S_N2 Character of Hydrolysis of Benzoyl Chloride

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Solvent effects on reactivity for hydrolysis/alcoholysis of benzoyl chloride are consistent with a direct displacement reaction having S_N2 character, in competition with a carbonyl addition reaction becoming dominant in less aqueous media.

Involvement of nucleophilic assistance has recently been demonstrated for S_N reactions of three 'classical' substrates, previously regarded as strongly prone to S_N1 reactions, *e.g.* nucleophilic displacements of methoxymethyl (**1**),[1a,b] α-phenylethyl (**2**),[1c] and t-butyl (**3**)[1d,e] substrates. We now report evidence that the hydrolysis of benzoyl chloride, also regarded previously as an S_N1 reaction,[2] is accelerated by nucleophilic solvent assistance (*i.e.* the reaction shows S_N2 character). Our conclusions are based on correlations of solvent effects on reactivity using equation (1),[3a] which has been applied successfully to characterise solvolyses in the S_N2–S_N1 spectrum according to the sensitivities (m and l) of

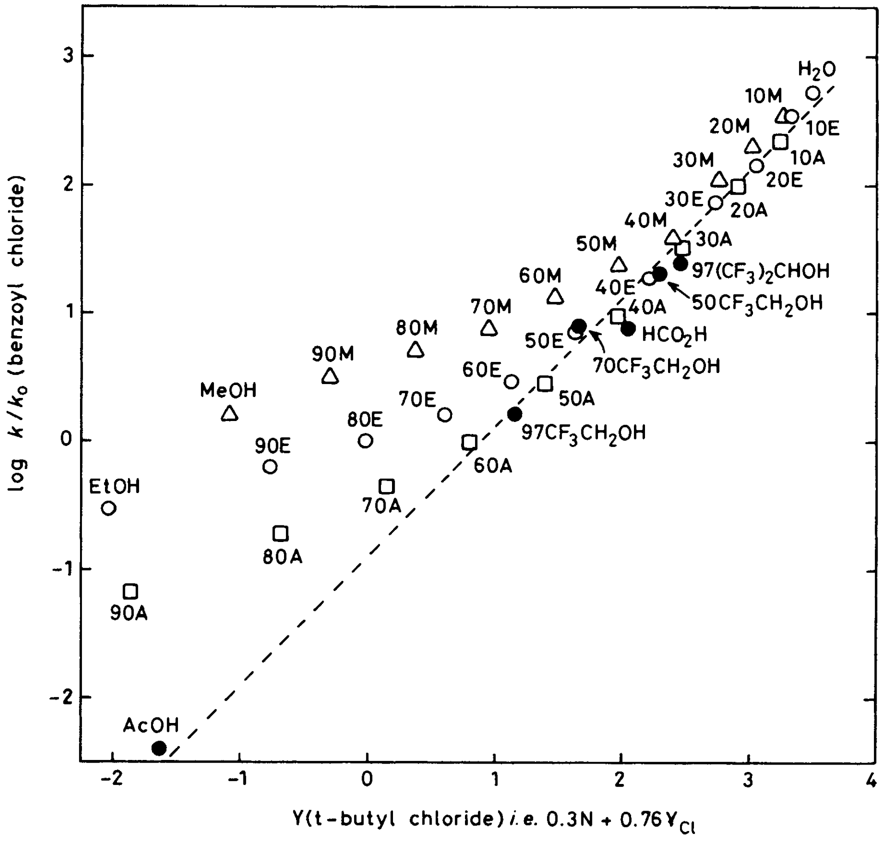

Figure 1. Correlation of rate data for solvolysis of benzoyl chloride (k) relative to k_0 (80% ethanol–water) at 25 °C *vs.* Y values.[3c] The hatched line is of unit slope; symbols A, E, and M refer to % acetone–, ethanol–, methanol–water (v/v) mixtures respectively; fluorinated alcohols are % w/w alcohol–water. Data for EtOH, 80E, 60E, 50E, 90A, 80A, 70A, AcOH (ref. 6a), and HCO_2H (ref. 6b) were obtained from the literature.

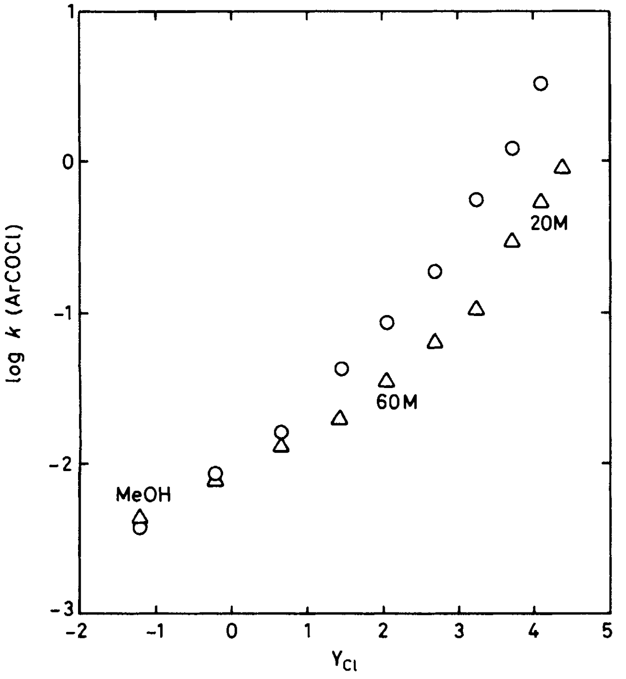

Figure 2. Rate data for benzoyl chloride (△) and *p*-toluoyl chloride (○) *vs.* Y_{Cl}.[1d]

the substrate (RX) to solvent ionising power Y and solvent nucleophilicity N respectively.[3] We also report the first application of equation (1) to the successful prediction of mechanistic change.

$$\underset{(1)}{MeOCH_2X} \quad \underset{(2)}{PhCHXMe} \quad \underset{(3)}{Me_3CX}$$

$$\log(k/k_0)_{RX} = m\mathrm{Y} + l\mathrm{N} \qquad (1)$$

Reactions of benzoyl halides are complicated by possible competition between S_N1, S_N2, and various carbonyl addition mechanisms.[2] Most published work is concerned with reactions in solvents of low ionising power (both protic and aprotic) where carbonyl addition is dominant.[2b] We have obtained kinetic data for highly aqueous media by combining experimental techniques for relatively fast solvolytic reactions[4a] with those for sparingly soluble solutes.[4b] Our direct measurement of the first order rate constant for hydrolysis of benzoyl chloride in water is 1.4 ± 0.1 s^{-1} at 25 °C (average of ten determinations, $t_{\frac{1}{2}} < 0.5$ s), 3000-fold[5a] or 16-fold[5b] greater than previously published values. Rates of solvolyses in solvents of high Y and/or low N, including acetolysis, correlate well with Y values[3c] (Figure 1). As the S_N2 character of solvolyses of t-butyl halides is now established,[1d,e] these results (Figure 1) show that hydrolysis of benzoyl chloride is also nucleophilically solvent-assisted, although the reaction probably has high carbocation character.[1,2b]

The feasibility of direct heterolytic cleavage of the C–Cl bond can be established from the gas phase equilibrium [equation (2)]. Using available experimental data,[7] we calculate for equation (2) that $\Delta H = ca.\ -12 \pm 4$ kcal/mol.† There are links between gas phase carbocation chemistry and solution reactions,[1d,8] and these results are consistent with the 10^2 greater reactivity of benzoyl chloride compared with t-butyl chloride[3c] in water at 25 °C (the argument can be applied to S_N1 reactions or to equally nucleophilically assisted S_N2 reactions).

$$\mathrm{PhCOCl} + \mathrm{Bu^{t+}} \rightleftharpoons \mathrm{PhCO^+} + \mathrm{Bu^tCl} \qquad (2)$$

Since equation (1) is known to correlate the kinetic data over the whole range of mechanistic changes within the S_N2–S_N1 spectrum,[3] we predict that the major deviations from the correlation line (for 50—100% methanol–water, 60—100% ethanol–water, and 70—90% acetone–water) are due to the incursion of a new solvolytic process, presumably carbonyl addition.[2] This mechanistic analysis is well supported by a comparison of kinetic data for solvolyses of *p*-toluoyl chloride with data for benzoyl chloride in methanol–water (Figure 2). In pure methanol the carbonyl addition process is favoured and benzoyl chloride reacts slightly the faster.[9] However, as the *p*-Me group stabilises the development of positive charge on the carbonyl carbon, the S_N2–S_N1 process for *p*-toluoyl chloride becomes predominant in media less aqueous than in the case of benzoyl chloride. Also solvolysis of *p*-toluoyl chloride proceeds by a close to parallel but faster reaction in the more aqueous media, consistent with the expected similarity of l values [equation (1)] for toluoyl and benzoyl chlorides.

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† 1 cal = 4.184 J.

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