Precise Dissection of Kinetic Data for Solvolyses of Benzoyl Chloride into Contributions from Two Simultaneous Reaction Channels

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Rate–rate profiles for solvolyses of benzoyl–p-methoxybenzoyl chlorides in ethanol–water and in methanol–water permit a precise dissection of the kinetic data into contributions from two simultaneous reaction channels.

Kinetic probes of mechanism are frequently used to characterise the properties of transition states, which may be presented on contour diagrams,[1] and it is generally assumed that there is only one reaction channel. Also, subtle kinetic probes such as isotope effects are usually reported as one rate ratio, even when several products are formed, although rare attempts have been made to dissect them.[2] A further complication is that reactions may proceed simultaneously by two reaction channels, e.g., for solvolytic reactions of carboxylic acid chlorides.[3—5] We now report precise quantitative evidence supporting this proposal, and a method of characterising the two reaction channels.

Kinetic data for solvolyses of (1, Z = H and Z = OMe) are plotted in Figure 1, showing results for methanol–water (M) and ethanol–water (E) 'dispersed' into two lines for less aqueous media. In more aqueous media there is upward curvature and reduced dispersion. A similar plot for solvolyses of (1, Z = OMe) and S_N1 solvolyses of 2,6-dimethylbenzoyl chloride[9] is linear and shows very little dispersion over the

experimentally accessible solvent range from 70% methanol–water to EtOH,[7] as expected from previous work on S_N2/S_N1 solvolyses of alkyl halides.[10,11] Hence, we assume that S_N2/S_N1 solvolyses of benzoyl chloride would also fit a single linear correlation, and that a second reaction channel (carbonyl addition) accounts for the deviations observed in less aqueous media (Figure 1).[3,5]

The expected S_N2/S_N1 correlation line (Figure 1) was defined from experimental data in three regions. (1) Experimental data points for 20% alcohol–water are furthest away from the curved parts of the plot, so observed rates are assumed to be dominated by the S_N2/S_N1 mechanism. (2) The point at which each of the two reaction channels contribute 50% of the observed solvolysis rate for benzoyl chloride in methanol–water is calculated from the intersection of the two
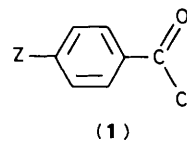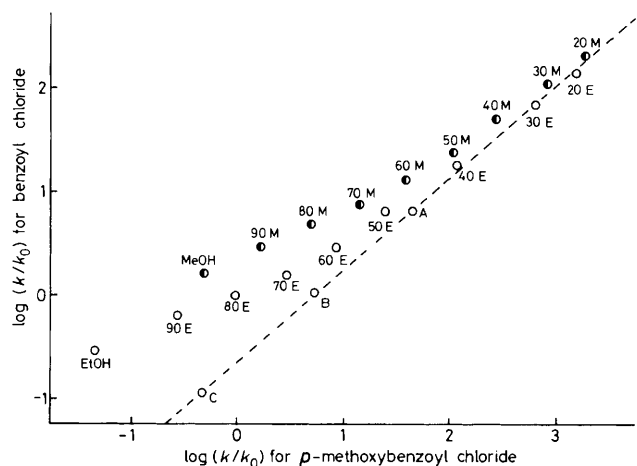
(1)

Figure 1. Correlation of rate data for solvolyses of benzoyl chloride (k) relative to k_0 (80% ethanol—water) at 25 °C vs. corresponding data for solvolyses of p-methoxybenzoyl chloride (**1**, Z = OMe). Symbols E and M refer to % v/v ethanol– and methanol–water mixtures, respectively. Points A, B, and C and the hatched line are discussed in the text. Kinetic data from references 5—8.

linear regions, MeOH → 70M and 20M → 50M; the rate of solvolysis via the S_N2/S_N1 reaction channel (point A in Figure 1) is half of the rate calculated for this intersection point. (3) Point B (Figure 1) is calculated for ethanol–water mixtures in an analogous way to point A. These four points give a precise correlation line (slope 0.89 ± 0.02, correlation coefficient 0.9994) covering over two log units in rate. Only by halving the rate constant to obtain points A and B (Figure 1) is such a precise correlation obtained. This halving can only be justified if there are two simultaneous reaction channels.

The above mechanistic analysis of the kinetic data is supported by the following additional results. (a) Data points for 30% alcohol–water mixtures are, as expected, close to the correlation line (Figure 1). (b) A similar analysis to Figure 1 of solvolysis data for p-methylbenzoyl chloride (**1**, Z = Me) is even more precise (slope 1.013 ± 0.004, correlation coefficient 0.9999). (c) Extrapolation of the correlation line to point C (Figure 1) gives the rate constant for S_N2/S_N1 solvolysis of benzoyl chloride in methanol (3.1 × 10^{-4} s^{-1}); for (**1**, Z = Me) the corresponding calculated rate constant is 7.0 × 10^{-4} and for (**1**, Z = OMe) the observed rate constant is 1.07 × 10^{-2}

s^{-1},[8] and these two values give a plausible $\rho^+ = -2.5$,[12] in comparison with $\rho^+ = -3.1$ for a range of substituents in 97% trifluoroethanol–water.[8] It appears that the transition state in the S_N2/S_N1 process for benzoyl chloride in methanol involves bond cleavage, but there is also weak bond formation by the nucleophile.[5]

Additional predictions can now be made, e.g., the S_N2/S_N1 reaction channel contributes 7% of the observed rate of solvolysis of benzoyl chloride in methanol. As water is added to methanol, the % contribution for the S_N2/S_N1 reaction channel increases. This channel shows expected trends in substituent and solvent effects, so a clearer understanding of these reactions is emerging. However, more complex trends in undissected rate data can be rationalised,[6] and further verification is desirable. As the two reaction channels show very different selectivities in competition for alcohol and water in product formation,[5,7] an independent dissection of the two reaction channels based on products rather than rates may be possible. More detailed mechanistic studies of the separated reaction channels are in progress.

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