**356.** *Acylation. Part V.* Acetylation by Acetic Anhydride in Acetic Acid Catalysed by Lewis Acids.*

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The use of acetic acid solutions of zinc chloride and stannic chloride as acidic solvents for effecting the acetylation of β-naphthol by acetic anhydride is described. The kinetic form of the reaction is reported, analysed, and compared with that found for solutions of Brønsted acids in acetic acid. It is concluded that stannic chloride solutions behave very like those of sulphuric acid, and that this supports previous suggestions concerning the reaction mechanism with strong-acid catalysts. Zinc chloride solutions provide unexpected behaviour.

SOLUTIONS of zinc chloride and stannic chloride (Lewis acids) in acetic acid exhibit in practice only acidity of the Brønsted variety,[1] because these substances, without undergoing solvolysis, form complex acids with the solvent,[1,2] *e.g.*, $H_2ZnCl_2(OAc)_2$. The acidic properties of such solutions have been studied in connexion with the ionisation of basic indicators,[1,2] and the velocities of aromatic alkylation,[3] of hydrogen isotope exchange,[1] and of depolymerisation of paraldehyde.[1] The acidic properties of similar solutions have also been used in preparative connexions, *e.g.*, to promote the anomerisation of sugars.[4] In all these cases the general acidic behaviour is similar to that observed when solutions of typical Brønsted acids (*e.g.*, hydrogen chloride) are employed. The zinc chloride solutions display rather feeble acidity, the complex zinc acids being weak, whereas the stannic chloride solutions exhibit acidity comparable with that of solutions of sulphuric acid in acetic acid.

Evidence has been presented in previous Parts of this series that acetylation of hydroxylic compounds by acetic anhydride in acetic acid, when catalysed by typical Brønsted acids, proceeds *via* the acetyl derivative of the catalysing acid:

$$Ac_2O + HX \rightleftharpoons AcX + AcOH \qquad \text{Fast}$$

$$AcX + ROH \longrightarrow ROAc + HX \qquad \text{Slow}$$
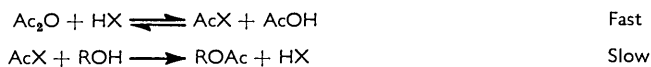
* Part IV, preceding paper.

[1] Satchell, *J.*, 1958, 3910, 1927, 2052.
[2] Bethell, Gold, and Satchell, *J.*, 1958, 1918.
[3] Bethell and Gold, *J.*, 1958, 1930.
[4] Hudson and Johnson, *J. Amer. Chem. Soc.*, 1915, **37**, 1270; Cramer and Pacsu, *ibid.*, 1937, **59**, 711.

With the halogen acids [5] the pre-equilibrium lies well to the right, but with strong acids,[5,6] *e.g.*, perchloric or sulphonic acids, it lies well to the left (though an alternative scheme is perhaps possible in the latter cases; see ref. 5 and below). Sulphuric acid occupies an intermediate, and also a special, position owing to its dibasic nature. Two acyl intermediates seem to be involved.[6]

In the following, the catalysis exhibited by the less typical, complex Brønsted acids mentioned in the opening paragraph, which are also dibasic, is described. The results are discussed in the light of previous Parts. As in Part I, β-naphthol has been the substance acylated.[5]

The ZnCl₂–AcOH Solvent System.—Experiments at 40° to determine the reaction orders are detailed in Table 1. The β-naphthol being acylated was always in great deficit compared with the acetic anhydride. The observed loss of β-naphthol was an accurately first-order process for several half lives. It will be seen that the rate (k_{obs}) is fairly closely proportional to acetic anhydride concentration even when this component is in excess of the acid component. (There is room nevertheless for a suspicion that the order in acetic anhydride may be slightly greater than unity.)

TABLE 1.

Acylation of β-naphthol by acetic anhydride in acetic acid catalysed by zinc chloride at 40°.

k_{obs} = First-order rate constant (in min.$^{-1}$). Square brackets represent concentration in both Tables.

[Ac₂O]	[ZnCl₂]	$10^2 k_{obs}$		[Ac₂O]	[ZnCl₂]	k_{obs}
(a) *Order in acetic anhydride*				(b) *Order in zinc chloride*		
0·08	0·133	0·077		1·0	0·04	0·20
1·00	0·133	1·2		1·0	0·067	0·36
0·03	0·266	0·11		1·0	0·133	1·2
0·08	0·266	0·32		1·0	0·266	4·9
0·18	0·266	0·77		0·1	0·53	1·1
0·38	0·266	1·6				

The effect of increasing the zinc chloride concentration at constant acetic anhydride concentration is marked, and the order in this component is greater than unity. Indeed if log k_{obs} is plotted against log I, where I is the ionisation ratio of a Brønsted base indicator [2] (*e.g.*, *o*-nitroaniline), a straight line of slope close to unity is obtained.

In this system [2] Brønsted bases (B) participate in equilibria such as:
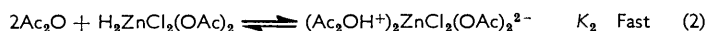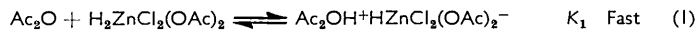
$$B + H_2ZnCl_2(OAc)_2 \rightleftharpoons BH^+HZnCl_2(OAc)_2^-$$

Secondary bases of type ROAc are also ionised as follows:

$$ROAc + H_2ZnCl_2(OAc)_2 \rightleftharpoons R^+HZnCl_2(OAc)_2^- + AcOH$$

Indicator data for the latter equilibria are not available for the zinc chloride concentrations used in the present experiments. However, the results which are available suggest that a plot of log k_{obs} against log I for such secondary bases would also be reasonably, though not so closely, linear.

The obvious inference from the kinetic results is that the acylation mechanism involves intermediates produced in ionisation equilibria similar to those involved in indicator ionisation. For instance:
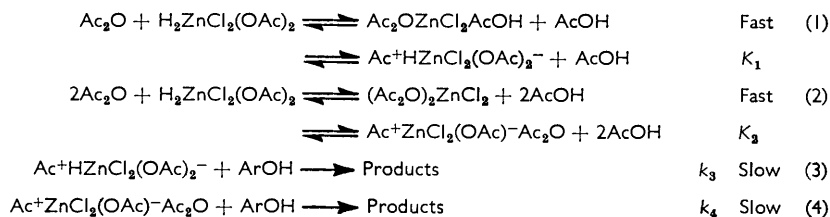
Mechanism 1.

$Ac_2O + H_2ZnCl_2(OAc)_2 \rightleftharpoons Ac_2OH^+HZnCl_2(OAc)_2^-$	K_1	Fast	(1)
$2Ac_2O + H_2ZnCl_2(OAc)_2 \rightleftharpoons (Ac_2OH^+)_2ZnCl_2(OAc)_2^{2-}$	K_2	Fast	(2)
$Ac_2OH^+HZnCl_2(OAc)_2^- + ArOH \longrightarrow Products$	k_3	Slow	(3)
$(Ac_2OH^+)_2ZnCl_2(OAc)_2^{2-} + ArOH \longrightarrow Products$	k_4	Slow	(4)

[5] Satchell, *J.*, 1960, 1752.
[6] Part IV, preceding paper.

This mechanism, with the pre-equilibria lying to the left, accounts formally for the observed kinetics, small contributions from steps (2) and (4) taking care of the slightly greater than first-order dependence on acetic anhydride (if this is real in this instance).*

Another possibility is mechanism 2, with ionisation like that for secondary bases, and the formation of what are in fact the acyl derivatives of the complex acid.

Mechanism 2.

$$Ac_2O + H_2ZnCl_2(OAc)_2 \rightleftharpoons Ac_2OZnCl_2AcOH + AcOH \qquad \text{Fast} \quad (I)$$

$$\rightleftharpoons Ac^+HZnCl_2(OAc)_2^- + AcOH \qquad K_1$$

$$2Ac_2O + H_2ZnCl_2(OAc)_2 \rightleftharpoons (Ac_2O)_2ZnCl_2 + 2AcOH \qquad \text{Fast} \quad (2)$$

$$\rightleftharpoons Ac^+ZnCl_2(OAc)^-Ac_2O + 2AcOH \qquad K_2$$

$$Ac^+HZnCl_2(OAc)_2^- + ArOH \longrightarrow \text{Products} \qquad k_3 \quad \text{Slow} \quad (3)$$

$$Ac^+ZnCl_2(OAc)^-Ac_2O + ArOH \longrightarrow \text{Products} \qquad k_4 \quad \text{Slow} \quad (4)$$

Apart from the possible intrusion of a small amount of second-order component arising from the dibasic character of the catalyst, the kinetic pattern shown by the zinc chloride catalysis is similar to that shown by the more conventional strong Brønsted acids, *e.g.*, perchloric and sulphonic acids. For these also we find [5] the close first-order dependence on acetic anhydride (implying that the significant intermediate-forming equilibria lie well to the left) and a rough parallelism to Brønsted base indicator ionisation, though this parallelism was sufficiently poor in perchloric acid catalysis for preference to go to a mechanism similar to the second of the above, involving acetyl perchlorate.

Such a mechanism certainly operates for the weaker acid hydrogen chloride, where the kinetics are different and proportionality to acetic anhydride concentration is not found, acetyl chloride being formed in an equilibrium which lies well to the right. It is noteworthy therefore that the even weaker acid $H_2ZnCl_2(OAc)_2$ is out of line in general behaviour: though weak, it behaves kinetically like a strong acid (though very much greater concentrations are needed to produce measurable reaction). In view of this fact and the good correlation with $\log I$, it is tempting to choose the (unusual) mechanism 1 for zinc chloride catalysis. In any event a species such as Ac_2OZnCl_2AcOH [and certainly $(Ac_2O)_2ZnCl_2$] cannot be formed to any great extent (cf. ref. 7).

An acceptance of mechanism 1 for zinc chloride catalysis, which is strange in being kinetically similar to strong-acid catalysis, nevertheless cannot open the way to a general acceptance of mechanism 1 for strong-acid catalysis also. For apart from the considerations noted previously in this connexion,[5,6] the results obtained under stannic chloride catalysis argue against it also.

TABLE 2.

Acylation of β-naphthol by acetic anhydride in acetic acid catalysed by stannic chloride at 40°.

k_{obs} = First-order rate constant (in min.$^{-1}$).

[Ac$_2$O]	10^3[SnCl$_4$]	$10^2 k_{obs}$	$10^2 k_{calc}$	[Ac$_2$O]	10^3[SnCl$_4$]	$10^2 k_{obs}$
(a) *Order in acetic anhydride*				(b) *Order in stannic chloride*		
0·01	8·6	0·9	0·9	0·50	0·69	0·088
0·03	8·6	1·8	1·8$_5$	0·50	2·0	0·61
0·08	8·6	3·0	2·8	0·50	4·1	1·8
0·25	8·6	4·8	4·6	0·50	6·1	4·0
0·50	8·6	6·6	7·0	0·50	8·6	6·6
1·00	8·6	11·5	12·0			

The SnCl$_4$–AcOH *Solvent System.*—Here the reaction was again of the first-order in loss of β-naphthol. The results are in Table 2. For this system the catalyst concen-

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* For a full argument from the rate equations see refs. 5 and 6.

[7] Burton and Praill, *J.*, 1951, 726.

tration needed was small, and that of the anhydride was always in some excess of it. Inspection of Table 2 reveals, besides a strong dependence on acidity, an order of somewhat less than unity in the anhydride at the lower anhydride concentrations, which, however, rises to close to unity at the higher concentrations. The observed order in anhydride will be dealt with first.

When an order of less than unity is involved a common reason is the intervention of an intermediate producing equilibrium which lies far, but not completely, to the right-hand side. A subsequent rise in order with further increase in reactant concentration can imply that a second reactive intermediate is being formed at the expense of the first, and which eventually contributes predominantly to the rate. There are thus, as for zinc chloride and strong-acid catalysis, at least two basic types of mechanism possible for the acylation. These may be envisaged by writing $SnCl_4$ for $ZnCl_2$ in the schemes on p. 1895. If, in these schemes, k represents a rate constant and K an equilibrium constant, and if it is also assumed that $K_1 \approx 10^2$ for mechanism 1 (or $K_1 \approx 16 \times 10^2$ for mechanism 2) and that K_2 is small, then the observed variation in k_{obs}, at constant catalyst concentration and varying anhydride concentration, may be very reasonably reproduced (see k_{calc} in Table 2) by either mechanism. They are, of course, of the same kinetic form. As for the zinc chloride catalysis, the detailed rate equations are not given here because the analyses are essentially similar to those presented previously.[5,6] The behaviour with stannic chloride is very similar to that obtained for catalysis by the dibasic sulphuric acid. The only differences are that in the present case the equilibrium (1) lies further to the right, and the contribution from step (4) is not sufficient to maintain the overall order in anhydride even as high as first over most of the range studied. K_1 was estimated by inspection for the present system, the special methods possible for sulphuric acid catalysis not being available. A value $1 \cdot 5 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$ is found for k_3. K_2 is assumed to be small, which implies a small amount of disubstituted intermediate. Therefore the value of k_4 must be large compared with that of k_3, for the disubstituted intermediate to contribute significantly to the rate. The greater reactivity of the di- than of the mono-substituted species seems at least a reasonable result on either mechanism. Values for K_2 and k_4 are not obtainable individually.

Thus the general form of mechanisms 1 and 2 is satisfactory so far as the order in anhydride is concerned. There remains the problem of choosing between them. The complex acid $H_2SnCl_4(OAc)_2$ is a strong acid—indeed comparable with sulphuric acid.[1] In fact these two acids probably exist in acetic acid in the ion-paired, ionised forms $AcOH_2^+HSO_4^-$ and $AcOH_2^+HSnCl_4(OAc)_2^-$, though this detail has been omitted so far. If mechanism 1 operates, the value of K_1 implies that there is fairly substantial replacement, in the concentration regions used, of acetic acid by acetic anhydride as the solvating base for $H_2SnCl_4(OAc)_2$:

$$AcOH_2^+HSnCl_4(OAc)_2^- + Ac_2O \rightleftharpoons Ac_2OH^+HSnCl_4(OAc)^- + AcOH$$
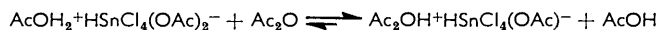
While when considered in the isolation of the present kinetics this is a satisfactory assumption, it is difficult to reconcile it with the observed kinetics for perchloric and sulphonic acids. These acids (especially perchloric) are as strong as, or even stronger [1,8] than, $H_2SnCl_4(OAc)_2$, and they will surely transfer a proton to acetic anhydride in an equilibrium like that above at least as well as the complex tin acid, e.g.:

$$AcOH_2^+ClO_4^- + Ac_2O \rightleftharpoons Ac_2OH^+ClO_4^- + AcOH$$

However, this sort of position for these equilibria is not compatible with first-order dependence on acetic anhydride concentration; and there is no dibasicity to counter the inevitable reduction in order. As for both perchloric acid and sulphonic acids a strict first-order dependence on anhydride is found; [5,6] therefore mechanism 1 must be rejected

[8] Kolthoff and Bruckenstein, *J. Amer. Chem. Soc.*, 1956, **78**, 1.

for stannic chloride catalysis. The alternative (mechanism 2), which we have in fact previously chosen [5,6] on other grounds for the other strong acids, involves the formation of the acetyl derivatives of the catalysing acids, and for catalysis by $H_2SnCl_4(OAc)_2$ these are (see above) Ac_2OSnCl_4AcOH and $(Ac_2O)_2SnCl_4$. While acetyl perchlorate only exists in acetic acid in very small amount, nevertheless, the formation of a considerable quantity of the species Ac_2OSnCl_4AcOH is perhaps not surprising. It seems probable that steric compression limits the formation of the disubstituted $(Ac_2O)_2SnCl_4$ by making it more reactive. Further evidence is presented in the following paper that these complex stannic chloride derivatives may indeed be active acetylating agents.

Two final points require comment. First, we have been led to assume the formation of considerable amounts of Ac_2OSnCl_4AcOH but of little of the corresponding Ac_2OZnCl_2AcOH. Apart from possible steric reasons, it is not clear why the formation of such a species should be so much more favourable in the one case. Secondly, we have not yet commented on the dependence on catalyst concentration for the stannic chloride-catalysed reaction. This dependence was determined in the region where acylation *via* $(Ac_2O)_2SnCl_4$ is dominant (see Table 2). A plot of log k_{obs} at constant anhydride concentration against log I for Brønsted bases shows that there is a rough correlation, the points falling, as for perchloric acid catalysis, on a smooth curve. The good linear relation found with zinc chloride is not obtained. As noted earlier, a rough correlation with indicator ionisation is probably compatible with the operation of equilibria such as:

$$Ac_2O + Ac_2OSnCl_4AcOH \rightleftharpoons (Ac_2O)_2SnCl_4 + AcOH$$

Experimental

Materials.—These were purified as described before.[1,5] The water content of the acetic acid solvent, determined by the Karl Fischer method, was <0.02M. Stock solutions of zinc chloride and stannic chloride in acetic acid were used in making up the reaction mixtures. Their strengths were estimated by a Fajans titration.

Kinetic Methods.—Measurements were at $40°$. The general kinetic procedure was as previously described.[5] It was shown that the traces of water in the solvent were acylated (to acetic acid) rapidly compared with the acetylation of β-naphthol that was being followed; the stoicheiometric anhydride concentrations were therefore corrected for the water contents of the medium. The obtained rate constants were reproducible to $\pm 5\%$.

Reaction Stoicheiometry.—Both the zinc chloride- and stannic chloride-catalysed reactions gave essentially quantitative yields of β-naphthyl acetate in independent preparative-scale reactions.

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