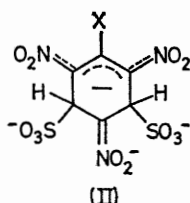
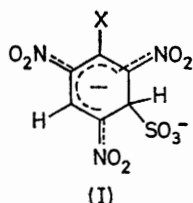


## The Stabilities of Meisenheimer Complexes. Part XII.<sup>1</sup> Some Kinetic Studies of the Reactions of Aromatic Nitro-compounds with Sodium Sulphite in Water

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Kinetic data are reported for the formation in water of 1 : 1 sulphite adducts from 2,4,6-trinitroanisole and from the picrate ion, and 1 : 2 adducts from these compounds and from picramide (2,4,6-trinitroaniline) and *N*-methyl- and *NN*-dimethyl-picramide. The values of  $k_2$  for formation of the diadducts vary little with substrate structure so that variations in complex stability derive mainly from differences in the values of  $k_{-2}$ . There is no evidence from the kinetic measurements or from <sup>1</sup>H n.m.r. spectra for *cis-trans*-isomerism in the 1 : 2 adducts and it seems likely that one isomer, probably the *trans*-form, is thermodynamically preferred.

IN 1967 spectroscopic and equilibrium data relating to the formation of sulphite adducts from 1-X-2,4,6-trinitrobenzenes (X = H, OMe, NH<sub>2</sub>, NHMe, NMe<sub>2</sub>, NHPH, or NMePh) were reported.<sup>2</sup> The results showed that in water 1 : 1 (I) and 1 : 2 complexes (II) were formed by sulphite addition at unsubstituted ring



positions. More recently kinetic studies of the reactions of 1,3,5-trinitrobenzene with sulphite have been made.<sup>3,4</sup> Bernasconi and Bergstrom's results<sup>3</sup> were of particular interest in that they provided evidence for the formation of two isomeric 1 : 2 complexes. Confirmation that these were the *cis*- and *trans*-forms, in which the sulphite ions are on the same or opposite sides of the ring plane, followed from <sup>1</sup>H n.m.r. measurements in water<sup>5</sup> and deuterium oxide.<sup>6</sup> At equilibrium these isomers are present in almost equal proportions. Kinetic data have also been reported<sup>7</sup> for the formation of 1 : 1 adducts from picramide (2,4,6-trinitroaniline) and *N*-

methyl- and *NN*-dimethyl-picramide. 2,4,6-Trinitrobenzaldehyde<sup>8</sup> is unusual in that sulphite addition apparently occurs at both the unsubstituted ring positions and at C-1. With this compound, as with 1,3,5-trinitrobenzene, there is n.m.r. evidence for *cis-trans*-isomerism in one of the 1 : 2 adducts.

In the present study we have extended previous work by determining kinetic data for the formation of 1 : 1 adducts from 2,4,6-trinitroanisole and the picrate ion, and 1 : 2 adducts from these compounds and picramide and *N*-methyl- and *NN*-dimethyl-picramide. We were particularly interested in examining the effects of a negative charge in the substrate (picrate ion) on adduct formation and to seek evidence for *cis-trans*-isomerism in the 1 : 2 complexes.

### EXPERIMENTAL

Parent nitro-compounds were prepared and purified as before.<sup>2</sup> Analytical grade sodium sulphite was used without purification. The distilled water used was boiled to remove carbon dioxide and subsequently protected from the atmosphere. <sup>1</sup>H N.m.r. measurements were made with Varian 60 MHz and Bruker 90 MHz instruments using sodium 4,4-dimethyl-4-silapentane-1-sulphonate as internal reference. Samples were prepared by dissolving the substrate in a solution of 1 or 2M-sodium sulphite in water or deuterium oxide to give *ca.* 0.2M solutions. Spectra were

<sup>1</sup> M. R. Crampton and M. J. Willison, preceding paper, 1973, 215.

<sup>2</sup> M. J. Strauss and S. P. B. Taylor, *J. Amer. Chem. Soc.*, 1973, **95**, 3813.

<sup>3</sup> E. Buncel, A. R. Norris, K. E. Russell, and P. J. Sheridan, *Canad. J. Chem.*, 1974, **52**, 25.

<sup>4</sup> N. Marendic and A. R. Norris, *Canad. J. Chem.*, 1973, **51**, 3927.

<sup>1</sup> Part XI, M. R. Crampton and M. J. Willison, preceding paper.

<sup>2</sup> M. R. Crampton, *J. Chem. Soc. (B)*, 1967, 1341; see this paper for references to earlier work.

<sup>3</sup> C. F. Bernasconi and R. G. Bergstrom, *J. Amer. Chem. Soc.*, 1973, **95**, 3603.

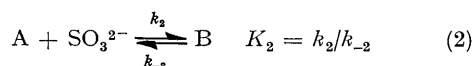
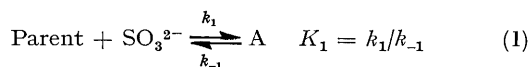
<sup>4</sup> M. Sasaki, *Chem. Letters (Tokyo)*, 1973, 205.

recorded between 5 and 80° as soon as possible after making up solutions.

Kinetic measurements were made by mixing aqueous solutions of the substrate with aqueous solutions of sodium sulphite in a Canterbury stopped-flow apparatus described previously.<sup>9</sup> All measurements were made at 25°. The concentration of the substrate was in the range 10<sup>-5</sup>–10<sup>-4</sup>M except in the case of picric acid where, because of the smaller changes in optical density observed, concentrations were 1–4 × 10<sup>-4</sup>M. In all cases the concentration of sodium sulphite was in large excess (>10) of the concentration of nitro-compound so that first-order kinetics were observed. Constant ionic strength was maintained with sodium sulphate

## RESULTS

Kinetic measurements were made by the stopped-flow technique in the visible spectral region. For each compound studied two relaxation times were observable. Comparisons of the visible spectra with those previously reported<sup>2</sup> showed that these correspond to the formation of 1 : 1 sulphite adducts, A, and 1 : 2 adducts, B. Under the



experimental conditions used the second relaxation time was in all cases much longer than the first. Thus equations (3) and (4) were derived using standard methods.<sup>10</sup>

$$1/\tau_1 = k_{-1} + k_1[\text{SO}_3^{2-}] \quad (3)$$

$$1/\tau_2 = k_{-2} + \frac{k_2 K_1 [\text{SO}_3^{2-}]^2}{1 + K_1 [\text{SO}_3^{2-}]} \quad (4)$$

**2,4,6-Trinitroanisole.**—The visible spectra reported previously<sup>2</sup> show that the 1 : 1 adduct has an absorption maximum at 446 nm with shoulder at longer wavelength while the 1 : 2 adduct has  $\lambda_{\text{max}}$  430 nm. Kinetic measurements were made at 400, 430, 500, and 550 nm. The formation of the 1 : 1 adduct always gave an increase in absorption while the second process corresponding to formation of the 1 : 2 adduct sometimes gave an increase and sometimes a decrease depending on the sulphite concentration and wavelength of measurement. However the measured relaxation times were, within experimental error, independent of the wavelength of measurement. There was no evidence for a third relaxation time.

Data are in Table 1. A plot of  $\tau_1^{-1}$  versus sulphite concentration was linear as required by equation (3); the intercept gave a value for  $k_{-1}$  of  $35 \pm 2 \text{ s}^{-1}$  and the slope a value for  $k_1$  of  $(4.8 \pm 0.4) \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ . Combination of these values gives a value for  $K_1$  of  $140 \pm 20 \text{ l mol}^{-1}$  which is in reasonable agreement with that  $(210 \pm 30 \text{ l mol}^{-1})$  previously determined<sup>2</sup> at 20° from equilibrium optical densities.

The values of  $\tau_2^{-1}$  depend markedly on the ionic strength of the medium as expected for formation of a multi-charged adduct.<sup>2</sup> The data at ionic strength 0.3M are well fitted by equation (4) with the values  $k_{-2} 0.12 \pm 0.02 \text{ s}^{-1}$ ;  $k_2 170 \pm$

10  $\text{l mol}^{-1} \text{ s}^{-1}$ ; and  $K_1 140 \text{ l mol}^{-1}$ . These results give a value for  $K_2$  of  $(1.4 \pm 0.3) \times 10^3 \text{ l mol}^{-1}$  which again is in reasonable agreement with that  $(0.9 \pm 0.2) \times 10^3 \text{ l mol}^{-1}$ ,

TABLE 1

Kinetic data for formation of sulphite adducts from 2,4,6-trinitroanisole in water at 25°

[Na <sub>2</sub> SO <sub>3</sub> ]/M	$\tau_1^{-1}/\text{s}^{-1}$	$\tau_2^{-1}/\text{s}^{-1}$ <sup>a</sup>	$\tau_2^{-1}/\text{s}^{-1}$ <sup>b</sup>
1.0 × 10 <sup>-3</sup>	40 ± 2	0.14 ± 0.02	
2.0 × 10 <sup>-3</sup>	45	0.18	
5.0 × 10 <sup>-3</sup>	60	0.31	
7.5 × 10 <sup>-3</sup>	70		
0.010	80	1.1	3.8 ± 0.2
0.025		3.4	
0.050		7.7	30.5
0.075		11.6	
0.10		16.9	58
0.20			125
0.30			170

<sup>a</sup> Ionic strength 0.3M with sodium sulphate. <sup>b</sup> Ionic strength 2.1M.

determined independently.<sup>2</sup> The data at  $I$  2.1M give a value for  $k_2$  of  $650 \pm 50 \text{ l mol}^{-1} \text{ s}^{-1}$  but do not allow the determination of  $k_{-2}$ .

**Picric Acid.**—Due to the high value for its acid dissociation constant<sup>11</sup> picric acid will be almost completely dissociated to the picrate ion in sulphite solutions. Hence the two relaxation processes observed correspond to the formation of 1 : 1 and 1 : 2 adducts of picrate ion with sulphite. Measurements were made at four wavelengths between 390 and 520 nm. Data are in Table 2.

TABLE 2

Kinetic data for the formation of sulphite adducts from picric acid in water at 25°

[Na <sub>2</sub> SO <sub>3</sub> ]/M	$\tau_1^{-1}/\text{s}^{-1}$ ( $I$ 0.3M)	$\tau_1^{-1}/\text{s}^{-1}$ ( $I$ 2.1M)	$\tau_2^{-1}/\text{s}^{-1}$ ( $I$ 2.1M)
0.020	116 ± 3	122 ± 3	
0.025			5.3 ± 0.3
0.040	120		
0.050		142	6.7
0.060	124		
0.080	132	156	
0.10	138		11.9
0.20			27
0.30			50
0.40			78

Plots according to equation (3) of  $\tau_1^{-1}$  versus sulphite concentration were linear and gave values at  $I$  0.3M of  $k_1 280 \pm 80 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_{-1} 110 \pm 5 \text{ s}^{-1}$ , leading to  $K_1 2.5 \pm 1 \text{ l mol}^{-1}$ ; and at  $I$  2.1M of  $k_1 600 \pm 50 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_{-1} 110 \pm 5 \text{ s}^{-1}$  leading to  $K_1 5.5 \pm 0.5 \text{ l mol}^{-1}$ . The values of  $\tau_2^{-1}$  at  $I$  2.1M are well fitted by equation (4) with  $k_2 250 \pm 50 \text{ l mol}^{-1} \text{ s}^{-1}$ ;  $k_{-2} 4 \pm 0.5 \text{ s}^{-1}$ ; and  $K_1 5.5 \text{ l mol}^{-1}$ . The values obtained for  $K_1$  and  $K_2$  from the kinetic data are somewhat smaller than those obtained previously<sup>12</sup> at 20° from equilibrium optical densities. For example at  $I$  0.3M values of  $K_1$  are  $2.5 \pm 1$  and  $6 \pm 2 \text{ l mol}^{-1}$  respectively. The negative values expected<sup>7</sup> for enthalpies of complex formation may to some extent account for these differences.

**Picramide and N-Methyl- and NN-Dimethyl-picramide.**—Kinetic data for 1 : 1 adduct formation<sup>7</sup> and equilibrium

<sup>11</sup> D. J. G. Ives and P. G. N. Moseley, *J. Chem. Soc. (B)*, 1966, 757.

<sup>12</sup> M. R. Crampton and M. A. El Ghariani, *J. Chem. Soc. (B)*, 1969, 330.

<sup>9</sup> M. R. Crampton, *J.C.S. Perkin II*, 1973, 2157.

<sup>10</sup> M. Eigen and L. De Maeyer in 'Technique of Organic Chemistry,' ed. A. Weissberger, Wiley-Interscience, New York, vol. VIII, part 2, p. 895.

data for both 1:1 and 1:2 adduct formation<sup>2,7</sup> have been reported previously. Kinetic results for 1:2 adduct formation are reported in Table 3. Measurements were

TABLE 3

Kinetic data for the formation of 1:2 adducts from picramide and *N*-methyl- and *NN*-dimethyl-picramide, with sodium sulphite in water at 25° and ionic strength 0.3M

[Na <sub>2</sub> SO <sub>3</sub> ]/M	Picramide $\tau_2^{-1}/s^{-1}$	<i>N</i> -Methyl- picramide $\tau_2^{-1}/s^{-1}$	<i>NN</i> -Dimethyl- picramide $\tau_2^{-1}/s^{-1}$
0.005	7.5	1.7	1.4
0.010	8.4	3.3	3.1
0.020	9.5	6.4	5.9
0.025	10.3		
0.030		10.2	
0.050	13.7	16	15.4
0.10	20.8	33	32.3

made in the region 460–470 nm where the fast formation of colour due to 1:1 adduct was followed by a slower decrease in absorption corresponding to 1:2 adduct formation. There was no evidence for a third relaxation time. For each of the three compounds values of  $K_1$  are large so that at the sulphite concentrations used  $K_1[\text{SO}_3^{2-}] \gg 1$ . Hence equation (4) simplifies to (5).

$$\tau_2^{-1} = k_{-2} + k_2[\text{SO}_3^{2-}] \quad (5)$$

Accordingly a plot of  $\tau_2^{-1}$  versus sulphite concentration for the data for picramide was linear and yielded values of  $k_2$   $140 \pm 10 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_{-2}$   $7 \pm 0.5 \text{ s}^{-1}$ . Combination of these values gives  $K_2$   $20 \pm 3 \text{ l mol}^{-1}$  which can be compared with the value of  $18.5 \pm 1.5 \text{ l mol}^{-1}$  obtained previously<sup>2</sup> at ionic strength 0.3M and 20°.

In the case of *N*-methylpicramide the data, as required by equation (5), give a straight line plot whose slope gives a value for  $k_2$  of  $330 \pm 20 \text{ l mol}^{-1} \text{ s}^{-1}$ . However the intercept is too small to allow the determination of  $k_{-2}$ . Nevertheless from previous work<sup>2,7</sup> a value is available for  $K_2$  of  $(2.0 \pm 0.5) \times 10^3 \text{ l mol}^{-1}$  at 25° and ionic strength 0.3M. Thus  $k_{-2}$  ( $= k_2/K_2$ ) has a value of  $0.16 \pm 0.04 \text{ s}^{-1}$ . Similarly for *NN*-dimethylpicramide a value of  $310 \text{ l mol}^{-1} \text{ s}^{-1}$  was found for  $k_2$  from a linear plot of  $\tau_2^{-1}$  versus sulphite concentration. This value together with the previously determined<sup>2,7</sup> value for  $K_2$ ,  $(5 \pm 1) \times 10^4 \text{ l mol}^{-1}$ , gives a value for  $k_{-2}$  of  $(6 \pm 1) \times 10^{-3} \text{ s}^{-1}$ .

<sup>1</sup>H *N.m.r.* Measurements.—The spectra of 1,3,5-trinitrobenzene in aqueous sodium sulphite solutions provide clear evidence for *cis-trans*-isomerism in the 1:2 adduct as previously reported.<sup>5,6</sup> Thus a solution cooled to 5° shows two sharp bands at  $\delta$  8.6 and 8.5 attributed to the hydrogens at the *sp*<sup>2</sup> hybridised carbon atoms in the diadducts and two sharp bands at  $\delta$  6.05 and 5.9 attributed to the hydrogens at the *sp*<sup>3</sup> hybridised carbon atoms. On warming the sample to 30° the bands at  $\delta$  8.6 and 6.05 remain sharp while the bands from the other isomer broaden considerably. Because of their broadness at probe temperature these latter bands were not detected in our original study.<sup>2</sup> We therefore thought it advisable to re-examine the spectra of the 1:2 adducts from other substrates over a wide temperature range. Also to reduce the intensity of the solvent peak measurements were made in deuterium oxide as well as in water.

Chemical shifts are in Table 4. For *N*-methyl- and *NN*-dimethyl picramide no new band or increased broadening

of existing bands was observed in the temperature range 10–70°. With picramide and 2,4,6-trinitroanisole no spectral changes were observed in the range 5–50° although at higher temperatures irreversible decomposition of these substrates occurred. In the case of 2,4,6-trinitroanisole the spectrum of the products showed bands at  $\delta$  6.27 and 2.82. This spectrum can be accounted for by demethylation of the substrate by sulphite to give picrate ions, which

TABLE 4

Chemical shifts of 1:2 adducts from 1-X-2,4,6-trinitrobenzenes and sodium sulphite in deuterium oxide<sup>a</sup>

X	Ring protons	Methyl protons
OMe	6.1 (2)	4.2 (3)
O <sup>-</sup>	6.3	
NH <sub>2</sub>	6.2	
NHMe	{ 6.30 (1) 6.15 (1)	3.23 (3)
NMe <sub>2</sub>	6.3 (1)	3.2 (3)

Measurements were made at 90 MHz using 4,4-dimethyl-4-silapentane-1-sulphonate as internal reference. Figures in parentheses are relative intensities.

will be present in these solutions as the sulphite diadducts and give rise to the low field band, and methanesulphonate ions. The spectrum of the diadduct from picric acid shows a single resonance at  $\delta$  6.3 which remains unchanged between 7 and 40°. Above this temperature the band broadens and new bands at  $\delta$  6.5 and 5.75 are observed. These latter bands almost certainly result from decomposition of the substrate. The broadening with increases in temperature of the resonance at  $\delta$  6.3 might, as in the case of one isomer of the trinitrobenzene-sulphite adduct, be due to increases in the rate of sulphite exchange or of ring 'flipping'.

The present results show, assuming that the spectra of *cis*- and *trans*-isomers are not identical, that in the case of the diadducts from 1-X-2,4,6-trinitrobenzenes (X = OMe, O<sup>-</sup>, NH<sub>2</sub>, NHMe, or NMe<sub>2</sub>) one isomer is formed preferentially. An upper limit of 5–10% can be set on the equilibrium proportion of the disfavoured isomer.

#### DISCUSSION

Equilibrium and kinetic data from this and previous studies are in Table 5. As expected the value of  $K_1$  for the picrate ion is reduced relative to uncharged compounds. However considering that this substrate carries a full negative charge the reduction in stability is not all that large. In these systems factors other than the electronic effects of substituents are likely to be important. These factors are likely to include solvation differences, steric factors, and in the case of picramide and of *N*-methylpicramide hydrogen-bonding of amino-protons to the adjacent nitro-groups. As regards solvation it is known<sup>2,13</sup> that multi-charged adducts are formed particularly readily in water by which they are presumably well solvated. Buncl, Norris, and their co-workers<sup>7</sup> have argued that differences in the extent of solvation of the complexes play an important part in determining their relative stabilities. This implies that

<sup>13</sup> M. R. Crampton and M. A. El Ghariani, *J. Chem. Soc. (B)*, 1971, 1043; M. R. Crampton and M. J. Willison, *J.C.S. Perkin II*, 1974, 1681.

complexes from *N*-methyl- and *NN*-dimethyl-picramide are particularly well solvated relative to the parent molecule. A further factor operating in those substrates carrying bulky substituents at C-1 may be the relief of steric interactions on complex formation. This factor would be expected to be largest in the 1:2 complexes where the requirement of ring planarity is removed. Any differences in the operation of these effects between *cis*- and *trans*-forms of the 1:2 complexes will account for varying stabilities of the isomers. The kinetic data show that except in the case of the picrate ion, where  $k_1$  is lowered, changes in the value of  $K_1$  with substituent

isomers. Nevertheless by analogy with the 1,3,5-trinitrobenzene system it might have been expected that if *cis*- and *trans*-isomers were present in anything approaching equal proportions then this isomerism should be kinetically detectable. This together with the failure in these systems to observe isomerism by  $^1\text{H}$  n.m.r. spectroscopy leads us to the conclusion that one of the isomers is thermodynamically preferred. We note that an energy difference between the isomers as small as 5 kJ would produce a distribution of 10:1. With such a distribution the less favoured isomer would almost certainly remain undetected by our methods.

TABLE 5

Summary of equilibrium and kinetic data for formation of 1:1 and 1:2 adducts from 1-X-2,4,6-trinitrobenzenes and sodium sulphite in water at 25°

	$k_1/\text{l mol}^{-1} \text{s}^{-1}$	$k_{-1}/\text{s}^{-1}$	$K_1/\text{l mol}^{-1}$	$k_2^a/\text{l mol}^{-1} \text{s}^{-1}$	$k_{-2}^a/\text{s}^{-1}$	$K_2^a/\text{l mol}^{-1}$
2,4,6-Trinitroanisole	$4.8 \times 10^3$	35	140	170	0.12	$1.4 \times 10^3$
Picrate ion	280 <sup>b</sup>	110 <sup>b</sup>	2.5 <sup>b</sup>	250 <sup>c</sup>	4 <sup>c</sup>	60 <sup>c</sup>
Picramide <sup>d</sup>	$5.7 \times 10^4$	7	$8.6 \times 10^3$	140	7	20
<i>N</i> -Methylpicramide <sup>d</sup>	$1.4 \times 10^4$	0.2	$6.8 \times 10^4$	330	0.16	$2 \times 10^3$
<i>NN</i> -Dimethylpicramide <sup>d</sup>	$4.1 \times 10^3$	0.14	$3.0 \times 10^4$	310	0.006	$5 \times 10^4$
1,3,5-Trinitrobenzene <sup>e</sup>	$3.5 \times 10_4$	125	290	{ 1.2 195	{ 0.13 21	{ 9.2 9.3

<sup>a</sup> Ionic strength 0.3M, with sodium sulphate, except where stated. <sup>b</sup> Ionic strength 0.3M. Values of  $K_1$  and  $k_1$  at zero ionic strength will be somewhat smaller than those quoted. <sup>c</sup> Ionic strength 2.1M. The value of  $K_2$  at ionic strength 0.3M will be smaller than that given. <sup>d</sup> Data for 1:1 complex formation from ref. 7. <sup>e</sup> From ref. 3. The two sets of data for 1:2 complex formation refer to *cis*- and *trans*-isomers.

derive largely from changes in values of  $k_{-1}$ . Similarly changes in the value of  $k_{-2}$  with substituent are very much larger than changes in values of  $k_2$ . This probably indicates that the respective transition states for complex formation are 'reactant-like' rather than 'product-like'. Thus changes in solvation and ring distortion will not have progressed very far in the transition state for reaction.

In contrast with the results for 1,3,5-trinitrobenzene<sup>3</sup> we were unable in the reactions of 1-X-2,4,6-trinitrobenzene (X = OMe, O<sup>-</sup>, NH<sub>2</sub>, NHMe, or NMe<sub>2</sub>) with sulphite to detect a third relaxation time corresponding to isomerisation in the 1:2 adducts. As a recent analysis has shown,<sup>14</sup> the failure to observe a third relaxation time in these systems does not necessarily indicate that only one of the possible isomers is present. If for a given compound the kinetic parameters for dissociation of *cis*- and *trans*-isomers are similar then they will be formed in a ratio which is equal to their equilibrium ratio so that their equilibration, giving rise to the third relaxation time, is unnecessary. Further even if the kinetic parameters are different but the visible spectra of *cis*- and *trans*-forms are identical, or very nearly identical, then the isomerisation might escape detection. We cannot therefore on the basis of kinetic data rule out the possibility that these 1:2 complexes exist as *cis-trans*-

If then, one isomer is thermodynamically preferred the question arises as to which isomer. The data in Table 5 show the values of  $k_2$  for formation of the 1:2 complexes examined in the present work are all very similar to the value, 195 l mol<sup>-1</sup> s<sup>-1</sup>, found previously<sup>3</sup> for formation of the kinetically preferred isomer from 1,3,5-trinitrobenzene. Bernasconi and Bergstrom argued that this was likely to correspond to formation of the *trans*-isomer. It is, then, tempting to infer that the 1:2 adducts from 1-X-2,4,6-trinitrobenzenes (X = OMe, O<sup>-</sup>, NH<sub>2</sub>, NHMe, or NMe<sub>2</sub>) are present mainly in the *trans*-form. In the case of 1,3,5-trinitrobenzene the *cis*-form has similar stability to its isomer but is formed less rapidly. This was rationalised<sup>3</sup> in terms of electrostatic repulsion between sulphite groups present in the transition state for formation of the *cis*-isomer but reduced by ring distortion in the complex itself. The results of the present study are in accord with this idea in so far as they indicate that transition-states are likely to be 'reactant-like' and thus little distorted.

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<sup>14</sup> C. F. Bernasconi and R. G. Bergstrom, *J. Amer. Chem. Soc.*, 1974, **96**, 2397.