The Stabilities of Meisenheimer Complexes. Part 40.[1] A Kinetic Study of the Reaction of 1-Chloro-2,4-dinitrobenzene with Sulphite Ions in Water–Dimethyl Sulphoxide Mixtures

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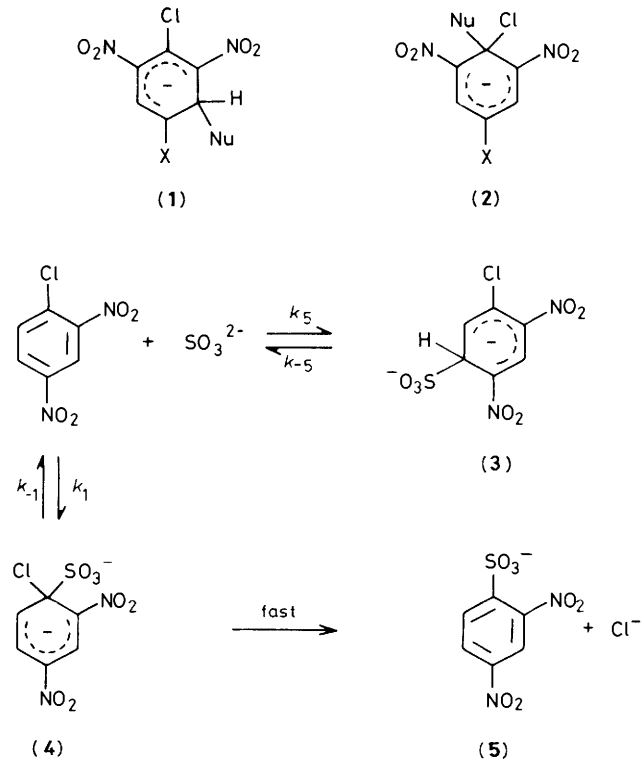
Kinetic and equilibrium data are reported for the reactions of 1-chloro-2,4-dinitrobenzene with sulphite ions in dimethyl sulphoxide–water mixtures. Attack at the unsubstituted 5-position yields an observable σ-adduct and is shown to be more rapid by a factor of *ca.* 12 than attack at the 1-position. The latter process which yields the substitution product is likely to involve intermolecular attack of sulphite on the substrate rather than intramolecular re-arrangement of the 5-adduct.

There have been several reports of the observation of σ-adducts during the reaction with nucleophiles of ring-activated chlorobenzenes. Spectroscopic studies[2,3] of the reactions of 1-chloro-2,6-dinitro-4-substituted benzenes with hydroxide, methoxide, and sulphite ions have shown that nucleophilic (Nu) attack occurs most rapidly at unsubstituted ring positions yielding adducts of structure (**1**) as observable species. The isomeric adducts (**2**) formed by attack at the chlorine-carrying ring-carbon atom are expected to be intermediates in the nucleophilic displacement of halide but, because of their instability with respect to loss of halide, are not observed spectroscopically. Kinetic data for the reactions of hydroxide ions with 1-substituted-2,4-dinitrobenzenes[4] and with 1-substituted-2,4,6-trinitrobenzenes[5,6] also accord with rapid attack at unsubstituted ring positions.

It was, then, not unexpected when the coloured species observed[7] during the reaction of 1-chloro-2,4-dinitrobenzene with sulphite ions was shown[8] by n.m.r. spectroscopy to be the adduct (**3**) formed by reaction at the unsubstituted 5-position rather than the adduct (**4**) at the 1-position. We report here a kinetic study of this reaction in dimethyl sulphoxide–water mixtures. The results are interpreted in terms of Scheme 1 and are important in that they allow a quantitative comparison of the rate coefficients for attack of sulphite at the 5-position and at the 1-position.



Scheme 1.

Experimental

1-Chloro-2,4-dinitrobenzene (DNClB) was a recrystallised commercial specimen, m.p. 52 °C (lit.,[9] 53 °C). AnalaR sodium sulphite was dried at 120 °C. Dimethyl sulphoxide was refluxed with calcium hydride and fractionated under reduced pressure. The distilled water used was boiled to remove carbon dioxide and subsequently protected from the atmosphere.

Kinetic and equilibrium measurements were made with freshly prepared solutions of reagents using a Hi-Tech SF3L stopped-flow spectrophotometer, a Pye Unicam SP8-100 recording spectrometer or a Beckman S25 instrument. Mixed solvents were prepared by volume and in stopped-flow work it was found most satisfactory to have solvents of the same composition in the two compartments. Rate coefficients at 25 °C measured under first-order conditions are the mean of five separate determinations and are precise to within ±5%.

Results and Discussion

Mixing solutions of 1-chloro-2,4-dinitrobenzene and sodium sulphite in water–dimethyl sulphoxide solvent resulted in the rapid production of a red-violet colour, $\lambda_{max.}$ *ca.* 540 nm, attributed to the adduct (**3**). The colour slowly faded and a new absorption at *ca.* 340 nm was observed due to the product (**5**). The rates of these two processes were sufficiently well separated for them to be measured separately. With the concentration of sulphite in large excess of that of the substrate the rate expressions relevant to the forming and fading reactions are equations (1) and (2), respectively.

$$k_{fast} = k_5[SO_3^{2-}] + k_{-5} \quad (1)$$

$$k_{slow} = \frac{k_1[SO_3^{2-}]}{1 + K_5[SO_3^{2-}]} \quad (2)$$

Measurements were made in solvent systems containing from 40 to 70% dimethyl sulphoxide by volume (14.3—36.8 mol% DMSO). The insolubility of sodium sulphite precluded measurements in media containing higher proportions of DMSO.

Table 1. Variation with solvent composition of the molar absorptivities of sulphite adducts

DMSO (% v/v)	Adduct (6),[a] 10^{-4} ε at 465 nm	Adduct (3) 10^{-4} ε at 540 nm
70	2.9	1.25[a]
65		1.18[b]
60	2.6	1.12[b]
50	2.45	1.06[b]
40	2.35	1.0[b]

[a] Measured experimentally. [b] Calculated, assuming similar variation to that of adduct (6)

Table 2. Data in 40 + 60 (v/v) DMSO–water at 25 °C

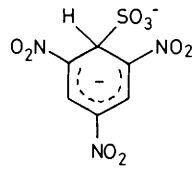
$[Na_2SO_3]$/M	[DNClB]/M	k_{fast}/s^{-1}	Absorbance (540 nm)[a]	K_5[b]/l mol^{-1}
0.020	5×10^{-4}	10.1	0.0115	0.58
0.020	1×10^{-3}	10.0	0.0214	0.54
0.040	1×10^{-3}	10.8	0.0372	0.47
0.040	5×10^{-4}	10.2	0.0196	0.50

[a] Measured with cell of 2 mm path length. [b] Calculated from absorbance values, using molar absorptivity of 1.0×10^4 l mol^{-1} cm^{-1} (Table 1)

Table 3. Data[a] in 50 + 50 (v/v) DMSO–water at 25 °C

$[Na_2SO_3]$/M	k_{fast}/s^{-1}	Absorbance (540 nm)[b]	K_5[c]/l mol^{-1}	k_{slow}[d]/s^{-1}	$k_{calc.}$[e]/s^{-1}
0.005	2.9	0.0030	5.8	0.0060	0.0063
0.010	3.2	0.0060	6.0	0.0114	0.0122
0.015	3.3	0.0090	6.2	0.0184	0.0179

[a] The concentration of 1-chloro-2,4-dinitrobenzene is 5×10^{-5}M. [b] Measured with cells of 2 mm path length. [c] Calculated from the absorbance values, using molar absorptivity of 1.06×10^4 l mol^{-1} cm^{-1} (Table 1). [d] Measured at 340 nm. [e] Calculated from equation (2) with k 1.3 l mol^{-1} s^{-1} and K_5 6 l mol^{-1}.



(6)

In a medium containing 70% (v/v) DMSO it was possible to achieve virtually complete conversion of the parent into adduct (3) and hence to obtain a value, 1.25×10^4 l mol^{-1} cm^{-1}, for the molar absorptivity at 540 nm.

It is, however, expected from previous work [10,11] that as the proportion of the hydroxylic component in the solvent is increased the value of the molar absorptivity will decrease slightly. In order to calculate molar absorptivities for (3) in more aqueous solvents we assume that the variation with solvent composition will be similar to that of the 1,3,5-trinitrobenzene–sulphite adduct (6). Data are given in Table 1.

40 + 60 (v/v) *DMSO–Water*.—Data relating to the colour-forming reaction are in Table 2. In this solvent system only small conversions of parent into adduct (3) are obtained leading to a relatively low value, 0.52 l mol^{-1}, for K_5. A consequence of this is that in equation (1) the k_{-5} term is dominant so that values

Table 4. Data[a] in 60 + 40 (v/v) DMSO–water at 25 °C

$[Na_2SO_3]$/M	k_{fast}/s^{-1}	$k_{calc.}$[b]/s^{-1}	Absorbance (540 nm)[c]	K_5[d]/l mol^{-1}	k_{slow}/s^{-1}	$k_{calc.}$[e]/s^{-1}
0.001	0.60	0.60	0.0048	94	0.004	0.004
0.002	0.64	0.65	0.0092	98	0.008	0.007
0.003	0.70	0.70	0.0123	93	0.009	0.009
0.004	0.74	0.75	0.0150	91	0.012	0.012
0.005	0.80	0.80	0.0173	90	0.014	0.014
0.006					0.015	0.015
0.008					0.020	0.019
0.009					0.020	0.020

[a] The concentration of 1-chloro-2,4-dinitrobenzene is 2.5×10^{-5}M. [b] Calculated from equation (1) with k_5 50 l mol^{-1} s^{-1} and k_{-5} 0.55 s^{-1}. [c] Measured with cell of 2 mm path length. [d] Calculated from the absorbance values using molar absorptivity of 1.12×10^4 l mol^{-1} cm^{-1}. [e] Calculated from equation (2) with k_1 4 l mol^{-1} s^{-1} and K_5 91 l mol^{-1}.

Table 5. Data[a] in 65 + 35 (v/v) DMSO–water at 25 °C

$[Na_2SO_3]$/M	k_{fast}/s^{-1}	$k_{calc.}$[b]/s^{-1}	Absorbance (540 nm)[c]	K_5[d]/l mol^{-1}	k_{slow}/s^{-1}	$k_{calc.}$[e]/s^{-1}
0.0007	0.32	0.32	0.012	490		
0.0012	0.38	0.38	0.019	560		
0.0017	0.45	0.45	0.023	560		
0.0010					0.008	0.008
0.0020					0.010	0.011
0.0030					0.013	0.013
0.0040					0.015	0.015

[a] With 1-chloro-2,4-dinitrobenzene, 2×10^{-5}M. [b] Calculated from equation (1) with k_5 130 l mol^{-1} s^{-1} and k_{-5} 0.23 s^{-1}. [c] Measured with cell of 2 mm path length. [d] Calculated from absorbance measurements using molar absorptivity of 1.18×10^4 l mol^{-1} cm^{-1}. [e] Calculated from equation (2) with k_1 12 l mol^{-1} s^{-1} and K_5 560 l mol^{-1}.

Table 6. Summary of rate and equilibrium data

DMSO (% v/v)	DMSO (mol-%)	k_5/l mol^{-1} s^{-1}	k_{-5}/s^{-1}	K_5/l mol^{-1}	k_1/l mol^{-1} s^{-1}
0	0[a]	0.40	230	0.0017	0.028
40	14.3	5.3	10.1	0.52	0.40
50	20.0	18	3.0	6.0	1.3
60	27.3	50	0.55	90	4.0
65	31.7	130	0.23	560	12

[a] By extrapolation.

of the rate coefficient for the colour-forming reaction are independent of the sulphite concentration. We obtain a value for k_5 ($= K_5 \cdot k_{-5}$) of 5.3 l mol^{-1} s^{-1}.

A value for k_1 of (0.40 ± 0.05) l mol^{-1} s^{-1} was obtained by following the formation of the product (5) at 340 nm in solutions containing 1—3 × 10^{-3}M sodium sulphite where the formation of the adduct (3) was negligible.

50 + 50 (v/v) *DMSO–Water*.—Data are in Table 3. The insolubility of sodium sulphite limited the concentration range available. The values of k_{fast}, again dominated by the reverse-rate coefficient, yield a value for k_{-5} of 3 s^{-1}. The value for k_5 ($= K_5 \cdot k_{-5}$) is 18 l mol^{-1} s^{-1}. Measurements of the slow product-forming reaction yield a value for k_1 of 1.3 l mol^{-1} s^{-1}.

60 + 40 (v/v) *DMSO–Water*.—The values in Table 4 of k_{fast} conform to equation (1) with values for k_5 of 50 l mol^{-1} s^{-1} and for k_{-5} of 0.55 s^{-1}. Combination of these yields a value for K_5 of 91 l mol^{-1}, in good accord with that obtained from the

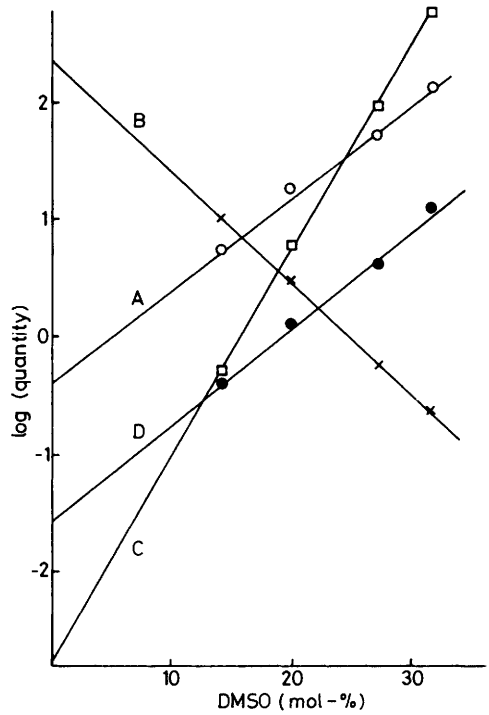
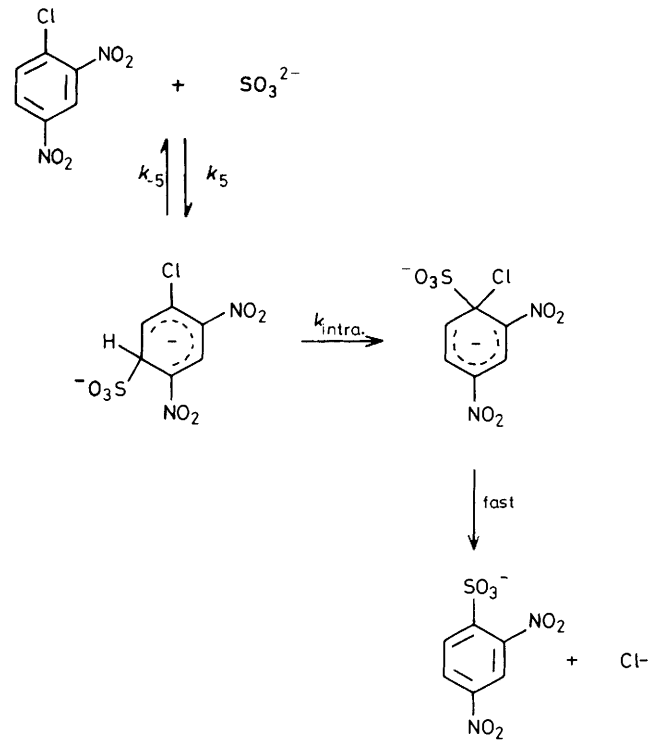


Figure. Variation with solvent composition of the logarithms of (A) k_5, (B) k_{-5}, (C) K_5, and (D) k_1



Scheme 2.

absorbance data. Measurement of the rates of the colour-fading reaction yield a value for k_1 of 4 l mol^{-1} s^{-1}.

65 + 35 (v/v) *DMSO–Water.*—The limited solubility of sodium sulphite allowed measurement only at low concentrations. The rate measurements for the forming reaction given in Table 5 yield values for k_5 130 l mol^{-1} s^{-1} and k_{-5} 0.23 s^{-1}. Combination of these values gives K_5 560 l mol^{-1}. The rates of the fading reaction allow the calculation of a value for k_1 of 12 l mol^{-1} s^{-1}.

Data are summarised in Table 6. In agreement with previous work [12–16] we find, Figure, that plots of the logarithms of rate and equilibrium constants *versus* the mole fraction of DMSO are linear. The increase in stability of the σ-adduct with increasing proportion of DMSO in the solvent probably reflects the poor solvation by DMSO of the sulphite ion and the good solvation of the polarisable adduct by this component.[16] Extrapolation to pure water allowed the determination of the values given in Table 6. The value of 0.0017 l mol^{-1} obtained for K_5 in water is considerably lower than the values previously reported [16,17] for sulphite addition at unsubstituted ring-positions of 1-X-2,4,6-trinitrobenzenes (*e.g.*, 290 l mol^{-1} for 1,3,5-trinitrobenzene). This decrease is consistent with the reduction from three to two of the ring nitro-groups.

The results in Table 6 show that sulphite attack at the unsubstituted 5-position is faster than attack at the chloro-substituted 1-position by a factor of 12 ± 2. The inductive withdrawal of the chlorine should favour attack at the 1-position. However, the steric and electrostatic repulsion [18] between entering and leaving groups will reduce the rate of attack. For comparison, the rates of hydroxide attack at the unsubstituted 3-position of 1-X-2,4,6-trinitrobenzenes [6] are faster than attack at the 1-position by factors of between 10 and 30 depending on the nature of X. In comparing the two systems we note two opposing effects; the absence of the 6-nitro group in 1-chloro-2,4-dinitrobenzene will reduce the steric effect while the change in nucleophile from hydroxide to the bulkier sulphite ion will increase steric repulsion.

Alternative Mechanisms.—We have interpreted our kinetic data in terms of Scheme 1, with (**3**) as the observed σ-adduct. There is strong n.m.r. support for this interpretation.[8] It is worth noting that the kinetic data allow us to discount the possibility that the σ-adduct we have observed is (**4**), the intermediate on the reaction pathway, rather than (**3**). The assumption that the observed adduct is (**4**) leads to the conclusion that expulsion from (**4**) of sulphite ion is faster by at least an order of magnitude than is expulsion of chloride ion and is hence untenable.[6]

A further possibility worth considering [8] is that rapid reaction to give (**3**) is followed by rate-determining intramolecular sulphite migration as shown in Scheme 2. Thus Gold *et al.*[19] have shown that the displacement by hydride of the 2-nitro group in 1-X-2,4-dinitrobenzenes may involve intramolecular migration from the initially formed hydride adduct at the adjacent 3-position. The fact that Scheme 2 requires migration between *meta*-oriented ring atoms reduces the likelihood of its occurrence. The kinetic dependence on sulphite concentration of the slow step is given in equation (3) and is similar to that of equation (2) so that the mechanism cannot be discounted for this reason. Using the data of Table 6 we calculate, from equation (3), values for $k_{intra.}$ which fall from 16

$$k_{slow} = \frac{k_{intra.}K_5[SO_3^{2-}]}{1 + K_5[SO_3^{2-}]} \quad (3)$$

s^{-1} in water to 0.02 s^{-1} in 65% (v/v) DMSO. This rather steep solvent dependence, similar in magnitude to the solvent dependence of k_{-5}, would indicate a transition state for the intramolecular step in which considerable negative charge is transferred from the ring to the sulphite group and is not compatible with a transition state in which the SO_3^- group

remains wholly bound to the ring. The dissociative mechanism of Scheme 1 seems more likely for the substitution reaction.

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