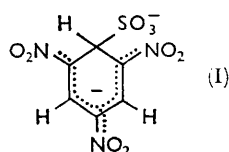


## A Spectroscopic Study of Complex Formation between Aromatic Nitro-compounds and Sodium Sulphite

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The interactions of a series of trinitrobenzene derivatives with sodium sulphite in water and in water-dimethyl sulphoxide mixtures have been investigated by  $^1\text{H}$  nuclear magnetic resonance and visible spectroscopy. In water each nitro-compound studied gives a 1:1 adduct at low sulphite concentrations resulting from covalent addition of sulphite at a ring carbon atom carrying hydrogen, while at higher sulphite concentrations di-adducts are formed by addition of sulphite at two ring positions carrying hydrogen. The equilibrium constants for formation of these complexes have been determined and are compared with the values for addition of hydroxide ion. The effects on the stabilities of the complexes of changes of the ionic strength or solvent are discussed.

It has been known<sup>1</sup> for some time that aqueous solutions of sodium sulphite will dissolve 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene to form highly coloured solutions from which the parent compounds can be re-formed. Cuta and Beranek<sup>2</sup> examined the visible spectra of trinitrobenzene in buffered solutions containing *ca.*  $10^{-3}\text{M}$ -potassium sulphite and showed that the absorption was due to a 1:1 interaction. They formulated the product as an addition complex (I) which would be similar to the addition complexes formed with alkoxides<sup>3</sup> and hydroxide.<sup>4</sup> On increasing the concentration of



sulphite ions the visible absorption decreased and this was attributed to the formation of higher complexes resulting from addition of two or three sulphite molecules per molecule of trinitrobenzene. The formation of higher complexes is also indicated by the isolation of a crystalline complex of stoichiometry 1 TNB :  $2\text{Na}_2\text{SO}_3$  from aqueous solutions.<sup>5</sup> Norris<sup>6</sup> also considered the possibility that the 1:1 complex in aqueous solution may result from a charge-transfer interaction similar to that formed between trinitrobenzene and aromatic amines or hydrocarbons.

This Paper deals with the interactions with sodium sulphite of 1,3,5-trinitrobenzene, 2,4,6-trinitroanisole, picramide, and various *N*-substituted picramides. The structures of the complexes formed have been determined by  $^1\text{H}$  n.m.r. spectroscopy, and the equilibrium constants for formation of the complexes by visible spectrophotometry. Most measurements were made in water, though in some cases dimethyl sulphoxide-water mixtures were used to examine the effect of change of solvent on the stabilities of the complexes.

### RESULTS AND DISCUSSION

**Visible Spectra.**—The visible spectra obtained in water indicate the presence of two equilibria between each nitro-compound studied and sodium sulphite. The

first is dominant at low sodium sulphite concentrations, and the second at higher sulphite concentrations. The spectra of trinitrobenzene (Figure 1) illustrate this behaviour. Increasing the concentration of sodium sulphite in the range 0–0.01M caused an increase in visible absorption, and the spectrum with maximum at 4620 Å was similar to that previously observed<sup>2,6</sup> in similar solutions. In this concentration range the shape of the spectrum was independent of the sulphite concentration,

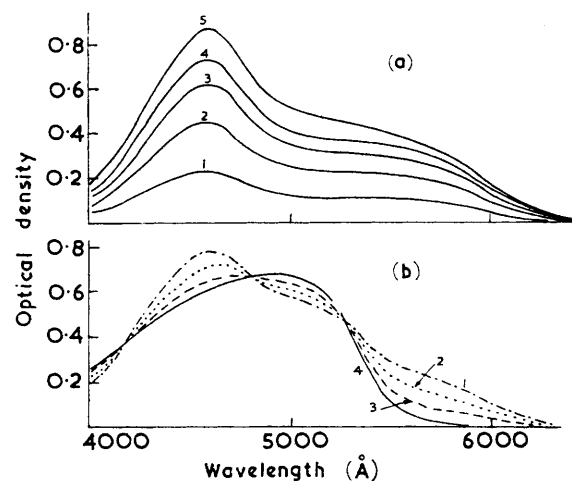


FIGURE 1 Absorption spectra of 1,3,5-trinitrobenzene ( $4 \times 10^{-5}\text{M}$ ) in water containing the following molarities of sodium sulphite: (a) 1, 0.001; 2, 0.003; 3, 0.006; 4, 0.012; 5, 0.03; (b) 1, 0.1; 2, 0.16; 3, 0.24; 4, 0.80

indicating the presence in addition to trinitrobenzene of a single complex (A). However, before conversion into (A) was complete, a second interaction occurred as indicated by changes in spectral shape above 0.01M-sulphite. These changes show the presence of a second complex (B), and conversion into B was complete in solutions containing 0.8M-sulphite. Increasing the sodium sulphite concentration above 0.8M caused no further spectral change.

Increasing the sodium sulphite concentration in the range 0–0.004M in solutions containing picramide caused a steady increase in absorption (from spectrum 1 to

<sup>1</sup> H. Muraour, *Bull. Soc. chim. France*, 1924, **35**, 367.

<sup>2</sup> F. Cuta and E. Beranek, *Coll. Czech. Chem. Comm.*, 1958, **23**, 1501.

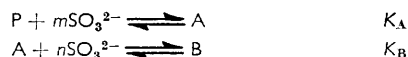
<sup>3</sup> See R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, 1966, **16**, 61, and references therein.

<sup>4</sup> V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1710.

<sup>5</sup> R. A. Henry, *J. Org. Chem.*, 1962, **27**, 2637.

<sup>6</sup> A. R. Norris, *Canad. J. Chem.*, 1967, **45**, 175.

spectrum 2 in Figure 2) indicating conversion into a complex (A). The spectrum remained unchanged up to 0.008M-sulphite but above this concentration a second interaction occurred, the spectral maximum shifting to shorter wavelength. Similar changes were observed with the other compounds studied. These equilibria can be represented in general by:



where P represents the parent nitro-compound, and the charges of A and B are neglected. In all cases only the initial reversible interactions were studied, though in some cases further irreversible changes occurred on long

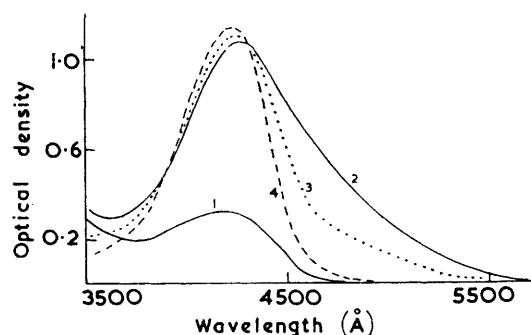


FIGURE 2 Absorption spectra of picramide ( $4 \times 10^{-5}\text{M}$ ) in water with  $[\text{Na}_2\text{SO}_3]$  (M): 1, 0; 2, 0.004; 3, 0.08; 4, 0.60

standing. The wavelengths of maximum absorption and extinction coefficients of the complexes are in Table I.

TABLE I

Visible absorption spectra of complexes [ $\lambda_{\text{max}}$  (Å),  $10^{-4}\epsilon$  \* in parentheses]

Parent	Complex A in water	Complex B in water	Complex A in water- $\text{Me}_2\text{SO}$
1,3,5-Trinitrobenzene	4620 (2.45)	4900 (1.7)	4740 (2.8)
2,4,6-Trinitroanisole	4460 (1.5)	4300 (1.2)	4620 (2.3)
Picramide	4260 (2.7)	4210 (2.8)	4340 (2.6)
N-Methylpicramide	4180 (2.4)	4020 (2.1)	4240 (2.6)
NN-Dimethylpicramide	4200 (2.0)	4170 (2.0)	4270 (2.4)

\* In some cases not determined directly; see Experimental section for method of determination.

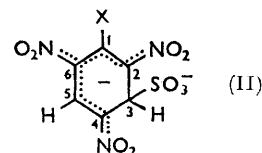
Visible spectra were also recorded in dimethyl sulphoxide-water mixtures (70 : 30 v/v). In this medium, in contrast to the behaviour in water, there was evidence for only one interaction between each nitro-compound and sodium sulphite. The shapes of the spectra were in each case closely similar to those of the 'A complexes' in water, with small shifts to longer wavelength. Thus it seems reasonable to assume that in this medium only the lower complexes (A) are formed.

The stoichiometries of the interactions and structures of the complexes were determined from  $^1\text{H}$  n.m.r. measurements.

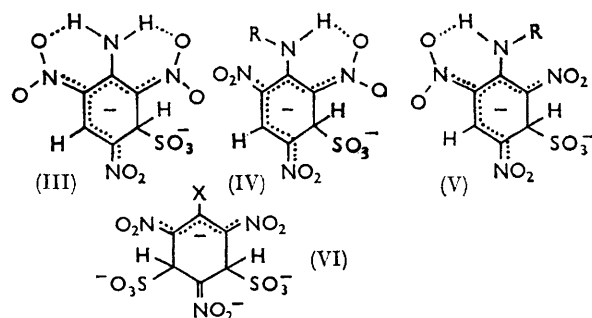
<sup>7</sup> M. R. Crampton and V. Gold, *J. Chem. Soc. (B)*, 1966, 893.

<sup>8</sup> L. K. Dyal and T. E. Kemp, *Spectrochim. Acta*, 1966, **22**, 467.

$^1\text{H}$  Nuclear Magnetic Resonance Spectra.—The structures of the lower complexes (A) were determined from measurements in dimethyl sulphoxide-water mixtures. The spectra of the nitro-compounds in the presence of sodium sulphite in this medium show in each case two sets of bands at *ca.*  $-8.40$  and  $-6.10$  p.p.m. exhibiting mutual spin-spin coupling. These are attributed to the ring protons of the 1 : 1 adducts (II). The hydrogen at C-3 shows in each case a large shift to high field relative



to the parent compound, consistent with a covalency change at this position, while the hydrogen at C-5 shows a smaller high-field shift compatible with increase screening in the negatively charged complex. These shifts are similar to those observed with the methoxide adducts of the nitro-compounds.<sup>7</sup> Also, it is interesting that the complexes derived from picramide and *N*-substituted picramides give resonances due to the amino-protons which are shifted to low field from the positions in the parent compounds. This low-field shift may be understood in terms of an increase in hydrogen-bonding on complex-formation. There is now good evidence<sup>8,9</sup> that intramolecular hydrogen-bonds exist in *o*-nitro-anilines, and in the complexes, where increased negative charge resides on the nitro-groups, this hydrogen-bonding is likely to be stronger than in the parent molecules. The fact that the amino-protons in the picramide complex give two bands shows their non-equivalence and a structure such as (III) may have some stability. The complexes derived from *N*-methyl- and *N*-phenylpicramide show only a single amino-proton resonance, suggesting that only one of the possible isomers (IV) or (V) is present in appreciable concentration.



In aqueous solutions containing *ca.* 1M-sodium sulphite where the visible spectra indicate that the nitro-compounds are present almost completely as the higher complexes (B), the  $^1\text{H}$  n.m.r. spectra indicate stoichiometries of 1 nitro-compound : 2 sodium sulphite. Thus the spectrum of trinitrobenzene shows two bands, with

<sup>9</sup> J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, 1964, **41**, 1033.

the more intense signal shifted strongly to high field at  $-6.05$  p.p.m. (indicating addition at two ring positions) and the less intense signal at  $-8.60$  p.p.m. This 1 : 2 stoichiometry is not unexpected in view of the isolation of a solid of this stoichiometry from solutions of trinitrobenzene in aqueous sodium sulphite. In contrast with the 1 : 1 complex, and perhaps unexpectedly, no spin-spin coupling was observed between the ring protons in the higher complex. The spectra of the compounds substituted at C-1 show a band or bands at *ca.*  $-6.20$  p.p.m. with intensity representing two protons, indicating addition at the two ring positions carrying hydrogen (VI).

was independent of the ionic strength of the medium, while the values of  $K_B$  ( $[B]/[A][SO_3^{2-}]$ ) increased sharply with increasing ionic strength. These changes no doubt largely reflect changes in the activity coefficients of the charged species in these solutions. The invariance of  $K_A$  indicates that the activity coefficient ratio  $f(A)/f(SO_3^{2-})$  must remain close to unity in these solutions, and this is perhaps not surprising in view of the double negative charge on A. However, species B carries four negative charges, so the ratio  $f(B)/f(A)f(SO_3^{2-})$  would not be expected to remain constant, with increasing ionic strength. It was found possible to correct the

TABLE 2

Chemical shifts (relative to internal tetramethylsilane) of 1-X-2,4,6-trinitrobenzenes and their adducts with sodium sulphite (figures in parentheses indicate relative intensities)

X	Parent molecule <sup>a</sup>			1 : 1 Complex <sup>a</sup> (addition at C-3)			1 : 2 Complex <sup>b, c</sup> (addition at C-3 and C-5)	
	Ring	Methyl	Amino	Ring <sup>e</sup>	Methyl	Amino	Ring <sup>f</sup>	Methyl
	Protons			Protons			Protons	
H	$-9.20$			$-6.00$ (1)	$-8.30$ (2)		$-6.05$ (2)	
OMe	$-9.05$	$-4.05$		$-6.05$ (1)	$-8.35$ (1)	$-3.85$ (3)	$-8.60$ (1)	
NH <sub>2</sub>	$-9.07$		$-9.00$	$-6.10$ (1)	$-8.38$ (1)		$-6.02$ (2)	$-4.08$ (3)
NHMe	$-8.92$	$-2.90$	$-9.20$	$-6.15$ (1)	$-8.30$ (1)	$-3.10$ (3)	$-6.07$ (1)	$-3.13$ <sup>d</sup> (3)
NMe <sub>2</sub>	$-8.80$	$-2.90$	—	$-6.15$ (1)	$-8.35$ (1)	$-3.03$ (6)	$-6.20$ (1)	$-3.07$ (6)
NHPh	$-8.95$		$-10.40$	$-6.17$ (1)	$-8.38$ (1)		$-6.26$	
NMePh	$-9.20$	$-3.30$		Not measured			$-6.20$ (1)	$-3.47$ (3)
							$-6.28$ (1)	

<sup>a</sup> In water-dimethyl sulphoxide (30 : 70 v/v). <sup>b</sup> In water. <sup>c</sup> In each case the bands at *ca.*  $-6.1$  and  $-8.3$  p.p.m. show spin-spin coupling with  $J \sim 1.5$  c./sec. All bands are doublets except the band at  $-6.00$  p.p.m. of the TNB spectrum which is a triplet. <sup>d</sup> Doublet,  $J \sim 6$  c./sec. <sup>e</sup> No separate band was observed due to the amino-protons here, possibly owing to their slow exchange with the solvent. <sup>f</sup> No spin-spin coupling observed between ring protons,  $J < 1$  c./sec.

TABLE 3

Equilibrium constants for complex formation in water

Parent	$K_A$ (l. mole <sup>-1</sup> )	$K_B^*$ (l. mole <sup>-1</sup> )	$K_B^\dagger$ (l. mole <sup>-1</sup> )	$K_B^\dagger \uparrow (= K_A K_B)$ (l. <sup>2</sup> mole <sup>-2</sup> )
1,3,5-Trinitrobenzene	$(2.5 \pm 0.1) \times 10^2$	$5 \times 10^{-1}$	$9.2 \pm 1$	$(2.25 \pm 0.35) \times 10^3$
2,4,6-Trinitroanisole	$(2.1 \pm 0.3) \times 10^2$	$5.8 \times 10^1$	$(9 \pm 2) \times 10^2$	$(1.9 \pm 0.7) \times 10^5$
Picramide	$(1.01 \pm 0.07) \times 10^4$	1.05	$(1.85 \pm 0.15) \times 10^1$	$(1.9 \pm 0.3) \times 10^5$
N-Methylpicramide	$(5.4 \pm 0.5) \times 10^4$	$1.1 \times 10^2$	$(1.8 \pm 0.2) \times 10^3$	$(9.7 \pm 2) \times 10^7$
N,N-Dimethylpicramide	$(5.4 \pm 0.6) \times 10^4$	$2.3 \times 10^3$	$(6.2 \pm 0.7) \times 10^4$	$(3.3 \pm 0.8) \times 10^9$

\* At zero ionic strength (by extrapolation). <sup>†</sup> At ionic strength 0.3.

The chemical shifts of the substituents, X, show only small changes from the positions in the parent molecule, indicating that no covalency change occurs at C-1. In the absence of an unsymmetrical substituent at C-1 the ring protons in the complex give a single peak indicating their equivalence. However, with the unsymmetrically substituted molecules (X = NHMe or NMePh) two bands were observed for the ring protons. The fact that N-phenylpicramide gives a single peak probably results from the fortuitous overlap of two bands due to non-equivalent protons.

**Equilibrium Constants.**—Measurements of optical density at either one or two wavelengths allowed the stoichiometric equilibrium constants for formation of the complexes in water to be determined (Experimental section). In each case the value of  $K_A$  ( $[A]/[P][SO_3^{2-}]$ )

values of  $K_B$  for ionic strength effects using the Debye-Hückel expression

$$-\log_{10} f_i = Az_i^2 \sqrt{I}/1 + Ba\sqrt{I}$$

where  $A = 0.507 \text{ mole}^{-\frac{1}{2}} \text{ l.}^{\frac{1}{2}}$  and  $B = 0.328 \times 10^8 \text{ cm.}^{-1} \text{ mole}^{-\frac{1}{2}} \text{ l.}^{\frac{1}{2}}$ .<sup>10</sup> The value of  $a$  was taken as  $3.65 \text{ \AA}$ , which is similar to that required by sodium sulphate.<sup>11</sup> Plots of  $\log_{10} K_B$  against  $\sqrt{I}/1 + 1.2\sqrt{I}$  were straight lines with slopes close to that predicted (4.06). These were extrapolated to give values of  $K_B$  at zero ionic strength. Three such plots are shown in Figure 3. Table 3 gives these values together with the more accurate values of  $K_B$  obtained in solutions made up to constant ionic

<sup>10</sup> R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1959, p. 468.

<sup>11</sup> R. A. Robinson and H. S. Harned, *Chem. Rev.*, 1941, **28**, 419.

strength ( $I = 0.3$ ) with sodium sulphate where  $K_B$  was invariant. Also given are values of  $K_B'$  ( $[B]/[P][SO_3^{2-}]^2$ ) at ionic strength 0.3. Our value of  $K_A$  for the formation of the 1:1 adduct from trinitrobenzene and sodium sulphite is in fair agreement with Norris's value<sup>6</sup> of  $3.12 \times 10^2$  l. mole<sup>-1</sup> but differs from the value of  $5.12 \times 10^2$  found by Cuta and Beranek<sup>2</sup> for the complex formed with potassium sulphite. Norris quotes values for the enthalpy and entropy of formation of the complex; however, in view of the fact that his measurements were made in solution of ionic strength 0.144, where we find significant conversion into the higher complex, these must be treated with reservation.

The value of  $K_A$  for 2,4,6-trinitroanisole is similar to that for 1,3,5-trinitrobenzene in this case where addition occurs at a ring carbon carrying hydrogen; cf. the values

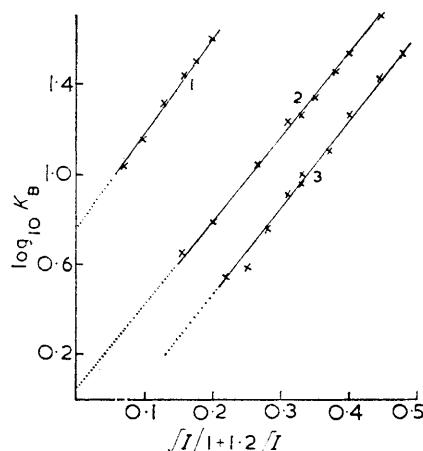


FIGURE 3 Variation of  $K_B$  with ionic strength

1, 2,4,6-Trinitroanisole; 2, picramide; 3, 1,3,5-trinitrobenzene.

for methoxide addition<sup>12</sup> where addition occurs at C-1 in the anisole and the equilibrium constant is *ca.* 500 times greater than for trinitrobenzene. This indicates that, as expected, the electronic effects of the substituent at C-1 are unlikely to affect the stabilities of the adducts greatly. The increase in stability of the picramide complex may result at least in part from some stabilisation through the strengthening of hydrogen-bonds between the amino-protons and the *o*-nitro-groups. A similar factor cannot of course apply to *NN*-dimethylpicramide; however, here the bulky substituent at C-1 will tend to twist the nitro-groups from the plane of the aromatic ring,<sup>9</sup> and this may facilitate sterically the addition of sulphite. With *N*-methylpicramide a combination of these two factors may occur.

The equilibrium constants ( $K_A$ ) for formation of the complexes in water can be compared with similar constants with hydroxide ion as the added base. Gold and Rochester<sup>4</sup> found a value of 2.7 l. mole<sup>-1</sup> for the formation of a 1:1 adduct from trinitrobenzene and hydroxide which is nearly one hundred times smaller than the value

for sulphite. With picramide the 1:1 complex with sulphite is about three hundred times more stable than the complex with hydroxide ion.<sup>13</sup> Evidently the carbon basicity<sup>14</sup> of the sulphite ion is greater than that of the hydroxide ion for these molecules.

The equilibrium constants for formation of the higher complexes indicate that the 1:2 adduct formed from *NN*-dimethylpicramide has special stability. This can be compared with the fact that Gold and Rochester<sup>13</sup> found evidence only for a 1:2 interaction between this compound and sodium hydroxide.

Measurements in water-dimethyl sulphoxide mixtures show that in this medium the formation of 1:1 complexes is enhanced. Thus, the equilibrium constant for formation of the 1:1 adduct of trinitrobenzene is at least one hundred times greater in a solution containing 70% (v/v) of dimethyl sulphoxide than in water. This stabilisation will in part result from the increased activity of the sulphite ions, which will be poorly solvated in the aprotic solvent.<sup>15</sup> Also, the complex, a large polarisable anion, will be well solvated in dimethyl sulphoxide, and this will favour its production. There is little tendency to form 1:2 complexes in media rich in dimethyl sulphoxide, and it might be argued that when two sulphite molecules are added to the ring the molecule begins to resemble an inorganic salt so that solvation by the aprotic solvent is poor. Thus, the 1:2 complex formed from trinitrobenzene is virtually insoluble in dimethyl sulphoxide. This may account for the small tendency to produce these ions in media rich in dimethyl sulphoxide.

#### EXPERIMENTAL

Picramide and its *N*-substituted derivatives were prepared by the addition of aqueous ammonia or the appropriate amine to methanolic picryl chloride<sup>16</sup> and recrystallised to constant m. p. The other nitro-compounds were recrystallised commercial specimens. Dimethyl sulphoxide was refluxed with calcium hydride and fractionated under reduced pressure. Analytical grade sodium sulphite was used without purification. The distilled water used was boiled to remove carbon dioxide and subsequently protected from the atmosphere. The trinitrobenzene-sodium sulphite complex was prepared by Henry's method.<sup>5</sup> The freshly prepared dark red crystals had an analysis corresponding to  $C_6H_3(NO_2)_3 \cdot 2Na_2SO_3 \cdot 4H_2O$  (Found: C, 14.0; H, 2.0. Calc.: C, 13.6; H, 2.05%). On gentle heating water was lost and analysis corresponded to  $C_6H_3(NO_2)_3 \cdot 2Na_2SO_3 \cdot H_2O$  (Found: C, 15.3; H, 1.0. Calc.: C, 15.1; H, 1.05%). The crystals were stable in air, and were soluble in water but insoluble (less than  $10^{-4}M$ ) in dimethyl sulphoxide.

<sup>1</sup>H N.m.r. spectra were recorded at 31° on a Perkin-Elmer R10 spectrometer operating at 60 Mc./sec., for solutions in water and in water-dimethyl sulphoxide. Solutions in water were prepared either by dissolving the parent nitro-compound directly in aqueous sodium sulphite solutions with gentle warming, or by dissolving it in carbon tetrachloride and shaking with aqueous sodium sulphite solution. The spectra were independent of the method of preparation

<sup>12</sup> V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1687.

<sup>13</sup> V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1727.

<sup>14</sup> A. J. Parker, *Proc. Chem. Soc.*, 1961, 371.

<sup>15</sup> A. J. Parker, *Quart. Rev.*, 1962, 163.

<sup>16</sup> J. Glazer, E. D. Hughes, C. K. Ingold, A. T. James, G. T. Jones, and E. Roberts, *J. Chem. Soc.*, 1950, 2674.



and of the sodium sulphite concentration in the range 0.5–2.0M. Solutions in water–dimethyl sulphoxide (30 : 70 v/v) were prepared by adding the parent compound in dimethyl sulphoxide to sodium sulphite in water. As the concentration of sulphite was increased up to that of the nitro-compound (*ca.*  $10^{-1}$ M) in this solvent, the  $^1\text{H}$  n.m.r. bands of the parent compound decreased in intensity and new bands attributed to complex increased in intensity. The change in spectrum was in most cases complete in solutions containing a stoichiometry of 1 nitro-compound : 1 sodium sulphite, and further increase in the sodium sulphite concentration did not affect the spectrum. In all cases acidification of the solutions soon after preparation resulted in precipitation of the parent nitro-compounds. Chemical shifts were measured relative to internal tetramethylsilane in media containing dimethyl sulphoxide. However, in water where this standard was insoluble shifts were measured relative to internal dioxan.<sup>17</sup> All shifts are quoted relative to tetramethylsilane assuming a difference of 3.70 p.p.m. between the two standards.<sup>17</sup>

Visible spectra were recorded with a Unicam SP 800 automatic instrument, to determine spectra shapes, and a Unicam SP 500 instrument, for the accurate measurements of optical density. All spectra were recorded at room temperature ( $20^\circ \pm 2^\circ$ ) using matched silica cells of 1 cm. or 4 cm. path-length. Test solutions were made up from stock solutions of the components which were prepared immediately prior to use. Spectra were recorded in aqueous sodium sulphite solutions and also in water–dimethyl sulphoxide mixtures containing sodium sulphite. The spectra of 1,3,5-trinitrobenzene, 2,4,6-trinitroanisole, picramide, *N*-methylpicramide, and *NN*-dimethylpicramide were examined. The behaviour of these compounds was similar, and to illustrate this behaviour and demonstrate the method of calculation of equilibrium constants we chose two examples.

**1,3,5-Trinitrobenzene.**—The visible spectrum of trinitrobenzene ( $4 \times 10^{-5}$ M) in water shows no absorption above 3500 Å. Spectra in the presence of various concentrations of sodium sulphite are shown in Figure 1. The addition of acid to these solutions resulted in decoloration, taken to indicate reversal to trinitrobenzene, and the addition of more sulphite to the acidified solutions renewed the colour, with visible spectra similar to those obtained previously. The absence of colour in acidic solutions removes the possibility that bisulphite rather than sulphite is the active species. Similarly, the absence of effects due to hydroxide ions present through salt hydrolysis was shown by the observation of similar spectra in solutions buffered at pH 9. The interaction of hydroxide with trinitrobenzene<sup>4</sup> only becomes appreciable at pH 12.

Measurements of optical density at 4620 and 5800 Å allowed the equilibrium constants for formation of the complexes to be found (Table 4). The extinction coefficients of B at these wavelengths were determined directly to be  $\epsilon_B(4620 \text{ Å}) = 1.45 \times 10^4 \text{ l. mole}^{-1} \text{ cm.}^{-1}$ , and  $\epsilon_B(5800 \text{ Å}) = 0$ . The extinction coefficients of A could not be determined directly since at no stage was conversion of trinitrobenzene into A complete. However, by application of the Benesi-Hildebrand equation<sup>18</sup> in the form,

$$a/\text{O.D.} = (1/K_A \epsilon)(1/b) + 1/\epsilon$$

(where *a* is the constant trinitrobenzene concentration, *b* is the varied sodium sulphite concentration,  $\epsilon$  is the extinction coefficient of the complex at the wavelength of measure-

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TABLE 4

Dependence of visible absorption of trinitrobenzene ( $4 \times 10^{-5}$ M) on sodium sulphite concentration in water, and calculated equilibrium constants

[Na <sub>2</sub> SO <sub>3</sub> ] (M)	Optical density		Relative concn.			$10^{-2}K_A$ (l. mole <sup>-1</sup> )	$K_B$
	4620 Å	5800 Å	B	A	TNB		
0	0.000	0.000	0	0	1	—	—
0.0005	0.110	0.036	0	0.11	0.89	2.48	—
0.0010	0.193	0.067	0	0.20	0.80	2.50	—
0.0020	0.323	0.110	0	0.33	0.67	2.46	—
0.0060	0.583	0.198	0	0.60	0.40	2.50	—
0.0100	0.705	0.237	0.01	0.71	0.28	2.54	—
0.030	0.840	0.270	0.08	0.82	0.10	2.7	3.3
0.040	0.845	0.262	0.12	0.79	0.09	2.2	3.8
0.060	0.814	0.230	0.24	0.70	0.06	—	5.7
0.080	0.790	0.193	0.38	0.58	0.04	—	8.2
0.100	0.760	0.162	0.49	0.49	0.02	—	10.0
0.150	0.700	0.110	0.66	0.33	0.01	—	13.3
0.200	0.655	0.070	0.78	0.21	0.01	—	18.5
0.30	0.620	0.036	0.89	0.11	0	—	27
0.40	0.602	0.022	0.935	0.065	0	—	35
0.80	0.580	0.004	1	0	0	—	—
1.00	0.580	0.003	1	0	0	—	—
0.0010 *	0.186	0.063	0	0.19	0.81	2.36	—
0.0040 *	0.480	0.160	0.02	0.48	0.50	2.40	—
0.0100 *	0.688	0.220	0.065	0.67	0.265	2.50	9.7
0.0200 *	0.785	0.240	0.13	0.73	0.14	2.60	9.0
0.040 *	0.820	0.230	0.24	0.695	0.065	2.66	8.7
0.080 *	0.780	0.182	0.42	0.55	0.03	—	9.6

\* Solutions made up to constant ionic strength ( $I = 0.3$ ) with sodium sulphate.

TABLE 5

Dependence of visible absorption of picramide ( $4 \times 10^{-5}$ M) on sodium sulphite concentration, and calculated equilibrium constants

[Na <sub>2</sub> SO <sub>3</sub> ] (stoich.) (M)	O.D.	Rel. concn.			$10^{-4}K_A$ (l. mole <sup>-1</sup> )	$K_B$
		[A]	[B]	[Pic] (free)		
0	0.000	0	0	1	—	—
$6.4 \times 10^{-5}$	0.151	0.33	0	0.67	1.01	—
$1.28 \times 10^{-4}$	0.238	0.52	0	0.48	1.01	—
$3.2 \times 10^{-4}$	0.340	0.74	0	0.26	0.98	—
$6.4 \times 10^{-4}$	0.400	0.88	0	0.12	1.20	—
$3.2 \times 10^{-3}$	0.450	0.99	0	0.01	—	—
$8.0 \times 10^{-3}$	0.455	1	0	0	—	—
$1.20 \times 10^{-2}$	0.432	0.95	0.05	0	—	4.5
$2.32 \times 10^{-2}$	0.398	0.875	0.125	0	—	6.1
$5.0 \times 10^{-2}$	0.290	0.64	0.36	0	—	11.2
$8.0 \times 10^{-2}$	0.193	0.425	0.575	0	—	17
0.120	0.130	0.28	0.72	0	—	22
0.160	0.087	0.18	0.82	0	—	29
0.60	0.004	0	1	0	—	—
$6.4 \times 10^{-5} *$	0.157	0.34	0	0.66	1.01	—
$2.24 \times 10^{-4} *$	0.302	0.66	0	0.34	0.97	—
$8.0 \times 10^{-4} *$	0.406	0.89	0	0.11	1.064	—
$1.20 \times 10^{-2} *$	0.383	0.84	0.16	0	—	16.5
$2.00 \times 10^{-2} *$	0.337	0.74	0.26	0	—	17.5
$4.00 \times 10^{-2} *$	0.262	0.575	0.425	0	—	18.5
0.100 *	0.157	0.35	0.65	0	—	18.5

\* Solutions made up to constant ionic strength ( $I = 0.3$ ) with sodium sulphate.

ment, and  $K_A$  is the equilibrium constant for formation of the complex) to solutions containing less than  $10^{-2}$ M-sodium sulphite, where no B is present, these were determined to be  $\epsilon_A(4620 \text{ Å}) = 2.45 \times 10^4$  and  $\epsilon_A(5800 \text{ Å}) = 8.3 \times 10^3 \text{ l. mole}^{-1} \text{ cm.}^{-1}$ . Absorption at the higher wavelength was thus due entirely to A, and the concentrations of A in all

<sup>17</sup> R. A. Y. Jones, A. R. Katritzky, J. N. Murrell, and N. Sheppard, *J. Chem. Soc.*, 1962, 2576.

<sup>18</sup> H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, 71, 2703.

solutions were determined. The concentrations of B and free trinitrobenzene were determined using, respectively,

$$\text{O.D.}(4620 \text{ \AA}) = [A] \cdot \epsilon_A(4620 \text{ \AA}) + [B] \cdot \epsilon_B(4620 \text{ \AA})$$

$$\text{and } [A] + [B] + [\text{TNB}]_{\text{free}} = 4 \times 10^{-5} \text{M}$$

A second series of measurements was made in solutions made up to constant ionic strength ( $I = 0.3$ ) with sodium sulphate.

In dimethyl sulphoxide–water (70:30 v/v) the visible spectrum of trinitrobenzene was similar to that of complex A in water. Conversion of trinitrobenzene into complex A was complete in a solutions containing  $2 \times 10^{-4} \text{M}$ -sodium sulphite. No detectable change in spectrum occurred on increasing the sulphite concentration to 0.01M, above which concentration sodium sulphite precipitated. Precise mea-

surements of equilibrium constants were not attempted but the value of  $K_A$  must be in excess of  $5 \times 10^4 \text{ l. mole}^{-1}$  and  $K_B$  must be less than  $10 \text{ l. mole}^{-1}$ .

*Picramide*.—The visible spectra of picramide in aqueous solutions containing sodium sulphite are shown in Figure 2. Measurements of optical density were made at 4800 Å, where absorption was due entirely to complex A, and the equilibrium constants determined (Table 5). The solutions contained a small concentration of buffer pH 9 to inhibit solvolysis of the sulphite.

In solutions containing dimethyl sulphoxide (70% v/v) the visible spectrum was that of complex A. In this medium the value of  $K_A$  was greater than  $10^5 \text{ l. mole}^{-1}$  while there was no measurable tendency to form the higher complex.

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