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A HAMMETT STUDY OF THE ALKALINE HYDROLYSIS OF BENZENESULPHONYL FLUORIDES

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The electronic requirements of nucleophilic substitution at sulphur have received considerable attention[1] in connection with the possible formation of a penta-co-ordinate intermediate along the reaction path and/or of d orbital participation in the transition state. It was expected that small rho values would indicate a direct, synchronous displacement, very similar to that of aliphatic nucleophilic substitution and large rho values would indicate a transition state where bond forming has progressed far more than bond breaking.[2]

The belief that nucleophilic substitution at sulphur occurs via a direct S_N2 type displacement is widespread because of much experimental evidence consistent with a reaction mechanism which does not require the formation of an intermediate (steric effects,[3] inversion of configuration,[4] lack of ^{18}O incorporation during hydrolysis,[5] etc.).

In this context, the few relatively large rho values to be found in the literature (1.8 and 2.2)[6,7] have been given little attention as indicative of an intermediate complex mechanism. We are reporting preliminary results on the alkaline hydrolysis of para substituted benzenesulphonyl fluorides in water-dioxan.

A plot of the data according to the Hammett equation is linear ($r = 0.9983$) with $\rho = 2.79$. This is the largest value determined so far. It clearly disproves any general belief that substituent effects for nucleophilic substitution at sulphur are small.

A rho value of 2.8 was found for nucleophilic substitution at silicon where other evidence for d orbital participation exists and it was considered a further proof for the mechanism.[8]

Rate Coefficients for the Alkaline Hydrolysis
of *para* Substituted Benzenesulphonyl Fluorides[a]

Substituent	*k*/mole^{-1} sec^{-1}	Substituent	*k*/mole^{-1} sec^{-1}
CH_3O	1.1	Cl	26.5
CH_3	2.9	NO_2	1100
None	8.2		

[a] Substrate concentration., *ca* 10^{-4}-10^{-3} *M*; solvent, water-dioxan, 55/45 (w/w); temp., 25° C; $[OH^-]$, 1.5-5.13 x 10^{-2} *M*; kinetics followed with a stopped flow spectrophotometer.

We are aware of the limitations of linear free energy relationships in mechanistic interpretations.[9] However, a vast amount of data shows that so far, there is no example of large rho value (>2) incompatible with a good deal of charge development in the transition state, in spite of the fact that small rho values have often been found either to give inconsistent evidence or to be difficult to interpret in terms of small charge development.[10]

Thus, the high rho value reported in this communication appears to provide some support to an addition-elimination mechanism in nucleophilic substitution at sulphur.

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