Reactions of Keten. Part III.[1] Kinetics of the Spontaneous and Acetic Acid-catalysed Reactions of Keten with Water

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The gas-phase spontaneous and acetic acid-catalysed additions of water to keten have been studied kinetically in the range 224—324 °C. The uncatalysed addition is heterogeneous, with an apparent activation energy of 10·7 kJ mol^{-1}, and is inhibited by acetic acid. The catalysed reaction is homogeneous and first order in all three reactants, $k = 10^{4\cdot34} \exp(-20{,}500/RT)$ l^2 mol^{-2} s^{-1}. The activation parameters agree with those calculated from the back reaction and equilibrium constant.

KETEN is known to react slowly with water to give acetic acid but there appear to have been no kinetic studies of the reaction.[2] Lillford and Satchell[3] studied the kinetics of the spontaneous and acid-catalysed additions of water to dimethylketen in diethyl ether. The former reaction is first order in dimethylketen and second order in water and the latter is first order in water, acid, and the keten. The catalysed reaction was believed to proceed through a cyclic transition state involving one molecule each of water, acid, and dimethylketen, and not *via* an anhydride intermediate. In the case of keten itself, the gas-phase reaction with water catalysed by acetic acid is the apparent back reaction of the bimolecular decomposition of acetic acid.[4] The results of kinetic studies of both the uncatalysed and acetic acid-catalysed addition of water to keten are reported here.

EXPERIMENTAL

Apparatus and Procedure.—A conventional static apparatus was used with heated dead spaces. The surface-to-volume ratios of the unpacked and packed silica reaction vessels used were 0·88 and 9·69 cm^{-1} respectively. Pressures were measured with a spiral gauge manometer. Temperatures were measured using calibrated Chromel–Alumel thermocouples, and controlled to within ±0·2° by an electronic platinum resistance thermometer controller. Reaction vessels were carbon-coated before use by pyrolysing isobutene or acetic acid in them at 600 °C until the rate of decomposition of the latter fell to the homogeneous value.[4]

In catalysed runs keten and acetic acid were first admitted to the vessel in amounts calculated from the known equilibrium constants[1] to give the required pressures once equilibrium (1) was set up. Water was then added to the vessel and initial rates of reaction were measured manometrically. Since both forward and back reactions in equilibrium (1) are very much (typically 100 times) faster than the reaction being studied[5] it was assumed that (1) remained at equilibrium. The reactions with water which may be taking place are shown in equilibria (2)—(4).

$$\mathrm{CH_3{\cdot}CO_2H + CH_2{:}CO \rightleftharpoons (CH_3{\cdot}CO)_2O} \qquad (1)$$

$$\mathrm{CH_2{:}CO + H_2O \rightleftharpoons CH_3{\cdot}CO_2H} \qquad (2)$$

$$\mathrm{CH_2{:}CO + H_2O + CH_3{\cdot}CO_2H \rightleftharpoons 2CH_3{\cdot}CO_2H} \qquad (3)$$

$$\mathrm{(CH_3{\cdot}CO)_2O + H_2O \rightleftharpoons 2CH_3{\cdot}CO_2H} \qquad (4)$$

The stoicheiometries of reactions (1)—(4) have been established[1,5,6] and, with the exception of diketen, only keten, water, acetic acid, and acetic anhydride were found in the reaction vessel. Keten was measured by i.r. absorption at 2150 cm^{-1}, acetic anhydride by u.v. absorption at 256 nm.

Corrections for loss of keten through dimerisation were usually small but increased with temperature, and the upper limit to the temperature range studied was set when the correction rose to 25% of the total rate. In view of the mobility of reaction (1), rates were expressed in terms of disappearance of water rather than that of keten. In the initial stages of the catalysed reaction $\Delta(\text{water}) \equiv \Delta p$ when initial pressures of keten and acetic acid are equal but, because of the mobility of (1), the ratio $\Delta p/\Delta(\text{water})$ typically rises to 1·3 : 1 at keten–acid ratios of 5 : 1 and falls to 0·7 : 1 when keten–acid is 1 : 5.

Materials.—Keten was prepared by the flow pyrolysis of

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[1] Part II, P. G. Blake, H. H. Davies, and A. Speis, *J. Chem. Soc.* (*B*), 1971, 2050.

[2] R. N. Lacey, 'The Chemistry of Alkenes,' Interscience, London, 1964, p. 1173.

[3] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 889.

[4] P. G. Blake and G. E. Jackson, *J. Chem. Soc.* (*B*), 1968, 1153.

[5] P. G. Blake and H. H. Davies, *J. Chem. Soc.* (*B*), 1971, 1727; P. G. Blake and A. Speis, *ibid.*, p. 1877.

[6] W. C. Child and A. J. Hay, *J. Amer. Chem. Soc.*, 1964, **86**, 182.

acetic anhydride at 400 °C, followed by low-temperature fractionation. It was stored *in vacuo* at liquid air temperature and the amount required for each run was re-distilled at −78 °C before use. Acetic acid was >99·8% pure and both it and water were degassed before use.

RESULTS AND DISCUSSION

The gas-phase reactions between keten and water alone and catalysed by acetic acid have been studied in the temperature range 224—324 °C with reactant partial pressures from 1 to 124 mmHg (1 mmHg = 133·28 N m^{-2}).

Kinetics.—The uncatalysed reaction is heterogeneous, the ratio of rates in the packed to those in the unpacked vessel being almost the same as the ratio of the surface-to-volume ratios, namely 11·0 : 1 (Table). (Rates in uncoated silica are very much greater than in coated vessels.) In both vessels the reaction is first order in keten and has an order of 0·4 in water (Figure 1). Apparent activation energies are 11·7 ± 3·3 and 9·6 ± 2·5 kJ mol^{-1} in unpacked and packed vessels respectively.

Effect of surface-to-volume ratio on initial rates of uncatalysed reaction and effect of 40 mmHg pentane. Rates, measured at $p_0(H_2O)$ of 10 mmHg, are expressed as nominal second order rate constants. (Ratio of surface-to-volume ratios packed–unpacked vessel 11·0 : 1)

Temp (°C)	Vessel	10^6k/ mmHg^{-1} s^{-1}	10^6k (mean)	k (packed) : k (unpacked)
227	P	4·37	4·37	12·5
	U	0·35	0·35	
284	P	6·1, 6·2, 7·1, 7·1	6·6	14·1
	U	0·50, 0·43	0·47	
254	P	5·0, 5·3, 6·1, 6·1	5·6	12·4
	U	0·40, 0·44, 0·47, 0·48	0·45	
254	U + pentane	0·48, 0·45	0·47	

P = Packed, U = unpacked.

The effect of addition of acetic acid to the system is shown in Figure 2. The heterogeneous reaction is rapidly inhibited and replaced by a homogeneous process which is first order in acetic acid. Inhibition shows up more clearly in the packed vessel and it appears that the surface reaction is negligible above 10 mmHg acetic acid pressure, the extrapolated line passing through zero rate when acid is absent. Thus the surface reaction between keten and water is strongly inhibited by acetic acid, presumably since acid is preferentially adsorbed on to the active sites. Supporting evidence comes from rate measurements on the keten–water reaction away from the initial stages when the auto-inhibitory nature shows up clearly. The triangles on Figure 2 refer to rates measured in the later stages of the reaction without added acid, the acetic acid present being product.

The homogeneous, acid-catalysed reaction is also first order in keten and in water (Figure 3). The rates (R_0) plotted in Figures 2 and 3 are initial rates divided by initial pressures of the reactants which are not being varied in the given plot. The acetic acid-catalysed addition of water to keten is therefore third order overall, first order in each component. The Arrhenius parameters at constant concentration, obtained from a least-squares plot of 33 unpacked and 16 packed rate constants, are given by $k = 10^{4\cdot34\pm0\cdot53} \exp(-20{,}500 \pm 1200/RT)$ l^2 mol^{-2} s^{-1}. A large number of observations was used because of the low value of the temperature coefficient.

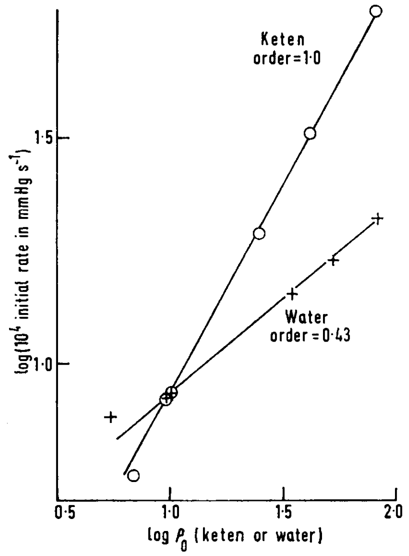

FIGURE 1 Orders in keten and water in the uncatalysed reaction. Plot of log (10^4 initial rate in mmHg s^{-1}) against log (keten or water initial pressure in mmHg), the pressure of the other remaining constant at 10 mmHg

Comparison with the Back Reaction.—The back reaction

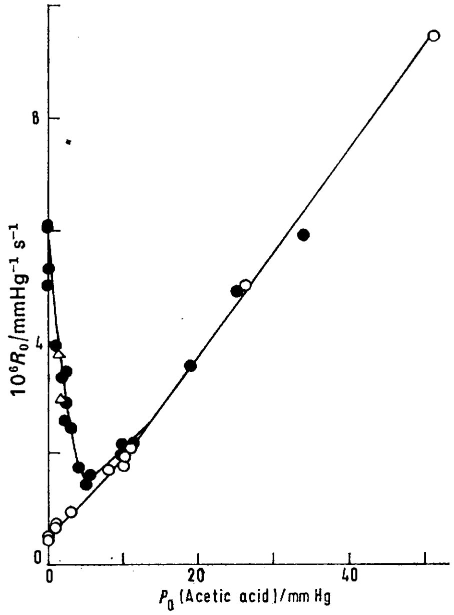

FIGURE 2 Dependence of initial rates on acetic acid pressure in unpacked and packed vessels, with keten and water initial pressures nominally 10 mmHg. R_0 = (Initial rate)/p_0(keten)-p_0(water). (○) unpacked vessel; (●) packed vessel; (△) self-inhibited rates (see text)

of (3) is the bimolecular thermal decomposition of acetic acid,[4] for which $A = 10^{8\cdot45\pm0\cdot18}$ l mol^{-1} s^{-1} and $E =$ 143·0 ± 4·5 kJ mol^{-1} at constant concentration. ΔH° (forward) has been calculated to be $-127\cdot9 \pm 4\cdot2$ kJ mol^{-1} from equilibrium measurements at 572 K, with ΔS° as $-135\cdot9 \pm 7\cdot6$ J K^{-1} mol^{-1}, both with respect to a standard state of one atmosphere.[6] Converting these to a 1 mol l^{-1} standard state at 550 K, A and E (forward) are calculated from the back reaction and equilibrium data to be $10^{3\cdot61\pm0\cdot57}$ l^2 mol^{-2} s^{-1}, and 19·7 ± 6·3 kJ mol^{-1}, respectively, in good agreement with the experimental values.

The activation energy of the unimolecular dehydration of acetic acid [7] is 272 kJ mol^{-1}, so that of the homogeneous uncatalysed addition of water to keten should be 144 kJ mol^{-1} (constant pressure). Consequently this reaction is not observed at the temperatures employed. Acetic acid decomposition changes from a bimolecular to a unimolecular mechanism around 650 °C,[7] so that the third-order, catalysed keten–water reaction would be expected to give way to the bimolecular uncatalysed addition above this temperature. However, dimerisation and decomposition of keten make this region experimentally inaccessible. It is of interest to note that the uncatalysed addition of water to dimethylketen in solution involves water dimer molecules only.[3] These are absent from the gas phase under our conditions.

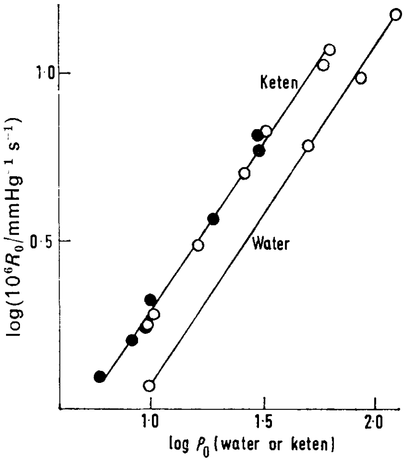

FIGURE 3 Orders in keten and water in the catalysed reaction at acetic acid pressures ⩾10mmHg. R_0 = (Initial rate)/ p_0(acid) p_0(keten or water). The water plot is displaced downwards by 0·2 log units for clarity

Mechanism of the Catalysed Reaction.—The reaction is homogeneous, first order in each component, and exothermic by 128 kJ mol^{-1}. Acetic acid is not acting merely as a third body since rates of the uncatalysed reaction are unaffected by the addition of pentane (Table). Two possible mechanisms are the termolecular process (3) involving one molecule each of keten, water, and acid in the transition state, and a pair of bimolecular reactions, (1), followed by a rate-determining hydrolysis of acetic anhydride as in (4). The mechanisms cannot be distinguished by the kinetic results, the former giving the rate expression $k_3[CH_2{:}CO]^1[H_2O]^1[CH_3{\cdot}CO_2H]^1$, the latter the expression $k_4K_1[CH_2{:}CO]^1[H_2O]^1[CH_3{\cdot}CO_2H]^1$. Similarly, $E_{obs} = E_4 + \Delta H_1^{\circ}$, which, with $\Delta H_1^{\circ} =$ -86 kJ mol^{-1} at 572 K, gives $E_4 = 106\cdot5$ kJ mol^{-1}. An attempt was made to decide between the mechanisms by following the very early stages of the back reaction, that is the homogeneous bimolecular decomposition of acetic acid at 330 °C and 450 mmHg pressure, when detectable amounts of acetic anhydride are formed. Keten–anhydride ratios greater than those expected if (1) is in equilibrium would support reaction (3), since anhydride would be formed in a second step; values less than equilibrium ratios favour (4) and (1). There was some scatter in the results, since amounts measured were small, but no indication of a real difference from the equilibrium ratio, confirming that (1) is fast compared with the other reactions. In the solution work of Lillford and Satchell with dimethylketen,[3] the keten reacts very slowly with isobutyric acid compared with the catalysed addition of water, so that anhydride cannot be involved in the rate-determining step. Thus a termolecular process is at least possible.

The Arrhenius constants ($A = 10^{4\cdot34}$ l^2 mol^{-2} s^{-1}, $E = 20\cdot5$ kJ mol^{-1}) are comparable with those of other termolecular reactions, the respective values for 2NO + Cl_2 for example [8] being $10^{3\cdot66}$ and 15·5, and correspond to a reasonable steric factor of about 10^{-5}. However, the value calculated for E_4, assuming the bimolecular route, also seems reasonable. The difference between the two mechanisms is blurred if the termolecular reaction is considered to proceed *via* a transient binary complex, for example one formed from keten and acid, which then reacts with water. Both mechanisms then consist of two bimolecular steps, distinguished by the lifetimes of the products of the first step, which would be about 10^{-13} s in the ' termolecular ' mechanism,[8] and very much longer in the bimolecular case.

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