# The Effect of Electrolytes on the Stabilities of Initial and Transition States in $S_N1$ Reactions

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THE rate coefficient ($k_1$) for the rate-determining heterolysis of $S_N1$ reactions in the presence of electrolytes is given by

$$\log (k_1/k_1^0) = \log (\gamma/\gamma^0) - \log (\gamma_\ddagger/\gamma_\ddagger^0)$$

where the superscript zero refers to zero ionic strength, and $\gamma$ and $\gamma_\ddagger$ are the activity coefficients of the initial and transition states, respectively. A knowledge of $\gamma/\gamma^0$ and $\gamma_\ddagger/\gamma_\ddagger^0$ can provide additional information about the operation of electrolyte effects but these parameters have only rarely been determined. We now report the relevant data for the $S_N1$ heterolysis of the sparingly soluble 4-nitro-4′-phenyldiphenylmethyl chloride in 70% aqueous acetone at 20° (see Table); a parallel study of 4-nitrodiphenylmethyl chloride in the 50% solvent gave very similar results.

The Table shows that $k_1/k_1^0$ is very sensitive to the nature of the electrolyte; similar patterns have been observed for other $S_N1$ reactions in aqueous organic solvents.[1] Apart from the two perchlorates which appear to be anomalous (see below), the different accelerating effects of the various

| *Electrolyte* (0·1M) | $\log (k_1/k_1^\circ)$* | $\log (\gamma/\gamma^\circ)$† | $\log (\gamma_\ddagger/\gamma_\ddagger^\circ)$‡ |
|---|---|---|---|
| $Me_4NF$ | −0·116 | −0·128 | −0·012 |
| NaCl | 0·021§ | −0·025 | −0·046§ |
| $NaSO_3Ph$ | 0·053 | −0·024 | −0·077 |
| $NaNO_3$ | 0·069 | 0·009 | −0·060 |
| $NaBF_4$ | 0·087 | 0·019 | −0·068 |
| NaBr | 0·109 | 0·018 | −0·091 |
| $HNO_3$ | 0·120 | 0·045 | −0·075 |
| $NaClO_4$ | 0·129 | 0·013 | −0·116 |
| $HClO_4$ | 0·163 | 0·048 | −0·115 |

* From the first-order rates for the production of chloride ions, error ⩽ 0·004. † From $\log (k_1/k_1^\circ)$ and $\log (\gamma_\ddagger/\gamma_\ddagger^\circ)$; error ⩽ 0·006. ‡ From the zeroth-order rates in solutions permanently saturated with respect to the substrate; error ⩽ 0·004. § Corrected for the common-ion effect.

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[1] (a) E. F. J. Duynstee, E. Grunwald, and M. L. Kaplan, *J. Amer. Chem. Soc.*, 1960, **82**, 5654; (b) G. R. Lucas and L. P. Hammett, *ibid.*, 1942, **64**, 1928; (c) K. D. McMichael and R. A. Clement, *J. Org. Chem.*, 1961, **26**, 620; (d) G. Kohnstam, A. Queen, and B. Shillaker, unpublished results.

electrolytes arise mainly from their different effects on the stability of the initial state [$\log(\gamma/\gamma^0)$], in contrast to the effect of chloride, bromide, and perchlorate ions on the hydrolysis of *exo*-norbornyl bromide.[1c*]

Previous determinations of $k_1/k_1^0$ in mixed solvents have led to the suggestion that the addition of electrolytes alters the stabilities of the initial and transition states by an electrostatic effect which is virtually independent of the nature of the electrolyte (the ionic strength effect[4]) and by a salt-induced medium effect[1a] which can roughly be regarded[1b] as arising from changes in the "effective" solvent composition caused by the solvation of the electrolyte. The magnitude of any salt-induced medium effect depends on the sensitivity of the rate to solvent changes, and on the nature of the electrolyte. As fluoride and chloride ions can be expected to "dry" aqueous acetone more than nitrate and perchlorate ions (*cf.* ref. 5), this interpretation predicts the smaller values of $k_1/k_1^0$ for the two halide ions, as now observed. The known effect of solvent changes on the stabilities of the initial and transition states in the present reaction[6] then requires that increasing values of $k_1/k_1^0$ should arise mainly from an increase in $\gamma/\gamma^0$ and only to a relatively small extent from a reduction of $\gamma_\ddagger/\gamma_\ddagger^0$; this applies to most of the electrolytes now employed.

Both the initial and the transition state appear to be excessively stabilised by the two perchlorates and (to a smaller extent) by benzenesulphonate ions, possibly because of specific short-range interactions with the substrate (*cf.* ref. 1a, 7). Bromide ions also reduce $\gamma_\ddagger/\gamma_\ddagger^0$ a little more than expected, but these ions represent the most powerful nucleophiles now reported and some bimolecular reactions between them and the substrate cannot be excluded.** In spite of these anomalies, the present results provide a clear demonstration of the importance of salt-induced medium effects in $S_\mathrm{N}1$ reactions. It is also noteworthy that the stability of the transition state is often relatively insensitive to the nature of the electrolyte, as originally postulated.[4]

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* For $S_\mathrm{N}1$ hydrolysis in water, $k_1/k_1^\circ$ is largely independent of the nature of the electrolyte which generally has the same effect on the values of $\gamma/\gamma^\circ$ and $\gamma_\ddagger/\gamma_\ddagger^\circ$.[2] Differences of solvolytic behaviour in water and in aqueous organic solvents are however not unexpected (*cf.* ref. 3).

** The more strongly nucleophilic azide ions clearly attacked the substrate bimolecularly in the present solvent.

[2] G. A. Clarke and R. W. Taft, *J. Amer. Chem. Soc.*, 1962, **84**, 2295.
[3] G. Kohnstam, "The Transition State," *Chem. Soc. Special Publ.*, No. 16, 1962, p. 179.
[4] L. C. Bateman, M. C. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 1940, 979.
[5] E. Grunwald, G. Baughman, and G. Kohnstam, *J. Amer. Chem. Soc.*, 1960, **82**, 5801.
[6] N. Featherstone, E. Jackson, and G. Kohnstam, *Proc. Chem. Soc.*, 1963, 175.
[7] G. M. Waind, *J. Chem. Soc.*, 1954, 2879.