the source of field effects is a major difference between models and the available data serve to distinguish the generally successful SUMCHIN models from those which are fundamentally incapable of describing certain substituent situations. However, less fundamental differences between models, such as the precise form of the field transmission coefficient in the SUMCHIN models, cannot be adequately evaluated from the present evidence. Indeed, if a few key series of substituent data were missing, it would be difficult to distinguish between any of the possible approaches. This points to the need for carefully designed studies to test the limits of applicability of substituent models; such tests may provide information for the further elucidation of the mechanisms of substituent effects.

Carefully designed substituent effect studies will help establish the best form for a substituent model, but the very nature of a semiempirical approach that makes it both practical and reasonably accurate also makes such distinctions difficult and somewhat limits its theoretical value. A semiempirical model is parameterized from experimental data so that regardless of its functional form it will reproduce exactly the correct results if it is applied to the system from which it was parameterized; it should also produce good results when applied to other systems which closely resemble the basis system. As long as the functional forms of the model equations approximate the "true" dependence of substituent effects on factors which vary between positions in aromatic systems, the process of parameterizing the equations from experimental data allows this type of semiempirical approach to produce excellent practical results, while showing a certain insensitivity to the precise form of the mathematical model. Furthermore, any interaction not explicitly accounted for in the model will be accommodated to some extent in the derived substituent parameters. For these reasons, we are also investigating other means of evaluating the variation of substituent effects in aromatic systems.

Acknowledgments. I would like to express my gratitude to Professor Donald S. Noyce for his suggestions and support in my work with him, and to Professor Andrew Streitwieser, Jr., for helpful discussions. I wish also to acknowledge helpful comments from B. Sandel, B. Bartman, and R. W. Nichols.

Intermediates in Nucleophilic Aromatic Substitution. IX.[1] 1:1 and 1:2 Sulfite Complexes of 1,3,5-Trinitrobenzene. Cis–Trans Isomerism in the 1:2 Complex

Claude F. Bernasconi*[2] and Robert G. Bergstrom

Contribution from the University of California, Santa Cruz, California 95060.

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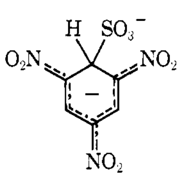
Abstract: A kinetic study by the stopped-flow method of the interaction of 1,3,5-trinitrobenzene with sulfite ion shows that three different anionic σ complexes are formed. The fastest process is associated with the reversible formation of a 1:1 complex, the two slower processes with the reversible formation of two different 1:2 complexes ($TNB:SO_3^{2-} = 1:2$). Evidence based on absorption spectra, reaction rates, and equilibrium properties indicates the two 1:2 complexes to be cis and trans isomers.

Sodium sulfite reacts with 1,3,5-trinitrobenzene (TNB) to yield the typically highly colored Jackson–Meisenheimer[3,4] complex. It has been shown that in aqueous solution both a 1:1 complex[5] (**1**) and a 1:2 complex[6] (**2**) are formed, depending upon the sulfite concentration. Previous investigators have determined equilibrium constants of complex formation from spectrophotometric data,[6,7] recorded nmr spectra[6] of both complexes (**1** and **2**), and isolated the 1:2 TNB-sulfite complex as a dark red crystalline material.[8]



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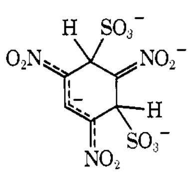

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Crampton[6] has reported nmr spectra of several other 1:2 complexes formed between sulfite ion and N-substituted picramides. Interestingly, it was observed that when the RR′N group of the complex was symmetrically substituted (R = R′), the sp^3 ring protons in the complex were equivalent, giving only a single peak. However, if the complex was unsymmetrically substituted (*i.e.*, Me-N-Ph), the sp^3 ring protons were nonequivalent and two resonance lines resulted. Strauss[9] has offered several possible interpretations for this result; one of them is that the nmr spectrum is actually that of an equimolar mixture of cis and trans

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[1] Part VIII: C. F. Bernasconi and R. H. de Rossi, *J. Org. Chem.*, **38**, 500 (1973).

[2] Alfred P. Sloan Fellow, 1971–1973.

[3] C. J. Jackson and F. H. Gazzolo, *J. Amer. Chem. Soc.*, **23**, 376 (1900).

[4] J. Meisenheimer, *Justus Liebigs Ann. Chem.*, **323**, 205 (1902).

[5] F. Čůta and E. Beránek, *Collect. Czech. Chem. Commun.*, **23**, 1501 (1958).

[6] M. R. Crampton, *J. Chem. Soc. B*, 1341 (1967).

[7] A. R. Norris, *Can. J. Chem.*, **45**, 175 (1967).

[8] R. A. Henry, *J. Org. Chem.*, **27**, 2637 (1962).

[9] M. J. Strauss, *Chem. Rev.*, 70, 667 (1970).

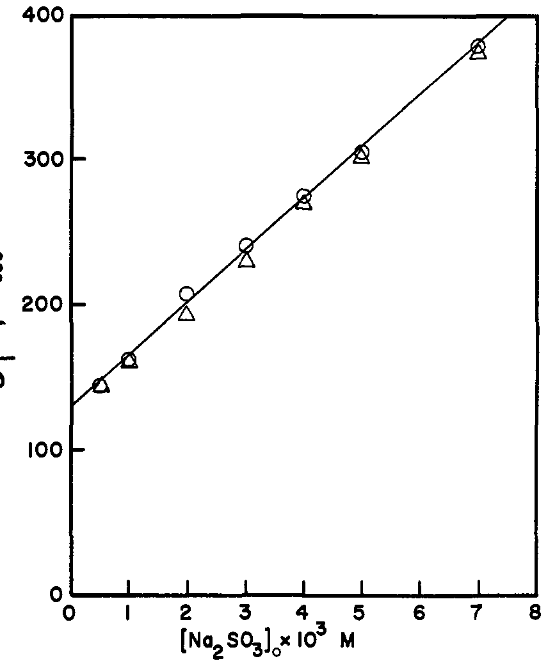


Figure 1. Kinetics of 1:1 complex formation: (△) without salt added; (○) at $\mu = 0.6$ *M*. Estimated error ±5% in any individual value of τ_1.

isomers (the two sulfites being located on the same or opposite sides of the ring system).

Regardless of the merits of this interpretation, Strauss has pointed out an interesting problem. No evidence for cis–trans isomerism has yet been reported in any 1:2 complex between activated aromatic compounds and nucleophiles. One wonders whether this is because one isomer is always so much less stable than the other as to escape detection or whether it reflects the experimental difficulty of recognizing as different two species which must have very similar spectral properties.

It is well known that by introducing time as an additional parameter one can gain enormously in "resolution" over static measurements on an equilibrium system. Thus a kinetic study of the interaction between TNB and sulfite ion, quite apart from being interesting in its own right for the sake of obtaining rates of complex formation and decay, was expected possibly to "separate" (on the time scale) the cis and trans isomers if both were present at all.

We now report such a study.

Results

Kinetics. We conducted our kinetic experiments by mixing aqueous solutions of TNB with aqueous solutions of Na_2SO_3 in the stopped-flow (SF) apparatus and monitoring changes in light absorption. The concentration of TNB was usually between 10^{-5} and 5×10^{-5} *M*, whereas the sulfite concentration was always much higher, assuring pseudo-first-order conditions throughout.

When the sulfite concentration was low (<0.003 *M*) we observed one single process giving rise to an increase in absorbance between about 400 and 600 nm (max around 462 nm) with a relaxation time, τ_1, of a few milliseconds. With increasing sulfite concentration, τ_1 became progressively shorter; furthermore, the first process was followed by two subsequent changes in absorbance which were much slower. Depending on the wavelength, the second process manifested itself either by an increase or a decrease in absorbance. For example, at 462 nm there was always a decrease, at 500 nm always an increase, regardless of sulfite concentration. This process was characterized by a relaxation time, τ_2, around 50 msec for $[Na_2SO_3]_0 \leqslant 10^{-2}$ *M*, becoming progressively shorter at higher concentrations or at higher ionic strength. The third process caused decreasing absorbance at 462 nm when the sulfite concentration was low (*e.g.*, for $[Na_2SO_3]_0 \leqslant 0.03$ *M* with $\mu = 5.4$ *M*) and was invisible at $[Na_2SO_3]_0 \simeq 0.03$ *M* but gave rise to an increase at $[Na_2SO_3]_0 > 0.03$ *M*; at 500 nm an increase in absorbance was always observed, regardless of sulfite concentration. The relaxation time, τ_3, was found to depend little on sulfite concentration or ionic strength and was around 5 sec. The three kinetic processes were sufficiently separated on the time scale as to allow the evaluation of each as an essentially single exponential.

τ_1^{-1} is plotted as a function of $[Na_2SO_3]_0$ in Figure 1. Experiments at high or low ionic strength gave virtually the same results. Data on τ_2^{-1} and τ_3^{-1} under various conditions are summarized in Tables I and II; Figures 2 and 3 show representative plots of τ_2^{-1} and τ_3^{-1}, respectively, *vs.* $[Na_2SO_3]_0$ at low and high ionic strength.

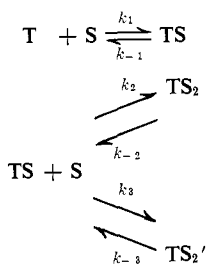
Table I. τ_2^{-1} for the Interaction between TNB and SO_3^{2-} in Aqueous Solution at 25°.[a] Formation of TS_2

$[Na_2SO_3]_0$, *M*	$[TNB]_0 \times 10^5$ *M*	Ionic strength[b] 0.3 *M*	0.6 *M*	0.9 *M*	4.5 *M*	5.4 *M*
0.005	3.0				22.7	22.3
0.010	3.0		19.6		28.0	29.8
0.015	3.0	22.8	20.2	23.8	31.0	41.7
0.020	1.0	23.0				
0.030	1.0		27.8	27.6	58.6	67.2
0.040	1.0	25.7				
0.050	1.0	26.8				
0.060	1.0	29.6	33.9	35.1	100	130
0.070	1.0	30.7				
0.080	1.0	35.5				
0.090	1.0		40.9			
0.100	1.0			50.8	149	206
0.120	1.0		47.6			
0.140	1.0			60.7	214	312
0.150	1.0		56.1			

[a] Estimated error ±4% in any individual value of τ_2. [b] Maintained by addition of Na_2SO_4.

The fact that each plot has a nonzero intercept means that each of the three processes characterized by τ_1, τ_2, and τ_3 is reversible. The concentration dependence of the 3 relaxation times is consistent with Scheme I under the assumption $k_1[S] + k_{-1} \gg k_2[S] + k_{-2} \gg k_3[S] + k_{-3}$. T stands for TNB and S for SO_3^{2-}; TS is a

Scheme I



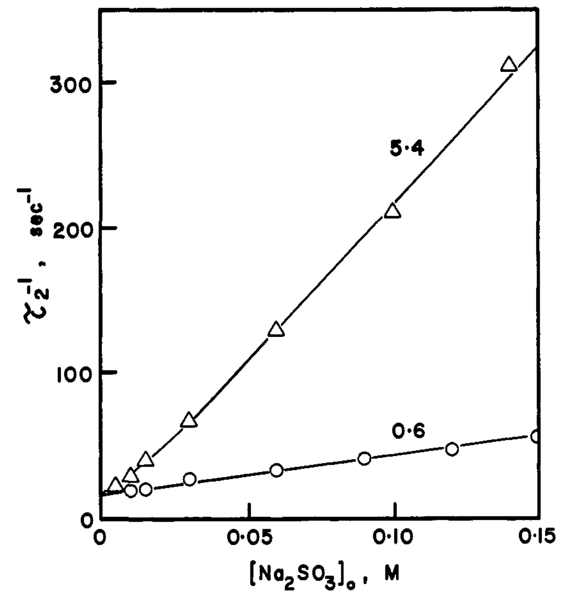


Figure 2. Kinetics of TS_2 formation: (○) at $\mu = 0.6$ *M*; (△) at $\mu = 5.4$ *M*.

Table II. τ_3^{-1} for the Interaction between TNB and SO_3^{2-} in Aqueous Solution at 25°.[a] Formation of TS_2'

$[Na_2SO_3]_0$, *M*	$[TNB]_0$ × 10^5 *M*	Ionic strength[b] 0.3 *M*	0.6 *M*	0.9 *M*	4.5 *M*	5.4 *M*
0.005	5.0	0.14	0.15	0.13	0.15	
0.010	5.0	0.15	0.16	0.14	0.16	0.15
0.015	5.0			0.16	0.19	0.20
0.020	5.0	0.15	0.16			
0.030	1.0	0.16		0.17	0.20	0.20
0.050	1.0	0.17				
0.060	1.0	0.17	0.18	0.17		0.21
0.070	1.0	0.18				
0.080	1.0	0.18				
0.090	1.0		0.19			
0.100	1.0			0.18	0.20	0.21
0.120	1.0		0.19			
0.140	1.0			0.19		0.21
0.150	1.0		0.19	0.19		
0.180	1.0				0.21	
0.750	1.0				0.22	
0.900	1.0					0.21

[a] Estimated error ±5% in any individual value of τ_3. [b] Maintained by addition of Na_2SO_4.

1:1 addition complex whereas TS_2 and TS_2' are two different 1:2 complexes. There is little doubt that TS and **1** are identical, as confirmed by a comparison of our kinetically determined equilibrium constant and the known spectrophotometric equilibrium constant (see below). We suggest that TS_2 and TS_2' are the trans and cis isomers, respectively, of the 1:2 complex **2**, as supported by several pieces of evidence presented in this paper.

The pertinent expressions for the relaxation times, derived according to standard procedures,[10] are given by eq 1, 2, and 3, where $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$.

$$\frac{1}{\tau_1} = k_1[S] + k_{-1} \tag{1}$$

$$\frac{1}{\tau_2} = \frac{k_2K_1[S]^2}{1 + K_1[S]} + k_{-2} \tag{2}$$

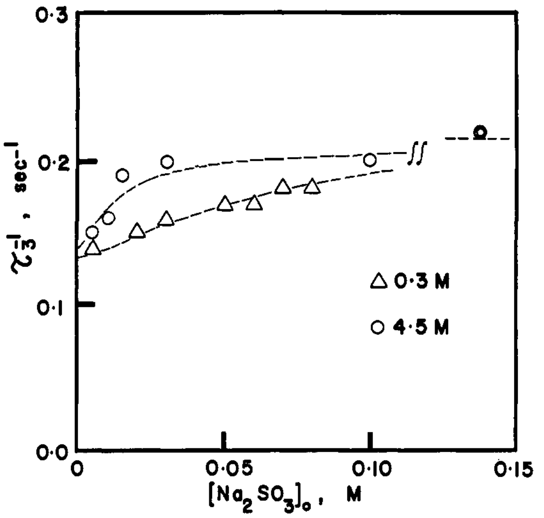


Figure 3. Kinetics of TS_2' formation: (△) at $\mu = 0.3$ *M*; (○) at $\mu = 4.5$ *M*; (⊙) at $[Na_2SO_3]_0 = 0.75$ *M*, $\mu = 4.5$ *M*.

$$\frac{1}{\tau_3} = \frac{k_3K_1[S]^2}{1 + K_1[S](1 + K_2[S])} + k_{-3} \tag{3}$$

According to eq 1, the slope in Figure 1 provides k_1, the intercept affords k_{-1}; they are reported in Table III as calculated from a least-squares analysis.

Equation 2 describes a somewhat complex dependence on [S] which is quadratic at low concentration ($K_1[S] \ll 1$, eq 4) but linear at high concentration

$$1/\tau_2 = k_2K_1[S]^2 + k_{-2} \tag{4}$$

($K_1[S] \gg 1$, eq 5). Since K_1 is in the order of 250,

$$1/\tau_2 = k_2[S] + k_{-2} \tag{5}$$

eq 5 prevails at $[S] \geqslant 0.04$ *M*, *i.e.*, for most experimental concentrations which were practical for obtaining τ_2. This is why the plots in Figure 2 look linear over almost the entire concentration range. k_2 was obtained from a least-squares analysis of the linear portion of τ_2^{-1} *vs.* [S] plots, whereas k_{-2} (intercept) was found by visual extrapolation of the curved portion; they are reported in Table III.

With respect to eq 3 there are four interesting limiting cases. In the first, eq 3 simplifies to eq 6 ($K_1[S] \ll 1$,

$$1/\tau_3 = k_3K_1[S]^2 + k_{-3} \tag{6}$$

$K_2[S] \ll 1$); when $K_1[S] \gg 1$ but $K_2[S] \ll 1$ one obtains eq 7, whereas for $K_1[S] \gg 1$, $K_2[S] \lesseqgtr 1$ one obtains eq 8.

$$1/\tau_3 = k_3[S] + k_{-3} \tag{7}$$

$$1/\tau_3 = \frac{k_3[S]}{1 + K_2[S]} + k_{-3} \tag{8}$$

Finally for $K_1[S] \gg 1$, $K_2[S] \gg 1$ eq 3 simplifies to eq 9,

$$1/\tau_3 = (k_3/K_2) + k_{-3} \tag{9}$$

i.e., τ_3^{-1} becomes independent of sulfite ion concentration. Thus τ_3^{-1} *vs.* [S] has a sigmoid shape as can be seen in Figure 3, where the curves were calculated according to eq 3 with the set of k_3 and k_{-3} giving the best fit with the experimental data. Because k_3/K_2 is quite small compared with k_{-3}, this curve fitting is not very sensitive to small variations in k_3 and k_{-3}; as a con-

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[10] M. Eigen and L. DeMaeyer in "Techniques of Organic Chemistry," Vol. VIII, part 2, A. Weissberger, Ed., Interscience, New York, N.Y., 1963, p 893.

sequence the uncertainty in k_3 and k_{-3} is higher than in k_1, k_{-1}, k_2, and k_{-2} as indicated in Table III.

Alternative interpretations, *e.g.*, that the third process is the attack of a further sulfite ion on TS_2 to form a 1:3 complex, that it is the attack of bisulfite ion on T or TS, or the attack of hydroxide ion on T or TS can easily be ruled out. They would lead to a qualitatively different concentration dependence of τ_3 and/or a pH dependence of τ_3 and possibly of τ_2 and τ_1, as well as a pH dependence of the absorbance changes associated with the various processes. No such pH dependence in the range investigated (pH 8.5–10.5) could be detected.

On the other hand, the changes in absorbance associated with the three processes as well as the dependence of the relaxation times on ionic strength are very much consistent with Scheme I. (1) Equilibration between T and TS is expected to be associated with an increase in absorbance at wavelengths between about 400 and 600 nm (visible spectrum of **1**[6,7]) regardless of sulfite concentration as is indeed observed. (2) On the assumption that TS_2 is a σ complex such as **2**, the decrease in absorbance at 462 nm and increase at 500 nm can be rationalized by the known fact the $\epsilon_2 < \epsilon_1$ at 462 but $\epsilon_2 > \epsilon_1$ at 500 nm[6] since formation of TS_2 is at the expense of TS. Only at very low sulfite concentrations, where but little of T has been converted to TS, would one expect an increase even at 462 nm, since the loss in TS to TS_2 would be made up by an approximately equal gain in TS from T. Some qualitative experiments to confirm this point were performed. However, the separation between τ_1 and τ_2 is insufficient at these low concentrations for good precision in the quantitative evaluation of τ_2, and therefore no τ_2 values are reported for these low concentrations. (3) The changes in absorbance associated with the third process are consistent with the following relations, confirmed by independent measurements described below: at 462 nm $\epsilon_{TS} > \epsilon_{TS_2'} > \epsilon_{TS_2}$, at 500 nm $\epsilon_{TS_2'} > \epsilon_{TS_2} > \epsilon_{TS}$. The decrease in absorbance at 462 nm when the sulfite concentration is low is due to the gain in TS_2' at the expense of some of the more strongly absorbing TS. At higher concentration only a little TS is present so that the third process essentially is an increase in the concentration of TS_2' at the expense of the more weakly absorbing TS_2.

The ionic strength is expected greatly to affect the reaction between TS and sulfite ion but not between T and sulfite ion, in agreement with experimental observation. The reason why τ_3 is relatively little affected by the ionic strength is not that the rate of formation of TS_2' (k_3) is independent of it (see Table III), but rather the consequence of a canceling effect; the ionic strength dependences of K_2 and k_3 are very similar and compensate each other, as is best illustrated in eq 9. On the other hand, k_{-3} depends little on ionic strength, again similar to k_{-2}.

Equilibrium Studies. The equilibrium constant K_1 was determined spectrophotometrically by means of the Benesi-Hildebrand[11] equation (eq 10) where A is

$$\frac{[T]_0}{A} = \frac{1}{\epsilon_{TS}K_1[S]} + \frac{1}{\epsilon_{TS}} \qquad (10)$$

the absorbance in a 1-cm cuvette. Our value of K_1 =

Table III. Rate and Equilibrium Constants for the Various Complexes between 1,3,5-Trinitrobenzene and SO_3^{2-} in Water at 25°

	No added salt	Ionic strength[a] 0.3 M	0.6 M	0.9 M	3.0 M	4.5 M	5.4 M
k_1, M^{-1} sec^{-1}	$(3.54 \pm 0.35) \times 10^4$		$(3.58 \pm 0.35) \times 10^4$				
k_{-1}, sec^{-1}	125 ± 10		130 ± 10				
$K_1 = k_1/k_{-1}$, M^{-1}	286 ± 43 $(221 \pm 25)^b$ $(225)^{b,c}$		272 ± 34				
k_2, M^{-1} sec^{-1}		195 ± 14	234 ± 16	311 ± 22	690 ± 48	1390 ± 100	2190 ± 150
k_{-2}, sec$^{-1\,e}$		21 ± 2	21 ± 2	20 ± 2	20 ± 2	16 ± 2	16 ± 2
$K_2 = k_2/k_{-2}$, M^{-1}		9.3 ± 1.4	11.1 ± 1.6	15.6 ± 2.3^d	35.5 ± 5.3	86.8 ± 13	137 ± 20
k_3, M^{-1} sec^{-1}		1.2 ± 0.24	1.1 ± 0.22	1.6 ± 0.32		6.3 ± 1.3	10.3 ± 2.1
k_{-3}, sec$^{-1\,e}$		0.13 ± 0.013	0.14 ± 0.014	0.12 ± 0.012		0.14 ± 0.014	0.14 ± 0.014
$K_3 = k_3/k_{-3}$, M^{-1}		9.2 ± 2.7	7.9 ± 2.4	13.3 ± 4.0^d		45 ± 14	73 ± 22

[a] Maintained by addition of sodium sulfate. [b] From equilibrium measurements. [c] Reference 7. [d] $K_2^{app} = K_2 + K_3 = 25 \pm 2$ from equilibrium measurements. [e] Not statistically corrected.

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(11) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 71, 2703 (1949).

221 ± 30 M^{-1} is practically identical with the one determined by Norris[7] but somewhat lower than the value from kinetics, $k_1/k_{-1} = 286 \pm 40\ M^{-1}$. The conservatively estimated error limits suggest that the two values might be indistinguishable. However, repeated determinations always gave the same results suggesting the presence of some unrecognized systematic error, possibly stemming from slow decomposition of the solutions,[7] or a temperature effect due to the difficulty in controlling the temperature in the SF apparatus with a Kel-F flow system.[12]

If cis and trans isomers of the 1:2 complex are formed, Crampton's[6] spectrophotometric measurements can only provide an apparent equilibrium constant for 1:2 complex formation, as defined by eq 11. Since the

$$K_2^{\mathrm{app}} = K_2 + K_3 \qquad (11)$$

experimental conditions in Crampton's work were not identical with ours, we did our own determination of K_2^{app}. At $\mu = 0.9\ M$ we obtain $K_2^{\mathrm{app}} = 25 \pm 2$ ($\epsilon_2^{\mathrm{app}}$ = 14,700 at 462 nm), whereas the kinetic equilibrium constants under the same conditions are $K_2 = 15.6 \pm 2.3$ and $K_3 = 13.3 \pm 4.0$, resulting in $K_2 + K_3 = 28.9 \pm 6.3$. Thus eq 11 is indeed obeyed within experimental error as called for by the cis and trans isomer hypothesis.

Spectra. Spectra of the 1:2 complex determined by Crampton[6] must be the sum of the contributions by the cis and trans isomers. The spectra of the cis and trans isomer are expected to be very similar though not necessarily identical. They can be determined separately by using the SF apparatus as a transient spectrophotometer in the following way. The absorbance reading, A_{SF}, in the SF apparatus for any wavelength at a time t, such that $\tau_2 \ll t \ll \tau_3$, is given by eq 12. If

$$A_{\mathrm{SF}} = \epsilon_{\mathrm{T}}[\mathrm{T}] + \epsilon_{\mathrm{TS}}[\mathrm{TS}] + \epsilon_{\mathrm{TS_2}}[\mathrm{TS_2}] \qquad (12)$$

the sulfite concentration and ionic strength are chosen so as to make $K_1[\mathrm{S}] \gg 1$ and $K_2[\mathrm{S}] \gg 1$ so that $[\mathrm{TS_2}] \gg [\mathrm{TS}] \gg [\mathrm{T}]$ and thus $[\mathrm{TS_2}] \cong [\mathrm{T}]_0$ where $[\mathrm{T}]_0$ is the stoichiometric TNB concentration, eq 12 simplifies to eq 13.

$$A_{\mathrm{SF}} = \epsilon_{\mathrm{TS_2}}[\mathrm{T}]_0 \qquad (13)$$

Spectra taken on an ordinary spectrophotometer at $t = \infty$ ($t \gg \tau_3$) under the same conditions provide an absorbance reading given by eq 14, where $[\mathrm{TS_2}] + [\mathrm{TS_2'}] = [\mathrm{T}]_0$. Expressing $[\mathrm{TS_2}]$ and $[\mathrm{TS_2'}]$ as functions of K_2, K_3, and $[\mathrm{T}]_0$ one obtains eq 15. Combining A_{SF}

$$A_\infty = \epsilon_{\mathrm{TS_2}}[\mathrm{TS_2}] + \epsilon_{\mathrm{TS_2'}}[\mathrm{TS_2'}] \qquad (14)$$

$$A_\infty = \left[\epsilon_{\mathrm{TS_2}}\frac{K_2}{K_2 + K_3} + \epsilon_{\mathrm{TS_2'}}\frac{K_3}{K_2 + K_3}\right][\mathrm{T}]_0 \qquad (15)$$

and A_∞ allows the calculation of $\epsilon_{\mathrm{TS_2}}$ and $\epsilon_{\mathrm{TS_2'}}$ as described in the Experimental Section. In Figure 4 we have plotted such calculated values of $\epsilon_{\mathrm{TS_2}}$ and $\epsilon_{\mathrm{TS_2'}}$ *vs.* wavelength. The spectra thus obtained ($\mathrm{TS_2}$: $\lambda_{\max}$ 500 nm (ϵ 16,000); $\mathrm{TS_2'}$: $\lambda_{\max}$ 490 nm (ϵ 18,100)) are less accurate than spectra determined under more ordinary circumstances because the respective extinction coefficients depend on K_2 and K_3 (eq 15) but also because absorbance readings in the SF apparatus (eq 13) are somewhat less precise than on a Cary 14 spectrophotometer. As a consequence, the absolute values of the extinction coefficients may be uncertain by as much as 15%. However, there is no uncertainty as to the spectral regions where $\epsilon_{\mathrm{TS_2}} > \epsilon_{\mathrm{TS_2'}}$ and where $\epsilon_{\mathrm{TS_2}} < \epsilon_{\mathrm{TS_2'}}$, and the conclusion that $\mathrm{TS_2}$ and $\mathrm{TS_2'}$ have very similar though not identical spectra is fully warranted.

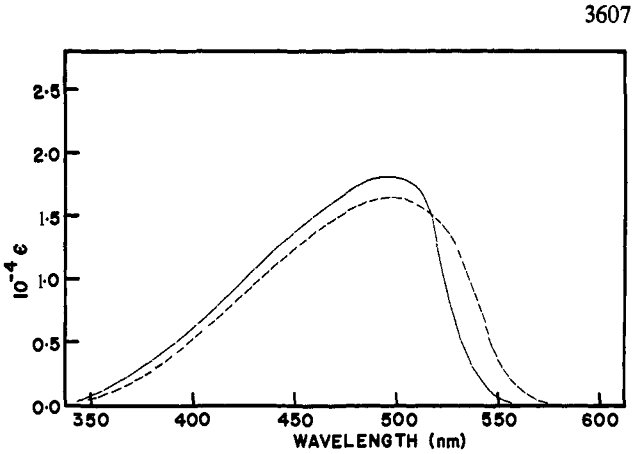
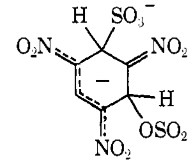


Figure 4. Spectra of the 1:2 complexes based on SF and spectrophotometric data at $[\mathrm{Na_2SO_3}]_0 = 0.75\ M$, $\mu = 4.5\ M$: (— — —) $\mathrm{TS_2}$, (- - - - -) $\mathrm{TS_2'}$. $\lambda_{\max}$ for $\mathrm{TS_2}$ at 500 nm (ϵ 16,000), $\lambda_{\max}$ for $\mathrm{TS_2'}$ at 490 nm (ϵ 18,100), $\lambda_{\mathrm{isosbest}}$ 515 nm.

Discussion

The most interesting and significant result of this study is that TNB forms two different 1:2 complexes with sulfite ion. The fact that not only the spectra but also the stability constants (K_2 and K_3) are very similar indicates that the two complexes must have a very similar structure; this led us to propose that they are the cis and the trans isomers of **2**.

In principle one can visualize another possibility, *viz.*, sulfite ion attack *via* the oxygen atom, to form the sulfite ester **3**.



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Although consistent with the spectral evidence and with the qualitative aspects of our kinetic results, such an interpretation must be rejected on several grounds. (1) Sulfite esters, $\mathrm{ROSO_2^-}$ and $\mathrm{ROSO_2H}$, are very unstable and decompose rapidly to give $\mathrm{ROH(RO^-)}$ and $\mathrm{SO_2}$.[13] This contrasts with the observation that an isolated mixture of $\mathrm{TS_2}$ and $\mathrm{TS_2'}$ can be heated to 100° for a short time without apparent decomposition and that such a mixture stored at room temperature was still unchanged after 6 years.[8] (2) Although some thallium complexes have been shown to involve sulfite bonded *via* oxygen,[14] the sulfite ion is not generally known as an ambident nucleophile in reactions with electrophilic carbon which it always appears to attack with the sulfur atom. This is in agreement with expectations based on Pearson's[15] concept of soft and

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[12] Some earlier experiments with a stainless steel flow system carried out by Miss Judith England provided $k_1/k_{-1} = 252 \pm 35\ M^{-1}$.

[13] W. Voss and E. Blanke, *Justus Liebigs Ann. Chem.*, **485**, 258 (1931).

[14] G. Newman and D. B. Powell, *Spectrochim. Acta*, **19**, 213 (1963).

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hard acids and bases. (3) If **3** were formed, one should expect to find a 1:1 complex from oxygen attack as well. There is no evidence for it although very small concentrations would of course escape both spectroscopic and kinetic detection. (4) Unless we assume that the reactive center in **1** is very soft, we expect the rates of nucleophilic attack by a series of oxygen bases to depend significantly on their p*K*. In this light it seems unreasonable that the rate of sulfite ($pK = 6.9$) attack *via* oxygen is of the same order of magnitude as the rates of hydroxide ion ($pK = 15.7$) or methoxide ion ($pK \approx 16.3$ in H_2O) attack on the 1:1 complex between TNB and hydroxide ion,[16] even if one allows for a possible α effect[17] due to the lone pair on sulfur and for a statistical factor. If, however, the reactive center in **1** were indeed very soft, oxygen attack could hardly compete with sulfur attack as pointed out above.

Each of these points inveighs against the possibility of sulfite attack *via* oxygen; taken together they make a convincing case.

Rate and Equilibrium Constants for the 1:1 Complex. Sulfite ion is known as a highly reactive nucleophile in various reactions,[17] including nucleophilic aromatic substitutions[18] where it was found to be about equally or even more reactive than methoxide and ethoxide ion toward nitrohalobenzenes. The same holds true toward TNB; the rate coefficient for methoxide ion attack in 22.5% MeOH–77.5% H_2O is 2425 M^{-1} sec^{-1} [19] and for ethoxide ion attack in 19% EtOH–81% H_2O it is 7700 M^{-1} sec^{-1} [19] whereas k_1 for SO_3^{2-} is 35,400 M^{-1} sec^{-1}. The rate coefficient, $k_{-1} = 125$ sec^{-1}, for sulfite expulsion is close to that for methoxide expulsion (254 sec^{-1})[19] but about four fold larger than for ethoxide expulsion (32 sec^{-1})[19] which makes the stability of the sulfite complex ($K_1 = 284$ M^{-1}) about the same as of the ethoxide complex (241 M^{-1})[19] but considerably higher than of the methoxide complex (9.55 M^{-1}).[19]

Rate and Equilibrium Constants for the 1:2 Complexes. It is noteworthy that the isomeric 1:2 complexes are of approximately the same stability[20] but that the rates in both directions differ by more than two orders of magnitude. For instance, at $\mu = 0.3$ *M*, $k_2/k_3 = 163$, $k_{-2}/k_{-3} = 161$, and $K_2/K_3 = 1.01$. This clearly indicates the operation of an effect on the respective transition states which is not present (or present to a smaller extent) in either the 1:1 complex or in the two 1:2 complexes.[22] We believe the following rationalization could explain the phenomenon. Assume TS_2 is the trans, TS_2' the cis isomer. In the cis form the two sulfonate groups are obviously closer to each other than in the trans form. Although the proximity of the two groups is not enough for direct steric interaction, electrostatic repulsion is likely to occur with an expected decrease in the relative stability of the cis isomer. The fact that the cis isomer is practically of the same stability as the trans isomer suggests that the ring system is somewhat distorted toward a nonplanar arrangement allowing for a greater separation between the sulfonate groups and a concomitant reduction in electrostatic repulsion. This distortion should not cost a lot since coplanarity of all ring atoms is no longer required for resonance stabilization, in contrast to the 1:1 complex.

In the transition state, on the other hand, there is a larger formal negative charge on the attacking sulfite ion than there is in the complex and probably not as much ring distortion as in the complex. Both these factors are expected to make electrostatic repulsion rather important in the transition state to or from the cis isomer and therefore to raise its energy.

Experimental Section

Materials. 1,3,5-Trinitrobenzene (Eastman White Label) was recrystallized twice from ethanol, mp 123°. Sodium sulfate (Mallinckrodt Analytical Reagent) and sodium sulfite (Mallinckrodt Analytical Reagent) were used without further purification.

Rate and Equilibrium Measurements. Spectral measurements were performed on the Cary Model 14 recording spectrophotometer (Applied Physics Corp.) equipped with thermostated cuvettes ($\pm 0.1°$).

The stopped-flow experiments were carried out on a Durrum-Gibson stopped-flow spectrophotometer.[24] The relaxation times were measured either at 462 nm (τ_1 and τ_2) or at 500 nm (τ_3). All relaxation times represent average values of three or four oscilloscope pictures of each solution.

Spectra of TS_2 and TS_2'. Since the output of our SF apparatus is in % *T* (transmission) rather than absorbance units, the following procedure proved the most useful. Let us define $\% T_{SF}$ as the % *T* reading at $\tau_2 \ll t \ll \tau_3$ on the SF apparatus, whereas $\% T_\infty$ is the absorbance reading from the spectrophotometer converted into % *T* units *via* eq 16. The change in % *T*, $\Delta(\% T)$, associated with τ_3 can be measured in the SF apparatus with relatively high precision. It is equivalent with $\% T_{SF} - \% T_\infty$. Thus from $\% T_\infty$ and $\Delta(\% T)$ one easily obtains $\% T_{SF}$ which is converted back to A_{SF} *via* eq 16. Direct measuring of $\% T_{SF}$ is also possible but less accurate.

$$A = \log 100/\% T \qquad (16)$$

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[16] C. F. Bernasconi and R. G. Bergstrom, unpublished results.

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[20] Note that the trans isomer is in fact a racemic mixture of two enantiomers whereas there is only one cis isomer. Consequently, similarly to K_2^{app}, the equilibrium constant for the trans isomer is in turn a sum of two equilibrium constants. These refer to the two enantiomers and are of course numerically identical. When relative stabilities of the cis and trans isomers are compared one has to keep in mind that the cis isomer is favored by a statistical factor of 2 over any one of the trans enantiomers;[21] no such statistical factor is, however, involved when the comparison is between the cis isomer and the racemic mixture of the trans isomers.

[21] S. W. Benson, *J. Amer. Chem. Soc.*, **80**, 5151 (1958).

[22] Recently some deviant Brønsted relations were rationalized by invoking effects which operate on the transition state but neither on on the initial nor on the final state.[23]

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