89. *Acylation. Part X.*[1] *Catalytic Salt Effects and Halogen Interchange between Acyl, Hydrogen, and Saline Halides: Two Factors in Acylation in Acetic Acid.*

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Experiments on the catalysis of the reactions between β-naphthol and acetyl chloride and bromide in acetic acid are reported. Catalysis of acetylation by both hydrogen and saline halides has been found. When the catalyst and the acyl halide have a common halogen, an electrophilic catalysis probably results, similar in principle, though not in power, to that found previously for the corresponding system involving the fluorides. When their halogen atoms are different, another form of catalysis appears owing to the possibility of rapid halogen interchange, *e.g.*:

$$\mathrm{AcCl + HBr \rightleftharpoons AcBr + HCl}$$
$$\mathrm{AcCl + Et_4NBr \rightleftharpoons AcBr + Et_4NCl}$$

From the measured rates for mixed halogen systems we have obtained approximate values for the equilibrium constants of the interchange reactions.

CURRENT work[1] with acetyl chloride in nitromethane as solvent redirected our attention to a few previous findings for acetic acid media,[2] and we amplify these here.

The reactions of acyl fluorides with hydroxylic compounds are powerfully catalysed by Brønsted acids, especially by molecular hydrogen fluoride. This phenomenon is exemplified by the behaviour of acetyl fluoride in acetic acid.[2] Previously we have also found that the rate of acetylation (of β-naphthol) by acetyl chloride in acetic acid is increased by added hydrogen chloride,[2] though the acceleration is much less than that observed when hydrogen fluoride is used with acetyl fluoride. We report now further measurements with hydrogen chloride and also similar new results for the pair acetyl bromide–hydrogen bromide.

TABLE 1.

Acylation of β-naphthol by acetyl chloride in acetic acid at 25°, catalysed by hydrogen chloride or tetraethylammonium chloride.

Initial [β-naphthol] ≈0·008M; k_{obs} = observed first-order rate constant.

[AcCl] (M)	1·0	1·0	1·0	1·0	1·0	0·50	1·0
[HCl] (M)	0·0	0·05	0·10	0·20	0·29	0·29	0·50
10^2k_{obs} (min.$^{-1}$)	1·90	2·13	2·10	2·47	2·65	1·30	2·88
[AcCl] (M)	1·0	1·0	1·0	1·0	1·0		
[Et_4NCl] (M)	0·025	0·05	0·10	0·20	0·28		
10^2k_{obs} (min.$^{-1}$)	2·12	2·31	2·75	3·40	3·75		

TABLE 2.

Acylation of β-naphthol by acetyl bromide in acetic acid at 25°, catalysed by hydrogen bromide and tetraethylammonium bromide.

Initial [β-naphthol] ≈0·005M.

[AcBr] (M)	0·05	0·05	0·05	0·05	0·10	0·05	0·05
[HBr] (M)	0·0	0·048	0·096	0·198	0·198	0·395	0·480
10^2k_{obs} (min.$^{-1}$)	1·27	1·49	1·61	2·09	4·20	2·90	3·32
[AcBr] (M)	0·05	0·05	0·05	0·05	0·10	0·05	0·05
[Et_4NBr] (M)	0·020	0·038	0·112	0·190	0·190	0·350	0·500
10^2k_{obs} (min.$^{-1}$)	1·45	1·43	1·68	2·16	4·25	2·55	2·60

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[1] Part IX, Satchell, preceding paper.

[2] Satchell, *J.*, 1960, 1752.

Kinetic Effects when Catalyst and Acylating Agent contain a Common Halogen.—(a) *The effect of added halogen acids.* The measured rates (see Experimental section) concern the first-order removal of β-naphthol in the presence of an excess of acyl halide and of varying amounts of acid, at 25°. The results are in Tables 1 and 2. Those referring to hydrogen chloride have the same general pattern as others previously noted [2] at 40°. The observed first-order constant (k_{obs}) may be represented, for convenience, as the sum of two terms referring respectively to the spontaneous (k_0) and the acid-promoted (k_{HX}) contribution. If ROH = naphthol, then:

$$-d[\mathrm{ROH}]/dt = k'[\mathrm{AcX}][\mathrm{ROH}] = k_{obs}[\mathrm{ROH}], \qquad (i)$$

and

$$k_{obs} = k_0 + k_{HX}[\mathrm{HX}]. \qquad (ii)$$

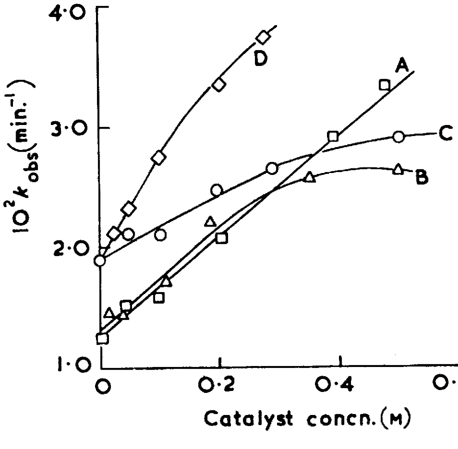
To compare the effects for hydrogen chloride–acetyl chloride with those found when using hydrogen bromide with the more reactive acetyl bromide, it is best to calculate the second-order constants, k'. The collected data (Table 3) show that k_0' for acetyl bromide is 13 times that for acetyl chloride [at 40° the factor is 15 (ref. 2)] and that the ratio $k'_{HBr}/k'_{HCl} = 32$ below *ca.* 0·30M. The bromide system, therefore, exhibits relatively greater susceptibility to catalysis. The Figure also shows that, whereas hydrogen bromide produces a linear increase in rate, at least up to *ca.* 0·45M, the effect of hydrogen chloride falls off after *ca.* 0·30M.

TABLE 3.

Collected second-order rate constants.*

Reactant	Catalyst	$10^2k'$ (l. mole^{-1} min.$^{-1}$)	Reactant	Catalyst	$10^2k'$ (l. mole^{-1} min.$^{-1}$)
AcCl	None	1·90 (= k_0')	AcBr	None	26 (= k_0')
,,	HCl (<0·3M)	2·5	,,	HBr	80
,,	Et_4NCl (<0·15M)	7·5	,,	Et_4NBr (<0·15M)	80

* For definitions of k' and k_0' see text.



Plots of k_{obs} against catalyst concentration. Catalyst: A, HBr; B, Et_4NBr; C, HCl; D, Et_4NCl.

(b) *The effect of added common-ion salts.* In contrast to the effects in nitromethane,[1] addition of common-ion salt enhances the reaction rate. The effects of tetraethylammonium chloride on the acetyl chloride reaction (Table 1), and those of the corresponding bromide on the acetyl bromide reaction (Table 2), may be analysed as for the acids above. For $\not>$0·15M-salt, $k'_{Et_4NBr}/k'_{Et_4NCl} = 10·6$ (Table 3). In this case, therefore, in view of the spontaneous rate ratio of 13, the chloride system displays the relatively greater susceptibility to catalysis. The catalytic effect of both chloride and bromide is linear below 0·15—0·2M, but falls thereafter (see Figure).

(c) *Reaction mechanism.* Because with acetyl chloride the rate enhancement by hydrogen chloride was much less than when hydrogen fluoride was used with acetyl fluoride, we previously [2] interpreted our preliminary data in terms of a " salt effect." And indeed, as may be seen from the present results, the effects of hydrogen chloride (and of hydrogen bromide) are in some respects similar to those produced by added salt. Nevertheless, we now interpret all such rate enhancement as due primarily to specific interaction between the added species and the acyl halide. Such interaction is properly termed catalysis, for the rate effects ensuing are additional to those which depend on changes in bulk dielectric constant or on modifications of activity coefficients.

We base our interpretation on the following reaction schemes in which X = halogen. (It is to be remembered that acids and salts are both little dissociated in acetic acid.)

$$\begin{array}{rll}
\mathrm{CH_3{\cdot}COX + ROH} \xrightarrow{k_0'} \mathrm{Products} & \text{Slow} & \text{Spontaneous reaction} \\
\mathrm{CH_3{\cdot}COX + HX} \rightleftharpoons \mathrm{CH_3{\cdot}CO^+(XHX)^-} & K_{\mathrm{HX}}\text{, Fast} & \multirow{2}{*}{$\left.\right\}$ Acid catalysis} \\
\mathrm{CH_3{\cdot}CO^+(XHX)^- + ROH} \longrightarrow \mathrm{Products} & k\text{, Slow} & \\
\mathrm{CH_3{\cdot}COX + Et_4N^+X^-} \rightleftharpoons \mathrm{CH_3{\cdot}CO^+X^-Et_4N^+X^-} & \text{Fast} & \text{Salt catalysis} \\
\mathrm{CH_3{\cdot}CO^+X^-Et_4N^+X^- + ROH} \longrightarrow \mathrm{Products} & \text{Slow} &
\end{array}$$

These schemes, in which the ionic intermediates are essentially similar for both salt and acid catalysis, provide, of course, for the observed spontaneous acylation and its linear acceleration by additive. Thus, for acid catalysis:

$$-\mathrm{d[ROH]/d}t = k_0'[\mathrm{CH_3{\cdot}COX}][\mathrm{ROH}] + kK_{\mathrm{HX}}[\mathrm{CH_3{\cdot}COX}][\mathrm{HX}][\mathrm{ROH}]$$

or

$$k_{\mathrm{obs}} = k_0 + k_{\mathrm{HX}}[\mathrm{HX}]$$

where $k_0 = k_0'[\mathrm{CH_3{\cdot}COX}]$ and $k_{\mathrm{HX}} = kK_{\mathrm{HX}}[\mathrm{CH_3{\cdot}COX}]$ [compare eqn. (ii)].

Our reasons for preferring the above catalytic interpretation to one based on general medium effects are three-fold: (i) The ionic intermediates involved for the catalytic routes are basically similar to those doubtless involved for the acyl fluoride–hydrogen fluoride system, for which the very marked effects make catalysis reasonably certain.[2]

$$\mathrm{CH_3{\cdot}COX + HF} \rightleftharpoons \underset{\left(\text{or } \mathrm{CH_3{\cdot}\overset{\delta_+}{C}O.\overset{\delta_-}{F}.\overset{\delta_+}{H}.\overset{\delta_-}{F}}\right)}{\mathrm{CH_3{\cdot}CO^+\ (FHF)^-}} \xrightarrow{\mathrm{ROH}} \mathrm{Products}$$

We have previously argued that no distinction of kind, but only one of degree, can be expected between the acid-catalysed routes for the various acyl halides. Both the units $\mathrm{HCl_2^-}$ and $\mathrm{HBr_2^-}$ are well known in other contexts and there is no reason why they should not play the kinetic role of low-concentration intermediate in acetic acid.[3]

(ii) Other workers,[4] in similar contexts concerning *alkyl* halides, have usually found it necessary to consider specific interaction to be the primary cause of rate enhancement in media of low dielectric constant.

(iii) In a medium of low dielectric constant such as the present, at relatively high catalyst concentrations, the ion-pairs will doubtless cluster into quadrupoles, and other, formally neutral, higher aggregates and therefore lose some catalytic power, as found (see Figure). Moreover, the concentration range in which this effect must be invoked in the present instance is compatible with the dielectric constant of the medium.[5] The effect should be less important for the acid catalysts, which are less completely ionised. Our data accommodate this prediction: hydrogen bromide catalysis is linear for concentrations

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[3] See, *e.g.*, Kaufler and Kunz, *Ber.*, 1909, **42**, 385; Peach and Waddington, *J.*, 1962, 600; Waddington and Klanberg, *J.*, 1960, 2333.

[4] *E.g.*, Patai and Zabricky, *J.*, 1961, 5479; Hart and Cassis, *J. Amer. Chem. Soc.*, 1954, **76**, 1634; Andrews and Keefer, *ibid.*, 1961, **83**, 3708; Gelles, Hughes, and Ingold, *J.*, 1954, 2918; de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2937; Leimu and Salomaa, *Acta Chem. Scand.*, 1947, **1**, 353; Swain and Pegues, *J. Amer. Chem. Soc.*, 1958, **80**, 812.

[5] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1935, **57**, 1.

up to 0·45M, and hydrogen chloride catalysis for concentrations up to *ca.* 0·30M. The eventual curvature of the hydrogen chloride plot is interesting. It is in the opposite direction to that obtained in nitromethane.[1] We here interpret it as due to phenomena which produce a similar effect on hydrogen fluoride catalysis,[2] that is to hydrogen-bonded poly-assocation. The distinction between ion-pair association and hydrogen-bonded association is obviously a fine one, though the mechanism of association is different. The effect on catalytic power is the same, for the higher aggregates will probably be less able to participate in the catalytic equilibria considered, *i.e.*, to accept another halide ion. On the other hand, were the catalysis dependent on proton transfer the higher aggregates (*e.g.*, H_2Cl_2) might prove more powerful than the monomer. The results in nitromethane may thus imply catalysis *via* protonation—a route we have considered.[1]

We feel the above explanations of the departures of the catalyses from linearity at high catalyst concentrations are at least as convincing as any that may be proposed, in the present state of knowledge about media of low dielectric constant, based on salt effects on activity coefficients.

In short, our results seem to us to provide some novel examples of salt catalysis in acetic acid—for, although linear salt effects have been found previously,[6] the salt concentration in such studies has seldom passed into the region beyond 0·2M where we now find significant deviations from linearity—and in particular some further examples of the rarely observed Brønsted-acid catalysis of reactions of acyl chlorides and bromides.

Kinetic Effects when Catalyst and Acylating Agent contain Different Halogens.—As noted above, if hydrogen bromide is added to a solution of acetyl chloride in acetic acid the possibility exists of halogen interchange:

$$\mathrm{AcCl} + \mathrm{HBr} \rightleftharpoons \mathrm{AcBr} + \mathrm{HCl} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The effect on the rate of acetylation of β-naphthol in such a system will thus depend on the rapidity with which the above equilibrium is set up and on its position at any moment. The position, of course, determines how much of each acetyl halide is available and how much of each of the two acids is present. Both facts are relevant because one acetyl halide—here acetyl bromide (see above)—will be the more reactive and one acid—here hydrogen bromide—will catalyse the reaction electrophilically (*i.e.*, in the sense dealt with in the first part of this paper) more than the other.

Were equilibria such as (1) attained at rates comparable with those of the acylation being studied, the kinetic result would be complex. This situation might arise for very reactive substrates, but in the present study halogen-interchange was probably always essentially complete before the naphthol was added and the acylation begun (see Experimental section): at 25°, such equilibria appear to be completely established within a very few minutes and probably much sooner. If, moreover, a deficit of naphthol is used (as is customary in our experiments) so as not to disturb the acyl concentration, and if also the total halogen concentration is kept relatively small, so that electrophilic catalysis is minimised, then the observed rate in a mixed halogen system, together with the known spontaneous rates for the separate acyl halides, leads to a conclusion concerning the approximate position of the exchange equilibrium. In this way we have studied the AcBr–AcCl and the AcBr–AcF system. Our kinetic data are in Table 4. (It was necessary to keep the total halogen content reasonably low, in spite of our quantitative knowledge concerning electrophilic catalysis, because in mixed halogen systems cross-catalytic terms appear, about the magnitude of which it is only possible to make a reasonable guess.)

Similar equilibria involving instead of the hydrogen halide a saline halide can also be studied this way. This too we have done for the Br–Cl and Br–F systems. The kinetic data are also in Table 4. Our comments on them are given below. The data are not very

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[6] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2763 and related papers; Winstein, Klinedinst, and Clippinger, *ibid.*, 1961, **83**, 4986.

TABLE 4.

Acylation in mixed halogen systems at 25°.

Initial [β-naphthol] ≃0·005M.

[AcCl]	[AcBr]	[AcF]	[HCl]	[HBr]	[Et$_4$NCl]	[Et$_4$NBr]	$10^2 k_{obs}$ * (min.$^{-1}$)
0·05	—	—	—	—	—	—	0·089
—	0·05	—	—	—	—	—	1·27
0·05	—	—	—	0·05	—	—	1·15
0·05	—	—	—	0·10	—	—	1·35
0·10	—	—	—	0·05	—	—	1·42
—	0·05	—	0·05	—	—	—	1·15
0·05	—	—	—	—	—	0·05	0·33
0·10	—	—	—	—	—	0·05	0·60
—	0·05	—	—	—	0·05	—	0·32
—	—	0·048	—	—	—	—	Negligible
—	—	0·048	—	0·048	—	—	0·10
—	—	0·048	—	—	—	0·048	0·02

* The constants quoted are all means of at least two determinations. Those for the fluoride systems correspond to initial slopes of autocatalytic plots, hydrogen fluoride being a powerful catalyst even at low concentrations.

numerous, nor are the equilibrium constants very accurate, but they are worth quoting because none of the equilibria appears to have been studied quantitatively before.

(a) *Chloride–bromide distribution.*

$$\mathrm{AcCl} + \mathrm{HBr} \rightleftharpoons \mathrm{AcBr} + \mathrm{HCl} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$
$$K_1 = [\mathrm{AcBr}][\mathrm{HCl}]/[\mathrm{AcCl}][\mathrm{HBr}].$$

We find $K_1 = 80 \pm 15$. (Fairly generous errors are quoted to cover known experimental errors and the unknown contributions from cross-catalytic terms noted above.) Thus for equal stoicheiometric molarities of total bromide and total chloride the equilibrium lies well towards acetyl bromide. Hydrogen bromide therefore powerfully catalyses acylation by acetyl chloride, whereas hydrogen chloride only slightly anti-catalyses acylation by acetyl bromide (see Table 4).

$$\mathrm{AcCl} + \mathrm{Et_4NBr} \rightleftharpoons \mathrm{AcBr} + \mathrm{Et_4NCl} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$
$$K_2 = [\mathrm{AcBr}][\mathrm{Et_4NCl}]/[\mathrm{AcCl}][\mathrm{Et_4NBr}].$$

We find $K_2 = (12 \pm 4) \times 10^{-2}$. Here, for equal stoicheiometric molarities of total bromide and total chloride, the equilibrium lies towards the acetyl chloride side. Thus addition of bromide has only a moderate catalytic effect on acylation by acetyl chloride, and chloride addition appropriately retards the reactions of acetyl bromide (see Table 4).

(b) *Fluoride–bromide distribution.*

$$\mathrm{AcF} + \mathrm{HBr} \rightleftharpoons \mathrm{AcBr} + \mathrm{HF} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$
$$K_3 = [\mathrm{AcBr}][\mathrm{HF}]/[\mathrm{AcF}][\mathrm{HBr}].$$

We find $K_3 < 10^{-2}$. Addition of moderate concentrations of hydrogen bromide in acetylation by acetyl fluoride does not produce a rate at all comparable with the corresponding rate for acetyl bromide (*i.e.*, the equilibrium constant is small) nevertheless, because acetyl fluoride is relatively so unreactive, a detectable catalysis is observed (Table 4).

$$\mathrm{AcF} + \mathrm{Et_4NBr} \rightleftharpoons \mathrm{AcBr} + \mathrm{Et_4NF} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$
$$K_4 = [\mathrm{AcBr}][\mathrm{Et_4NF}]/[\mathrm{AcF}][\mathrm{Et_4NBr}].$$

We find $K_4 < 4 \times 10^{-4}$. Added bromide had almost no effect on acylation by acetyl fluoride in our experiments (Table 4). For reasons noted in the Experimental section the constants quoted for these fluoride equilibria are to be treated with some reserve.

(c) *Fluoride–chloride distribution.* The equilibrium constants quoted may be used to estimate those for the fluoride–chloride systems:

$$\mathrm{AcF + HCl \rightleftharpoons AcCl + HF} \quad \ldots\ldots\ldots\ldots \quad (5)$$

$$K_5 = \mathrm{[AcCl][HF]/[AcF][HCl]} = K_3/K_1 < 1{\cdot}5 \times 10^{-4}$$

$$\mathrm{AcF + Et_4NCl \rightleftharpoons AcCl + Et_4NF} \quad \ldots\ldots\ldots\ldots \quad (6)$$

$$K_6 = \mathrm{[AcCl][Et_4NF]/[AcF][Et_4NCl]} = K_4/K_2 < 3 \times 10^{-3}.$$

It follows that acetyl fluoride (and probably also other acyl fluorides) will be formed readily from the corresponding chloride and either hydrogen fluoride or fluoride salts. The success of preparative methods based on these reactions is therefore understandable.[7]

Comparison with the Work of Winstein.[6]—The effects of salts (and acids) recorded above for acylation could be described as normal and special. The special effect involves the formation of a new reagent, the normal effect an enhancement of ionisation by short-range complex formation. In his work on ester solvolysis in acetic acid, Winstein also finds evidence for two salt effects—normal and special. Within his own context his interpretation of the special effect is, like ours, based essentially on the formation of a new reagent. He does not speculate on the mechanism of the normal effect, but it is probable that the phenomena have a similar origin for both reactions. As in Winstein's examples two types of ion-pair—the intimate and the solvent separated—no doubt exist in our systems. However, our data are not concerned with phenomena which require this elaboration. Our conclusions would, in any case, be unaffected.

EXPERIMENTAL

Materials.—Pure acetic acid and acetyl fluoride, chloride, and bromide were prepared as before.[2] A Karl Fischer estimation showed the acetic acid (solvent) to contain *ca.* 0·005 mole of water per l. The β-naphthol was a recrystallised sample, of m. p. 122°. Dry hydrogen chloride was prepared as before.[2] Dry hydrogen bromide was prepared by adding bromine to tetrahydronaphthalene, the evolved gases being passed through more of the organic liquid to remove traces of bromine. The preparation of anhydrous tetraethylammonium chloride has been described.[1] That of the corresponding bromide was similar; analysis (for bromide) showed 99·95% purity.

Kinetic Arrangements.—These were essentially as previously described,[2] except that all experiments were at 25°. The lower temperature made higher molarities (*ca.* 1·0M) than usual desirable for the experiments in which only chlorides were used. Significantly, however, experiments at lower concentrations showed the medium effect thus incurred to be small (see Tables 3 and 4). The basic kinetics for the uncatalysed systems have been established previously at 40° and were assumed to hold also at 25°. It was verified (see Tables 1 and 2) that the order in acetyl chloride remained unity in the presence of electrophilic catalysis. The reaction mixtures were made up from all the components, except the naphthol, and left to acquire bath-temperature as previously described.[2] The water content of the solvent was allowed for as previously.

For the mixed halogen systems, to demonstrate that the attainment of the halogen-exchange equilibrium was probably complete before the addition of naphthol, reaction mixtures of the same composition were left for different periods (*ca.* 8 min. to several hours) before addition of the naphthol. In no case was the observed rate affected by this procedure. Individual rate constants were reproducible within 2%. It therefore follows from the other results that bromide–chloride equilibration must be rapid in the sense used. That involving bromide–fluoride must either be rapid or very slow; the latter would invalidate our deductions about the relevant equilibrium constants. However, the latter alternative is most unlikely, since the equilibria each contain, as one of their opposing pair of reactions, a step involving acetyl bromide. In our view the reaction of this compound with hydrogen fluoride or tetraethylammonium fluoride is hardly likely to be much slower than its reaction with, say, β-naphthol. Nevertheless, as noted above, the equilibrium constants for the fluoride systems should perhaps be treated with reserve.

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[7] See, *e.g.*, Fredenhagen, *Z. phys. Chem.*, 1933, *A*, **164**, 176; Hickinbottom, " Reactions of Organic Compounds," Longmans, Green and Co., 1959; Sonntag, *Chem. Rev.*, 1953, **53**, 237.