The Stabilities of Meisenheimer Complexes. Part 21.[1] Sulphite Additions to 2,4,6-Trinitrotoluene and 2,4,6-Trinitrobenzyl Chloride

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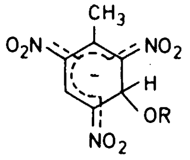
In aqueous sodium sulphite solutions, 2,4,6-trinitrotoluene and 2,4,6-trinitrobenzyl chloride give 1 : 1 and 1 : 2 adducts by addition at unsubstituted ring positions. Rate and equilibrium data for these reactions have been obtained by the stopped-flow method and are compared with similar data for other nitro-compounds.

THE reaction of 2,4,6-trinitrotoluene (TNT) with alkaline sodium hypochlorite is of current interest [2,3] as it provides a route to the commercially important 2,2',4,4',6,6'-hexanitrostilbene. 2,4,6-Trinitrobenzyl chloride (TNBCl) is likely to be an intermediate in this reaction.[2,3] Likely modes of interaction of TNT, or TNBCl, with alkali are formation of the conjugate base by transfer of a side-chain proton or formation of σ-adducts by base addition.[4] In the case of TNT there is good evidence [5] that in the presence of alkoxide ions rapid formation of the adduct (1) is followed by production of the thermodynamically more stable anion (2). In liquid ammonia TNT gives a 1 : 1 adduct by amide ion addition at an unsubstituted ring-position and a 1 : 2 adduct (3), in which geometrical isomerism is possible, by addition at the 1- and 3-positions.[6]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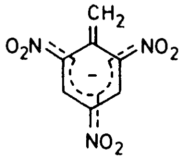
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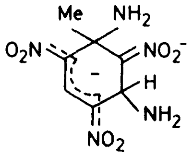
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Here we report structural, kinetic, and equilibrium data relating to reaction of TNT and TNBCl with sulphite ions. We chose sulphite for the initial studies since it is known readily to form σ-adducts with polynitrobenzenes [4,7-10] but has a relatively low affinity for protons. Hence we expected formation of the conjugate bases, (2) in the case of TNT, to be of minor importance, thus simplifying the analysis. It has been known for many years that aqueous sodium sulphite solutions will dissolve TNT to give highly coloured solutions; [11] but the only recent work [12] is the observation that in dilute solutions a species of unspecified structure with $\lambda_{max.}$ 465 nm and equilibrium constant 5.6 l mol^{-1} is formed.

RESULTS AND DISCUSSION

Spectroscopic Studies.—The visible spectra obtained in water indicate the presence of two equilibria between each nitro-compound and sodium sulphite. In dilute (<0.01M) sulphite solutions, TNT gives a pink species with $\lambda_{max.}$ 460 and 550sh nm, attributed to 1 : 1 interaction. In more concentrated (>0.1M) solutions an orange species showing a broad absorption maximum at 420 nm is the predominant species. This is likely to have 1 : 2 stoicheiometry. Previous work [7] with other substrates indicates that dimethyl sulphoxide (DMSO) stabilises 1 : 1 adducts relative to 1 : 2 adducts, and we find that in water–DMSO mixtures containing sulphite the visible spectra obtained are similar to those of the lower adduct in water but showing small bathochromic shifts.

The behaviour of TNBCl is similar to that of TNT in that at low sulphite concentrations a species with $\lambda_{max.}$ 460 and 550sh nm is formed while in more concentrated solutions a species with broad maximum at 440 nm predominates.

^{1}H N.m.r. data for the parent molecules and sulphite adducts are in Table 1. The spectra of the 1 : 1 adducts were obtained in a 70 : 30 DMSO–water mixture and the observation of spin-coupled bands at δ 8.50 and 6.14 due to ring protons is clear evidence for structure (4; X = H or Cl). The spectra of the 1 : 2 adducts were obtained

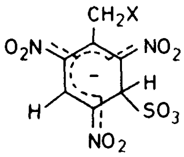
TABLE 1

^{1}H N.m.r. data for TNT and TNBCl and their adducts with sodium sulphite

	Solvent [a]	δ (ring)	δ (side chain)
TNT	DMSO	9.04	2.56
(4; X = H)	70 : 30 v/v DMSO–water	8.50 (d, *J* 2 Hz) 6.14 (d *J* 2 Hz)	2.41
(5; X = H)	Water	6.0	2.48
TNBCl	DMSO	9.08	5.00
(4; X = Cl)	70 : 30 v/v DMSO–water	8.50 6.13	5.05 (d, *J* 11 Hz) 5.18 (d, *J* 11 Hz)
(5; X = Cl)	Water	6.0	4.8 (d, *J* 11 Hz) 5.1 (d, *J* 11 Hz)

[a] Deuteriated solvents were used.

by dissolving the parent compounds in 1M-sodium sulphite in D_2O. In each case a single band due to ring protons was observed at δ 6.0 indicating structure (5; X = H or Cl). There was no evidence for *cis–trans*-isomerism in the 1 : 2 adducts as has been observed in the di-adduct from 1,3,5-trinitrobenzene.[9,13] The shifts of



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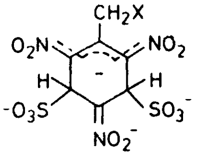


(5)

the side-chain protons vary little on complex formation but in the adducts formed from TNBCl non-equivalence of the CH_2Cl protons is observed presumably due to restricted rotation of this group.

Kinetic and Equilibrium Data.—Examination by stopped-flow spectrophotometry of the reactions of TNT, or TNBCl, with sodium sulphite in water indicated the presence of two processes whose rates were well separated. We attribute these to the formation of 1 : 1 and 1 : 2 adducts. Since all measurements were made with

$$\text{Parent} + SO_3^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (4)$$

$$(4) + SO_3^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (5)$$

sulphite in large excess over the parent, equations (1) and (2), respectively, will apply to these processes.[8]

$$k_{\text{fast}} = k_{-1} + k_1[SO_3^{2-}] \qquad (1)$$

$$k_{\text{slow}} = k_{-2} + \frac{k_2K_1[SO_3^{2-}]^2}{1 + K_1[SO_3^{2-}]} \qquad (2)$$

2,4,6-*Trinitrobenzyl chloride*. Rate and equilibrium measurements were made at 460 nm, the absorption maximum of (4; X = Cl), and are in Table 2. A plot according to equation (1) of the rate data for the faster reaction was linear and yielded values of k_1, 4 000 l mol^{-1} s^{-1}, and k_{-1}, 77 s^{-1}. Combination of these values gives K_1 ($=k_1/k_{-1}$) 52 l mol^{-1}, in good agreement with the value obtained from the optical densities at completion of the rapid reaction.

Extrapolation to zero sulphite concentration of the rates of the slower reaction gave a value for k_{-2} of 1.7 s^{-1}. Using this value and the known value of K_1, values of k_2 were calculated using equation (2). Good agreement between the observed and calculated rates is observed in Table 2.

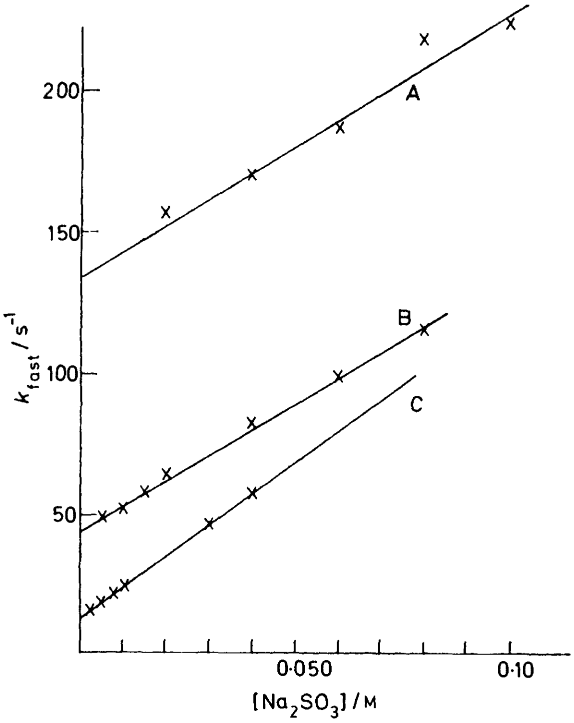
TABLE 2

Kinetic and equilibrium data for reaction of 2,4,6-trinitrobenzyl chloride (5×10^{-5}M) with sodium sulphite in water at 25°

$[Na_2SO_3]$ [a]/ M	k_{fast}/ s^{-1}	O.D. (460 nm) [b]	K_1/ l mol^{-1}	k_{slow}/ s^{-1}	k_{slow} [c] (calc)/ s^{-1}
0.002	86 ± 5	0.0131	61		
0.004	98	0.0214	54		
0.006	110	0.0302	56		
0.008	110	0.0371	56		
0.010	118	0.0427	55	1.94 ± 0.1	1.90
0.015	126	0.0537	54		
0.020				2.27	2.27
0.040				3.10	3.20
0.060				4.05	4.20
0.080				5.32	5.25
0.100		0.105		6.33	6.35

[a] Ionic strength 0.3M with sodium sulphite. [b] After completion of rapid colour-forming process, but before second process. Measurements relate to a 2 mm pathlength cell. A Benesi–Hildebrand plot gives a value of 0.120 for complete conversion. [c] Calculated from equation (2) with k_{-2} 1.7 s^{-1}, k_2 55 l mol^{-1} s^{-1}, and K_1 55 l mol^{-1}

2,4,6-*Trinitrotoluene*. In water a very fast process is associated with the formation of (4; X = H). Rate coefficients were in excess of 250 s^{-1} in the most dilute sulphite solutions which gave measurable absorption, and were too rapid for accurate measurement by the stopped-flow method. We made use of the stabilisation of the 1 : 1 adduct by dimethyl sulphoxide [4,7] to obtain data in mixed solvent systems. Rate measurements obtained at 460 nm in media containing 10, 20, and 30% dimethyl sulphoxide by volume are in the Figure and derived parameters are in Table 3. Measurements of optical density at the completion of the rapid colour-forming reaction were also obtained using the stopped-flow spectrophotometer and were used to calculate values of K_1, which were in each case in excellent agreement with those derived from rate measurements. In agreement with previous work [14] we find that log plots of K_1 and k_{-1} *versus* mol % dimethyl sulphoxide were linear and allowed values for these parameters in water to be found.



Rate data for formation of (4; X = H) in water containing the following percentage of DMSO by volume: A, 10; B, 20; C 30

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.

The kinetic data show that the changes in value of K_1 with solvent composition derive largely from changes in k_{-1}. This indicates that, as found in previous work,[8] the transition state for formation of the 1 : 1 adduct is 'reactant-like'.

Rate measurements of the slower process relating to the formation of (5; X = H) were conveniently made in water at 25°. Data are in Table 4. The values for this process depend markedly on the ionic strength of the medium as expected for formation of a multi-charged adduct.[8]

Comparison with Other Compounds.—Rate and equilibrium data at I 0.3M are summarised in Table 5 where they are compared with similar data for 1,3,5-trinitrobenzene and 2,4,6-trinitroanisole. As with other compounds we were unable to detect addition of sulphite at the 1-substituted position.[8] The higher value of K_1 for TNBCl than for TNT can be attributed to the greater inductive effect of the CH_2Cl substituent compared with the CH_3 group. However steric effects are also likely to be important and the presence of bulky groups at the 1-position will hinder planarity of nitro-groups, an important factor in charge delocalisation in the adducts. The decreased stability of the 1 : 1 adducts from TNT and TNBCl relative to TNB may be due to this factor. Buncel and his co-workers[10] have suggested that differences in the extent of solvation of adducts plays an important part in determining their relative stabilities, and the presence of a hydrophobic group (CH_3) may to some extent hinder the solvation of adjacent nitro groups which will be particularly important in the negatively charged adducts.

TABLE 3

Variation with solvent composition of rate and equilibrium data for formation of (4; X = H) from TNT and sodium sulphite at 25°

Vol % DMSO	Mol % DMSO	k_1/ l mol^{-1} s^{-1}	k_{-1}/ s^{-1}	K_1 [a]/ l mol^{-1}	K_1 [b]/ l mol^{-1}
30	9.6	1 100 ± 50	14 ± 0.5	80 ± 5	80 ± 8
20	5.9	920 ± 70	45 ± 2	21 ± 2	21 ± 2
10	2.7	900 ± 100	135 ± 10	7 ± 1	7 ± 1
0 [c]	0	800 ± 100	300 ± 30	2.6 ± 0.5	2.6 ± 0.5

[a] From kinetic data, $K_1 = k_1/k_{-1}$. [b] From optical density data. [c] Extrapolated values.

TABLE 5

Summary of equilibrium and kinetic data for sulphite additions in water at 25° with I 0.3M

	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K_1/l mol^{-1}	k_2/ l mol^{-1} s^{-1}	k_{-2}/s^{-1}	K_2/l mol^{-1}
1,3,5-Trinitrobenzene [b]	3.5 × 10^4	125	290	1.2 [a] 195	0.13 21	9.2 9.3
2,4,6-Trinitroanisole [c]	4.8 × 10^3	35	140	170	0.12	1.4 × 10^3
2,4,6-Trinitrotoluene	800	300	2.6	42	1.16	36
2,4,6-Trinitrobenzyl chloride	4 × 10^3	77	55	55	1.7	32

[a] Data refer to formation of *cis*- and *trans*-isomers. [b] From ref. 9. [c] From ref. 8.

We were unable to detect either from the n.m.r. or kinetic measurements any evidence for *cis–trans*-isomerism in the 1 : 2 adducts.[8,9,13,15] As in other cases[8] it seems likely that one isomer, probably *trans*, is favoured.

TABLE 4

Rate data for the formation of (5; X = H) in water at 25°

$[Na_2SO_3]$/M	k_{slow}[a]/s^{-1}	k_{slow}[b] (calc)	k_{slow}[c]/s^{-1}	k_{slow}[d] (calc)
0.010	1.19 ± 0.03	1.17		
0.020	1.20	1.20	1.01	1.01
0.040	1.27	1.32		
0.050			1.79	1.77
0.060	1.49	1.50		
0.080	1.74	1.74		
0.10	2.10	2.03	4.00	4.13
0.20			11.3	11.7
0.30			22.3	21.9
0.40			34.3	33.6

[a] I 0.3M with sodium sulphate. $I = \Sigma c_i Z_i^2$. [b] Calculated with k_{-2} 1.16 s^{-1}; k_2 42 l mol^{-1} s^{-1}; and K_1 2.6 l mol^{-1}. [c] I 1.5M with sodium sulphate. [d] Calculated with k_{-2} 0.85 s^{-1}; k_2 160 l mol^{-1} s^{-1}; and K_1 2.6 l mol^{-1}.

EXPERIMENTAL

2,4,6-Trinitrotoluene and 2,4,6-trinitrobenzyl chloride were recrystallised specimens supplied by Ministry of Defence, P.E.R.M.E., Waltham Abbey. Analytical grade sodium sulphite was used without purification. The distilled water used was boiled to remove carbon dioxide and subsequently protected from the atmosphere. ^1H N.m.r. measurements were made with a Bruker HX90E instrument modified for Fourier transform operation and using a deuterium lock. Measurements in media containing DMSO were made relative to internal tetramethylsilane. In water where this standard was insoluble shifts were measured relative to internal dioxan assuming a difference of 3.70 p.p.m. between the two references.[7]

Kinetic measurements were made by mixing freshly prepared solutions of reagents in a Canterbury stopped-flow apparatus. All measurements were made at 25° with sulphite in large excess over nitro-compound, so that first-order kinetics were observed.

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