° C. is given as an example in Table I. There is no doubt that the excess ketene is formed by the thermal decomposition of acetic anhydride. A few dark runs performed at temperatures up to 300° C. showed no evidence of any radicals formed during the thermal decomposition, while the only gaseous product found was ketene. This is in accordance with the findings of Szwarc and Murawski (9), who studied the pyrolysis of acetic anhydride by the toluene carrier technique and concluded that the decomposition occurs by a molecular rearrangement:

$$(CH_3CO)_2O = CH_2CO + CH_3COOH, \qquad E = 34.5 \text{ kcal./mole.}$$

In order to obtain information about the formation of CH_4 and C_2H_6, a few runs (6 to 13) were performed at higher pressures and varying intensities. If both compounds are only formed by reactions 1 and 2,

$$CH_3 + (CH_3CO)_2O = CH_4 + CH_3COCOOCH_2, \qquad [1]$$

$$CH_3 + CH_3 = C_2H_6, \qquad [2]$$

the following relationship exists:

$$k_1/k_2^{\frac{1}{2}} = R_M/R_E^{\frac{1}{2}}\,(A)\ .$$

R_M and R_E represent respectively the rate of formation of methane and ethane. (A) indicates the concentration of acetic anhydride.

Values of $R_M/R_E^{\frac{1}{2}}$ (A) are given in Table I. Runs 10, 11, and 12 indicate that a 70-fold variation of the intensity affects this ratio only to a small extent. This may be considered as evidence for the fact that CH_4 and C_2H_6 are only produced by reactions 1 and 2. In Fig. 1, $k_1/k_2^{\frac{1}{2}}$ has been plotted against $1/T$. A value of 9.6 kcal./mole can be obtained from the slope of the Arrhenius plot. This value is comparable to the activation energy found for the abstraction of a H-atom from acetone, although the steric factor is about two times lower.

The values of $(\frac{1}{2}CH_4 + C_2H_6)/CO$ for the high pressure runs have been given in the last column of Table I. This ratio should be equal to one if the CH_3 radicals are only consumed by reactions 1 and 2. Values close to one were obtained for the high intensity runs 6, 7, 9, and 10, while lower values were found for the other runs. This is mainly due to the photochemical decomposition of ketene and the occurrence of the recombination reaction:

$$CH_3 + CH_3COCOOH_2 = CH_3COCOOC_2H_5.$$

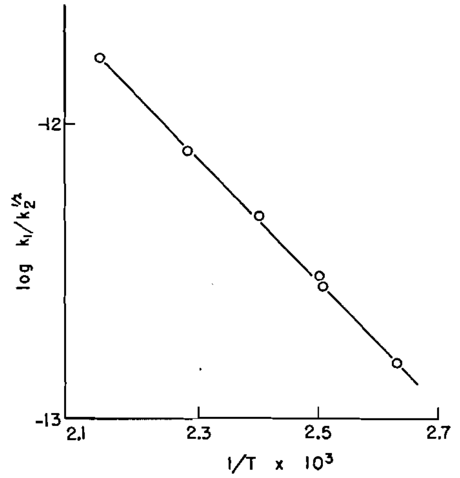

FIG. 1.

Propionic Anhydride

For comparison, the photochemical decomposition of propionic anhydride has been investigated very briefly. The average values for the rates of the reaction products of three runs performed at 115° C., 1.55 cm. pressure, and constant intensity are given in Table II.

TABLE II

GAS PHASE PHOTOLYSIS OF PROPIONIC ANHYDRIDE (RATE, CC./MIN. $\times 10^4$)
Temp., 115° C. Pressure, 1.55 cm.

CO	24.0	C_2H_4	2.8	CH_3CHCO	17.6
CO_2	23.8	C_2H_6	6.5	C_4H_{10}	17.0

These results point to primary processes analogous to those proposed for acetic anhydride:

$$(C_2H_5CO)_2O + h\nu = C_2H_5CO + C_2H_5COO, \qquad [Ib]$$

$$(C_2H_5CO)_2O + h\nu = CH_3CHO + C_2H_5COOH. \qquad [IIb]$$

The fact that the CO and CO_2 rates are equal indicates that under these conditions C_2H_5CO and C_2H_5COO are entirely decomposed. Ethylene and butane are mainly produced by the disproportionation and combination of the ethyl radicals.

CONCLUSION

Primary processes [II*a*] and [II*b*] as well as the thermal decomposition of acetic and propionic anhydride probably involve a "cyclic hydrogen bridge" as proposed for the thermal decomposition of esters (6). Pyrolysis studies of esters with a β-hydrogen in the alkyl group (1, 3) have indeed shown that these compounds decompose into the corresponding acid and alkene. Recently (2) it has been found that absorption of a photon by these molecules may also lead to a direct decomposition into an acid and an alkene.

The thermal and photochemical decomposition of certain molecules following the same pattern can be explained (5) by considering the primary process as an internal conversion directly followed by a molecular elimination. This internal conversion probably produces a "hot" molecule in the electronic ground state, which may be expected to behave like a normal thermally excited molecule.

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