# Nucleophilic Substitution at Dico-ordinated Sulphur in Substituted Arylsulphenanilides

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*Summary* The bimolecular substitution reactions of 2,4-dichloroaniline with sulphenamides (**1a—e**) gave a negative value for the reaction constant $\rho$, and correlated with enhanced $\sigma$ values ($\sigma^-$).

NUCLEOPHILIC substitution reactions at dico-ordinated sulphur have recently received considerable attention.[1] Although evidence has been obtained for metastable intermediates for displacement reactions at dico-ordinated sulphur in a few cases,[2] the insensivity of reaction rates to electronic effects,[3] the lack of free energy relationships,[4] and the large steric effects[5] seem to support a synchronous $S_N2$ mechanism for displacement reactions at dico-ordinated sulphur in most cases. In an investigation of substitution reactions of 2,4-dichloroaniline with substituted arylsulphenanilides, $XC_6H_4{\cdot}SNHPh$, (**1a—e**) (**a**; X=H, **b**; X=*p*-Cl, **c**; X=*p*-Br, **d**; X=*m*-$NO_2$, **e**; X=*p*-$NO_2$), we have observed substantial substituent electronic effects, a negative value for $\rho$, and a correlation with enhanced $\sigma$ values for (**1e**).

When 1·7M-solutions of sulphenamides (**1a**—**e**)[6]† in 2,4-dichloroaniline were heated at 109·3°, equilibrium mixtures of starting materials and (**2a**—**e**) were obtained (equation 1). Under the conditions used, the rates of parasitic reactions were negligible,[6] while the rate of substitution remained measurable. The composition of the reaction mixtures at each time interval was calculated from the n.m.r. spectra of the individual samples, first quenched by cooling and dilution with $CDCl_3$.

$$\underset{(\mathbf{1})}{XC_6H_4\cdot SNHPh} + 2,4\text{-}Cl_2C_6H_3\cdot NH_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(\mathbf{2})}{XC_6H_4\cdot SNH\cdot C_6H_3Cl_2\text{-}2,4} + PhNH_2 \quad (1)$$

Graphical analysis of the experimental data proved that the reaction was first-order in both amine and sulphenamide. Rate constants were calculated from the rate of disappearance of sulphenanilides.[7] Equilibrium constants were obtained from the final composition of the reaction mixtures (Table). A plot of log $k_1$ *vs.* $\sigma$ [8] for sulphenamides (**1a, d, e**) gave a good linear correlation (Figure). The reaction constant $\rho$, calculated from the least-squares treatment of experimental data, was −1·71 ($s$ = 0·995, $r$ = 0·02).

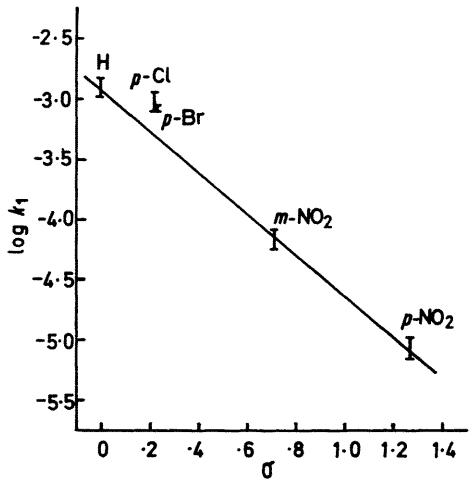


FIGURE. *Log $k_1$ vs. a for substitution of 2,4-dichloroaniline with substituted arylsulphenanilides (error ranges represent actual spread of experimental data).*

the excess of electron density on sulphur may be dispersed in the ground state by resonance interaction. This interpretation is then compatible with an $S_N2$ transition state.

Additional experimental evidence to support this interpretation was obtained from the correlation of the chemical shifts for the NH protons in the n.m.r. spectra of (**1a**—**e**)

*Kinetic data for the reaction of 2,4-dichloroaniline with sulphenanilides at* 109·3 ± 0·3°

| Sulphenamide | $k_1$ ($M^{-1}$ $s^{-1}$)[a] | $K_{eqm}(k_1/k_2)$[a] | No. of runs |
|---|---|---|---|
| (**1a**) | (1·3 ± 0·1) × $10^{-3}$ | (1·8 ± 0·5) × $10^{-1}$ | 4 |
| (**1b**) | (9·4 ± 0·7) × $10^{-4}$ | (1·01 ± 0·01) × $10^{-1}$ | 3 |
| (**1c**) | (8·5 ± 0·5) × $10^{-4}$ | (1·2 ± 0·2) × $10^{-1}$ | 3 |
| (**1d**) | (7·9 ± 0·5) × $10^{-5}$ | (8·2 ± 0·1) × $10^{-2}$ | 5 |
| (**1e**) | (8·3 ± 0·7) × $10^{-6}$ | (4·4 ± 0·1) × $10^{-2}$ | 3 |

[a] Error ranges are linear least-squares standard deviations.

The negative value for $\rho$ and the correlation with $\sigma^-$ are incompatible with a truly synchronous $S_N2$ mechanism without additional considerations. One interpretation of these results is that interaction between sulphur and nitrogen stabilizes the ground state relative to the transition state. Electron donation from nitrogen to sulphur should be facilitated by electronegative substituents on sulphur and the resulting increase in electron density on sulphur makes it less susceptible to nucleophilic attack. The correlation with $\sigma^-$ for (**1e**) is also explained because with enhanced $\sigma$ values and the u.v. spectrum of (**1e**) (cyclohexane) which showed a broad absorption at 315 nm ($\epsilon$ 13·700) which was absent in (**1a**—**d**).

A similar explanation has also been suggested for the torsional barriers to rotation found in certain *N*-sulphenylsulphonamides.[9]

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† All compounds were prepared by the reaction of the appropriate sulphenyl chloride with aniline and had elemental analysis, i.r. and n.m.r. spectra consistent with their structures.

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