Reactions of Keten. Part VI.[1] Kinetics of Gas-phase Reactions with Halogenated and Unsaturated Acids, Formic Acid, and Acetic [^{2}H]Acid

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

The homogeneous bimolecular reactions of keten with carboxylic acids in the gas phase have been studied for halogenated and unsaturated acids, and formic acid. Rates increase proportionately to the increase in intrinsic strength of the acid, except for the very strongest acids which react more rapidly than expected. A large deuterium isotope effect is found at the acid hydrogen atom. Reactions with dimethylketen are slower than with keten by a factor of 2.4. A concerted but non-synchronous mechanism involving a six-centre transition state is proposed. The results and mechanism are compared with those for ester decomposition and for the reactions of dimethylketen with acids in solution.

KETEN adds to carboxylic acids in the gas phase to give anhydrides in a reaction which is homogeneous, molecular, and first-order in each reactant.[2] Rates increase with increasing size and polarisability of the acid's alkyl group, which is also the order of increasing acidity in the gas phase,[1] although not in aqueous solution. Larger alkyl groups stabilise both the acid anion and the transition state in reaction with keten, which suggests that the latter is moderately polar in character. In the work reported here the effect of the acid on the rate of reaction with keten has been studied for eight halogenated and four unsaturated acids, and activation parameters have been measured for one representative of each group. In addition the effect of isotopic substitution at the carboxylic acid hydrogen atom has been examined, and the untypical reaction of keten with formic acid studied.

EXPERIMENTAL

The apparatus and general procedures used have been described previously.[2] Acids used were of greater than 98% purity except for 3,3-dimethylpropenoic acid (97%) which was further purified by fractional crystallisation from the melt, and thiopropanoic acid (94%), which was fractionally redistilled *in vacuo*. The latter acid was also redistilled immediately before use in order to remove the hydrogen sulphide which accumulates in the liquid. Runs with benzoic acid were restricted to acid pressures of 5 Torr in order to avoid errors caused by low volatility. Thermal decomposition of propynoic acid was negligible under the conditions used for reaction with keten.

Keten was prepared by pyrolysis of acetic anhydride at 400 °C and dimethylketen from 2-methylpropanoic anhydride at 475 °C.

RESULTS AND DISCUSSION

The reactions of keten with carboxylic acids already studied have been found to be homogeneous, molecular, and of the first-order in keten and in acid, and to give anhydride as the only product. Rates were measured in both packed and unpacked carbon-coated vessels for the three fluorinated acetic acids, mono- and di-chloroacetic acids, 2- and 3-chloropropanoic acids, propenoic, and propynoic acids in this work and, in all cases, were unaffected by surface-to-volume ratio. Reaction stoicheiometries were checked with propenoic, difluoroacetic, and acetic [^{2}H]acids by comparing pressure change with keten consumed, and these were again equivalent within experimental error. Orders of reaction in keten and in acid were measured for propenoic acid by plotting log (initial rate) against log (initial pressure), varying the initial pressure of one reactant while the other remained constant. The order in keten was 0.96 ± 0.05, that in acid 1.06 ± 0.10. Except in the case of formic acid (see below) the only product found was the appropriate anhydride.

Second-order rate constants were calculated from initial rates or from integrated second-order plots. The methods agreed well except for the fastest reactions, when second-order plots were preferred. Arrhenius constants were measured for acetic [^{2}H]acid, propenoic acid, and 2-chloropropanoic acid over the temperature range 108—216 °C using at least 12 rate constants for each plot. The results are given in Table 1 along with those for acetic acid for comparison. Rate constants for all other acid–keten reactions were measured at 155 °C (except formic acid) and the mean values for all reactions at this temperature are listed in Table 2.

TABLE 1

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})
$MeCO_2D$	55.82 ± 0.60	6.25 ± 0.07
$MeCO_2H$	49.91 ± 0.95	6.10 ± 0.11
$CH_2{:}CH{\cdot}CO_2H$	49.59 ± 0.88	6.28 ± 0.11
$MeCHCl{\cdot}CO_2H$	41.37 ± 1.76	5.73 ± 0.21

TABLE 2

Second-order rate constants at 155 °C

Acid	10^5k/ Torr^{-1} s^{-1}	Acid	10^5k/ Torr^{-1} s^{-1}
$MeCO_2D$	1.04	$CH{\vdots}C{\cdot}CO_2H$	15.9
$MeCO_2H$	3.83	$MeCHCl{\cdot}CO_2H$	18.0
$CH_2{:}CH{\cdot}CO_2H$	6.35	$CH_2Cl{\cdot}CO_2H$	20.7
$Me_2C{:}CH{\cdot}CO_2H$	6.65	$MeCH_2{\cdot}COSH$	30.6
HCO_2H	8.98	$CF_2H{\cdot}CO_2H$	40.4
$CH_2Cl{\cdot}CH_2{\cdot}CO_2H$	9.85	$CCl_2H{\cdot}CO_2H$	158
$PhCO_2H$	12.2	$CF_3{\cdot}CO_2H$	316
$CH_2F{\cdot}CO_2H$	13.2	$CCl_3{\cdot}CO_2H$	>500

Reaction with Formic Acid.—When keten reacts with formic acid at 155 °C the pressure at first falls but then rises again to near the initial value. The final products of reaction are carbon monoxide and acetic acid (or

---

[1] P. G. Blake and M. H. B. Vayjooee, *J.C.S. Perkin II*, 1976, 988.

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

acetic anhydride if keten is in excess). The initial product is acetic formic anhydride, which was identified by means of its i.r. absorptions at 1 045, 1 200, 1 380, 1 780, and 1 810 cm^{-1} (*ca.* 10—15 cm^{-1} above the values published for a solution in chloroform [3]). The course of the reaction is seen more clearly at lower temperatures. For example, when keten and formic acid are mixed in an i.r. gas cell at 25 °C and the spectrum is scanned repeatedly, acetic formic anhydride absorbances increase at first as formic acid is consumed. After *ca.* 20 min acetic anhydride and/or acetic acid (depending on the keten-to-formic acid ratio) begin to appear. Eventually the amount of mixed anhydride begins to fall, acetic acid and anhydride are still increasing and carbon monoxide is detectable.

Results of this sort and the work of Van Es and Stevens [3] indicate that the reactions (1)—(6) take place

$$\mathrm{CH_2{:}CO + HCO_2H \longrightarrow MeCO{\cdot}O{\cdot}COH} \qquad (1)$$

$$\mathrm{2MeCO{\cdot}O{\cdot}COH \rightleftharpoons (MeCO)_2O + (HCO)_2O} \qquad (2)$$

$$\mathrm{MeCO{\cdot}O{\cdot}COH + HCO_2H \rightleftharpoons (HCO)_2O + MeCO_2H} \qquad (3)$$

$$\mathrm{(HCO)_2O \longrightarrow HCO_2H + CO} \qquad (4)$$

$$\mathrm{CH_2{:}CO + MeCO_2H \longrightarrow (MeCO)_2O} \qquad (5)$$

$$\mathrm{MeCO{\cdot}O{\cdot}COH + MeCO_2H \rightleftharpoons (MeCO)_2O + HCO_2H} \qquad (6)$$

when keten reacts with formic acid. The main aim here was to obtain an estimate for the rate constant of reaction (1) at 155 °C to compare with those for other acids. In steps (1) and (5) pressure change equals keten consumed; in (4) pressure change equals CO formed, and thus overall,

$$\Delta p = \Delta\text{keten} + \text{CO}$$

In the early stages reaction (5) is negligible compared with (1), and therefore the rate of loss of keten in (1) is equal to the rate of pressure change minus the rate of formation of CO. Rates at 155 °C could not be measured accurately in this way, but four values obtained at 117 °C agreed within $\pm 10\%$. The rate constant at 155 °C was then estimated by multiplying the 117 °C value by k (155 °C)/k (117 °C) for 2,2-dimethylpropanoic acid, which has a very similar rate constant. This procedure assumes that the two acids have similar A factors, which is true for all the acids whose Arrhenius factors have been determined. Clearly there is substantially greater uncertainty in the formic acid value than for the other acids.

Isotope Effect.—Substituting the acidic hydrogen atom in acetic acid by deuterium lowers the rate of reaction with keten by a factor of 3.68 at 155 °C, and Table 1 shows that change in activation energy is responsible. The effect is 62% of the maximum possible in simple theory and shows that the O–H bond is substantially broken in the transition state. No isotopic data are available for the C–H bond in the anhydride decomposition back reaction but C–H isotope effects in thermolysis of esters [4] are also fairly large. The value obtained here may also be compared with that of k_H/k_D (3.0) obtained for the addition of diphenylketen to dichloroacetic acid.[5]

Rate and Acid Strength.—In the gas phase the rate of addition of a carboxylic acid to keten generally increases with its strength. Figure 1 is a plot of log (rate constant) against pK_a of the acid in aqueous solution, and includes data for straight-chain and branched lower aliphatic acids.[1] Discrepancies with the main trend of the results are that all chloro-acetic acids react faster than their fluoro-counterparts, that rates with alkyl-substituted acetic acids increase with decreasing acidity, and that 3,3-dimethylation of propenoic acid has a substantial effect on acid strength but very little on the rate of reaction with keten. pK_a Values are influenced by contributions from hydration terms. Measurements of intrinsic (gas-phase) acidities have been made in some cases [6] and should provide a sounder guide to the effect of acid strength on the reaction with keten. Intrinsic acidity is related to the energy term (D — EA), that is the O–H bond dissociation energy minus the electron affinity of the anion, and a plot of log k against (D — EA) is shown in Figure 2. Values of (D — EA) are not available for all the acids used here, but a linear plot is obtained except for the very strongest acids and formic acid. Thus substituents which increase intrinsic acidity also increase the rate of reaction with keten. The apparent anomalies in Figure 1 are due, in the case of the alkyl substituents, to pK_a changes being governed by hydration factors and similarly, in the reversals shown by halogenated acetic acids, to the fact that, although chlorine is the more polarisable, the fluorine-containing anions are more stabilised by hydration. A Taft plot of log k versus σ^* (Figure 3) shows the

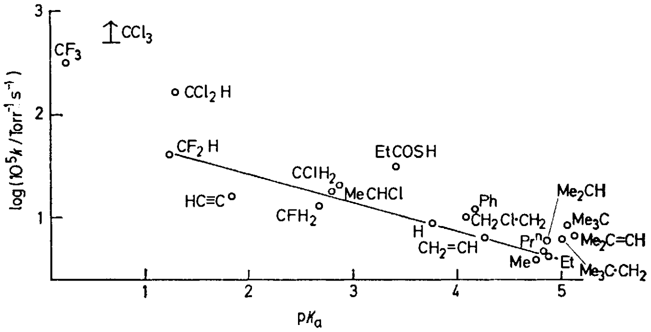

FIGURE 1 Plot of log k for reactions of carboxylic acids (RCO_2H) with keten against their pK_a values in aqueous solution

---

[3] W. Stevens and A. Van Es, *Rec. Trav. chim.*, 1964, **83**, 863; I. Muramatsu, M. Murakami, T. Toneda, and A. Hagitani, *Bull. Chem. Soc. Japan*, 1965, **38**, 244.

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

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

[6] R. Yamdagni and P. Kebarle, *Canad. J. Chem.*, 1974, **52**, 861.

anomalies above but gives a value for ρ^* of $+0.43$ if the fastest acids and branched alkyl substituents in the plot are ignored.

Mechanism.—Figures 2 and 3 suggest that trifluoro-, trichloro-, and dichloro-acetic acids may react with keten by a mechanism different from that of the remaining acids. The latter will be considered first. The constancy of A factors at *ca.* 10^6 l mol^{-1} s^{-1}, the fact that the additions are the reverse of anhydride decompositions [7] with A factors around $10^{11.5}$ s^{-1}, and the close similarity of these to ester decompositions, all favour a concerted mechanism with a six-centre transition state, as illustrated. The effects of substituents at the γ-carbon atom show that electron withdrawing groups stabilise the transition state and that this carbon atom must then be less positive than in the ground state. This parallels the situation in ester decompositions where $\rho = +0.33$ in the decomposition of isopropyl benzoates,[8] and where rate increases with the strength of the product acid.[9] Table 3 compares the two cases.

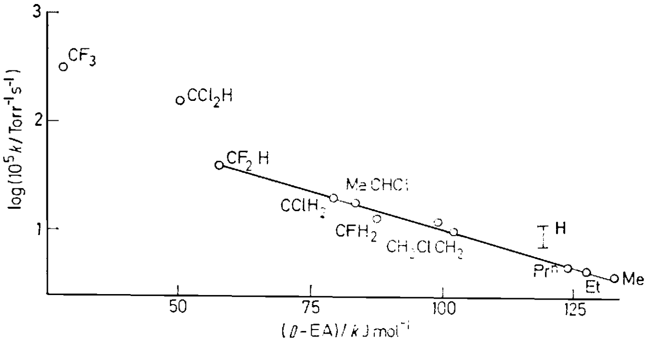

FIGURE 2 Plot of log k for reaction with keten against $(D - \mathrm{EA})$ for the acid RCO_2H

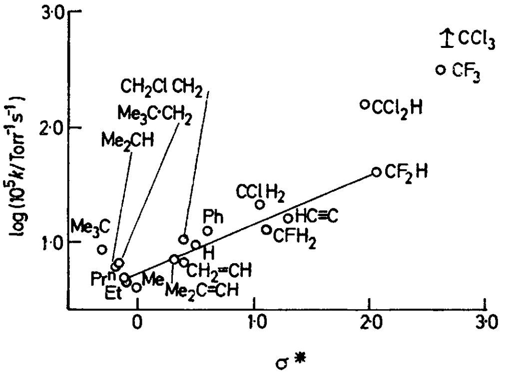

FIGURE 3 Taft plot of log k versus σ^* for RCO_2H

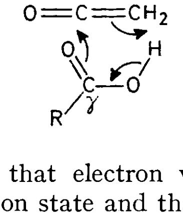

TABLE 3

Effect of the acid group on the relative rates of pyrolysis of t-butyl esters and additions of acids to keten

Acid group	Rate of ester pyrolysis	Rate of keten addition
$MeCO_2^-$	1.0	1.0
HCO_2^-	1.6	2.3
$CH_2Cl{\cdot}CO_2^-$	5.5	5.4
$CHCl_2{\cdot}CO_2^-$	18.6	41

Evidence concerning the β-carbon position is provided by measurements of the rate of reaction of dimethylketen with acetic and 2-methylpropanoic acids. At 155 °C rate constants were 1.64×10^{-5} and 2.30×10^{-5} Torr^{-1} s^{-1}, giving values of 2.34 and 2.55, respectively, for the expression k(keten)/k(dimethylketen). Also in the back reactions the relative rates of decomposition per β-hydrogen atom of acetic, propanoic, and 2-methylpropanoic anhydrides are 5.4 : 3.0 : 1.0. The latter values include contributions from the R group at the γ- as well as the β-carbon atom; the former will tend to increase the rate as R is larger but by not very much.[1] A similar reduction in rate with methyl substitution at the β-carbon atom takes place in the reaction of ketens with *m*-chloroaniline where k(keten)/k(dimethylketen) has a value of six in the second-order reaction.[10] The effects seem to be electronic rather than steric and calculations show that negative charge density on the β-carbon atom of keten is reduced by methyl substitution.[10]

The large isotope effect and close parallel between rate and intrinsic acid strength point to the importance of O–H bond breaking and, together with the ρ^* value, suggest a non-synchronised mechanism where movement of electrons out of this bond into the carboxylate area precedes the other indicated shifts. The effect of substituents on the keten addition follows their ability to stabilise the anion in acid dissociation.

A problem arises when the work reported here is compared with results on the addition of carboxylic acids to dimethylketen in ether.[5] In solution the trend is for the rate of addition of weaker acids to *decrease* with increasing acid strength, but to increase again for the strongest acids. This discrepancy is not due to differences between intrinsic acid strength and that in solution nor, apparently, to solvent effects on the rate. For example, with 2,2-dimethylpropanoic acid the rate constant for addition to dimethylketen in ether at 25 °C is 5.5×10^{-3} l mol^{-1} s^{-1}, and the gas-phase value with keten extrapolated to 25 °C is 7.2×10^{-3} l mol^{-1} s^{-1}. It was noted above that relative rates of keten and dimethylketen additions in the gas phase were 2.4 : 1, which gives an estimate of 3.0×10^{-3} l mol^{-1} s^{-1} for the gas-phase value with dimethylketen. This suggests

---

[7] P. G. Blake, A. Craggs, and M. H. B. Vayjooee, *J.C.S. Perkin II*, 1976, 986.

[8] G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, 1963, **28**, 3496.

[9] E. V. Emovon, *J. Chem. Soc.*, 1963, 1246.

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

that the same mechanism operates in both phases. The solution results pointed to the importance of nucleophilic attack by the carboxyl oxygen on the α-carbon atom of the keten, which became weaker with increasing acid strength. Thio-acids add to keten preferentially in the thiono-form,[11] and the rate of gas-phase addition is greater than would be expected from their acid strength (Figure 1), indicating that the increased nucleophilicity of sulphur as against oxygen is having an effect. However it is clear that in the gas phase at least stabilisation of the negative charge developed on the carboxy-residue during O–H bond breaking is of dominant importance.

Turning to the three fastest acids, rates lie well above the general trend whichever plot is considered. An obvious possibility is the onset of a surface reaction with the very polar acids, but changing the surface-to-volume ratio has no effect, at least for dichloro- and trifluoroacetic acids. The reaction with trichloroacetic acid was too fast to be measured accurately. In solution the behaviour of the strongest acids is explained by invoking a separate proton-transfer step.[5] It is tempting to suggest something similar in the gas phase, but the energy requirement for reaction (7) is 500 kJ mol^{-1}

$$CH_2{:}CO(g) + CF_3{\cdot}CO_2H(g) \longrightarrow CF_3{\cdot}CO_2^-(g) + MeCO^+(g) \quad (7)$$

and, even allowing for a large reduction due to ion pair formation, it seems improbable that this could compete successfully with the concerted mechanism, which requires *ca.* 40 kJ mol^{-1}. It is therefore likely that the same mechanism operates in all cases but that transition states become increasingly polar with the strongest acids. The upward curvature in the log k/σ^* plot is thus accounted for, since ρ^* will be more positive in these cases. The proton-transfer step above would represent the limit of the trend towards increasing polarity.†

[6/435 *Received, 3rd March,* 1976]

---

† We thank a referee for this suggestion.

[11] P. G. Blake and A. Speis, *J.C.S. Perkin II*, 1974, 1879.