

Rates of Addition of 4-Substituted-2-nitrobenzenesulphenyl Chlorides to Cyclohexene

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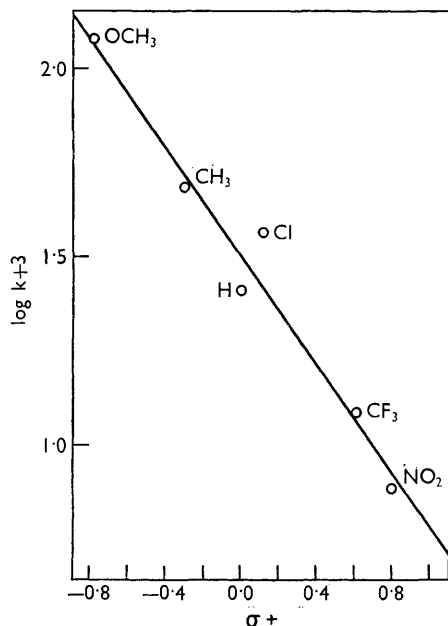
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THE reaction of 2,4-dinitrobenzenesulphenyl chloride with *para*-substituted styrenes gives a value of -2.20 for the Hammett reaction constant,

ρ ,¹ suggesting that in the transition state the α -carbon atom is appreciably electron deficient. Variation of the substituents in the arylsulphenyl

¹ W. S. Orr and N. Kharasch, *J. Amer. Chem. Soc.*, 1956, **78**, 1201.

chloride should give an indication of the extent of the electron deficiency on the sulphur atom in the transition state. The second order velocity constants for the reaction of a series of 4-substituted-2-nitrobenzenesulphenyl chlorides with cyclohexene in acetic acid solution at 25.0° have been measured using a dilatometric technique,² and $\log k$ plotted against the substituent constant, σ^+ , as shown. The value for 2,4-dinitrobenzenesulphenyl chloride has been previously recorded.³ From a



Plot of $\log k$ against the substituent constant, σ^+ , for the reaction of 4-substituted-2-nitrobenzenesulphenyl chloride with cyclohexene in acetic acid solution at 25°.

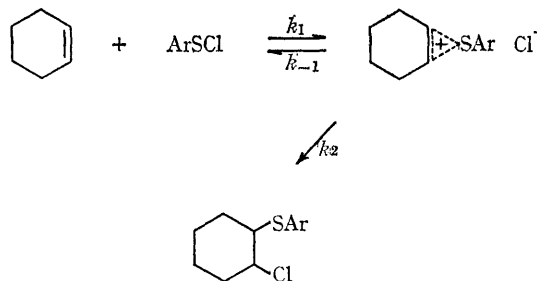
least-squares treatment the reaction constant, ρ^+ , equals -0.714 ($r = 0.955$). The corresponding

plot against the Hammett substituent constant, σ , is approximately linear for all the substituents except *p*-methoxy, for which the experimentally determined velocity constant is approximately twice that required for linearity. In all cases the reaction gave the appropriate 2-chlorocyclohexyl aryl sulphide in over 95% yield under the conditions used for the rate measurements.

These results are in agreement with the mechanism previously proposed:^{2,4}

The need to allow for an enhanced mesomeric electron release from the *para*-substituents by the use of σ^+ strongly supports the postulation of an intermediate episulphonium ion, rather than an open carbonium ion. The sign and magnitude of ρ^+ can be explained only if the first step is rate limiting and the transition state resembles the intermediate, which will become more stable with increasing electron release from the *para*-substituents. This order of reactivity supports the conclusion² that slight variations in the initial positive charge on the sulphur atom do not directly play an important part in determining the relative rate of these electrophilic addition reactions.

All the new compounds, sulphenyl chlorides, sulphides, and the corresponding sulphones gave satisfactory analyses.



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² D. S. Campbell and D. R. Hogg, *J. Chem. Soc.*, in press.

³ D. R. Hogg and N. Kharasch, *J. Amer. Chem. Soc.*, 1956, **78**, 2728.

⁴ N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, 1949, **71**, 2724.