Sequential Displacement of Chloride in *N*-Aryl- and *N*-Aroyl-carbonimidoyl Dichlorides

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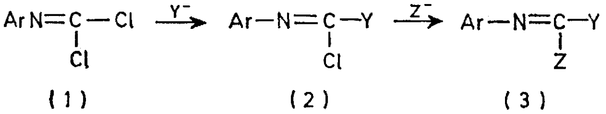
Hydrolysis of carbonimidoyl dichlorides (1) occurs *via* base catalysed and uncatalysed pathways in 1 : 4 dioxan–water at 25°. Hammett ρ values measured under basic (ρ +1.26) and neutral (ρ −2.30) conditions indicate that the former involves direct attack by hydroxide ion on the substrate while in the latter unimolecular C–Cl bond cleavage (to give an azocarbonium ion intermediate) occurs. The observed solvent and common ion effects support this. The products of hydrolysis are the corresponding amines except at high pH where the decarboxylation of *N*-arylcarbamates formed as intermediates is slow. The reaction of (1) with morpholine is S_N2 to give the *N*-iminomethylmorpholine (2; Y = morpholino) initially; however, the intermediate (2; Y = morpholino) undergoes further hydrolysis (by an S_N1 mechanism) more rapidly than the initial bimolecular step in all the dioxan–water solvent mixtures studied. *N*-Aroyl dichlorides (9) undergo nucleophilic displacement *ca.* 10^3-fold more rapidly than (1) while the rate of the subsequent S_N1 step is reduced *ca.* 10^6-fold due to the destabilization of azocarbonium ion formation by the neighbouring carbonyl group. In general then at high nucleophile concentration and in solvents of low dielectric constant the intermediates (14) may be isolated (Y = S, NMe, or O). The dichloride (9) also shows a pH independent rate of hydrolysis at low pH but this is attributed to nucleophilic attack by solvent water, representing the first time that this has been observed in an imidoyl halide system.

CARBONIMIDOYL DICHLORIDES (1) are structurally similar to phosgene and like the latter may undergo sequential displacement of the two chlorines (Scheme 1). In most cases reaction of (1) with nucleophiles such as amines or alkoxide ions leads to direct disubstitution (3; Y = Z).[1] However, some cases have been reported in which the monosubstituted product (2) has been isolated.[2] This clearly enhances the utility of the dichloride reagents since a different nucleophile can now be used in the second displacement to yield (3; Y ≠ Z). The successful isolation of compounds (2) depends upon the relative magnitudes of the rate constants for both steps [(1) ⟶ (2) and (2) ⟶ (3)]. We have investigated the mechanism of reaction of several aryl- and aroyl-carbonimidoyl chlorides and report on how the mechanism of the two displacement reactions varies with the reaction conditions and with the nature of the imidoyl substrate.



SCHEME 1

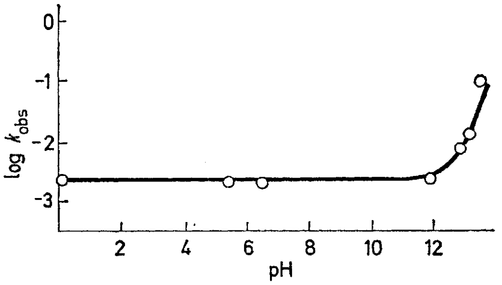
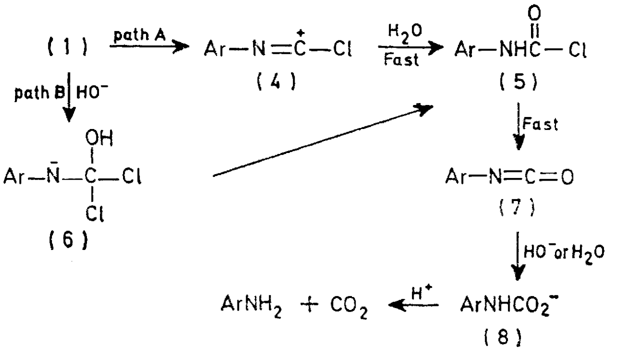


FIGURE 1 Plot of log of the observed rate constants against pH for the hydrolysis of (1; Ar = Ph) at 25° in 1 : 4 dioxan–water (μ = 1.0; $NaClO_4$)

RESULTS AND DISCUSSION

(a) *Hydrolysis of Arylcarbonimidoyl Dichlorides* (1).—The rates of hydrolysis of phenylcarbonimidoyl dichloride (1; Ar = Ph) were studied in 1 : 4 dioxan–water (v/v) at 25° as a function of pH (Figure 1). The solutions were buffered where appropriate, but in all cases a constant ionic strength (μ = 1.0 using sodium perchlorate or sodium chloride) was maintained. The final products of reaction were aniline and carbon dioxide and good rate constants with stable infinity values were obtained, except in the pH region *ca.* pH 11.

The results obtained are consistent with the reaction Scheme 2. Above pH *ca.* 12.5, the rate of hydrolysis is proportional to the hydroxide ion concentration. This implies an overall bimolecular mechanism (path B, Scheme 2); consistent with this is the ρ value of +1.26 (*r* 0.993) obtained for variation of the *N*-aryl substituent at high pH (Table 1). The *p*-nitro-substituted compound (1; Ar = *p*-$NO_2C_6H_4$) reacted too rapidly in the presence of 0.20M-hydroxide ion; however, from data measured at lower [HO^-] a σ value of +0.93 was required to bring the datum point for this compound onto the correlation line for the other substituted compounds. This value is intermediate between the ordinary σ and σ^- values of the *p*-nitro-substituent[3] implying some resonance delocalisation of charge onto Ar in the transition state [see (6)].



SCHEME 2

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[1] H. Ulrich, 'The Chemistry of the Imidoyl Halides,' Plenum Press, New York, 1968.

[2] A. F. Hegarty, J. D. Cronin, and F. L. Scott, *J.C.S. Perkin II*, 1975, 429.

[3] J. Shorter, 'Correlation Analysis in Organic Chemistry,' Clarendon Press, Oxford, 1973, ch. 2.

A surprising feature of the results in Figure 1 is the large pH region where the rate of reaction is pH-independent. This is due to a mechanism involving unimolecular C–Cl bond cleavage giving rise initially to the azocarbonium ion (4) (see path A, Scheme 2). Clearly this path predominates in the absence of a strong nucleophile.

TABLE 1

First-order rate constants (s^{-1}) for the hydrolysis of the arylcarbonimidoyl dichlorides (1) in 1 : 4 dioxan–water (a) containing 0.20M-NaOH (μ = 1.0; NaCl), and (b) at pH 6.5 (μ = 1.0; $NaClO_4$)

Ar	*p*-MeC_6H_4	Ph	*p*-ClC_6H_4	*m*-ClC_6H_4	*m*-$NO_2C_6H_4$
(a) 10^3k_{obs}	9.7	13.1	31.4	52.5	110
(b) 10^4k_{obs}	36	18	4.6	0.83	

This mechanistic pathway is consistent with the observation (Table 1) that in the neutral pH region the effect of substituents is opposite to that observed in basic solution. From these data a ρ of -2.30 (*r* 0.995) is calculated; this large value which arises from considerable delocalisation of charge onto the nitrogen in (4) is similar to values reported previously in related systems.[2] The solvent *m* value of 0.89 (obtained from data in various dioxan–water mixtures),[4] and the common ion effect [a 3.5-fold rate depression for the hydrolysis of (1; Ar = Ph) at pH 6.5 in the presence of 0.1M-Cl^-] also support the formation of a stabilized carbonium ion species.

Reaction of (1) by either path A or B would be expected to give initially the *N*-carbamoyl chloride (5). We have synthesised *N*-phenylcarbamoyl chloride (5; Ar = Ph) independently and examined its reactivity in 1 : 4 dioxan–water at 25° (Figure 2, triangles). However, the apparent reactivity of (5; Ar = Ph) is the same as that shown by phenyl isocyanate (7; Ar = Ph) under the same conditions (Figure 2, open circles). Clearly therefore (5) undergoes rapid elimination to (7) at all pH values. The observed decrease in the rate of hydrolysis of (5) or (7; Ar = Ph) is most likely due to a change in the rate-determining step to subsequent decomposition of the carbamate (8; Ar = Ph) at high pH.[5] This is consistent with the observed rates of hydrolysis of (8; Ar = Ph) measured under the same conditions (solid circles, Figure 2). The changeover in the rate-determining step to carbamate decomposition occurs because the latter process is acid catalysed even at high pH.[6]

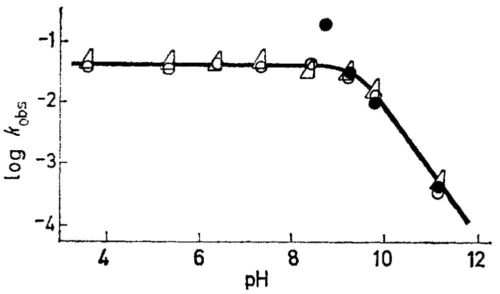

FIGURE 2 Plot of log of the observed rate constants against pH for the hydrolysis of: *N*-phenylcarbamoyl chloride (5; Ar = Ph) (△); phenyl isocyanate (7; Ar = Ph) (○); and *N*-phenylcarbamate (8; Ar = Ph) (●)

Thus all the steps involved in the neutral hydrolysis of (1) (subsequent to azocarbonium ion formation) are relatively rapid; this accounts for the clear kinetics and products observed. However at pH *ca.* 11 repetitive scans of the u.v. spectrum of (1; Ar = Ph) clearly show that two reactions of comparable rate are occurring (there are no isosbestic points, see Figure 3).

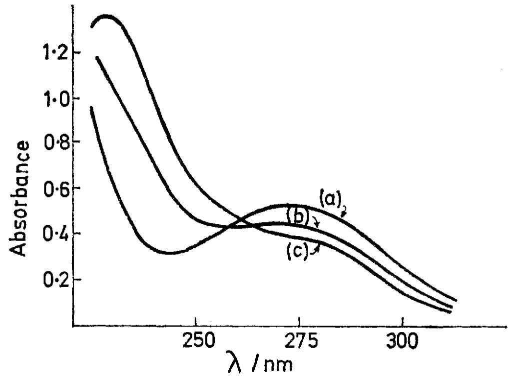

FIGURE 3 Repetitive scans of the u.v. region for the hydrolysis of (1; Ar = Ph) at pH 11.0 in 1 : 4 dioxan–water at 25° (a) at *t* = 0, (b) after 10 min, and (c) after 60 min

From the data in Figures 1 and 2 it is clear that the rate of the initial reaction of (1; Ar = Ph) and the subsequent hydrolysis of (8; Ar = Ph) are comparable at this pH.

(b) *Reaction of Phenylcarbonimidoyl Dichloride with Morpholine.*—The reaction of (1; Ar = Ph) with morpholine was also examined. The secondary amine morpholine was chosen for study since (a) rapid loss of HCl from the intermediate is blocked [unlike (5)] and (b) the reactivity of the intermediate (2; Y = morpholino) has already been established.[2] At all pH values the rate of reaction was proportional to the total morpholine concentration present, while experiments around the pK_a of morpholine indicated that the only reactive species was morpholine free base. From these data a second-order rate constant of 7.4 l mol^{-1} s^{-1} can be calculated for the reaction of (1) with morpholine in 1 : 4 dioxan–water at 25°. Clearly then the S_N2 displacement of chloride ion by the nucleophile morpholine is more rapid than hydrolysis of (1; Ar = Ph) at pH <11 when the free morpholine concentration $>2.4 \times 10^{-4}$M.

In spite of the observed rapid bimolecular displacement of Cl^- from (1) by morpholine, the intermediate (2; Y = morpholino) reacts further even more rapidly. From available data[2] it can be calculated that the

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[4] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770; E. Grunwald and S. Winstein, *ibid.*, 1948, **70**, 846.

[5] S. L. Johnson and D. L. Morrison, *J. Amer. Chem. Soc.*, 1972, **94**, 1323.

[6] A. F. Hegarty, C. N. Hegarty, and F. L. Scott, *J.C.S. Perkin II*, 1975, in the press.

observed rate constant for the loss of Cl^- from (2; Ar = Ph, X = morpholino) in 1 : 4 dioxan–water is *ca.* 3.8×10^4 s^{-1}. Therefore even at the most concentrated amine solution possible, (2) reacts $>10^3$-fold more rapidly than it is formed from (1).

However the fact that the two displacements occur *via* different mechanisms (arising from the differing abilities of the amino- and chloro-groups to stabilize an azocarbonium ion centre) can be used to partly reverse the order of reactivity. Thus the S_N1 (or second) step, being highly sensitive to the ionizing power of the solvent, will be appreciably slower on transfer to a solvent with a lower aqueous content, while the first (S_N2) step should remain relatively unchanged. This was in fact observed since at pH 8.35 in 9 : 1 dioxan–water k_{obs} for the reaction of morpholine (10^{-2}M) and (1; Ar = Ph) is 1.24×10^{-3} s^{-1}; under the same conditions the rate of reaction of the morpholino adduct (2; Y = morpholino) is of the same order of magnitude ($k_{obs} = 3.0 \times 10^{-3}$ s^{-1}). On transfer of the reaction medium to a non-aqueous solvent, *e.g.* benzene, the S_N1 step can be entirely suppressed and under these conditions the intermediate (2) can be isolated.

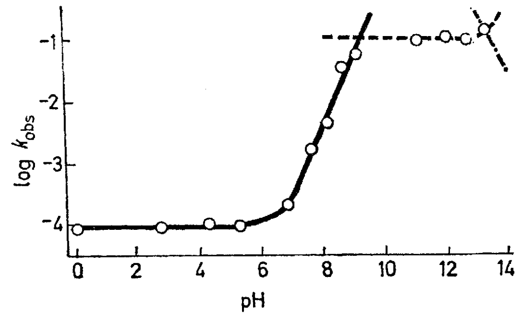


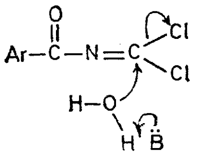
FIGURE 4 Plot of the log of the observed rate constants against pH for the hydrolysis of benzoylcarbonimidoyl dichloride (9; Ar = Ph) (solid line) and the subsequent hydrolysis of benzoylisocyanate (— — —) and *N*-benzoylcarbamate (— · — · —) at 25° in 1 : 4 dioxan–water (μ = 1.0; $NaClO_4$)

(c) *Hydrolysis of Aroylcarbonimidoyl Dichlorides.*—The insertion of a carbonyl group between the aryl group and nitrogen in (1) had a profound effect on the reactivity of the dichloride. The rates of hydrolysis of benzoylcarbonimidoyl dichloride (9; Ar = Ph) are summarised in Figure 4. The pH profile is broadly of the same type as shown by (1) except that the bimolecular reaction with hydroxide ion occurs at a far lower pH [>pH 6 for (9), >pH 11 for (1)] and the pH independent rate is >10-fold slower. The large enhancement (*ca.* 3000-fold) in the rate of displacement of Cl^- from (9) by hydroxide ion relative to (1) is explicable in terms of the greater susceptibility of (9) to nucleophilic attack [see (9b)] and the stabilization of a transition state such as (6) by the adjacent aroyl group.

(9a) (9b)

Although (9) shows a region where the rate is pH independent (Figure 4), several pieces of evidence indicate that this does not represent rate determining unimolecular C–Cl bond cleavage [to give an azocarbonium ion (10)], as observed for (1). Thus when $Ar = p\text{-}ClC_6H_4$, (9) reacts *more* rapidly at pH 3.0 ($k_{obs} = 1.6 \times 10^{-4}$ s^{-1}) than when Ar = Ph ($k_{obs} = 0.96 \times 10^{-4}$ s^{-1}, solvent 1 : 4 dioxan–water at 25°); this implies the development of *negative* charge in the transition state. This suggested that nucleophilic attack by water on (9) [see (11)] might be responsible for the pH independent rate. This was confirmed by the 2.2-fold slower rate in this pH region when the water in the solvent was replaced by deuterium oxide. No rate depression in the presence of added chloride ion was detected and experiments in various dioxan–water mixtures gave a low *m* value of 0.17, clearly indicating the absence of a charged intermediate [such as (10)].[4] General base catalysis of the addition of water (11; B = AcO^-) or nucleophilic attack by acetate ion was also observed; the rate constants in Figure 4 were obtained by extrapolation to zero buffer concentration. The solvolysis of (9) *via* nucleophilic attack by water in the pH range 0—4 represents the first example in which this mode of reaction for an imidoyl halide system has been observed; normally in the absence of strong nucleophiles, a unimolecular C–Cl bond cleavage is the preferred pathway.[7]

(10a) (10b)



(11)

Between pH 8 and 13 the observed rate constants for the hydrolysis of (9) change from first- to zero-order dependence on [HO^-] (see Figure 4). This is most likely due (see above) to a change in the rate determining step to hydrolysis of benzoyl isocyanate. Although the rate of hydrolysis of the isocyanate should increase at high pH, the observed rate at pH 13 and 14 is actually lower; in view of the evidence presented earlier this probably arises from a second changeover in mechanism to rate determining hydrolysis of the *N*-benzoylcarbamate.

(d) *Reaction of Aroylcarbonimidoyl Dichlorides with Morpholine.*—The rates of reaction of morpholine with (9; Ar = Ph) at pH 6.32 were examined and show (Figure 5) that at low morpholine concentration [total morpholine (B_T) $< 5 \times 10^{-3}$M] the observed rate increases as the amine concentration is increased. How-

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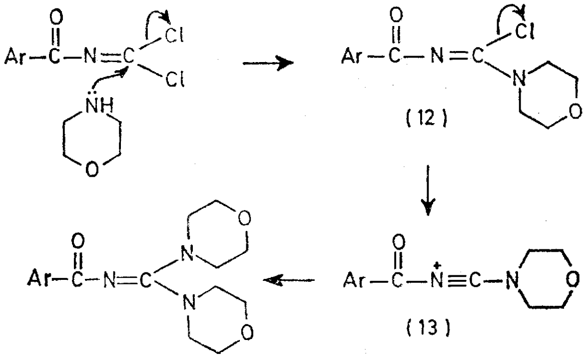
[7] See, for example, A. F. Hegarty, T. A. F. O'Mahony, P. Quain, and F. L. Scott, *J.C.S. Perkin II*, 1973, 2047.

ever when $B_T > 5 \times 10^{-3}$M the observed rate was independent of added buffer concentration (Figure 5). By carrying out the reaction at various pH values it was demonstrated that the reaction at low B_T represented a second-order process between the substrate and morpholine free base. The 'plateau' rate at high buffer concentration was on the other hand shown to be independent of both the buffer concentration and of the pH of the reaction medium. This suggested the mechanism of Scheme 3; at low morpholine concentration (or at low pH, which acts to reduce the concentration of free morpholine available) the initial S_N1 step is rate determining. However at sufficiently high morpholine concentration formation of (12) is so rapid that its reaction with a further mole of morpholine [*via* an S_N1 mechanism involving (13)] is rate determining. Consistent with this, the pH independent rate at high morpholine concentration was reduced in the presence of the common ion, Cl⁻.



SCHEME 3

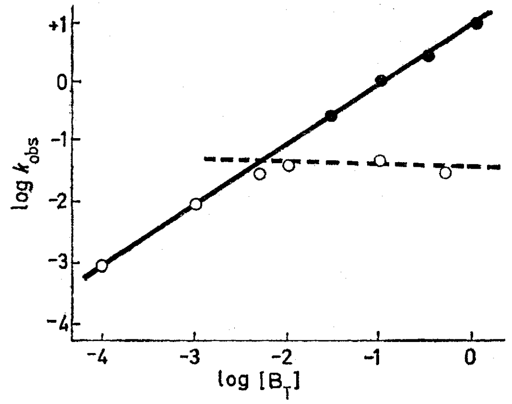


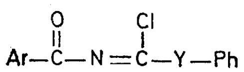
FIGURE 5 Plot of the log of the observed rate constants against log of total morpholine concentration. The substrate is (9; Ar = Ph), pH = 6.32, solvent 1 : 4 dioxan–water at 25° (μ = 1.0; $NaClO_4$). The open circles were obtained using conventional spectrophotometric measurements and represent (at low buffer concentration) rate-determining nucleophilic attack on (9) while at high buffer concentration the further reaction of the intermediate (12; Ar = Ph) is rate determining. The closed circles (obtained using the stopped-flow technique) represent the rates of nucleophilic attack in all cases

Although the initial nucleophilic step was quite rapid at high morpholine concentration, it was possible to follow the reaction under these conditions using the stopped-flow technique. An example of the results is shown in Figure 5 (solid circles); there is a rapid initial increase in absorption at 270 nm followed by a relatively slow decrease. Rate constants for both processes were calculated and the rapid reaction (solid circles, Figure 5) clearly corresponds to the values obtained for the initial bimolecular reaction at low [morpholine]. The rate constants for the second (slow) reaction correspond to the S_N1 or plateau rate.

Finally (12; Ar = Ph) was synthesised using a low dielectric constant solvent. Its rate of hydrolysis was pH independent and corresponds exactly to the plateau rate obtained for (9; Ar = Ph) at high morpholine concentration (Figure 5).

The enhancement in the S_N2 displacement of Cl⁻ by morpholine on (9) is 400-fold relative to the same reaction with (1). Concomitantly the subsequent S_N1 displacement of Cl⁻ from the intermediate (12) is reduced by *ca.* 10^6-fold [relative to (2; Y = morpholino)]. This large increase in the rate of the first S_N2 step coupled with the decrease in the subsequent S_N1 step may reverse the order of reactivity of the dichloride and the monosubstituted intermediate, permitting the isolation of the latter. In addition, to suppress further reaction of the intermediate a solvent of low dielectric constant should be used, moreover a high nucleophile concentration speeds up the first step while leaving the rate of reaction of the intermediate unaffected. We have used this technique to prepare monosubstituted compounds in which different heteroatoms oxygen, nitrogen, and sulphur are attached to carbon.

(e) *Hydrolysis of* C-*Substituted Aroylimidoyl Chlorides.*—Since displacement of Cl⁻ from (9) by the very weak nucleophile water is an S_N2 process, it is likely that all displacements would follow this mechanistic course. Thus the key question with regard to the isolation of monodisplacement products from (9) is the mechanism of further displacement from the intermediate. We have examined a series of compounds (14; Y = NMe, O, and S, Ar = *p*-ClC_6H_4).



$$\mathrm{Ar{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N{=}\overset{\overset{\displaystyle Cl}{|}}{C}{-}Y{-}Ph}$$

(14)

The rates of hydrolysis of *N*-(*p*-chlorobenzoyl)-*C*-(*N*-methylanilino)imidoyl chloride (14; Y = NMe, Ar = *p*-ClC_6H_4) in 1 : 4 dioxan–water at 25° are pH independent over the region 1—13 ($k_{obs} = 1.60 \times 10^{-2}$ s^{-1} at 25°); at $HO^- = 1.0$M a small rate increase is observed ($k_{obs} = 6.0 \times 10^{-2}$ s^{-1}) (see Figure 6). The criteria of salt effect, common ion rate depression, and solvent *m* value (+0.88) confirm an S_N1 mechanism in the pH-independent region.

The results for *N*-(*p*-chlorobenzoyl)-*C*-thiophenoxyimidoyl chloride (14; Y = S, Ar = *p*-ClC_6H_4) are parallel; a large pH independent region is observed where $k_{obs} = 2.2 \times 10^{-3}$ s^{-1} (Figure 6). The same criteria (see above) support an S_N1 type mechanism of displacement (m +0.95).

The rates of hydrolysis of *N*-(*p*-chlorobenzoyl)-*C*-phenoxyimidoyl chloride (14; Y = O, Ar = *p*-ClC_6H_4) which are summarised in Figure 6 contrast with those for Y = NMe and S. Thus no low pH region was observed where the rate was independent of pH. Experiments at 60° showed that even at pH 4, the rate is proportional to [HO^-]. The results for (4; Y = O) are therefore akin to those observed for (9) itself (see Figure 4) in that only S_N2 reactivity is observed. Also, like (9), (14; Y = O) shows a plateau at high pH which can be attributed to a change in the rate determining step to hydration of the subsequently formed *p*-chlorobenzoyl isocyanate.

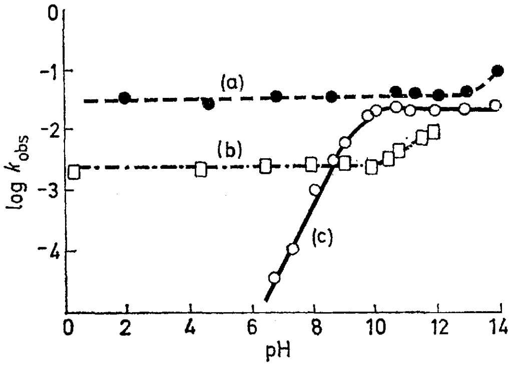


FIGURE 6 Plot of the log of the observed rate constants against pH for the hydrolysis of (a) (14; Ar = *p*-ClC_6H_4, Y = NMe) (●); (b) (14; Ar = *p*-ClC_6H_4, Y = S) (□); and (c) (14; Ar = *p*-ClC_6H_4, Y = O) (○). The solvent was 1 : 4 dioxan–water at 25° (μ = 1.0; $NaClO_4$)

Table 2 summarises the relative rates of carbonium ion formation for various *N*-aroyl- (14) and *N*-aryl-imidoyl chlorides (2). In all cases where a measureable S_N1 reactivity is demonstrated, the presence of the aroyl (rather than the aryl) group causes a 10^6-fold decrease in reactivity. In the aroyl compounds (9) (where Y = Cl) a different mechanism becomes operative (nucleophilic attack by water) while when Y = O the S_N1 reactivity is too slow to measure. Because of the similarity both in mechanism and in rate of displacement of chloride ion from (9) and from (14; Y = Cl), the isolation of the intermediate (14; Y = O), uncontaminated by disubstituted products, is difficult.

TABLE 2

Relative rates of azocarbonium ion formation from *N*-aryl- and *N*-aroyl-imidoyl chlorides

	k_{rel}	
Substituent X	ArCON=C(Cl)X	ArN=C(Cl)X
N(Me)Ph	8	8×10^6 [a]
SPh	1	8×10^5 [a]
Cl	*b*	55
OPh	*c*	0.32 [a]

[a] Data from ref. 2. [b] Reacts *via* different mechanism. [c] Too slow to measure.

EXPERIMENTAL

M.p.s were determined on a Thomas capillary apparatus and are uncorrected. U.v. spectra for product analysis were run on either a Unicam SP 800 or Perkin-Elmer 124 spectrophotometer. Combustion analyses were carried out by the Microanalytical Laboratory, University College, Cork.

Materials.—All inorganic salts were AnalaR grade and were dried at 120° before use. AnalaR dioxan (B.D.H.) was used directly as supplied. The solvent mixtures, *e.g.* 1 : 4 dioxan–water, are v/v, made up at 20°. The aqueous potassium hydroxide and sodium hydroxide solutions were made up from Volucon (M and B) standard ampoules and the perchloric acid solutions from 60—62% AnalaR perchloric acid.

Substrates.—*N*-(*p*-Chlorophenyl)formamide was prepared by refluxing *p*-chloroaniline in an excess of formic acid (90% w/w) for 3 h. The solid which precipitated was recrystallised from 95% ethanol and had m.p. 101—102° (lit.,[8] 102°). The following analogues were similarly prepared: *p*-nitro, m.p. 194° (lit.,[9] 194—195°); *m*-nitro, m.p. 133° (lit.,[9] 133—134°); *p*-methyl, m.p. 53° (lit.,[10] 53°); *m*-chloro, m.p. 57° (lit.,[10] 57—58°). Arylcarbonimidoyl dichlorides (1) were prepared by the method of Kuhle *et al.*[11] by treating the formamides with thionyl and sulphuryl chlorides. The dichlorides were purified by distillation and where possible, (1; Ar = *p*-$NO_2C_6H_4$ and *m*-$NO_2C_6H_4$), by recrystallisation from light petroleum (b.p. 60—80°); the physical properties and spectra of the dichlorides agreed with reported values.[11] Sodium *N*-phenylcarbamate (8) was prepared from phenyl isocyanate and sodium hydroxide by the method of Johnson and Morrison.[5] Phenylcarbamoyl chloride (5) was prepared by bubbling dry hydrogen chloride gas through a solution of phenyl isocyanate in hexane and had m.p. 44—45° (lit.,[12] 45—46°). Benzoylcarbonimidoyl dichloride was prepared by bubbling dry chlorine gas through a solution of benzoyl isothiocyanate[13] in carbon tetrachloride at 0° for 5 h. The solution was stirred at room temperature for two days and after filtration the sulphur dichloride and carbon tetrachloride were removed *in vacuo*; distillation gave the dichloride, b.p. 80° at 1 mmHg (lit.,[13] 131° at 17 mmHg). The p-*chlorobenzoyl analogue* was similarly prepared and had b.p. 120° at 3 mmHg (Found: C, 40.4; H, 1.7; Cl, 44.8; N, 5.7. $C_8H_4Cl_3NO$ requires C, 40.6; H, 1.7; Cl, 45.0; N, 5.9%).

C-*Substituted* N-*Aroylimidoyl Chlorides* (14).—The following is a general procedure. *p*-Chlorobenzoylcarbonimidoyl dichloride (1 equiv.) was dissolved in dry benzene with phenol (1 equiv.). Triethylamine (1 equiv.) also dissolved in dry benzene was added dropwise over 30 min. The precipitated triethylamine hydrochloride was filtered off and the residue obtained on evaporation of the benzene was distilled *in vacuo* (see Table 3 for physical and analytical details). The *C*-thiophenoxy and *C*-(*N*-methylanilino)

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[8] F. D. Chattaway, K. Orton, and W. Hurtley, *Ber.*, 1899, **32**, 3636.

[9] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, vol. 4.

[10] H. Hirst and J. Cohen, *J. Chem. Soc.*, 1895, 830.

[11] E. Kuhle, B. Anders, and G. Zumack, *Angew. Chem. Internat. Edn.*, 1967, **6**, 649.

[12] R. Bacaloglu and C. A. Bunton, *Tetrahedron*, 1973, **29**, 2721.

[13] J. Ambelang and T. Johnson, *J. Amer. Chem. Soc.*, 1939, **61**, 632.

analogues were similarly prepared (Table 3). For the *C*-(morpholino)-compound two equivalents of morpholine were used without triethylamine; morpholine hydrochloride was recovered in this case as a by-product.

Kinetic Method.—The dioxan–water solutions used for the kinetic experiments were made up by mixing appropriate volumes of solution containing 1.0M-sodium perchlorate or -sodium chloride with 1.0M-perchloric acid or -sodium hydroxide made up in the same solvent. The solutions were thus of constant ionic strength and had known concentrations of acid or hydroxide ion. The pH values used in the text refer for convenience to the pH of the corresponding 100% aqueous solution containing the same quantity of acid or base. The indicated pH values of the dioxan–water solutions were also measured using a Radiometer model PHM 26 pH meter with a Metrohm EA 125U glass combination electrode, having first standardized the electrode in aqueous buffers. The values obtained were within ±0.3 pH unit of theoretical values.

The kinetics of hydrolysis were followed spectrophotometrically at appropriate wavelengths in the u.v. region using apparatus and techniques which have already been fully described.[14] The products of hydrolysis were determined in all cases by comparing the u.v. spectrum obtained at the completion of a kinetic experiment with the spectrum of the product, run at the same concentration and under the same conditions. In some cases (*e.g.* when the product was *p*-nitroaniline) actual isolation of the product was also possible. As an additional check of the products formed, t.l.c. (on silica gel) with authentic samples proved useful and was widely employed.

TABLE 3

Physical and analytical data for the *N*-aroyl monochlorides $p\text{-ClC}_6\text{H}_4\text{CON=C(Cl)-Y}$

		Found (%)				Required (%)		
Y	M.p. (°C)	C	H	N	Formula	C	H	N
N(Me)Ph	59	58.4	4.2	8.9	$C_{15}H_{12}Cl_2N_2O$	58.7	3.9	9.1
OPh	103	57.6	3.6	5.2	$C_{14}H_9Cl_2NO_2$	57.2	3.1	4.8
SPh	63	54.3	3.0	4.6	$C_{14}H_9Cl_2NOS$	54.2	2.9	4.5
Morpholino	98	49.9	4.6	9.8	$C_{12}H_{12}Cl_2N_2O_2$	50.2	4.2	9.8

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[14] A. F. Hegarty and L. N. Frost, *J.C.S. Perkin II*, 1973, 1719.