# **26.** *Acylation. Part XIV.* A Comparison of the Reactivities of Acetyl and Chloroacetyl Chloride towards Phenols in Acetonitrile.*

By J. M. Briody and D. P. N. Satchell.

Kinetic data are provided for the reactions of acetyl, propionyl, butyryl, β-chloropropionyl, and chloroacetyl chloride with phenols in acetonitrile. The effects of added tetraethylammonium chloride and bromide have been studied. The behaviour of the acetyl, propionyl, and butyryl compounds fits reasonably into the pattern previously established for acetyl chloride in nitromethane and for acetyl bromide in acetonitrile. The mechanism of acylation is presumably similar in all these systems, ionisation (acylium ion) routes predominating. However, with chloroacetyl chloride the mechanism is essentially a synchronous displacement of covalently bound chlorine by the phenol, and this process is powerfully catalysed by added salt, bond-breaking being dominant kinetically. In the absence of added salt, the rate of acylation by chloroacetyl chloride is *ca.* 8000 fold slower than that by acetyl chloride in the present systems. The behaviour of β-chloropropionyl chloride falls satisfactorily between that of the acetyl and chloroacetyl derivatives.

This is the first assignment of prime kinetic importance to bond-breaking in an essentially bimolecular acylation; although substituents with the greatest electron demand have always previously been found to lead to the fastest rates for such processes, the reverse is true here.

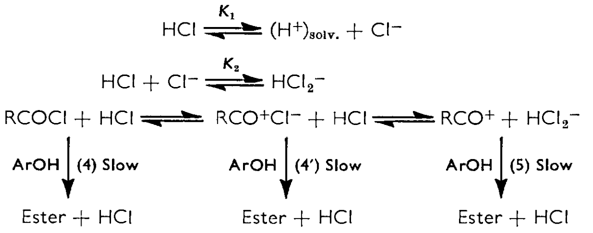
The results exclude, for the present systems, the participation of carbonyl addition intermediates in acylation, and are significant for the interpretation of experiments involving unsymmetrical carboxylic anhydrides.

We have studied the kinetics and mechanism of the reaction between phenols and acetyl chloride in nitromethane [1] and acetyl bromide in acetonitrile.[2] We now present data for the reactions of β-naphthol and *p*-methoxyphenol with substituted acetyl chlorides in acetonitrile. The comparison between acetyl and chloroacetyl chloride is of particular interest.

(1) *Acetyl, Propionyl, and n-Butyryl chloride.*—The data for these compounds (Tables 1, 2, and 3) fit reasonably into the pattern established in Parts IX [1] and XIII.[2]

(i) *Reaction orders.* The observed rate ($k_{\mathrm{obs}}$), that of the removal of phenol (always in at least a ten-fold deficit compared with the acyl halide), was, except as noted below, an accurately first-order process. The order in acyl halide, in the absence of added saline chloride, was also unity. In the presence of added chloride the reaction rate is reduced, eventually becoming constant at the " repressed rate," further salt additions then having a negligible effect.

We have argued [1,2] that such facts imply a reaction mechanism of the following type:



$$\mathrm{HCl} \overset{K_1}{\rightleftharpoons} (\mathrm{H^+})_{\mathrm{solv.}} + \mathrm{Cl^-} \qquad (1)\ \text{Fast}$$

$$\mathrm{HCl} + \mathrm{Cl^-} \overset{K_2}{\rightleftharpoons} \mathrm{HCl_2^-} \qquad (2)\ \text{Fast}$$

$$\begin{tikzcd} \mathrm{RCOCl + HCl} \arrow[r, leftrightharpoons] \arrow[d, "\mathrm{ArOH}"', "(4)\ \text{Slow}"] & \mathrm{RCO^+Cl^- + HCl} \arrow[r, leftrightharpoons] \arrow[d, "\mathrm{ArOH}"', "(4')\ \text{Slow}"] & \mathrm{RCO^+ + HCl_2^-} \arrow[d, "\mathrm{ArOH}"', "(5)\ \text{Slow}"] & (3)\ \text{Fast} \\ \text{Ester} + \mathrm{HCl} & \text{Ester} + \mathrm{HCl} & \text{Ester} + \mathrm{HCl} & \end{tikzcd}$$

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* Part XIII, *J.*, 1964, 3724.

[1] Satchell, *J.*, 1963, 558.

[2] Briody and Satchell, *J.*, 1964, 3724.

TABLE 1.

Acylation by acetyl chloride.

$[\text{Phenol}]_{\text{initial}} \approx 10^{-2}$M in all Tables; $k_{\text{obs}}$ in min.$^{-1}$.

(*a*) Reaction with β-naphthol at 25·1°.

(i) Order in acetyl chloride in absence of salt.

| [AcCl] | 0·42 | 0·56 | 0·70 | 0·98 | 1·12 |
|---|---|---|---|---|---|
| $10^3k_{\text{obs}}$ | 1·59 | 2·08 | 2·70 | 3·45 | 3·89 |

(ii) Effect of added saline chloride ([AcCl] = 0·70M).

| $10[Et_4NCl]$ | 0·0 | 0·114 | 0·238 | 0·495 | 0·830 | 1·10 |
|---|---|---|---|---|---|---|
| $10^3k_{\text{obs}}$ | 2·70 | 1·47 | 1·21 | 0·55 | 0·35 | 0·35 |

(iii) Order in acetyl chloride in presence of 0·13M-$Et_4NCl$.

| [AcCl] | 0·42 | 0·56 | 0·70 | 0·84 |
|---|---|---|---|---|
| $10^3k_{\text{obs}}$ | 0·19 | 0·27 | 0·35 | 0·44 |

(*b*) Reaction with *p*-methoxyphenol at 49·7°.

(i) Effect of added saline chloride ([AcCl] = 0·70M).

| $[Et_4NCl]$ | 0·0 | 0·093 | 0·145 |
|---|---|---|---|
| $10^2k_{\text{obs}}$ | 5·40 | 1·38 | 1·38 |

(ii) Order in acetyl chloride in presence of 0·13M-$Et_4NCl$.

| [AcCl] | 0·42 | 0·56 | 0·70 | 0·84 |
|---|---|---|---|---|
| $10^2k_{\text{obs}}$ | 0·66 | 0·96 | 1·34 | 1·74 |

TABLE 2.

Acylation by propionyl and butyryl chlorides at 25·1°.

[Acyl halide] = 0·70M.

(*a*) Propionyl chloride.

| $[Et_4NCl]$ | 0·0 | 0·13 |
|---|---|---|
| $10^3k_{\text{obs}}$ | 1·46 | 0·20 |

(*b*) n-Butyryl chloride.

| $[Et_4NCl]$ | 0·0 | 0·13 |
|---|---|---|
| $10^3k_{\text{obs}}$ | 1·74 | 0·24 |

TABLE 3.

Acylation of *p*-methoxyphenol by chloroacetyl chloride at 70·2°.

(i) Effect of added saline chloride ($[ClCH_2{\cdot}COCl]$ = 0·70M).

| $10^2[Et_4NCl]$ | 0·0 | 0·64 | 1·27 | 1·36 | 2·54 |
|---|---|---|---|---|---|
| $10^2k_{\text{obs}}$ | 0·02 | 1·01 | 2·15 | 2·56 | 4·24 |

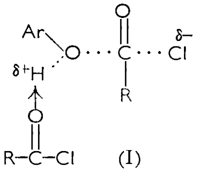
(ii) Effect of added saline bromide ($[ClCH_2{\cdot}COCl]$ = 0·70M).

| $10^2[Et_4NBr]$ | 0·0 | 0·21 | 0·50 | 0·92 | 1·63 |
|---|---|---|---|---|---|
| $10^2k_{\text{obs}}$ | 0·02 | 0·32 | 0·93 | 2·13 | 4·13 |

(iii) Order in acyl halide in presence of saline chloride ($10^2[Et_4NCl]$ = 2·54).

| $[ClCH_2{\cdot}COCl]$ | 0·395 | 0·53 | 0·70 | 0·87 |
|---|---|---|---|---|
| $10^2k_{\text{obs}}$ | 2·18 | 3·22 | 4·24 | 5·06 |

The hydrogen chloride arises during the early stages of the reaction, or before reaction begins from the acylation of traces of water. Its concentration is not important provided that $[H^+] > [RCO^+]$, for then, if the equilibrium constants of (1) and (2) are such that $[HCCl_2^-] > [Cl^-]$, these equilibria effectively buffer the chloride ion concentration and hence the ratio $[HCl]/[HCl_2^-]$. As saline chloride is added step (5) is removed. Whether (4) or (4′) is chiefly responsible for the repressed rate is not certain. We argued in Part XIII that (4′) was the more likely in acetonitrile. We return to this point below. Nevertheless, because $[RCO^+Cl^-]$ will always be proportional to [RCOCl], the mechanism implies a first-order dependence of the repressed rate on the stoicheiometric acyl halide concentration. This predicted dependence was indeed found for acetyl chloride in nitromethane[1] and for acetyl bromide in acetonitrile.[2] However, Table 1 shows that for the present systems the order may be somewhat greater than unity. With substrate *p*-methoxyphenol it is *ca.* 1·4 and with β-naphthol *ca.* 1·2 for the acetyl chloride reaction. The unrepressed rate appears closely of the first-order, in spite of this non-integral dependence of the repressed rate, presumably because the latter contributes only about one eighth to the total (unrepressed) rate (see Table 1) so that the small disturbance is largely lost.


(I)

The enhancement of the expected order appears to depend on the phenol. The results could imply that the help of an additional molecule of acyl halide is more beneficial for the *p*-methoxyphenol than for the β-naphthol reaction. We conclude tentatively that the loss of the phenolic proton is kinetically significant in route (4) [or (4′)] and that an additional molecule of acyl halide can sometimes accept this proton (see I) (the solvent, acetonitrile, is a poor acceptor of protons). The repressed rate could now be a sum for two routes:

$$\mathrm{RCOCl} + \mathrm{ArOH} \xrightarrow{k_{4A}} \mathrm{Ester} + \mathrm{HCl} \qquad (4A)$$

$$2\mathrm{RCOCl} + \mathrm{ArOH} \xrightarrow{k_{4B}} \mathrm{Ester} + \mathrm{HCl} + \mathrm{RCOCl} \qquad (4B)$$

Thus, $$d[\mathrm{ArOH}]/dt = (k_{4A} + k_{4B}[\mathrm{RCOCl}])[\mathrm{RCOCl}][\mathrm{ArOH}].$$

Such circumstances would explain the observed orders of between first and second. β-Naphthol, the more acidic phenol of the two, would need less of this assistance, and yields the lower order (Table 1). In nitromethane, or for the more reactive acylating agent acetyl bromide, such assistance could be less important, so leading to the more closely integral orders observed in these cases.[1,2]

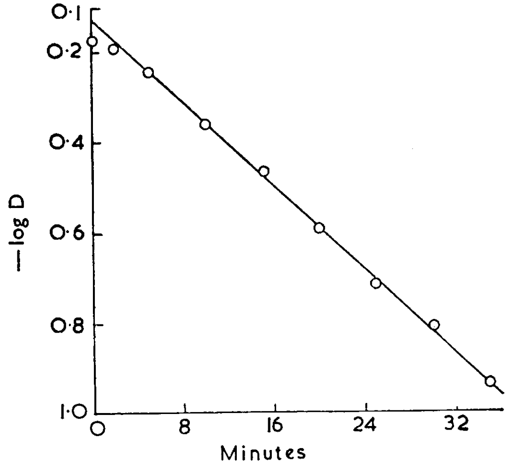


FIG. 1. First-order plot for reaction of acetyl chloride with *p*-methoxyphenol at 49·7°. [AcCl] = 0·70M; $10^2k_{\mathrm{obs}}$ = 5·40.

As noted, the unrepressed rate [*i.e.*, mainly (5)] does not involve these effects. The implication that the details of step (5) and those of the repressed route are significantly different might be considered to argue against (4′) as the main contributor for the repressed rate.

The observed order in phenol was always accurately of first order over the greater part of all runs. With added salt present the plots were linear throughout, but in its absence the initial 10—20% of reaction appeared like an induction period (Fig. 1). This effect was absent from corresponding experiments [1,2] with acyl bromides, and in those with chlorides in nitromethane. We attribute it to the absence of sufficient hydrogen chloride in the early stages to satisfy the mechanistic requirements (p. 169). The solvent was probably very dry [2] and for hydrogen chloride $K_1$ and $K_2$ are perhaps such that these requirements are only met after a significant amount of HCl has been produced. The induction periods might, therefore, be considered as circumstantial support for the proposed scheme. Since presence of salt reduces the importance of the dissociation step, the induction period should then be much less prominent, as found.

The essentially first-order loss of phenol under all conditions implies that in our concentration ranges ($[\text{Phenol}]_{\text{initial}} \approx 10^{-2}\text{M}$) either monomeric and polymeric phenol species have the same reactivity, or that phenolic association or, expressed differently, self-catalysis by other phenol molecules) does not intrude. The suggestion above that acyl halide molecules may accept protons in the transition state is compatible with the fact that other molecules of the phenol itself do not appear to do this: the phenol may well be the less basic species.

(ii) *Relative reactivities.* A given batch of solvent gave reproducible results but different batches, though producing closely similar kinetic patterns, showed irreproducibility ($\pm 25\%$) in the absolute magnitudes of the rate constants. This prevents *exact* comparison of the present data with those for acetyl chloride in nitromethane and for acetyl bromide in acetonitrile, but qualitatively the position is clear. The present data, measured with a single large batch of solvent, are directly comparable among themselves.

(*a*) With a given phenol, at the same temperature, acetyl bromide reacts *ca.* 80 fold more rapidly than does acetyl chloride. This result is compatible with previous comparisons of their reactivities.[3]

(*b*) Both propionyl and *n*-butyryl chlorides react with β-naphthol about half as fast as does acetyl chloride in both the repressed and unrepressed reactions. This means that acetyl, propionyl, and butyryl chloride all suffer rate repression by salt by about the same factors, 7·9, 7·3, and 7·3, respectively. Possible reasons for the generally lower rates produced by alkyl substitution are in Part XIII. Even if all the effect is steric, which is unlikely, this steric effect is clearly reasonably small.

(*c*) In nitromethane acetyl chloride has a rate repression factor of *ca.* 2·5 in the reaction with β-naphthol.[1] There are fairly obvious possible reasons for the change to the value of *ca.* 8 in acetonitrile. With *p*-methoxyphenol in acetonitrile the factor is *ca.* 4 (Table 4). For acetyl bromide with β-naphthol and *p*-methoxyphenol they are 3·8 and 2·7, respectively.[2] The pattern seems consistent.

(iii) *Activation energies.* Data for the reaction of acetyl chloride with *p*-methoxyphenol at different temperatures are in Table 4. (*a*) The value of $E$ appears very similar for both the repressed [(4) or (4′)] and the unrepressed [mainly (5)] reactions, as found for the acetyl bromide reaction.[2] (*b*) The actual magnitude of $E$ must be very close to that in the analogous reactions of acetyl bromide.

The implications of (*a*) and of results like those noted under (ii)(*b*), were discussed in Part XIII, and led us to prefer a mechanism based on routes (5) and (4′) (in which the active entities are presumably very similar in reactivity) to one based on routes (5) and (4). We consider that result (*b*) further supports this, the common reactant throughout being an approximation to a free acetylium ion and thus leading to an essentially constant activation energy with a given phenol (but cf. p. 170).

The differences in absolute magnitude between the rate constants for acetyl chloride and bromide may be due to (*a*) greater ionisation for acetyl bromide (to be expected) and/or (*b*) a more favourable entropy of activation.

(iv) *Rate repression by added saline chloride* (*Table* 1). The comments and explanations in Part XIII apply here. The published values for $K_1$ and $K_2$ again appear based on somewhat suspect data.[4]

(2) *Chloroacetyl Chloride.*—To spread the reactivities we also studied chloroacetyl chloride. Available evidence[5] led us to expect reduced ionisation but, because of the

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[3] Venkataraman and Hinshelwood, *J.*, 1960, 4977.

[4] Kolthoff, Bruckenstein and Chantooni, *J. Amer. Chem. Soc.*, 1961, **83**, 3927.

[5] Bender, *Chem. Rev.*, 1960, **60**, 53; Satchell, *Quart. Rev.*, 1963, **17**, 160.

withdrawal of electrons from the carbonyl carbon atom, a faster step (4) and therefore a faster repressed rate. In the event, chloroacetyl chloride reacted immeasurably slowly with *p*-methoxyphenol in acetonitrile, carbon tetrachloride, or *o*-dichlorobenzene at 25°, though it was possible to prepare the ester in the refluxing solvents. In acetonitrile at 70° (the temperature range is limited by the b. p.) the rate was just measurable and was greatly and linearly accelerated by added saline chloride (Table 3). The effect of temperature (also determined in the presence of salt) is shown in Table 4. In the presence of 0·0136M-tetraethylammonium chloride the activation energy is *ca.* 37 kcal. mole$^{-1}$. It would doubtless be greater in the absence of salt, for the latter clearly acts as a catalyst. Even so, the value of 37 contrasts markedly with that of 12 for acetyl chloride. Tables 1 and 3 show that chloroacetyl chloride is *ca.* 8000 fold less reactive than acetyl chloride. In view of the results with propionyl and butyryl chloride, steric effects can hardly account for this, and the mechanism given above must obviously be modified in this case.

TABLE 4.

Effect of temperature on the reactions of the acyl chlorides with *p*-methoxyphenol.

[Acyl halide] = 0·70M.

| | | | | |
|---|---|---|---|---|
| (*a*) Acetyl chloride. | | | | |
| (i) Unrepressed rates. | | | | |
| $T$ (°c) | 25·1 | 35·1 | 49·7 | $E^* \approx 12$ kcal. mole$^{-1}$ |
| $10^2k_{\text{obs}}$ | 1·16 | 2·41 | 5·40 | |
| (ii) Repressed rates ([$Et_4NCl$] = 0·13M). | | | | |
| $T$ (°c) | 25·1 | 35·1 | 49·7 | $E^* \approx 12$ kcal. mole$^{-1}$ |
| $10^2k_{\text{obs}}$ | 0·28 | 0·61 | 1·34 | |
| (*b*) Chloroacetyl chloride (in the presence of 0·0136M-$Et_4NCl$). | | | | |
| $T$ (°c) | 49·7 | 70·2 | | $E \approx 37$ kcal. mole$^{-1}$ |
| $10^2k_{\text{obs}}$ | 0·084 | 2·56 | | |
| (*c*) β-Chloropropionyl chloride. | | | | |
| (i) Uncatalysed. | | | | |
| $T$ (°c) | 49·7 | 70·2 | | $E \approx 28$ kcal. mole$^{-1}$ |
| $10^2k_{\text{obs}}$ | 0·010 | 0·140 | | |
| (ii) Catalysed ($10^2$[$Et_4NCl$] = 15·0M). | | | | |
| $T$ (°c) | 49·7 | 70·2 | | $E \approx 14$ kcal. mole$^{-1}$ |
| $10^2k_{\text{obs}}$ | 0·121 | 0·480 | | |

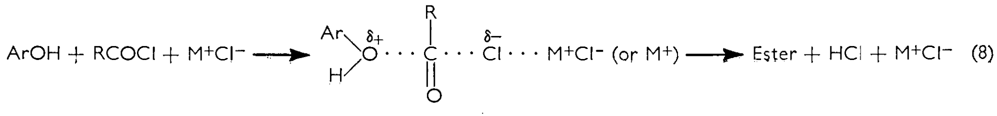
* $E$ is probably somewhat temperature-dependent. The calculated values are based on the best straight lines for the Arrhenius plots.

As noted, it seems clear that the salt is acting as a catalyst and assisting the departure of the chloride ion from the acyl halide. Two ways in which it could do this are (6) and

$$RCOCl + M^+ \rightleftharpoons RCO^+ + M^+Cl^- \qquad (6)$$

$$RCOCl + M^+Cl^- \rightleftharpoons RCO^+ + Cl^-M^+Cl^- \qquad (7)$$

(7) ($M^+$ represents $Et_4N^+$). We rejected[2] processes like (7) as unimportant because of the absence of sustained positive catalysis by salt in the reactions of acetyl chloride and bromide. Moreover, although we consider that (6) contributes in the latter cases, its contribution is small and becomes less at the higher salt concentrations where the ratio $M^+Cl^-/M^+$ increases because of incomplete dissociation. Yet because the acceleration



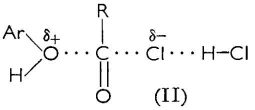
$$ArOH + RCOCl + M^+Cl^- \longrightarrow \overset{Ar}{\underset{H}{>}}\overset{\delta+}{O}\cdots\overset{R}{\underset{O}{C}}\cdots\overset{\delta-}{Cl}\cdots M^+Cl^-\ (\text{or } M^+) \longrightarrow \text{Ester} + HCl + M^+Cl^- \qquad (8)$$

(Transition state)

by salt for chloroacetyl chloride is so strong, the highest salt concentration used is necessarily rather small (Table 3) and therefore process (6) *could* be the origin of the catalysis. We believe that it is not the principal origin because with β-chloropropionyl chloride the catalysis, although marked, is less extreme, and continues unabated to fairly high salt concentrations. We therefore favour processes like (8) for the major catalytic routes for chloroacetyl and β-chloropropionyl chlorides. Such assistance at the leaving group will be unimportant for the reactions of acetyl chloride and bromide, where reactants with an already fully ionised halide ion are always available [routes (4′) and (5)]. We conclude that, in acetonitrile, chloroacetyl chloride always reacts *via* the un-ionised acyl halide molecule and that this unexpectedly slow process is greatly facilitated by the presence of a suitable acceptor for the leaving group. In acetonitrile, and presumably also in carbon tetrachloride and *o*-dichlorobenzene, this departure clearly dominates the kinetics and accounts for the slowness of the reaction of chloroacetyl compared with acetyl chloride. The data appear to provide the first clear example of the dominance of leaving-group departure in an acylation of formal $S_N2$ character.[5] It is expected that when the medium has a structure which sufficiently facilitates the departure of the leaving group, bond formation will become dominant for chloroacetyl chloride and then this compound will react faster than acetyl chloride. Such is the usual situation (*e.g.*, in hydroxylic media). It is clearly also the situation in the presence of sufficient salt (cf. Tables 1 and 3).

Why does the hydrogen chloride present not itself catalyse the chloroacetyl chloride reaction? First, since acylation is very slow, very little water will have been esterified before the start of the reaction and therefore little hydrogen chloride will be present (see also p. 171). However, if hydrogen chloride could act as a catalyst an acceleration, as the products build up, would be expected. This is not found.

The hydrogen chloride might exert an influence (i) *via* an equilibrium like (3), (ii) *via* formation of ion-paired structures like $RCO^+HCl_2^-$, and (iii) *via* hydrogen-bonded structures like (II) [analogous to (8)]. The low tendency of chloroacetyl chloride to form acylium ions accounts for the absence of (i) and (ii). Since the data for acetyl chloride and bromide all point to a greater tendency to behaviour like (i) and (ii) for hydrogen halide catalysis compared with salt-catalysis, the absence of these effects for hydrogen chloride with chloroacetyl chloride is good supporting evidence that the mechanism of salt catalysis in the latter case is *via* a process like (8) rather than (say) (6) or a similar ionisation route. The reasons that hydrogen chloride does not contribute significantly *via* (II) are presumably that (*a*) rather little is present, and (*b*) it is much less polar than are salts. If sufficient added hydrogen chloride were used in acetonitrile it probably would cause acceleration.



(II)

A final result, which again argues very strongly against any ionisation route for chloroacetyl chloride, is that added tetraethylammonium *bromide* has about the same effect on the rate as has the chloride (Table 3). If ionisation equilibria were involved, chloroacetyl bromide would form rapidly and give *considerably faster* rates.

(3) *β-Chloropropionyl Chloride*.—Our data are somewhat suspect, but fit well into the general pattern emerging. Thus the rate is much slower than for acetyl chloride but substantially faster than for chloroacetyl chloride, and the effect of added salt appears to combine the effects noted for these two compounds (Fig. 2).

The activation energy data are particularly interesting (Table 4). In the absence of salt $E \approx 28$ kcal./mole, between the values for acetyl and chloroacetyl chlorides. With 0·15M salt present, $E$ is reduced to *ca.* 14 kcal/mole. No doubt if sufficient salt were present for bond-forming components to dominate kinetically, it would fall below the value of 12 kcal. found for acetyl chloride.

(4) *Some General Consequences of the Data*.—(i) Reactions of β-chloropropionyl and chloroacetyl chlorides with phenols in acetonitrile provide the first examples of retardation

of an $S_N2$ acylation by an increase in the electron-withdrawing power of the substituent carried by the carbonyl carbon atom. In all acylations such an increase has previously been found to accelerate the reaction,[5] and this effect has usually been assumed in speculations on mechanism. Our results emphasise the role of solvent structure in determining the relative kinetic importance of bond-forming and -breaking processes in bimolecular acylation, and clarify problems posed by Bonner and Gabb's recent work [6] on trifluoroacetic acetic anhydride in carbon tetrachloride. Moreover Gold and Emery's rationalisations [7] of the directions of cleavage of unsymmetrical anhydrides generally, in non-hydroxylic media, now appear ambiguous. It is doubtful if steric factors play the prominent role assumed by these authors.

(ii) The dominance of bond-breaking (at moderate salt concentrations) in the reactions of chloroacetyl and β-chloropripionyl chlorides, together with these reactions' essential freedom from acylium ion participation, means that these processes must be synchronous, as depicted in (8), rather than modifications of the carbonyl addition mechanism [5] [*e.g.*,

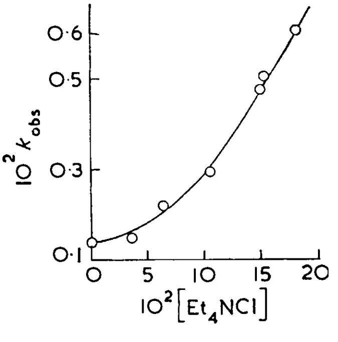
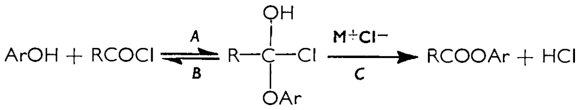


FIG. 2. Effect of salt on the reaction of β-chloropropionyl chloride with *p*-methoxyphenol at 70·2°.
$[Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Cl] = 0{\cdot}70M.$



$$ArOH + RCOCl \underset{B}{\overset{A}{\rightleftharpoons}} R{-}\underset{OAr}{\overset{OH}{C}}{-}Cl \xrightarrow[C]{M^+Cl^-} RCOOAr + HCl \qquad (9)$$

9]. This follows because, if step *C* is slow, *B* must surely be slow also,[8] and thus the addition intermediate would accumulate and we find no kinetic or spectrophotometric evidence for this. We consider that the formation of carbonyl addition products as the intermediates in acylation has been too uncritically accepted, except perhaps by Bunton.[9] No doubt it often occurs, but even the observation of oxygen exchange during solvolysis (the basis of the postulate) does not demand it: the acylation could remain synchronous, as we conclude it is in the above example.

## EXPERIMENTAL

*Materials and Reaction Stoicheiometry.*—Samples of acetonitrile, purified and stored as previously described,[2] from the same makers gave the same (±3%) kinetic results but in contrast to our findings with acyl bromides, samples from different sources often led to rate constants of different absolute magnitudes (±25%), despite more rigorous purification.

Dry carbon tetrachloride and *o*-dichlorobenzene, fractionally distilled from calcium hydride or phosphoric oxide, had b. p. 77 and 178—179°, respectively.

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[6] Bonner and Gabb, *J.*, 1963, 3291.
[7] Gold and Emery, *J.*, 1950, 1443.
[8] Bender, in " Technique of Organic Chemistry," Vol. 8, Interscience, 1963.
[9] *E.g.*, Bunton, *Ann. Reports Chem. Soc.*, 1958, **15**, 186.

Acetyl, propionyl, butyryl, and chloroacetyl chlorides, distilled from isoquinoline, had b. p. 51·5, 79, 102, and 108°, respectively. β-Chloropropionyl chloride, prepared from thionyl chloride and β-chloropropionic acid, had b. p. 84°/100 mm. β-Naphthol, *p*-methoxyphenol, and tetraethylammonium chloride and bromide were previous samples.[2] Specimens of some expected reaction products (esters) were prepared from the phenols and the acid anhydrides by Vogel's method.[10] Others were made in preparative scale reactions which reasonably simulated the kinetic conditions. In all the latter experiments (save for the reaction between β-chloropropionyl chloride and *p*-methoxyphenol) the esterifications were apparently straightforward and the products obtained in high yields (>85%). The chloro-acyl chlorides react rather slowly, so temperatures close to the b. p. of the solvent were employed in both preparative and kinetic work. The kinetic data show the reactions of these compounds to be powerfully catalysed by added salt, but high yields are eventually obtained (several days) even in absence of salt. Both acetonitrile and carbon tetrachloride can be used as preparative solvents. β-Naphthyl acetate, *p*-methoxyphenyl acetate, β-naphthyl β-chloropropionate, *p*-methoxyphenyl chloroacetate, and β-naphthyl chloroacetate had m. p. 71, 31, 55, 44, and 96°, respectively. β-Naphthyl butyrate had b. p. 123°/0·05 mm. β-*Naphthyl* β-*chloropropionate* (Found: C, 66·6; H, 5·27; Cl, 15·06. $C_{13}H_{12}ClO_2$ requires C, 66·5; H, 4·73; Cl, 15·15%), p-*methoxyphenyl chloroacetate* (Found: C, 53·7; H, 4·08; Cl, 17·4. $C_9H_9ClO_3$ requires C, 53·8; H, 4·53; Cl, 17·7%), and β-*naphthyl chloroacetate* (Found: C, 65·3; H, 4·21; Cl, 15·9. $C_{12}H_{10}ClO_2$ requires C, 65·4; H, 4·12; Cl, 16·1%) showed single spots on a thin-layer chromatogram. Attempts to prepare *p*-methoxyphenyl β-chloropropionate in acetonitrile and carbon tetrachloride provided only an oil, which chromatography showed to contain two main components. Yet the corresponding ester from β-naphthol is formed cleanly, and chloroacetyl chloride gives the *p*-methoxyphenyl derivative normally. We consider that the initial esterification between *p*-methoxyphenol and β-chloropropionyl chloride is followed by some (unknown) process.

*Kinetic Arrangements.*—Acetyl, propionyl, and butyryl chlorides reacted sufficiently rapidly at 25°, but higher temperatures (*e.g.*, 70°) were necessary for the chloro-substituted compounds. For measurements of the activation energies temperatures differing by at least 20° were chosen. With the kinetic arrangements previously described [2] the measured rate ($k_{obs}$) was the first-order loss of phenol in the presence of excess of acyl halide. Final optical densities ($D_\infty$) usually fell close to those for synthetic product mixtures, providing further evidence that the reactions proceed cleanly and in good yield. For chloroacyl chlorides with β-naphthol, the solutions develop a fluorescence which interfered with the optical analysis. The corresponding esterifications with *p*-methoxyphenol were not so affected and the behaviour of chloroacetyl chloride could be studied. Unfortunately, for β-chloropropionyl chloride uncertainties exist as to the exact course of its reaction with *p*-methoxyphenol, but we made a few kinetic measurements on this reaction on the assumption that, at least at first, esterification dominates. Reasonable first-order plots for loss of phenol could be obtained over two or more half-lives, using assumed values of $D_\infty$ based on *p*-methoxyphenyl chloroacetate.

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[10] Vogel, " Practical Organic Chemistry," Longmans, 1959.