Reactions of Keten. Part V.† Gas-phase Reactions with Carboxylic Acids. Effect of Alkyl Substituents

By **Peter G. Blake** * and **Mohammad Baghal Vayjooee**, Chemistry Department, University College, Cardiff CF1 1XL

Keten reacts homogeneously in the gas phase with carboxylic acids between 95 and 216 °C to give anhydrides in a reaction which is first order in keten and in acid monomer. Rates of reaction increase with increasing alkyl substitution and branching in the acid. This increase does not correlate well with the pK_a values of the acids but runs parallel to their gas-phase acidities.

KETEN reacts with acetic acid homogeneously in the gas phase to give acetic anhydride.[1] This bimolecular reaction is the reverse of the unimolecular decomposition of acetic anhydride,[2] both reactions proceeding through the same six-centre transition state. In the work reported here the kinetics of reaction of keten with several other carboxylic acids have been studied, first to see whether these reactions are also well behaved and, secondly, to examine the effect that changing the alkyl group of the acid has on the rate. The latter is of interest since any connection between such rates and acid strength throws light on the nature of the transition state, and the recent work on gas-phase acidities [3] enables the intrinsic effects of alkyl substitution to be distinguished from those due to solvation differences.

EXPERIMENTAL

Apparatus and Procedure.—The static apparatus and procedures used have been described previously.[1] Packed and unpacked vessels were carbon-coated before use by pyrolysing isobutene in them at 550 °C. Premixing of reactants is not feasible in this system [1] and the use of a normal type of packed vessel containing large numbers of narrow tubes causes mixing problems which result in a slightly sigmoid initial rate curve. To overcome this a redesigned packed vessel was used which had fluted walls and contained a few larger bore tubes with small holes along their length. The surface to volume ratio of this vessel was three times that of the unpacked vessel and rate curves obtained with it were of normal shape.

The only reaction product detected was the appropriate anhydride which was normally unsymmetrical. The latter may disproportionate to give a mixture of symmetrical anhydrides; no evidence of this occurrence was seen, but to avoid any possible complications on this count, rate constants were measured from initial rates only. Keten was separated from unchanged acid and anhydride product by passing the vessel contents through a trap at −78 °C, and was measured in a gas burette and by i.r. spectroscopy.

Materials.—Keten was prepared from acetic anhydride and purified and stored as described previously.[1] The carboxylic acids used were of better than 99% purity, except for 3,3-dimethylbutanoic acid, which was 98%. All were degassed before use.

RESULTS AND DISCUSSION

The reactions between keten and propanoic, 2-methylpropanoic, 2,2-dimethylpropanoic, acetic, butanoic, and 3,3-dimethylbutanoic acids have been studied in the gas phase in the temperature range 95—216 °C using keten pressures from 7—50 Torr and acid pressures from 8—100 Torr (1 Torr $\equiv$ 133.28 N m^{-2}). Some stoicheiometric measurements comparing pressure change with keten reacted are recorded in Table 1. Those for acetic acid have already been reported.[1] The results and the fact that anhydride was the only product detected show that in each case the reaction involves one molecule of keten reacting with one of acid to give anhydride.

TABLE 1

Relation between pressure change and keten reacted during the addition to carboxylic acids

T/°C	Acid	Δp/Torr	Δp(keten)/Torr
156	Propanoic	6.9	6.9
		23.6	24.4
		42.4	43.5
		24.4	23.6
172	Propanoic	24.9	23.9
186	Propanoic	24.9	23.5
154	2,2-Dimethylpropanoic	11.9	12.0
170	2,2-Dimethylpropanoic	11.8	11.8

Kinetics.—All the reactions are homogeneous in carbon-coated vessels, rates in packed and unpacked vessels being the same within experimental error. The order of reaction with respect to keten is unity at all temperatures measured (Table 2). The order in acid is also one but at and below the lowest temperatures used for kinetic runs the pressure of acid dimer may become appreciable.[1] The order in acetic acid was measured at 95 °C and found to be 0.73 ± 0.06 in total acid pressure and 0.99 ± 0.10 in acid monomer. Keten seems therefore to react with monomer molecules rather than dimer. It may be noted that $\Delta H°$ for dissociation of dimer is, at 60 kJ mol^{-1}, greater than the activation energy of the acid–keten reaction. All reactions are thus second order overall, first in keten and first in acid monomer, which under most conditions used here is almost the same as total acid present.

Rates of reaction increase with increasing alkyl substitution near the carboxy-group (Table 3). Activation

---

† Part IV, P. G. Blake and A. Speis, *J.C.S. Perkin II*, 1974, 1879.

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

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

[3] R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, 1973, **95**, 4050.

parameters were measured for acetic, propanoic, and 2,2-dimethylpropanoic acids and are shown in Table 4.

TABLE 2

Reactions of carboxylic acids with keten. Orders in keten and acid

T/°C	Acid	p_0(acid)/ Torr	p_0(keten)/ Torr	10^5k/ $Torr^{-1}$ s^{-1}
(*a*) Order in keten				
156	Propanoic	50	8.3	4.10
		50	25.5	3.91
		50	50.7	4.31
170	2,2-Dimethylpropanoic	12.5	8.1	11.5
		12.5	12.9	13.0
		12.5	25.0	14.1
		12.5	38.6	11.7
156	Acetic	50	7.5	3.94
		50	25.9	4.24
		50	50.8	3.93
(*b*) Order in acid				
156	Propanoic	7.3	50	4.03
		25.2	50	3.96
		49.9	50	4.13
170	2,2-Dimethylpropanoic	7.6	13	12.8
		12.6	13	13.1
		18.1	13	13.2
		30.5	13	11.9

Differences in E_a and A between propanoic and acetic acids are about the size of the standard deviations but the results for 2,2-dimethylpropanoic acid indicate that the increase in rate is due to a lower activation energy. All the reactions studied are the reverse of unimolecular decompositions of anhydrides which, from their natures and A factors, are taken to involve a six-centre transition state. This state will consequently be involved here and altering the R group should have little effect on the A factor.

TABLE 3

Relative rates of reaction of carboxylic acids with keten at 155 °C

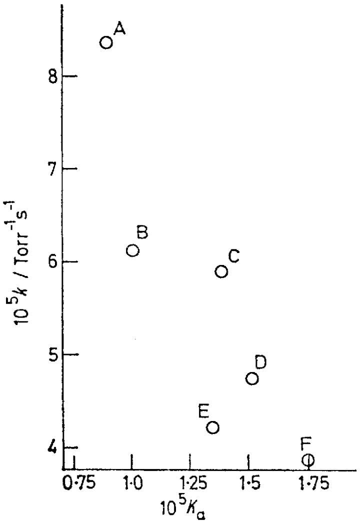
Acid	10^5k/$Torr^{-1}$ s^{-1}
Acetic	3.83
Propanoic	4.21
Butanoic	4.73
2-Methylpropanoic	5.88
3,3-Dimethylbutanoic	6.11
2,2-Dimethylpropanoic	8.35

TABLE 4

Activation energies and A factors for reactions of carboxylic acids with keten

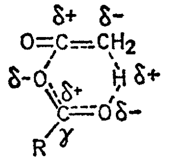
Acid	E_a/kJ mol^{-1}	log (A/l mol^{-1} s^{-1})
Acetic	49.91 ± 0.95	6.10 ± 0.11
Propanoic	50.73 ± 0.75	6.24 ± 0.09
2,2-Dimethylpropanoic	47.84 ± 0.83	6.19 ± 0.10

If rate is plotted against acid strength in water as in the Figure the correlation is poor, although the broad trend is for rate to decrease with increasing strength. It is more appropriate to compare rate with intrinsic acidity measured in the gas phase, free from the complication of hydration effects, and some data are available. Kebarle[3] has shown that intrinsic acidity increases in the order acetic, propanoic, and butanoic acids, that is with increasing size and therefore polarisability of alkyl group. In addition Brauman's work[4] on gas-phase acidities of alcohols, which also includes branched alkylation, gives the sequence of increasing acidity of methyl, ethyl, isopropyl, t-butyl, neopentyl. Thus the more polarisable the alkyl group the greater is the stabilisation of the anion and thus the acidity. The order of increasing intrinsic acidity for the acids used here would therefore seem to be acetic, propanoic, n-butanoic, 2-methylpropanoic, 3,3-dimethylbutanoic, and 2,2-dimethylpropanoic, with some doubt about the relative positions of the last two. Brauman found neopentyl alcohol to be more acidic than t-butyl alcohol whereas it might be expected that the effect of the t-butyl group would be attenuated by the intervening methylene group.



Plot of rate of reaction of carboxylic acid with keten against acid strength in aqueous solution: A, $Me_3C{\cdot}CO_2H$; B, $Me_3C{\cdot}CH_2{\cdot}CO_2H$; C, $Me_2CH{\cdot}CO_2H$; D, $Me(CH_2)_2{\cdot}CO_2H$; E, $Et{\cdot}CO_2H$; F, $Me{\cdot}CO_2H$

It may be seen from Table 3 that the rate of reaction of an acid with keten increases with increasing gas-phase acidity, and the increasing ability of the alkyl groups to stabilise anions parallels their stabilisation of the transition state. This fact suggests that the transition state here is fairly polar with stabilisation of the partial negative charges on the acid oxygen atoms by the alkyl



J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, 1968, **90**, 6561.

groups. The situation resembles the decomposition of esters where electron-withdrawing groups at the γ-carbon increase the rate and the polarity of the transition state.[5] There is also some positive correlation between rate of ester decomposition and the pK_a of the parent acid.[6] An alternative explanation of the trend in rate, suggested by a referee, is that the larger alkyl groups increase the inductive electronic repulsion towards the carboxylic oxygen, and that this facilitates the rate-controlling attack of this oxygen on the carbonyl carbon atom of keten. In either case a fairly polar transition state is involved.

The rate of addition of carboxylic acids to dimethylketen in ether solution is also first order in each reactant [7] and rates are known at 25 °C for two of the acids used in this work, namely 2,2-dimethylpropanoic and 2-methylpropanoic acids. The ratio of the rates in solution is almost identical with that in the gas phase, $k(\mathrm{Me_3C\cdot CO_2H})/k(\mathrm{Me_2CH\cdot CO_2H})$ being 1.44 and 1.42 respectively.

[5/2175 *Received*, 10*th November*, 1975]

---

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

[6] E. U. Emovon, *J. Chem. Soc.*, 1963, 1246.

[7] J. M. Briody, P. J. Lillford, and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 885.