Grunwald–Winstein Plots exhibiting a Maximum. Solvolysis of Methyl Perchlorate

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Summary Maxima are observed in Grunwald–Winstein plots for the solvolyses of methyl perchlorate in aqueous acetone and aqueous dioxan; they may be associated with the unusual solvation characteristics of the perchlorate ion.

ALTHOUGH the Grunwald–Winstein equation[1] was originally intended for use with S_N1 (and $E1$) solvolyses, many bimolecular solvolyses in a given mixed aqueous–organic solvent have also been found to give linear plots, but with considerably reduced slopes (m-values). The S_N2 solvoyses can be better described in terms of the extended Grunwald–Winstein equation[2,3] (1) where the first term relates to

$$\log(k/k_0) = lN + mY \qquad (1)$$

solvent nucleophilicity in a parallel manner to that in which the second relates to solvent ionizing power. The frequent observation of linear log k *vs.* Y plots for S_N2 solvolyses arises from a proportionality between the N- and the Y-scales;[4] indeed, the slopes can be predicted from the appropriate proportionality constant and the l- and m-values of the four-parameter equation.[5] A corollary is that, while negative slopes are, in principle, possible ($l >> m$), simple Grunwald–Winstein plots should, in the absence of superimposed perturbations, be linear for those solvent systems for which $N \propto Y$.

Methyl perchlorate differs from previously studied initially neutral alkyl derivatives (such as halides or toluene-*p*-sulphonates) in that, owing to its small tendency for hydration,[6] the leaving group is better solvated in dipolar aprotic solvents than in water.[7] This could lead to unusual solvolysis characteristics, which would be reflected in Grunwald–Winstein plots. The rate data for solvolysis of methyl perchlorate in aqueous–acetone and aqueous–dioxan mixtures, obtained following the procedure outlined previously,[8] are reported in the Table. Grunwald–

TABLE. Specific rates (k_1/s^{-1}) for solvolysis of methyl perchlorate in aqueous–acetone (A–W) and aqueous dioxan (D–W) mixtures at 25·0 °C.[a]

% of organic component[b]	10^3k_1(A–W)	10^3k_1(D–W)
95	0·64	0·254
90	1·26	0·72
80	2·03	1·64
70	2·37	2·34
60	2·57	2·80
50	2·61	2·89
40	2·34	2·78
30	2·07	2·32
20	1·84	2·04
10	1·67	1·74
0	1·58[c]	

[a] Standard deviations, determined for each run, were between 1 and 3% of the reported values. [b] By volume; owing to use of a concentrated stock solution of $MeOClO_3$ in dioxan, the solvent was 98% of that indicated plus 2% of dioxan. [c] D. N. Kevill and B. Shen [*Chem. Ind.* (*London*), 1971, 1466] report a value of 1·54(± 0·03) × 10^{-3} s^{-1}.

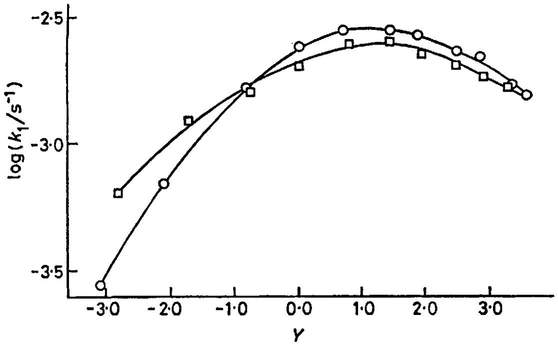

FIGURE. Grunwald–Winstein plots for solvolysis of methyl perchlorate in acetone–water (□) and dioxan–water (○) at 25·0 °C. The Y-values are from P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

Winstein plots of the data are given in the Figure and the regions of decreasing rate with increasing solvent ionizing power (negative m-values) are, to the best of our knowledge, the first reported examples for solvolysis by a nucleophilic substitution mechanism of an initially neutral substrate. For the < 50% water content region, the average m-values of 0·14 ± 0·03 for aqueous acetone and 0·18 ± 0·03 for aqueous dioxan are consistent with the values of 0·11 and 0·13 previously obtained for studies in water, 80% ethanol, and methanol[8] and in water and methanol.[9]

In contrast, no maximum is observed in a Grunwald–Winstein plot constructed using the specific solvolysis rates of methyl iodide in aqueous dioxan at 60 °C.[10] A curved plot is obtained with m-values of 0·37 at the Y-value corresponding to 80% dioxan and 0·12 at the Y-value corresponding to 20% dioxan.

(*Received*, 30*th September* 1980; *Com.* 1076.)

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