The Hydrolysis of Acetic Anhydride. Part IV. Catalysis by Hydrochloric Acid and the Hydrolysis of Acetyl Chloride.*

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The rates of hydrolysis of acetic anhydride and of acetyl chloride in aqueous hydrochloric acid have been studied at 0° as a function of acid concentration over the range 0—9·28M. For acetic anhydride the rate increases steeply with acidity, whereas there is a very small decrease in the case of acetyl chloride. At the highest acid concentrations acetic anhydride is hydrolysed more rapidly than acetyl chloride. It is therefore concluded that acetyl chloride is not an intermediate in the hydrochloric acid-catalysed hydrolysis of acetic anhydride.

The reaction velocities were measured by a modification of the thermal maximum method.

It has been known for some time that the hydrolysis of acetic anhydride in aqueous solution is catalysed by hydrochloric acid and other acids (Szabo, *Z. physikal. Chem.*, 1926, **122**, 405; Kilpatrick, *J. Amer. Chem. Soc.*, 1928, **50**, 2896) but these earlier measurements do not throw much light on the mechanism of this catalysis. The problem is treated in a more general manner in Part V (succeeding paper). The present paper is concerned with an examination of the particular hypothesis that the catalysing acid HX reacts with acetic anhydride according to $Ac_2O + HX \longrightarrow AcX + AcOH$, the subsequent hydrolysis of the compound AcX being rapid compared with the hydrolysis of acetic anhydride. On general grounds this is a reasonable and attractive hypothesis. For example, there is evidence that, in anhydrous mixtures of nitric acid and acetic anhydride, acetyl nitrate is formed by this reaction (Gold, Hughes, and Ingold, *J.*, 1950, 2467), and there have been similar suggestions concerning acetyl hydrogen sulphate (Russell and Cameron, *J. Amer. Chem. Soc.*, 1938, **60**, 1345; Murray and Kenyon, *ibid.*, 1940, **62**, 1230) and acetyl perchlorate (Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159). Further, it is known that the solvolyses of acetyl chloride (Branch and Nixon *J. Amer. Chem. Soc.*, 1936, **58**, 2499) and of acetyl dihydrogen orthophosphate (Bentley, *ibid.*, 1949, **71**, 2765) are more rapid than the corresponding reactions of acetic anhydride, and Burton and Praill (*Quart. Rev.*, 1952, **6**, 302) have concluded that acetyl perchlorate is a more powerful acetylating agent than acetic anhydride.

EXPERIMENTAL

Materials.—Acetic anhydride ("AnalaR") was allowed to reflux over magnesium turnings for several hours and then fractionally distilled in a dry atmosphere, a middle portion being retained for kinetic measurements. Acetyl chloride ("AnalaR") was allowed to reflux for several hours in order to drive off hydrogen chloride, and was then distilled similarly. The hydrochloric acid solutions were prepared by dilution of "laboratory reagent as recommended for analysis." The concentration of the stock reagent was found by density determinations.

Kinetic Measurements.—Since the reactions were too rapid for investigation by conventional methods, the rate constants were obtained by a modification of the thermal maximum method of Bell and Clunie (*Proc. Roy. Soc.*, 1952, *A*, **212**, 16; cf. Bell, Gold, Hilton, and Rand, *Discuss. Faraday Soc.*, 1954, **17**, 151). In this modification the time taken between the mixing of the reagents and the attainment of the temperature maximum of a reaction mixture which is losing heat to its surroundings at a controlled rate is measured.

Apparatus.—Reactions vessels. The reactions were carried out in one of a matched pair of rectangular vessels of sheet platinum (4 × 4 × 16 cm.) supported in a brass frame. The vessels were placed symmetrically in the apparatus. They contained the same solution (except for the low concentration of acid chloride or anhydride in one of them) and were stirred at the same constant rate (1500 r.p.m.) by identical twisted-leaf glass stirrers driven *via* a gear box by a 1/16 h.p. constant-speed induction motor.

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* Part III, *J.*, 1953, 1409.

Temperature measurement. The temperature difference between the two vessels was measured by means of a rigidly held " Pallador " thermo-couple (Messrs. Johnson, Matthey and Co. Ltd.) directly immersed in the liquid and connected across a critically damped Cambridge short-period galvanometer. This (primary) galvanometer gave a deflection of 1 cm./0·1°, and approximately 30-fold sensitivity was obtained by means of a simple photo-amplifier in which the light reflected by the primary galvanometer was made to fall on a knife edge and then on to a high-impedance " Cintel " photo-cell which, in turn, actuated a secondary critically damped galvanometer (Tinsley, short-period). The optical arrangement was such that the movement of the primary galvanometer mirror did not change the position of the illuminated area of the photo-cell electrode, and that the intensity of illumination of the photo-cell was strictly proportional to the deflection of the primary galvanometer. The light source for the primary galvanometer was a Mazda Exciter lamp (Projection lamp, Class G, Exciter G/8) run off a stabilised mains supply stepped down to 8 v.

For calibration purposes a current of about 0·03 μA could be passed through the primary galvanometer from two Weston cadmium cells with a 60-megohm resistance in series. The use of twin vessels ensures that both junctions are exposed to identical influences, in particular to the same heat of stirring which causes an appreciable temperature rise above the temperature of the bath in solutions of high viscosity.

Temperature control. The temperature of the bath was kept constant at 0° by water in contact with a large mass of ice, generated as a frozen sheet at the bottom of the tank by pumping refrigerant liquid (temperature $< -3°$) through 10 ft. of copper tubing. The thermostat liquid was agitated by a circulating pump driven by a second constant-speed motor, which pumped a steady flow of liquid past the two platinum vessels, and by rotary blades attached to the extended shaft of the centrifugal pump, substantially as in the single-vessel apparatus of Bell and Clunie (*loc. cit.*).

Mixing of reagents. Acetic anhydride or acetyl chloride was injected into the stirred reaction mixture from an all-glass syringe with an outlet 0·02 cm. in diameter. The narrow outlet ensured that there was no interdiffusion of liquids in the capillary and allowed the reactant to enter in a finely divided form, thus hastening solution. The construction was such that the reservoir of injected liquid was below the level of the liquid in the reaction vessel, thus ensuring that the reagent was at the same temperature as the solvent. Since the reaction time was short compared with the time necessary for the transfer of heat through the wall of the reservoir, no measurable temperature effect was produced by the replacement of the injected reagent by reagent not previously below this level. This method of mixing suffers from the drawback that a time of the order of ½ sec. is required for the injection. The zero-time for the reaction was taken half-way between starting and finishing the injection. Since the concentration of injected reagent was low (~0·01M), several runs could be made in succession without changing the solvent.

Assembly. The construction of all non-rigid parts allowed their accurate re-alignment. The galvanometer circuits were screened, and all vessels, screens, and other metallic components were connected to earth. A platinum heating coil was incorporated in the reaction vessel to allow the determination of the effective water equivalent of the system and calibration of the thermocouple.

Procedure.—For the determination of the cooling constant the temperature of the acid in the reaction vessel was raised 0·4—0·6° above the equilibrium temperature by withdrawing about 20 ml. of the acid from the vessel into a pipette whose bulb was warmed by hand and then returning it to the vessel (or else by electrical heating). When the excess temperature had fallen to 0·15°, readings of the secondary galvanometer were taken at 6-sec. intervals, and the first-order cooling constant $[k_2 = -(1/T_{\text{excess}})\mathrm{d}T/\mathrm{d}t]$ calculated by Guggenheim's method. For each acid the value of the cooling constant was determined 4—8 times, and a mean value taken.

For carrying out reactions sufficient reactant was injected to cause a maximum temperature rise (T_m) of 0·1° or slightly less. Readings of the secondary galvanometer were taken for about three times the time needed to reach the maximum (t_m). The time t_m was estimated from a graph of the experimental points (Fig. 1). As a rule, three values of t_m were measured and their agreement was within ±3%.

It was verified by numerical calculation that, if the galvanometer system is critically damped and the time taken to reach 90% of full deflection—when an e.m.f. is applied instantaneously—is less than about one-fifth of the value of t_m, the inertia of the galvanometer system is insignificant and the observed maximum of the deflection is practically synchronous with the temperature maximum. For faster reactions the measurement of T_m, rather than t_m, is to be preferred.

Theory.—The time of attainment of maximum temperature (t_m) for an exothermic first-order reaction is given by

$$t_m = \frac{1}{(k_2 - k_1)} \ln \left[\frac{k_2}{k_1}\left(1 + \frac{T_i}{T_0} - \frac{k_2 T_i}{k_1 T_0}\right)\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[Bell and Clunie's equation (3), *loc. cit.*], where T_0 is the rise in temperature due to the reaction which would be observed under adiabatic conditions, T_i is the initial instantaneous rise in temperature due to the heat of mixing of the reactants, k_1 is the rate constant of the reaction, and k_2 is the cooling constant. The ratio T_i/T_0 ($\equiv \rho$) may be found or eliminated from this expression by carrying out each experiment twice in vessels with different cooling constants. A reduction of about 30% in k_2 could be achieved by masking two of the external faces of the reaction vessel with Perspex spacers. It was shown in this way that, for the reactions considered, ρ is of the order of $+0{\cdot}1$ to $+0{\cdot}2$. Procedures for the determination of T_i and T_0 have been described in previous papers on this method. In the present investigation the precise determination of T_i is difficult, and since the highest accuracy attainable by the method was not required, a less rigorous and experimentally much easier approach was adopted. From this point of view the following examination of equation (1) is profitable.

FIG. 1. *Temperature–time curves of the thermal maximum method. (Hydrolysis of acetyl chloride in water at* 0°.)

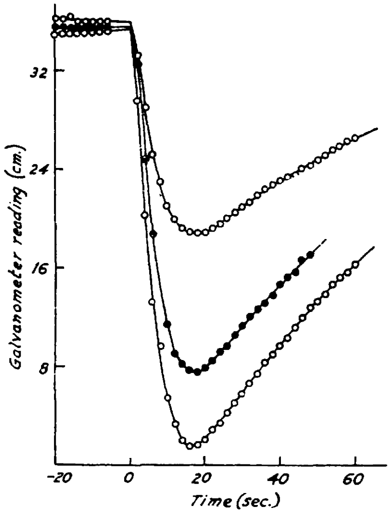
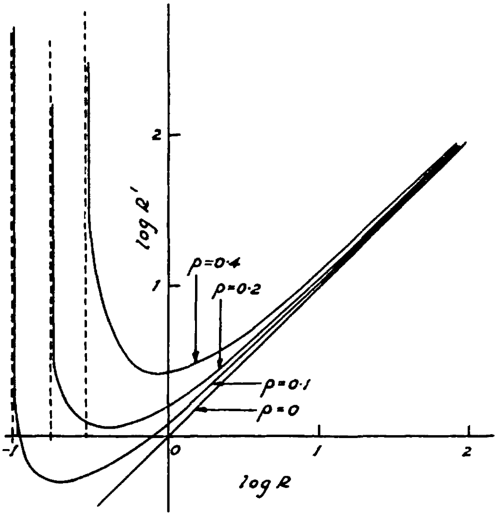


FIG. 2. *Relation between R and R'.*



Let k' be defined by the equation

$$t_m = [1/(k_2 - k')] \ln k_2/k' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and let $R' = k'/k_2$ and $R = k_1/k_2$. When $\rho = 0$, $k' = k_1$; for other values of ρ, k' will deviate from k_1, and therefore R' from R. The manner in which R' and R diverge has been calculated numerically for different values of ρ and is shown in Table 1 and Fig. 2. It is seen that as $R \longrightarrow \infty$, $R' \longrightarrow R$, but that there is a large difference between R' and R for low values of R.

The values of k' in Tables 2 and 3 were derived from the experimentally observed t_m values by solution of equation (2). For acetic anhydride the range of R' covered is from 1 to 28 approximately. From the systematic variation of R' with acidity it may be concluded that only the higher root of R need be considered. It will be seen from Table 1 that for the fastest of these reactions R' will exceed R by 10% at the most, and that, for the slowest of these reactions it is possible that R is less than R' by as much as 35% of the value of R'. For acetyl chloride R is in the range 5—9. Since, in this case, we do not have a systematic variation of the observed value with acidity it is possible that the found value of R' corresponds to either one of two possible values of R. The lower of these two values corresponds to a reaction velocity which is slow enough for measurement by conventional methods. Since it is known that the hydrolysis of acetyl chloride is too fast for such measurements, only the higher value of R has significance in this case.

It is assumed in the calculation that the hydrolysis reaction is kinetically of the first order. This is reasonable, since the hydrolysed reagent is in both reactions the only component of the reaction mixture whose concentration is expected to vary significantly during the course of the reaction. A first-order law has been found to be rigorously obeyed in all similar reactions where the progress of the reaction can be followed with precision. The assumption is further justified by the absence of any dependence of t_m upon the initial concentration of hydrolysed reagent (see Fig. 1). In both cases the identification of the observed rate process with the hydrolysis reaction is supported by a variety of circumstantial evidence. The case of acetic anhydride is discussed more fully in Part V.

TABLE 1. *The relationship between* R *and* R′ *for different values of* ρ.

	R'				R'				R'		
R	$\rho = 0{\cdot}1$	$\rho = 0{\cdot}2$	$\rho = 0{\cdot}4$	R	$\rho = 0{\cdot}1$	$\rho = 0{\cdot}2$	$\rho = 0{\cdot}4$	R	$\rho = 0{\cdot}1$	$\rho = 0{\cdot}2$	$\rho = 0{\cdot}4$
0·5	0·72	1·13	5·84	4·0	4·37	4·75	5·59	32·0	33·2	34·4	36·5
1·0	1·23	1·54	2·58	8·0	8·52	9·03	10·08	64·0	65·9	67·8	71·2
2·0	2·28	2·60	3·39	16·0	16·7	17·5	19·0				

Results are summarised in Tables 2 and 3.

TABLE 2. *The hydrolysis of acetic anhydride in aqueous hydrochloric acid at* 0°.

$[\mathrm{Ac_2O}]_{\text{initial}} = 0{\cdot}01$—$0{\cdot}04$M.

[HCl] (M)	$-H_0$ *	t_m,(1) sec.	10^2k_2,(2) sec.$^{-1}$	$10^2k'$, sec.$^{-1}$	$10^2k'_{\text{cat.}}$(4)	$\log k'_{\text{cat.}} + 5{\cdot}0$
0·00	—	—	—	0·046 (3)	—	—
4·64	1·37	56	1·98	1·94	1·89	3·28
5·56	1·62	42	2·21	2·60	2·55	3·41
6·50	1·89	28	2·06	5·55	5·50	3·74
6·96	2·01	22·5	1·93	8·5	8·5	3·93
9·28	2·64	6·1	2·07	56·0	56·0	4·75

TABLE 3. *The hydrolysis of acetyl chloride in aqueous hydrochloric acid at* 0°.

$[\mathrm{AcCl}]_{\text{initial}} = 0{\cdot}01$—$0{\cdot}02$M.

[HCl] (M)	t_m,(1) sec.	10^2k_2,(2) sec.$^{-1}$	$10^2k'$, sec.$^{-1}$	[HCl] (M)	t_m,(1) sec.	10^2k_2,(2) sec.$^{-1}$	$10^2k'$, sec.$^{-1}$	[HCl] (M)	t_m,(1) sec.	10^2k_2,(2) sec.$^{-1}$	$10^2k'$, sec.$^{-1}$
0·00	17·5	1·79	13·3	2·32	17·5	1·91	12·7	9·28	17·0	2·31	12·1
1·16	16·8	1·83	13·7	4·64	17·5	2·12	12·0				

(1) Mean of 3—6 determinations. (2) Mean of 4—8 determinations. (3) Value obtained by dilatometry. (4) $k'_{\text{cat.}} = k' - k_1^{\circ}$, where k_1° = first-order rate constant in water.

* Hammett's acidity function.

DISCUSSION

The results show that the hydrolysis of acetyl chloride in water is not catalysed by hydrochloric acid even in very high concentration. On the other hand, the velocity of the hydrolysis of acetic anhydride increases rapidly over the same concentration range. At concentrations of hydrochloric acid which are higher than about 7·5M, the reaction of acetic anhydride is more rapid than that of acetyl chloride (Fig. 3). These conclusions hold even if the experimental error of the method is considerably greater than that considered probable (see p. 840). If the catalysis of the hydrolysis of acetic anhydride by hydrochloric acid were due to intermediate formation of acetyl chloride, the velocity of this reaction would be expected to remain less than that for acetyl chloride and, possibly, to approach that of acetyl chloride hydrolysis asymptotically at high acidities. For this reason the catalysis by hydrochloric acid must have a different explanation.

The retardation of the rate of hydrolysis of acetyl chloride by hydrochloric acid is hardly outside the limits of experimental accuracy and cannot be given a precise interpretation. It could be due to the decreased stoicheiometric concentration of water in concentrated solutions of hydrochloric acid. It indicates that there is no common-ion retardation of the reaction by chloride ion, as found for certain types of the S_N1 mechanism.

On the basis of the present results—which are the only ones available for the hydrolysis of acetyl chloride in water—it is impossible to draw incontrovertible conclusions concerning reaction mechanisms. The following comparison of the rates of reaction of acetyl chloride and benzoyl chloride favours the view that the reaction follows a bimolecular rather than a unimolecular mechanism. Branch and Nixon (*loc. cit.*) found that the rates of bimolecular acylation of ethanol by acetyl chloride and benzoyl chloride were in the ratio 204 : 1. The hydrolysis of benzoyl chloride in water is thought to be a predominantly unimolecular reaction (Gold, Hilton, and Jefferson, *J.*, 1954, 2756), but the bimolecular velocity constant can be approximately estimated by extrapolating the linear relation between log k and $(\varepsilon - 1)/(2\varepsilon + 1)$ (ε = dielectric constant) for low values of ε in acetone–water mixtures, in which the reaction is known to be predominantly bimolecular, to the value of $(\varepsilon - 1)/(2\varepsilon + 1)$ appropriate for water (*idem, ibid.*, Fig. 1). The value of the first-order rate constant for the bimolecular reaction thus found is 5×10^{-4} sec.$^{-1}$. The value of k' for acetyl chloride in water is $13{\cdot}5 \times 10^{-2}$ sec.$^{-1}$, *i.e.*, 270 times greater, and hence of the order of magnitude expected if the hydrolysis of acetyl chloride in water is indeed bimolecular.

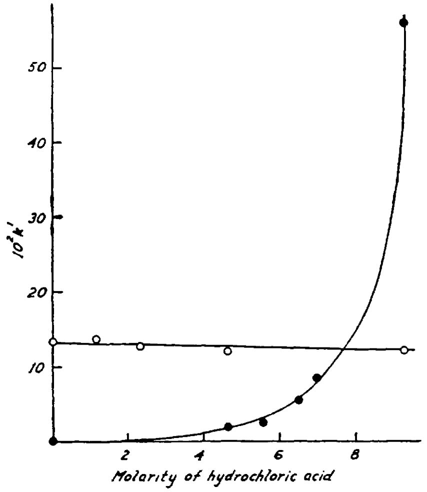


FIG. 3. *Dependence of hydrolysis velocity on concentration of hydrochloric acid.*

● Ac_2O. ○ AcCl.

The lower ionisation tendency of acetyl chloride than of benzoyl chloride is consistent with the idea that the stability of aromatic acylium ions is partly derived from the conjugation between the carbonyl group and the aromatic ring, which is impossible for aliphatic acylium ions :

This conjugation will begin to assume importance in the transition state of the ionisation reaction, and hence stability and ease of formation of acylium ions are expected to run parallel.

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