The Thermal Decomposition of Propanoic and 2-Methylpropanoic Anhydrides in the Gas Phase

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The homogeneous gas-phase thermal decompositions of propanoic anhydride and 2-methylpropanoic anhydride have been studied over the temperature ranges 220—294 and 246—283 °C respectively. Both reactions obey first-order kinetics, are unaffected by chain inhibitors and give the parent acid and methylketen or dimethylketen respectively as sole products.

Kinetic parameters are given by the equations $k/\mathrm{s}^{-1} = 10^{11.38} \exp(-140\ 400\ \mathrm{J\ mol^{-1}}/RT)$ in the case of propanoic anhydride, and $k/\mathrm{s}^{-1} = 10^{11.81} \exp(-151\ 500\ \mathrm{J\ mol^{-1}}/RT)$ for 2-methylpropanoic anhydride. Equilibrium constants were also measured in the propanoic anhydride system and gave $\Delta H^\circ = 95\ 095\ \mathrm{J\ mol^{-1}}$ and $\Delta S^\circ = 132.2\ \mathrm{J\ K^{-1}\ mol^{-1}}$ in the direction of decomposition. The effect of alkyl substitution on the transition states for anhydride decomposition is discussed.

THE gas-phase thermal decomposition of acetic anhydride has been studied in static and flow apparatus,[1] and found to be homogeneous and unimolecular giving acetic acid and keten as sole products. The decomposition is analogous to those of carboxylic esters and, like them, may proceed through a six-centre transition state. In this paper the results of studies on higher symmetric anhydrides, namely propanoic and 2-methylpropanoic, are reported. These prove to behave similarly to acetic anhydride and to show a trend of decreasing decomposition rate with increasing alkyl substitution.

EXPERIMENTAL

Apparatus and Procedure.—The static apparatus used was of conventional design with heated dead spaces and a glass spiral manometer. The flow apparatus has been described previously,[2] packed and unpacked vessels had surface-to-volume ratios of 11.5 and 1.3 cm^{-1}. Contact times were varied by changing capillary flow restrictors. Temperatures were electronically controlled to within ±0.2 °C and measured by calibrated chromel–alumel thermocouples. In some cases vessels were carbon-coated before use by pyrolysing isobutene in them several times at 550 °C. Once the stoicheiometry of reaction was established rates were measured by pressure change in the static system and by measurement of the keten produced in the flow work.

In both anhydrides the only decomposition products detected were the appropriate acid and keten, and there was no sign of further decomposition of the ketens, in that no CO, CO_2, or hydrocarbons were present. However, in measuring equilibrium constants with higher pressures of propanoic anhydride, disturbance due to polymerisation of methylketen became apparent. Methylketen was separated from propanoic acid and unchanged propanoic anhydride by passing the vessel contents through a packed trap at −78 °C, and was measured in a gas burette and by i.r. absorption at 2 150 cm^{-1}. The same procedure was used with dimethylketen except that the packed trap was maintained at −38 °C.

Materials.—Methylketen was prepared by the pyrolysis of propanoic anhydride in a flow system at 425 °C, and dimethylketen by the pyrolysis of 2-methylpropanoic anhydride at 475 °C. Both ketens were purified by low-temperature fractionation and stored under vacuum at −183 °C. Methylketen is especially prone to polymerisation on warming and was redistilled at −95 °C before use. Propanoic acid, 2-methylpropanoic acid, and their anhydrides ($\geqslant 99\%$) obtained from Aldrich Chemical Co. were redistilled *in vacuo*.

RESULTS AND DISCUSSION

The kinetics of thermal decomposition of propanoic anhydride have been studied in a flow system between 256 and 375 °C and in a static apparatus between 220 and 294 °C, the pressure range being 10—100 Torr in both cases (1 Torr = 133.28 N m^{-2}). Equilibrium constants were also measured in the static system between 225 and 294 °C. The kinetics of decomposition of 2-methylpropanoic anhydride have also been studied over the temperature range 246—283 °C in static apparatus. The lower limit of temperature in this anhydride was imposed by the relatively small degree of dissociation at equilibrium.

The results of stoicheiometry measurements, and the absence of products other than propanoic acid and methylketen, and 2-methylpropanoic acid and dimethylketen respectively show that the thermal decompositions are correctly represented by equations (1) and (2).

$$(\mathrm{MeCH_2{\cdot}CO})_2\mathrm{O} \longrightarrow \mathrm{MeCH_2{\cdot}CO_2H} + \mathrm{MeCH{:}C{:}O} \quad (1)$$

$$(\mathrm{Me_2CH{\cdot}CO})_2\mathrm{O} \longrightarrow \mathrm{Me_2CH{\cdot}CO_2H} + \mathrm{Me_2C{:}C{:}O} \quad (2)$$

Kinetics.—The propanoic anhydride decomposition was homogeneous giving the same rates in both packed and unpacked vessels (see Figure). The carbon-coating procedure was not essential here since after one or two runs both clean packed and unpacked vessels gave the same results as coated ones. First-order kinetics were obeyed in both static and flow systems, and first-order rate constants were independent of pressure in the range 10—76 Torr. Addition of isobutene as chain inhibitor at three different temperatures had no effect on the rate of decomposition (see Figure). The Arrhenius equation for results in the static system is $k/\mathrm{s}^{-1} = 10^{11.38\pm0.32} \exp(-140\ 400 \pm 3\ 250\ \mathrm{J\ mol^{-1}}/RT)$ and $k/\mathrm{s}^{-1} = 10^{11.11\pm0.21} \exp(-138\ 300 \pm 2\ 300\ \mathrm{J\ mol^{-1}}/RT)$ for flow and static results together, where $R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$. It may be seen from these results and from the Figure that

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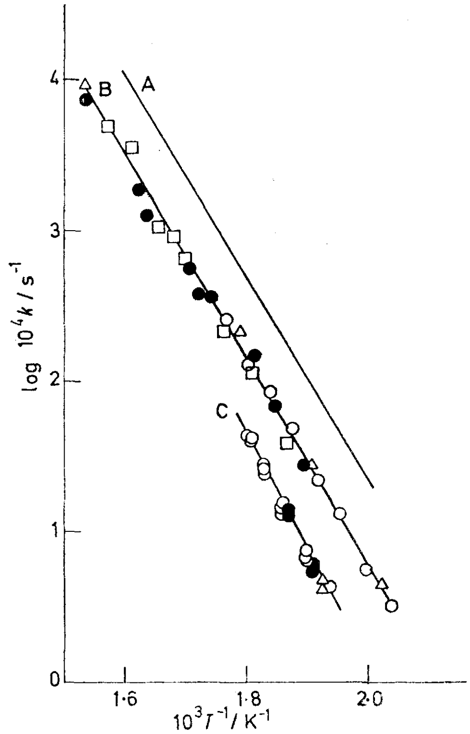
[1] M. Szwarc and J. Murawski, *Trans. Faraday Soc.*, 1951, **47**, 269; P. G. Blake and A. Speis, *J. Chem. Soc.* (*B*), 1971, 1877.

[2] P. G. Blake and G. E. Jackson, *J. Chem. Soc.* (*B*), 1969, 94.

essentially the same rates were obtained in flow and static apparatus.

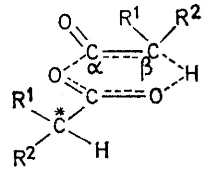
The decomposition of 2-methylpropanoic anhydride was also homogeneous, unaffected by isobutene (see Figure), and had a kinetic order of one. The Arrhenius equation, obtained from a least-squares treatment of 24 rate constants at six different temperatures, was $k/\mathrm{s}^{-1} = 10^{11.81\pm0.29} \exp(-151\,500 \pm 3\,040 \mathrm{\ J\ mol^{-1}}/RT)$.



Arrhenius plots for the thermal decomposition of anhydrides [A = $(\mathrm{MeCO})_2\mathrm{O}$ included for reference, B = $(\mathrm{MeCH_2{\cdot}CO})_2\mathrm{O}$, and C = $(\mathrm{Me_2CH{\cdot}CO})_2\mathrm{O}$]: (○) = static unpacked vessel, (□) flow unpacked vessel, (●) packed vessels, and (△) isobutene present.

Equilibria.—Equilibrium constants for propanoic anhydride decomposition were independent of pressure up to *ca*. 40 Torr. At higher pressures more erratic results were obtained and there were signs of polymerisation of methyl keten. Consequently, only results at pressures below 40 Torr were used. From the temperature dependence of K were obtained $\Delta H^\circ = 95\,050 \pm 4\,036$ J mol^{-1} and $\Delta S^\circ = 132.2 \pm 7.6$ J K^{-1} mol^{-1} at 532 K and 1 atm. These values may be compared with those of acetic anhydride ($\Delta H^\circ = 89.0 \pm 3.5$ kJ mol^{-1}, $\Delta S^\circ = 131.7 \pm 7.0$ J K^{-1} mol^{-1}). The equilibrium constant for acetic anhydride decomposition is approximately four times that for propanoic anhydride at experimental temperatures due apparently to the enthalpy difference. The trend of increasing thermodynamic stability of anhydrides, with respect to their decomposition products, with alkyl substitution is supported by comparing the equilibrium constants for the above, extrapolated to 155 °C, with a value obtained for 2-methylpropanoic anhydride from the rate constants of the forward and back reactions. The values of 10^2K/Torr are acetic 6.3, propanoic 1.6, and 2-methylpropanoic anhydride 0.86.

Mechanism.—Both decompositions are homogeneous and unimolecular, and the values of the A factors and general resemblance to acetic anhydride make it probable that, like it, they decompose *via* a six-centre transition state. The effect that changing the alkyl group has on the rate may be discussed in terms of this model.



The Table gives the relevant data for the three anhydrides using the static results. It is seen that the decrease in rate constant with increasing alkyl substitution is quite marked, even when the reaction path degeneracy ratios of 3 : 2 : 1 are taken into account, and is reflected in the increasing activation energy. This may be caused by the effect of the electron-donating methyl groups (Taft $\sigma^*_{\mathrm{H}} = +0.49$, $\sigma^*_{\mathrm{Me}} = 0.00$) in destabilising the partial negative charge at the carbon atom in the transition state. Any effect of methyl substitution at the asterisked carbon 2 is likely to be small but by analogy with ester decompositions, will tend to reduce the rate.[3]

Rate data for acetic, propanoic, and 2-methylpropanoic anhydrides

Anhydride	E_a/ kJ mol^{-1}	log (A/s^{-1})	10^4k (500 K)/s^{-1}	Relative k per βH
Acetic	134.7	11.27	15.5	5.4
Propanoic	140.4	11.38	5.62	3.0
2-Methylpropanoic	151.5	11.81	0.95	1.0

Transition states in ester decompositions are closely similar to those proposed here. β-Substitution in esters gives rise to some anomalous results[3] but, in general, substituents which increase electron density at the β-carbon reduce the rate.[4] However the effects are much smaller than those observed here and the weak effect in esters has been attributed in part to the relatively small charge on the partial carbanion developed at the β-position in the transition state.[5] The greater effect in anhydrides may be due to the presence of a larger negative charge here. The charge at the β-position in the product keten has been calculated to be as much as -0.53 [6]e, although lower estimates have also been made.[7] Since the activation energy of the back reaction is small[8] the charge distribution in this part of the transition state may reflect that in ketens to some extent and thus be significantly larger than in the ester case.

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[3] R. Taylor, *J.C.S. Perkin II*, 1975, 1025.

[4] G. G. Smith, F. D. Bagley, and R. Taylor, *J. Amer. Chem. Soc.*, 1961, **83**, 3647.

[5] R. Taylor, *J.C.S. Perkin II*, 1972, 165.

[6] A. Hopkinson, *J.C.S. Perkin II*, 1973, 795.

[7] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1970, 1016.

[8] P. G. Blake and H. H. Davies, *J. Chem. Soc.* (*B*), 1971, 1727.