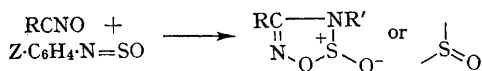


Kinetic Evidence for a Two-step 1,3-Cycloaddition

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IN 1,3-cycloadditions of benzonitrile oxides to arylacetylenes, the kinetic effect of substituents on the phenyl rings of both reagents is variable and/or weak.^{1,2} A concerted reaction mechanism is favoured in those cases which fit the general proposal about "1,3-dipolar cycloadditions".³ It seemed worth checking whether this could be true also in a cycloaddition to an unsaturated bond connecting markedly different atoms.

The reaction between nitrile oxides and *N*-sulphonylanilines, that gives 1,2,3,5-oxathiadiazole-2-oxide derivatives,⁴ was kinetically studied:



with 3,5-dichloro-2,4,6-trimethylbenzonitrile oxide¹ and the following *N*-sulphonylanilines (I), with Z = *p*-OMe (a), *p*-Me (b), *p*-H (c), *m*-Cl (d). Cycloadducts were isolated, and their structure confirmed both by infrared spectra and by decomposition to diarylcarbodi-imides.⁴ The kinetics were measured in carbon tetrachloride and in chlorobenzene, and followed by infrared spectrophotometric determination of both the reagents and often also of the product: the rate was found to be of the first order with respect to both reagents.

The following rate constants were obtained at 25.0°, each one being the average of several values (probable errors are shown):

	$10^4 k$ (l. mole ⁻¹ sec. ⁻¹) at 25°	
	in CCl ₄	in PhCl
(Ia)	5.75 ± 0.41	3.44 ± 0.34
(Ib)	15.5 ± 1.7	12.0 ± 1.3
(Ic)	25.1 ± 1.4	—
(Id)	33.3 ± 2.5	29.7 ± 4.5

For runs in carbon tetrachloride the plot of $\log k$ against Hammett σ -values (see Figure) is a curve. Reaction constants, roughly evaluated from chords between (Ia) and (Ib), and between (Ic) and (Id), are as different as $\rho_1 = 4.4$ and

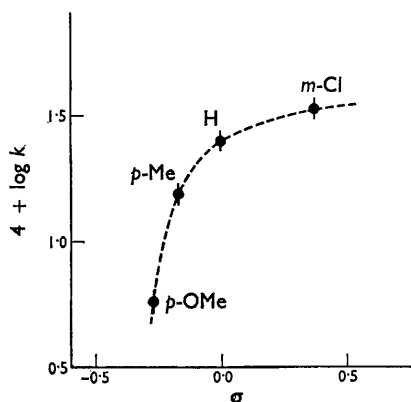


FIGURE. ρ - σ Relationship for reactions in carbon tetrachloride at 25.0°.

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² A. Dondoni, *Tetrahedron Letters*, 1967, 2397.

³ R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, 2, 565, 633.

⁴ P. Rajagopalan and H. U. Daeniker, *Angew. Chem. Internat. Edn.*, 1963, 2, 46; P. Rajagopalan and B. G. Advani, *J. Org. Chem.*, 1965, 30, 3369.

⁵ G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem. Internat. Edn.*, 1962, 1, 89.

$\rho_1 = 0.33$, respectively. In chlorobenzene, the trend is the same; ρ_1 equals 5.6.

Such behaviour can be explained as being due to a two-step reaction mechanism, the first step being a reversible nucleophilic attack on the sulphur from sulphinylaniline by the oxygen from the nitrile oxide, followed by ring closure as a second step. Nucleophilic attack appears to be rate limiting in the case of the electron-releasing Z substituents on the aniline, as is shown by the ρ_1 -values being around 5. Acceleration of this step by substituents of higher σ -constant makes it fast as compared with the second one, which gains kinetic control.

When chlorobenzene (dielectric constant $D_{20} = 5.71$) is used instead of carbon tetrachloride ($D_{20} = 2.24$), the reaction rates are slightly decreased. This is difficult to reconcile with the proposed mechanism, at least for (Ia) and (Ib), since nucleophilic reactions between neutral molecules are usually accelerated by polar solvents. However, as the reactants have large dipole moments,^{1,5} it seems possible that the transition state of the nucleophilic attack is slightly less solvated than the initial system.

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