A Comparison of the Mechanisms of the Solvolytic Hydrolysis Reactions of Acetic Anhydride and Benzoyl Chloride.

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The hydrolysis of benzoyl chloride and acetic anhydride in aqueous acetone has been studied kinetically. By examining the influence of different amounts of an added aromatic amine (which can compete with the solvent for the acylating agent) on the rate and on the final product composition, it has been possible to determine the relative contributions of unimolecular and bimolecular mechanisms to the acylation of the amine and to the acylation of water. Acetic anhydride in acetone–water (50 : 50 w/w), and benzoyl chloride in acetone–water (80 : 20 w/w) react by bimolecular mechanisms, but in the hydrolysis of benzoyl chloride in acetone–water (50 : 50 w/w) approximately half of the total reaction proceeds by a rate-determining process in the benzoyl chloride molecule, which does not involve participation of the molecule undergoing acylation. The analysis shows that it is preferable to regard a border-line (*i.e.*, between S_N1 and S_N2) solvolysis to be the sum of two simultaneously occurring processes rather than as a single reaction involving an intermediate degree of solvent participation.

The use of the relation between log k and $(\varepsilon - 1)/(2\varepsilon + 1)$ (ε = dielectric constant) as a criterion of reaction mechanism is discussed, and it is concluded that in the present state of knowledge the existence of a non-linear relation between these two quantities is insufficient evidence for a change of mechanism. For the hydrolysis of benzoyl chloride the application of this method leads to the same conclusion as the kinetic analysis of the competition experiments.

The unambiguous assignment of a detailed mechanism to a reaction between two species in a condensed phase is more difficult when the reaction partners are a solvent and a solute species than when both are solutes in low concentration. In the former case, the variation of the stoicheiometric concentration of one of the species by an order of magnitude or so is usually attended by a large change in the properties of the medium * and, therefore, the molecularity of the reaction with respect to the solvent cannot be deduced from the relation between concentration and reaction velocity. In addition to a consequent "medium effect" on the rate there is also the problem as to what kind of a concentration scale is a correct measure of the collision frequency or *a priori* probability of the activation process. This problem does not arise in reactions between solutes, since at sufficiently low concentrations the molarity, molality, mole fraction, volume fraction, partial vapour pressure, etc., are nearly proportional to each other and a satisfactory analysis of the reaction in terms of reaction order is possible whatever concentration scale is used.

For these reasons less direct methods for determining the molecularity of a reaction with respect to a solvent are usually employed (see Hughes, *Trans. Faraday Soc.*, 1941, **37**, 611). Not all these methods are useful in every instance. The applications of some of them to the hydrolysis of acetic anhydride (Gold, *ibid.*, 1948, **44**, 506) and to that of benzoyl chloride (Hudson and Wardill, *J.*, 1950, 1729; Archer and Hudson, *ibid.*, p. 3259; Brown and Hudson, *J.*, 1953, 883; Archer, Hudson, and Wardill, *ibid.*, p. 888) have recently been discussed. However, some of these criteria of mechanism are rather indirect and, moreover, are diagnostic only in a qualitative fashion; *i.e.*, they do not allow the quantitative analysis of a border-line case where processes of different mechanism may proceed

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* Although it may be unsound to draw a sharp division between "solutes" and "solvents," the foregoing statement appears to provide a useful distinction for the purpose of chemical kinetics in solution. The solution property whose variation is significant in this connection is the rate in that solution of a similar but non-solvolytic reaction.

simultaneously, as has been suggested for the hydrolysis of benzoyl chloride in certain acetone–water mixtures (Hudson *et al.*, *locc. cit.*).

A method, applicable to acylation reactions, which is independent of these indirect criteria of mechanism and allows at the same time an estimate of the relative importance of two simultaneously occurring different mechanisms, has accordingly been developed. Such a direct approach has also seemed desirable in view of certain doubts which have been raised regarding the physical meaning of the molecularity of a reaction with respect to the solvent (Winstein, Grunwald, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700).

With regard to terminology: we recognise that solvent molecules play a part in all reactions in solution, *i.e.*, even in so-called unimolecular solvolyses (*e.g.*, S_N1). Nevertheless, since the slow first step in these reactions is not peculiar to solvolysis but is common to all reactions proceeding by this mechanism, irrespective of whether the subsequent reaction of the ion is with a solvent or a solute, these reactions have continued to be called unimolecular.

The experimental procedure followed consisted in examining the influence of varying concentrations of a solute aromatic amine, which competes with the water in the solvent for the acylating agent, on (i) the total velocity of the disappearance of the acylating agent, and (ii) the relative amounts of the reaction products (anilide and acid).

The study of the intervention of azide ions in the unimolecular solvolysis of alkyl halides (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979; Hawdon, Hughes, and Ingold, *J.*, 1952, 2499) illustrates another application of the same basic approach.

For the sake of definiteness, let us represent the relevant mechanisms for benzoyl chloride by the following chemical equations, although it will be seen later that a slightly different interpretation of the data would also be acceptable.

$$\text{Bimolecular } (S_N2)\text{:}\quad \mathrm{BzCl} + \mathrm{H_2O} \xrightarrow{k_2} \mathrm{BzOH} + \mathrm{HCl}$$

$$\mathrm{BzCl} + \mathrm{R{\cdot}NH_2} \xrightarrow{k_2'} \mathrm{Bz{\cdot}NHR} + \mathrm{HCl}$$

$$\text{Unimolecular } (S_N1)\text{:}\quad \mathrm{BzCl} \xrightarrow{k_1} \mathrm{Bz^+} + \mathrm{Cl^-}$$

$$\mathrm{Bz^+} + \mathrm{H_2O} \xrightarrow{\kappa_1} \mathrm{BzOH} + \mathrm{H^+}$$

$$\mathrm{Bz^+} + \mathrm{R{\cdot}NH_2} \xrightarrow{\kappa_1'} \mathrm{Bz{\cdot}NHR} + \mathrm{H^+}$$

The symbol above a reaction arrow represents the rate constant of the reaction concerned, which is supposed to be of the molecularity indicated by the stoicheiometry. The acylation reactions of acetic anhydride may be written in an analogous manner. The proved absence of common-ion effects in the hydrolysis of benzoyl chloride (Table 3; cf. Archer, Hudson, and Wardill, *loc. cit.*) allows us to disregard the association reaction between $\mathrm{Bz^+}$ and $\mathrm{Cl^-}$ ions.

The kinetic features of the simultaneous occurrence of the above two mechanisms are then represented by the following set of equations. Let x and y be the concentration changes of the acylating agent A, due to hydrolysis and anilide formation respectively. The concentrations of acylating agent and amine are denoted by a and b respectively; w stands for the concentration of water in the appropriate (unspecified) units, as discussed above. The subscripts 0 and ∞ used in connection with concentration symbols refer to times from the mixing of the reagents:

$$\mathrm{d}x/\mathrm{d}t = k_1 a \kappa_1 w/(\kappa_1 w + \kappa_1' b) + k_2 a w \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{d}y/\mathrm{d}t = k_1 a\, \kappa_1' b/(\kappa_1 w + \kappa_1' b) + k_2' a b \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the first term on the right-hand side of each expression accounts for the unimolecular portion of the reaction and the second term for the bimolecular one. If b and w can be assumed to remain constant during the reactions the total reaction velocities in the absence and in the presence of amine will follow the first-order law. The respective first-order rate constants k_H and k_T will be related to the rate constants of the fundamental steps of the above reaction scheme:

$$k_H = k_1 + k_2w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$k_T = k_1 + k_2w + k_2'b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Also, from (1) and (2):

$$\frac{dx}{dy} = \frac{k_2w + k_1\kappa_1w/(\kappa_1w + \kappa_1'b)}{k_2'b + k_1\kappa_1'b/(\kappa_1w + \kappa_1'b)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and, if w and b can again be assumed to stay sensibly constant during the course of the reaction or, at least, to be adequately represented by a mean value, integration is possible and

$$\frac{dx}{dy} = \frac{x_\infty}{y_\infty} = \frac{\%\ \text{Hydrolysis}}{\%\ \text{Anilide formation}} \equiv \rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

[This integrated expression is *not* equivalent to the expression previously given (Emery and Gold, *J.*, 1950, 1449), which was derived on the assumption that only one mechanism operates, although the nature of the mechanism was immaterial.] The product ratio ρ can be determined by acidimetry of the solution after completion of the reaction. The extent of conversion of the amines into their conjugate acids was negligible.

It will at first be assumed that the addition of aromatic amine does not change the rate of hydrolysis for a given acetone–water mixture, *i.e.*, that the medium properties and the kinetically effective water concentration are unaffected. Then, for a given solvent mixture, $k_2'b = k_T - k_H$. The large value of this difference between k_T and k_H for moderate values of b demonstrates that a significant amount of bimolecular acylation occurs for all the conditions studied by us (Table 1). Equations (3)—(6) can also be combined to give

$$k_1 \cdot \frac{\kappa_1'b}{\kappa_1w + \kappa_1'b} = \frac{k_T}{\rho + 1} - (k_T - k_H) \equiv \chi \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which allows the unimolecular contribution to the amine acylation reaction to be deduced. The evaluation of χ from the experimental data is given in Table 2.

TABLE 1. *Dependence of overall rate of disappearance of acylating agent on concentration of added amine.*

Acetic anhydride: B = *o*-Chloroaniline. Temp.: 30·06°. Solvent: acetone–water (50 : 50 w/w). $[Ac_2O]_0$ ~0·04M.

$[B]_{mean}$ *	0	0·086	0·118	0·466
10^4k_T (sec.$^{-1}$)	1·39	3·58	4·65	10·4

Benzoyl chloride: B = *o*-Nitroaniline. Temp.: 0°. $[BzCl]_0$ ~0·05M.

Wt. (%) of acetone in solvent					
80	$[B]_{mean}$ *	0	0·091	0·187	0·285
	10^5k_T (sec.$^{-1}$)	3·9	6·5	8·0	10·0
50	$[B]_{mean}$ *	0	0·092	0·188	0·286
	10^5k_T	27·7	32·1	36·3	39·6

* In some of the experiments the concentration of amine was not in large excess over the concentration of acylating agent. The mean concentration of amine in these experiments was calculated from the independent determination of ρ. The rate of change of the amine concentration was sufficiently small not to impair the evaluation of the first-order rate coefficient after exactly one half-life.

For acetic anhydride in acetone–water (50 : 50 w/w) and benzoyl chloride in acetone–water (80 : 20 w/w), χ is found to be zero within the experimental error. On the other hand, this analysis leads to an appreciable value for χ (amounting to up to a quarter of the total rate) in the case of benzoyl chloride in acetone–water (50 : 50 w/w), and from the dependence of χ on the concentration of added base, *viz.*,

$$1/\chi = (1 + \kappa_1w/\kappa_1'b)/k_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

it is possible to derive graphically that $k_1 = (14{\cdot}5 \pm^{4}_{2}) \times 10^{-5}$ sec.$^{-1}$, *i.e.*, that in the hydrolysis of benzoyl chloride in acetone–water (50 : 50 w/w) the unimolecular and the

TABLE 2. *Values of* ρ *and the evaluation of* χ.

Acetic anhydride in acetone–water (50 : 50 w/w) at 30·06°.

[o-Chloroaniline]$_{\text{mean}}$, M	10^4k_T (sec.$^{-1}$)	ρ *	$10^4k_T/(\rho+1)$	$10^4(k_T - k_H)$	$10^4\chi$
0·086	3·58	$0{\cdot}62_5$	2·20	2·19	+0·01
0·118	4·65	$0{\cdot}44_5$	3·22	3·26	−0·04
0·466	10·4	$0{\cdot}16_5$	8·9	9·0	−0·1

* Obtained by interpolation from a more extensive set of measurements at different concentrations.

Benzoyl chloride in acetone–water (80 : 20 w/w) at 0°.

[o-Nitroaniline]$_{\text{mean}}$, M	10^5k_T (sec.$^{-1}$)	ρ	$10^5k_T/(\rho+1)$	$10^5(k_T - k_H)$	$10^5\chi$
0·091	6·5	1·88	2·3	2·6	−0·3
0·187	8·0	1·04	3·9	4·1	−0·2
0·285	10·0	$0{\cdot}72_5$	5·8	6·1	−0·3

Benzoyl chloride in acetone–water (50 : 50 w/w) at 0°.

[o-Nitroaniline]$_{\text{mean}}$, M	10^5k_T (sec.$^{-1}$)	ρ	$10^5k_T/(\rho+1)$	$10^5(k_T - k_H)$	$10^5\chi$
0·092	32·1	2·20	9·7	4·4	5·3
0·188	36·3	1·25	16·1	8·6	7·5
0·286	39·6	0·86	21·3	11·9	9·4

TABLE 3. *Salt effects in hydrolysis of* BzCl *in acetone–water* (50 : 50 *w/w*) *at* 0°.

Added salt :	0·1M-NaCl	0·2M-NaCl	0·3M-NaCl	0·1M-Li_2SO_4
$10^5(k_H - k^\circ_H)$ (sec.$^{-1}$)............	1·8	2·4	2·6	2·5

TABLE 4. *First-order rate constants for the hydrolysis of benzoyl chloride in acetone–water mixtures at* 0°.

Wt. (%) of acetone in solvent	85	80	75	70	65	60	55	50	45
10^5k_H(sec.$^{-1}$)	2·6	3·9	5·4	7·4	9·5	13·2	19·4	27·7	42·6

TABLE 5. *Medium effects in the hydrolysis of benzoyl chloride and acetic anhydride in* 50% *acetone–water at* 0°.*

	Added substance	Percentage reduction † of k_H, $100(k_H - k^\circ_H)/k^\circ_H$
Benzoyl chloride	0·08M-Nitrobenzene	7
Acetic anhydride	0·08M-Nitrobenzene	4
,, ...	0·30M-Nitroaniline	6

* Experiments carried out by Mr. D. Bethell.

† Each of these values is the mean of several pairs of experiments agreeing to within approx. 1·5%.

bimolecular mechanism are of roughly equal importance. In principle, it should also be possible to obtain in this way the values of k_2w/k_2' and κ_1w/κ_1', *i.e.*, the relative reactivities of water and aromatic amine for benzoyl chloride and benzoylium ions, but the accuracy of the derived quantities is inadequate for this purpose. It seems, however, that the two ratios have rather similar values.

Medium Effects.—To allow for the possibility that the addition of a certain concentration of amine might exert a medium effect, equations (4), (6), and (7) may, as a second approximation, be modified to give

$$k_T = k_1(1-\lambda) + k_2(1-\mu)w + k_2'(1-\nu)b \quad . \quad . \quad . \quad . \quad . \quad (4')$$

$$\rho = \frac{k_2(1-\mu)w + k_1(1-\lambda)\cdot\kappa_1w/(\kappa_1w+\kappa_1'b)}{k_2'(1-\nu)b + k_1(1-\lambda)\cdot\kappa_1'b/(\kappa_1w+\kappa_1'b)} \quad . \quad . \quad . \quad . \quad (6')$$

$$\chi = k_1(1-\lambda)\cdot\kappa_1'b/(\kappa_1'w+\kappa_1'b) + k_1\lambda + k_2\mu \quad . \quad . \quad . \quad . \quad (7')$$

where χ, μ, and ν express the (retarding) medium effects.

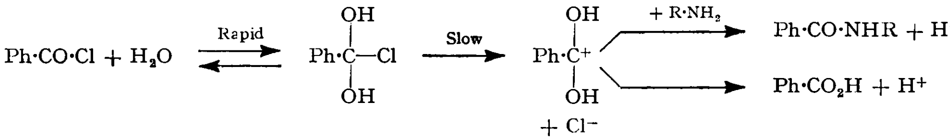
It follows from equation (7′) that an appreciable value of χ could arise even when there is no unimolecular contribution to the rate at all (*i.e.*, $k_1 = 0$) in the event of μ being positive and large. Although it would be very difficult to allow rigorously for the effect of λ and μ on the value of the unimolecular contribution to the amine acylation calculated by the previous analysis, yet the following experiments render it exceedingly unlikely that this supposedly unimolecular rate is entirely, or for the most part, attributable to the medium effect of o-nitroaniline, *i.e.*, to the term $k_2\mu$ in equation (7′).

Table 5 shows the effect of added substances on the rates of hydrolysis of acetic anhydride and benzoyl chloride. It is seen from this that the addition of 0·3M-*o*-nitroaniline (which does not undergo acylation under these conditions) reduced the rate of hydrolysis of acetic anhydride only slightly more than the addition of 0·08M-nitrobenzene. The effect of 0·08M-nitrobenzene on the rate of hydrolysis of benzoyl chloride can be measured and, in view of the similarity of the two hydrolyses, it seems justifiable to conclude that 0·286M-*o*-nitroaniline would depress the bimolecular hydrolysis of benzoyl chloride by not more than 12—14% at the most. On the other hand, it would be necessary to assume that this value is about 34% if one were to account for the value of χ found in the competition experiment with that concentration of *o*-nitroaniline on the basis of a medium effect alone.

Further support for the view that χ is not the consequence of a medium effect comes from the close agreement between $(k_T - k_H)$ and $k_T/(\rho + 1)$ for acetic anhydride in 50% acetone–water and for benzoyl chloride in 80% acetone–water, *i.e.*, under conditions where an ionisation mechanism is expected to be less likely.

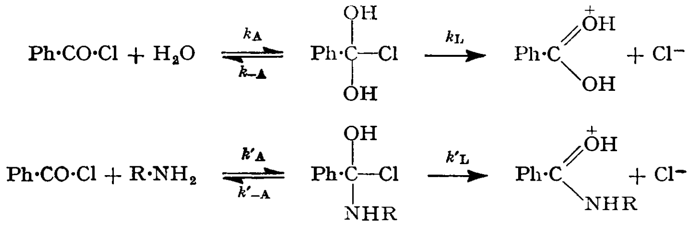
We estimate from the data of Table 5 that the value of k_1 for the hydrolysis of benzoyl chloride in 50% acetone–water, calculated above without consideration of the medium effect, is only slightly too large, and that the corrected figure would be $(11 \pm {}^{4}_{2}) \times 10^{-5}$ sec.$^{-1}$. It is possible to consider more quantitative methods of analysing the data, but this seems hardly justified by their experimental accuracy.

Chemical Interpretations of Kinetic Results.—The immediate inference from the kinetic analysis for benzoyl chloride in 50% acetone–water is that some of the reaction proceeds by a mechanism in which the rate-determining step is the same and independent of amine concentration whether the outcome of the reaction is the acylation of amine or of water, and that some of it goes by a mechanism in which the rate-determining steps are different for the two reactions, that of amine benzoylation being kinetically of the first order with respect to the amine. It is impossible to decide from the results whether benzoyl chloride is first converted by one or more rapid equilibria into some intermediate which then undergoes the rate-determining process common to amine acylation and hydrolysis. However, the most reasonable rate-determining step is the heterolysis of the C–Cl bond and the assumption of a rapid and reversible intermediate hydration of benzoyl chloride preceding this step, *i.e.*,



does not appear attractive when it is remembered that the conjugate acid of benzoic acid (formed, for instance, in solutions of benzoic acid in sulphuric acid) is not a particularly good benzoylating agent.

On the other hand, it is not incompatible with the results that the bimolecular mechanism is composite, involving, as in the case of ester hydrolysis (Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626), an addition reaction as the first step, *i.e.*,

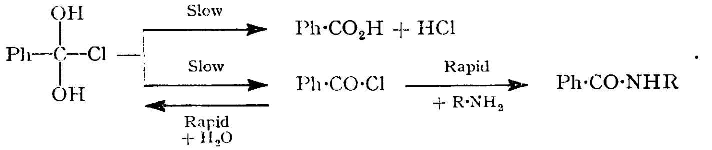


in which case the rate constants of the two bimolecular reactions are given by

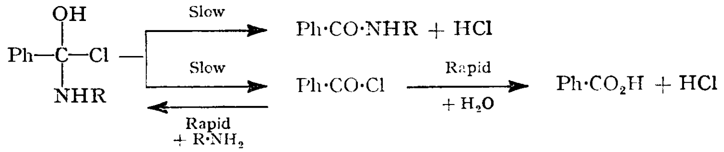
$$k_2 = k_A k_L/(k_{-A} + k_L)\,;\ k_2' = k'_A k'_L/(k'_{-A} + k'_L)$$

but, as far as our method of kinetic analysis goes, this mechanism is indistinguishable from a direct substitution mechanism.

We have also considered the mechanisms



. . . . (A)



. . . (B)

in which it is supposed that the benzoyl chloride is virtually completely converted into adducts which then undergo unimolecular reversion to benzoyl chloride for one of the reactions. Neither of these schemes is satisfactory for the reactions of benzoyl chloride in 50% acetone–water. For instance, scheme (A) predicts $k_T/(\rho + 1)$ and $(k_T - k_H)$ to be equal, whereas scheme (B) would require $k_T/(\rho + 1)$ to be independent of the concentration of amine. Scheme (A) and more complicated schemes based on the hypothesis of rapid hydration are also rendered improbable by our observation that the instantaneous heat of mixing of benzoyl chloride and acetone–water is negligible compared with the heat of hydrolysis, the rate of evolution of which agrees with the experimental rate of hydrolysis.

Winstein, Grunwald, and Jones (*loc. cit.*) have recently suggested that it is not correct to assume two kinds of processes (*i.e.*, unimolecular and bimolecular heterolyses) to occur simultaneously in the solvolysis of " border-line " cases (*i.e.*, between S_N1 and S_N2) in any one solvent, but that it is more profitable to describe the reaction in terms of one single process, intermediate in character between the extreme mechanistic categories. A similar point has also been made by Bird, Hughes, and Ingold (*J.*, 1954, 634). It is now suggested that this approach makes too great a distinction between solvolytic and non-solvolytic reactions, and that the inadequacy of the underlying physical picture can be demonstrated by the following considerations. Let us try to apply their ideas to the situation found in the simultaneous hydrolysis and amine acylation reaction of benzoyl chloride in 50% acetone–water. Suppose the rate of hydrolysis to be given by $dx/dt = k_2^*aw^*$, where w^* is now a function of the water concentration appropriate to this intermediate type of solvent participation in the reaction. In order to explain the experimental difference between $(k_T - k_H)$ and $k_T/(\rho + 1)$ it is still necessary to assume that the rate of amine acylation be given by $dy/dt = k_2^{*\prime}ab^*$, where b^* is a function of b which increases less rapidly than the first power of b, *i.e.*, the acylation is kinetically between zero and first order. Such a reaction order cannot be attributed to an incomplete participation of an amine molecule in the transition state of the reaction : if it takes part at all, however weakly, the reaction is of the first order with respect to the amine, although other characteristics of the reaction (such as substituent effects) may indicate that the C–Cl bond rupture rather than the C–N bond formation is the more important aspect of the reaction. We are therefore bound to conclude that the intermediate reaction order indicates that amine molecules are involved in some, though not all, of the transition states of this reaction. This is equivalent to the statement that unimolecular and bimolecular acylations proceed simultaneously, *i.e.*, that

$$k_2^{*\prime}ab = k_2'b + k_1\kappa_1'b/(\kappa_1 w + \kappa_1'b)$$

as previously derived. Now it is still conceivable that—notwithstanding the experimental evidence that some of the anilide formation proceeds *via* the intermediate formation of Bz^+ ions—none of the acylation of the solvent follows this route. This would involve the assumption that the Bz^+ ions are infintiely more reactive towards amine than they are towards water, *i.e.*, that $\kappa_1'b \gg \kappa_1 w$ or $\kappa_1 w/\kappa_1'b \ll 1$, but this can be disproved from the experimental data by application of equation (8). If no part of the hydrolysis proceeded *via* the common unimolecular step, χ should be independent of the value of b, which it is not (Table 1).

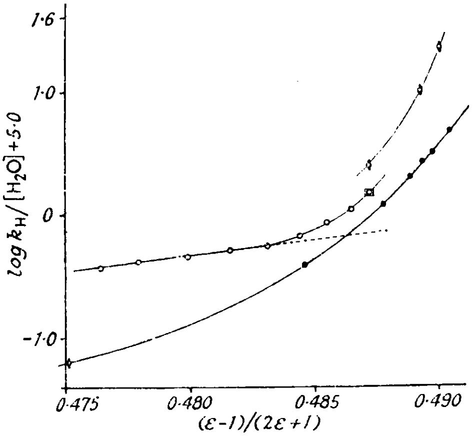
The observation that $\kappa_1'b$ is neither very much smaller nor very much larger than $\kappa_1 w$ for acetone–water (50 : 50 w/w) confirms that the good agreement between $(k_T - k_H)$ and $k_T/(\rho + 1)$ in the experiments in acetone–water (80 : 20 w/w) is to be attributed to the complete predominance of the bimolecular mechanisms. An alternative explanation would have been to attribute the smallness of χ to a very low value of the ratio $\kappa_1'b/(\kappa_1 w + \kappa_1'b)$, when the unimolecular amine acylation would escape detection, although k_1 would be quite large and there would be an appreciable amount of unimolecular hydrolysis. However, it is unreasonable to suppose $\kappa_1 w/(\kappa_1 w + \kappa_1'b)$ to have a lower value in the solvent poorer in water, and therefore if, as is found, $\kappa_1'b/(\kappa_1 w + \kappa_1'b)$ is not very small in 50% acetone–water, it is even less likely to be negligible in acetone–water (80 : 20 w/w).

Similar considerations lead us to accept a bimolecular mechanism for the hydrolysis of acetic anhydride in 50% acetone–water.

Our demonstration of the operation of two physically distinct mechanisms in the hydrolysis of benzoyl chloride also argues against Swain and Langsdorf's point of view (*J. Amer. Chem. Soc.*, 1951, **73**, 2813) according to which " there are no clear dividing lines to distinguish between " mechanisms " such as S_N1, S_N2, $B'2$, etc." Our work links up in this respect with a recent paper by Swain, Scott, and Lohmann (*ibid.*, 1953, **75**, 136) who, by use of a kinetic technique similar to ours, employing both ionic and non-ionic competing solutes, have shown that the rate of disappearance of triphenylmethyl halides is independent of the presence of added substances although the composition of the products is thereby appreciably altered. Swain, Scott, and Lohmann draw the plausible conclusion that their results can be interpreted only by postulating an unstable intermediate which they suggest is the solvated triphenylcarbonium ion, in agreement with generally accepted views. The authors should also have pointed out that their work elegantly demonstrates an example of what is commonly known as the S_N1 mechanism and, since they implicitly accept the occurrence of a different (S_N2) mechanism in other cases (Swain and Scott, *ibid.*, p. 141), that it invalidates the earlier conclusions of Swain and Langsdorf. These, like the statement by Winstein, Grunwald, and Jones (*loc. cit.*), appear to have been founded on incorrect indirect criteria of mechanism.

The Dependence of Reaction Velocity on Dielectric Constant as a Mechanistic Criterion.— It has been suggested by Archer and Hudson (*loc. cit.*) that curvature of the relation between log k and $(\varepsilon - 1)/(2\varepsilon + 1)$ (where k is obtained by dividing the experimental rate constant by the molarity of water in the solvent) indicates a change of mechanism in a solvolytic reaction in a mixed solvent (cf. Cowan, McCabe, and Warner, *J. Amer. Chem. Soc.*, 1950, **72**, 1194). A linear relation of this form follows from Kirkwood's treatment of dipole solvation (*J. Chem. Phys.*, 1934, **2**, 351; cf. Bell, *Trans. Faraday Soc.*, 1931, **27**, 797) by assuming that reagent molecules and transition states can be regarded as electric dipoles immersed in a structureless medium of dielectric constant ε and that all non-electrostatic interactions are unimportant. The figure includes a plot of rate data on benzoyl chloride in acetone–water mixtures which shows that a linear relation of the type mentioned holds for media containing between 15 and ~35% of water by weight. On continuation of the curve to more aqueous media, a departure from linearity appears to set in fairly suddenly. On this basis one would conclude that over the linear portion of the curve the hydrolysis occurs entirely by a single mechanism only, presumably a bimolecular reaction, and that for higher water concentrations a unimolecular mechanism is responsible for part of the rate. One may then attempt to derive from the difference between the experimental points in this region and the extrapolation of the linear portion of the curve (shown as a broken line) values for the unimolecular contribution to the rate. For 50% acetone–water it is thus found that the rate constant for unimolecular hydrolysis (k_1) has a value of $\sim 11 \times 10^{-5}$ sec.$^{-1}$, which is in good agreement with the value derived from the competition experiments. Internal consistency is given to this analysis by the fact that a plot of the values for log k_1 derived from experiments with different acetone–water mixtures against $(\varepsilon - 1)/(2\varepsilon + 1)$ is linear.

Nevertheless, it should be pointed out that application of this mechanistic criterion to an unknown system does not seem justified until there is more evidence that linear relations of this type are in fact the rule for solvolytic reactions for which it is known from a kinetic analysis that one mechanism alone is important. It was reported earlier (Gold, *loc. cit.*) that the hydrolysis of acetic anhydride in acetone–water is an example of a reaction for which log k is a linear function of $(\varepsilon - 1)/(2\varepsilon + 1)$. It follows from the Figure, where that curve for the hydrolysis of acetic anhydride is extended by the inclusion of a more recent experimental result (Emery and Gold, *J.*, 1950, 1450) (at the same time correcting an error in the drawing of the earlier paper), that this conclusion does not seem justified when the more extensive graph is considered. This curvature occurs for regions of the graph for which the bimolecular mechanism is certain to preponderate.



* *Rec. Trav. chim.*, 1927, **46**, 516.

EXPERIMENTAL

Acetone and acetic anhydride were purified as in previous work (Gold and Jefferson, *J.*, 1953, 1409). Benzoyl chloride ("AnalaR") was used without purification, but the purity was repeatedly checked by chemical analysis (cf. Emery and Gold, *J.*, 1950, 1443), and appropriate corrections were applied for the presence of free acids in the specimens used in kinetic experiments. *o*-Chloroaniline was purified by King and Orton's method (*J.*, 1911, **99**, 1380); *o*-nitroaniline was crystallised from aqueous alcohol.

Rate Measurements with Acetic Anhydride.—The velocity of hydrolysis was determined as previously described (Bafna and Gold, *J.*, 1953, 1406). The course of the disappearance of acetic anhydride in the presence of *o*-chloroaniline was followed by simultaneously withdrawing two samples of the reaction mixture and discharging one into an excess of aniline (*a*) and the other into an excess of standard ammonia solution (*b*) (cf. Caudri, *Rec. Trav. chim.*, 1930, **49**, 1). In order to minimise the loss of acetone from the solvent during the run the sampling procedure was similar to that described by Gold, Hughes, Ingold, and Williams (*J.*, 1950, 2466). Solution (*a*) was titrated with standard sodium hydroxide solution. The acetic anhydride reacts very rapidly with the aniline, with the result that in this titration we determine (i) the acid initially present in the preparation ($\equiv z$); (ii) the acid produced by hydrolysis ($= 2x$); (iii) the acid produced by acetylation of *o*-chloroaniline ($= y$); (iv) the acid produced by acetylation of aniline ($= a_0 - x - y$). The total acid concentration in the sample (*a*) is therefore equal to $(a_0 + x + z)$. To solution (*b*) an excess of standard hydrochloric acid solution was added and then back-titrated potentiometrically with standard sodium hydroxide, a quinhydrone electrode being used. The solution was well diluted with water before titration, and any precipitated amine and anilide were removed by filtration. Delivery into an arresting solution of ammonia produces almost instantaneous hydrolysis of the remaining acetic anhydride. Hence the amount of standard ammonia solution neutralised is a measure of (i) the acid initially present ($= z$); (ii) the acid produced by hydrolysis up to the time of sampling ($= 2x$); (iii) the acid produced by acetylation of *o*-chloroaniline ($= y$); (iv) the acid produced by the instantaneous hydrolysis of the anhydride after sampling [$= 2(a_0 - x - y)$]. The total of these four sources of acid is ($z + 2a_0 - y$). The difference in the amounts of acid produced in samples (*a*) and (*b*) is equal to $a_0 - x - y$, *i.e.*, the amount of acetic anhydride remaining in the reaction solution at the time of sampling. First-order rate coefficients were evaluated graphically (cf. footnote to Table 1).

Rate Measurements with Benzoyl Chloride.—The measurements on benzoyl chloride summarised in Tables 1 and 4 were obtained by dilatometric observation of the reaction velocity. The dilatometer reservoir consisted of a thin-walled narrow helix of 50 ml. capacity, a design intended to minimise heating effects in strongly exothermic reactions. It was verified by independent chemically-followed runs that the dilatometric observations relate to the two acylation reactions.

The observations on salt and medium effects (Tables 3 and 5) relate to such chemical runs, the experimental method being an adaptation of the aniline–water method used in most of our work on the kinetics of the hydrolysis of acid anhydrides.

Determination of ρ.—The total acidity developed in the solution after completion of the reaction (X_∞) from an initial concentration a_0 of acylating agent was determined by titration of aliquot parts of the solution. Each result is the mean of six determinations. The following relations hold between x_∞, y_∞, a_0, and X_∞, after allowance for the traces of free acid initially present in the acylating agent:

$$X_\infty = 2x_\infty + y_\infty; \; a_0 = x_\infty + y_\infty;$$

and hence

$$(\rho + 1) = a_0/(2a_0 - X_\infty).$$

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