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KINETIC AND EQUILIBRIUM STUDIES ON σ-COMPLEXES OF 2, 4, 6-TRINITROANISOLE AND PICRYLSULPHONATE WITH SULPHITE ION IN AQUEOUS SOLUTION

BY MUNEO SASAKI

The reactions of 2, 4, 6-trinitroanisole (TNA) and picrylsulphonate with sulphite ion in aqueous solution take place to give intensely colored σ-complexes. Kinetic studies on the formations of these complexes have been carried out by the stopped-flow method in the temperature range, 15.0~30.0°C. The respective rate constants for the formation and the decomposition (reverse reaction) of σ-complexes were well consistent with the results of the separate equilibrium study. The effect of ionic strength on the anion-anion reaction was well explained by taking into account of the Debye-Hückel equation. Kinetic and thermodynamic parameters were determined and compared with the previous data on the interaction of 1, 3, 5-trinitrobenzene with sulphite ion, and with the results of methoxide attack to TNB and TNA.

Introduction

The reactions of 1, 3, 5-trinitrobenzene (TNB) with aromatic amines are known to be the charge-transfer interactions[1], but with aliphatic amines or anionic nucleophiles the predominant reactions have been known to be σ-complex formations[2,3]. The reactions of TNB and its related compounds with nucleophiles, such as CH_3O^- and SO_3^{2-}, are quite interesting. Complex (I) is only formed from TNB and methoxide ion at low methoxide concentration in methyl alcohol. Since it was suggested by Servis[4] that complex (II) formed by methoxide attack at C_1 position of 2, 4, 6-trinitroanisole (TNA) —— henceforth abbreviated 1, 1-complex —— is preceded by a much faster attack at C_3 position —— the formation of 1, 3-complex (III), considerable attention has been directed to the spectra, relative stability and reactivity of these isomeric complexes[5~7]. Bernasconi has revealed[7a] using the "stopped-

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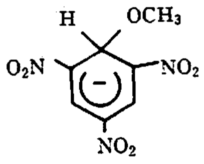
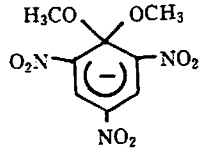
1) For example, R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952)
2) (a) J. Osugi and M. Sasaki, *This Journal*, **37**, 43 (1967)
   (b) R. Foster and C. A. Fyfe, *Tetrahedron*, **21**, 3363 (1965)
   (c) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966)
   (d) E. Buncell, A. R. Norris and K. E. Russell, *Quart. Rev.*, **22**, 123 (1968)
3) M. R. Crampton, *Adv. Phys. Org. Chem.*, **7**, 211 (1969)
4) (a) K. L. Servis, *J. Amer. Chem. Soc.*, **87**, 5495 (1965)
   (b) K. L. Servis, *ibid.*, **89**, 1508 (1967)
5) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970)
6) M. R. Crampton and H. A. Khan, *J. C. S. Perkin II*, 773 (1972)
7) (a) C. F. Bernasconi, *J. Amer. Chem. Soc.*, **93**, 6975 (1971)
   (b) C. F. Bernasconi, *ibid.*, **92**, 4682 (1970)

flow temperature-jump" method that (III) is, though thermodynamically less stable, kinetically much more favored than (II). It has been found that, by NMR spectroscopy in DMSO-H_2O mixed solvent, the predominant interaction of sulphite ion with 1-X-2, 4, 6-trinitrobenzene (X=CH_3O, NH_2, $NHCH_3$, *etc.*) results in only the formation of 1, 3-complex at low sulphite ion concentration[8]; no evidence has been found for the formation of 1, 1-complex.



(I)



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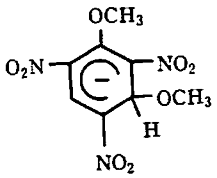

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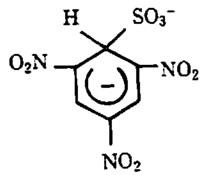

(IV)

The reaction of TNB with sulphite ion was studied previously[9]. The kinetic and thermodynamic parameters for complex (IV) were determined. Moreover, it was found that picrylchloride reacts with sulphite ion to form both 1, 1-complex and 1, 3-complex[10], and that picrylsulphonate ion (PS^-) is produced, which reacts further with sulphite ion.

With sulphite ion as a nucleophile, not only kinetic study but equilibrium one is not so enough, and the present paper deals with the reactions of TNA and PS^- with sodium sulphite especially from the view point of kinetics.

Experimental

Materials

TNA was synthesized from dinitroanisole by nitration in the usual way, and repeatedly recrystallized from methyl alcohol until constant melting point, 56.5°C (*lit.* 56–57°C). Commercial picrylsulphonic acid sodium salt (Guaranteed reagent grade) was recrystallized several times from water-ethyl alcohol (1 : 3 v/v), and dried under reduced pressure at about 90°C until constant weight. Sodium sulphite and sodium sulphate were crystallized from aqueous solutions by adding ethyl alcohol, and dried

8) M. R. Crampton, *J. Chem. Soc.* (*B*), **1967**, 1341
9) M. Sasaki, *Chem. Letters*, 205 (1973)
10) M. Sasaki, Paper Presented at 7th Symposium on Fast Reactions, Nagoya (1972)

under reduced pressure at about 100°C until constant weight. Water as a solvent was passed through ion-exchange resin and distilled. Spectrograde DMSO was used without further purification. All reacting solutions were prepared immediately before the use.

Apparatus and procedure

Kinetics: Kinetic measurements were carried out by the use of a Union Giken SF-71 Stopped-Flow Spectrophotometer which is operated by the gaseous pressure-drive method,——two reacting solutions are drived into a mixing chamber by pressurizing directly two separate reservoirs with compressed gas. The dead time in this study was kept constant, about 1.0 msec. Thermostated water was circulated around the observation cell compartment (2.0 mm quartz cell) and the reservoirs; the temperature was regulated within ±0.1°C.

All kinetic and equilibrium runs were performed with sodium sulphite in large excess over substrates. The concentrations of TNA varied from 0.6×10^{-4} to 1.8×10^{-4} mole/*l*. The concentrations of PS^- varied from 1.0×10^{-4} to 4.3×10^{-4} mole/*l*. Sulphite concentrations were in the range, 0.002~0.015 mole/*l* in the case of TNA, and 0.010~0.100 mole/*l* in the case of PS^-. The ionic strength, if necessary, was maintained constant by adding sodium sulphate. The pseudo first-order rate constants were determined according to Guggenheim's plot.

Equilibrium: The equilibrium measurements for PS^-—SO_3^{2-} system were performed by the use of the same spectrophotometer. The overall change of amplitude on kinetic oscilloscope trace cannot give accurate optical density, because the change in the dead time is withdrawn. So the equilibrium measurements were carried out independently from kinetic runs, being referred to the solvent. A Shimadzu UV-200 Spectrophotometer equipped with 10 mm quartz cell was used in recording the spectra.

NMR spectra were recorded with a JOEL-C-60 HL (60 MHz) spectrometer at room temperature. The NMR spectra of TNA-SO_3^{2-} complex were observed in water-DMSO mixed solvent (30:70 v/v). The solutions were prepared by adding TNA in DMSO to sodium sulphite in water. The sodium sulphite was in the range, 0.1~0.5 mole/*l*, and TNA was about 0.07 mole/*l*.

For PS^-—SO_3^{2-} system, NMR spectra were recorded in water. The measurements in water-DMSO mixture were unsuccessful owing to the low formation constant of the complex and to the too low solubility of sodium sulphite to detect the signal.

Chemical shifts were measured relative to internal tetramethylsilane in media containing DMSO. However, in water where TMS is insoluble shifts were relative to internal dioxane. A difference of 3.70 ppm was assumed between the two standards[11].

Results and Considerations

Reactions of TNA with SO_3^{2-}

11) R. A. Y. Jones, A. R. Katritzky, J. N. Murrell and N. Sheppard, *J. Chem. Soc.*, **1962**, 2576

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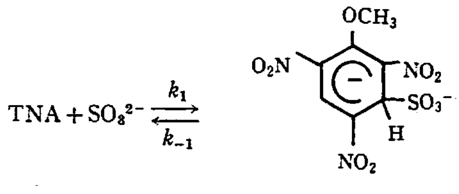
The reaction of TNA and SO_3^{2-} under the conditions employed in this study leads to the reversible formation of 1 : 1 σ-complex (V).



(V) (1)

The absorption spectrum of TNA in water shows no absorption above 400 nm. However, the spectrum in the presence of sodium sulphite is shown in Fig. 1; a maximum appears at 443 nm. On increasing the concentration of sulphite ion ($\geq$0.02 mole/l), a higher complex results from the addition of two sulphite ions per molecule of TNA: λ_{max}=430 nm. The chemical shifts ($-\delta$) of TNA in the presence of sodium sulphite were, in addition to the bands of parent molecule, 6.06 (d 1H) and 8.37 (d 1H); both could be attributed to the ring protons of complex (V). These spectral properties were fully in accordance with Crampton's results[8], and the formation of σ-complex (V) was confirmed.

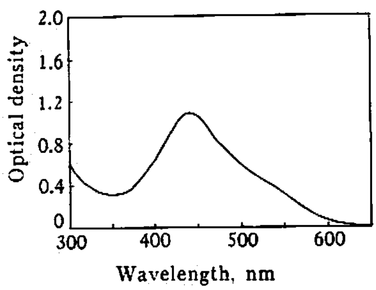


Fig. 1 Absorption spectrum of complex (V) formed by mixing TNA (2.39 $\times 10^{-4}$ mole/l) and Na_2SO_3 (1.08 $\times$ 10^{-2} mole/l) in water

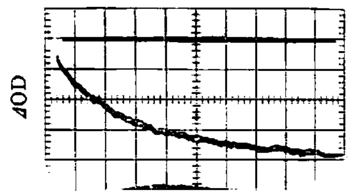


Fig. 2 Representative stopped-flow trace at 443 nm (25.0°C). $[TNA]_0$=1.5 $\times$ 10^{-4} mole/l, $[Na_2SO_3]_0$=0.75 $\times 10^{-2}$ mole/l.
Vertical scale: ΔOD/div =0.01, Horizontal scale: 5 msec/div. An upper line shows a flow signal.

Kinetic measurements for the formation of (V) were carried out spectrophotometrically in the region of wavelength, 410~560 nm. When sulphite ion was less than 0.016 mole/l, the kinetic curve for the formation of (V) obeyed the first-order rate equation. The observed rate constant, $1/\tau_1$, was almost constant despite the different wavelength within the experimental error. A representative oscilloscope trace is shown in Fig. 2. The pseudo first-order rate constant, $1/\tau_1$, was linearly related to the initial concentration of sodium sulphite as shown in Fig. 3, where all the rate constants were determined from the measurements at 443 nm. Since $[Na_2SO_3]_0 \gg [TNA]$ in all runs, $1/\tau_1$ can be expressed by Eq. (2), taking reaction (1) into account.

$$\frac{1}{\tau_1}=k_1[Na_2SO_3]_0+k_{-1}. \tag{2}$$

At each temperature, k_1 and k_{-1} were obtained from the slope and the intercept, respectively, and the

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equilibrium constant K_1 ($=k_1/k_{-1}$) was calculated. These are listed in Table 1, where K_1 is in good accord with that determined separately by NMR spectroscopy.

Table 1 Rate constants k_1, k_{-1} and equilibrium constant K_1 for the formation of complex (V)

Temp. (°C)	k_1 (l mole^{-1} sec^{-1})	k_{-1} (sec^{-1})	$K_1=k_1/k_{-1}$ (l mole^{-1})
15.0	$(3.83\pm0.10)\times10^3$	13.8 ± 1.6	$(2.78\pm0.35)\times10^2$
20.0	$(4.70\pm0.32)\times10^3$	22.0 ± 2.3	$(2.14\pm0.36)\times10^2$
			$(2.1\pm0.3)\times10^2$ [a]
25.0	$(6.69\pm0.24)\times10^3$	32.0 ± 2.3	$(2.09\pm0.24)\times10^2$
30.0	$(8.40\pm0.41)\times10^3$	50.0 ± 4.1	$(1.68\pm0.22)\times10^2$

a) Reference 8, determined by NMR spectra

There appears no significant effect of ionic strength in the range, $\mu=0.045\sim0.15$. The similar insensitivity to ionic strength was also found in σ-complex formation from TNB and sulphite ion[9]. This fact is well understood because the reaction takes place between a neutral molecule and an ion.

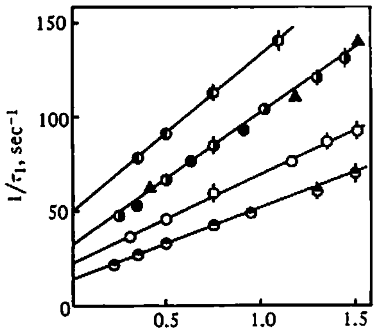

Fig. 3 Pseudo first-order rate constant, $1/\tau_1$, as a function of $[Na_2SO_3]_0$
◐: 30.0°C, ◑: 25.0°C,
●: 25.0°C $\mu=0.045$,
▲: 25.0°C $\mu=0.15$,
○: 20.0°C, ◓: 15.0°C

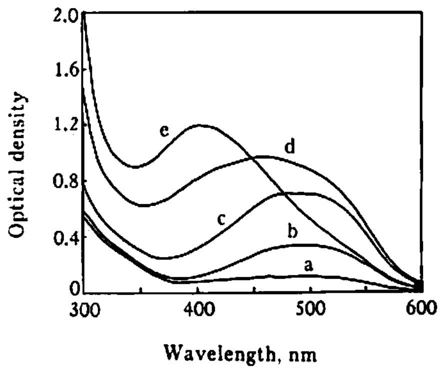

Fig. 4 Absorption spectra of PS^- (4.4×10^{-4} mole/l) in the presence of the following concentration (in mole/l) of Na_2SO_3 in water
(a): 0.02, (b): 0.05, (c): 0.10,
(d): 0.20, (e): 0.40

Reactions of PS^- with SO_3^{2-}

The NMR spectra of PS^- in water in the presence of sodium sulphite (*ca.* 0.1 mole/l) showed the bands owing to complex (VI); $-\delta=6.10$ (d 1H) and 8.35 (d 1H). This spectrum could be attributed to the adduct (VI). The visible absorption spectra of solutions containing PS^- and sodium sulphite are shown in Fig. 4, which indicate, at least, the presence of two interactions. Increasing the concentrations of sodium sulphite up to 0.1 mole/l caused an increase of optical density with broad maximum at about 500 nm. A second interaction occurred with increasing sulphite ion concentration above 0.2 mole/l. The 1:1 stoichiometry of the complex with maximum at 500 nm was preliminarily also confirmed by

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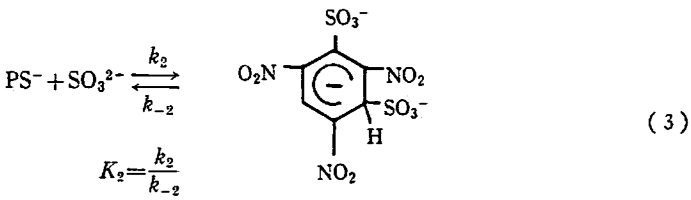
the continuous variation plot[12].

Equilibrium measurement: The equilibrium at low sulphite ion concentration was studied spectrophotometrically.



(VI)

Based on Eq. (3), the Benesi-Hildebrand relationship[13] could be applied to a series of solutions in which one of the components (sodium sulphite in this case) was in considerable excess.

$$\frac{a}{\mathrm{OD}}=\frac{1}{K_2\varepsilon l}\times\frac{1}{b}+\frac{1}{\varepsilon l}, \tag{4}$$

where a is the constant initial concentration of PS^-, b is the varied initial concentration of sodium sulphite, OD is the optical density for l cm light path length, ε is the molar extinction coefficient of the complex, and K_2 is, of course, equilibrium constant. The typical plots are shown in Fig. 5, at 25.0°C. The linearity is quite satisfactory: hence values of K_2 and ε can be calculated from the slopes and intercepts at each ionic strength. In this study $l=0.20$ cm and the values of ε was almost constant, 1.0×10^4 l mole^{-1} cm^{-1}, despite different temperature and various ionic strength. These results are in

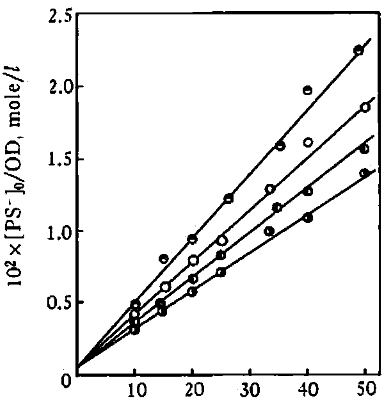


Fig. 5 Benesi-Hildebrand plot for equilibrium (3) at the following ionic strength
◓: 0.15, ○: 0.30,
◐: 0.45, ◑: 0.75

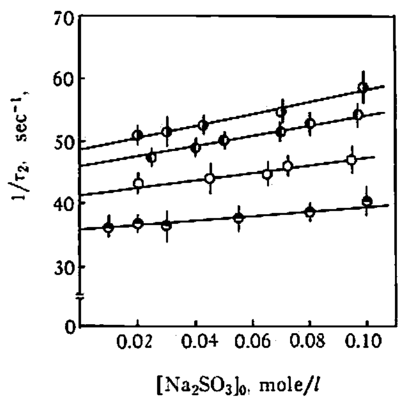


Fig. 6 Pseudo first-order rate constant, $1/\tau_2$, as a function of [Na_2SO_3]$_0$ at various ionic strength (25.0°C).
Symbols represent the same as those in Fig. 5

12) P. Job, *Compt. Rend.*, **180**, 928 (1925)
13) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949)

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Table 2 Rate and equilibrium constants for the formation of complex (VI)

Temp. (°C)	Ionic strength[a] μ	k_2 ($l\ mole^{-1}\ sec^{-1}$)	k_{-2} (sec^{-1})	$K_{2(kinetic)}$[b] ($l\ mole^{-1}$)	$K_{2(equil.)}$[c] ($l\ mole^{-1}$)
15.0	0.30	23.2± 7.0	12.7±2.1	1.83±0.74	1.49±0.15
20.0	0.30	33.5± 9.0	25.1±3.0	1.33±0.50	1.51±0.10
25.0	0.15	41.5± 6.9	35.7±1.4	1.61±0.25	1.11±0.15
	0.30	57.6± 5.1	41.4±1.3	1.39±0.16	1.39±0.14
	0.45	78.3±11.5	46.5±2.3	1.68±0.31	1.58±0.10
	0.75	94.4±11.5	48.8±2.3	1.93±0.32	1.88±0.10
30.0	0.15	69.1± 8.0	52.0±1.5	1.33±0.19	1.14±0.10
	0.30	92.1±12.0	56.7±2.6	1.62±0.30	1.48±0.12
	0.75	115 ±13	61.7±2.6	1.86±0.27	1.87±0.10

a) Ionic strength was maintained by adding Na_2SO_4. The concentration of Na_2SO_3 was 0.010～0.100 mole/l.

b) K_2 was calculated as k_2/k_{-2}.

c) K_2 was determined spectrophotometrically by a separate method.

the last column of Table 2.

Kinetic measurement: The kinetic curve for the formation of (VI) obeyed the first-order rate equation at low sulphite concentration. The pseudo first-order rate constant, $1/\tau_2$, measured at 500 nm slightly increased with increasing sulphite concentration. The linear relationship expressed by Eq. (5) can be undertaken, based on reaction (3).

$$\frac{1}{\tau_2}=k_2[\mathrm{Na_2SO_3}]_0+k_{-2}. \tag{5}$$

The experimental results were approximately related to a straight line according to equation (5) as shown in Fig. 6. The numerical values of k_2 and k_{-2} were read from the graph and they were listed in Table 2. The uncertainty accompanied with K_2 calculated from k_2 and k_{-2} is larger than that from static equilibrium determination. However, the agreement between the results determined by the separate methods is quite satisfactory.

Effect of ionic strength: The value of K_2 increased with increasing ionic strength. These changes are no doubt largely due to the changes in the activity coefficients of the charged species in aqueous ionic solutions. The equilibrium constant, K_2^0 at zero ionic strength has to be expressed as

$$K_2^0=K_2\times\frac{f(\mathrm{VI})}{f(\mathrm{PS}^-)\cdot f(\mathrm{SO_3}^{2-})}, \tag{6}$$

where f's are the activity coefficients of respective species. Here, the Debye-Hückel equation (7) was applied.

$$\log f_i=\frac{-Az_i^2\sqrt{\mu}}{1+Ba\sqrt{\mu}}. \tag{7}$$

One may imagine that the ion size parameter, a, will be variable depending on respective ions. How-

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ever, the quantity a was implicitly assumed to be the same for all pairs of ions[14], when it was introduced. It does not seem so unreasonable to take the mean value of a for all anionic species in the present study[8]. Calculating used with the parameters at 25°C, $A=0.511\, l^{1/2}$ mole$^{-1/2}$, $B=0.329\times 10^8$ cm^{-1} $l^{1/2}$mole$^{-1/2}$[14], and $a=3.65\times 10^{-8}$cm[15] which is similar to that required by sodium sulphate, one can take the form:

$$\log K_2 = \log K_2{}^0 + \frac{2.04\sqrt{\mu}}{1+1.20\sqrt{\mu}}. \tag{8}$$

The experimental data give a straight line with a slope 1.5 in the plot of $\log K_2$ against $\sqrt{\mu}/(1+1.20\sqrt{\mu})$ as shown in Fig. 7. A similar plot for the formation constant of 1:2 adduct complex from TNB and sulphite ion was linear with slope 4.2, in agreement with that expected (4.06)[8].

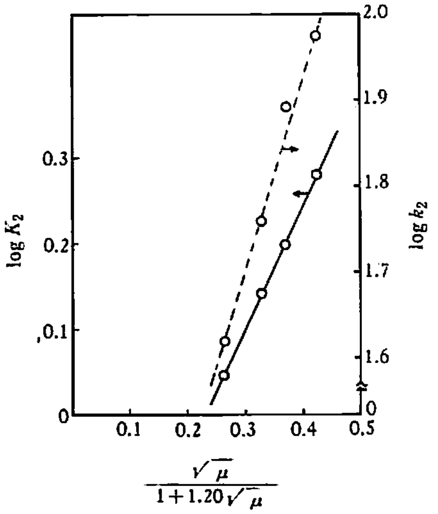


Fig. 7 Variations of K_2 and k_2 with ionic strength

The same account can be applied to the reaction rate of complex formation. The rate constant at constant temperature can be formulated, on the assumption that the reacting ions and the activated complex are all spherical with symmetrically distributed charges[16], and neglecting the non-electrostatic term,

$$\log k_2 = \log k_2{}^0 + \frac{z_1 z_2 A\sqrt{\mu}}{1+Ba\sqrt{\mu}}, \tag{9a}$$

where $k_2{}^0$ is the rate constant at zero ionic strength, and z_1 and z_2 are the charges of reacting ions. An unjustified but simplifying assumption was made that a mean value a was taken for the distance of closest approach of various ions. By using the same values for A, B and a as in the treatment of

14) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", 2nd ed., p. 235, 468, Butterworths, London (1957)
15) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941)
16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", p. 426, McGraw-Hill Book Company, Inc., N. Y. and London (1941)

equilibrium constant, we have Eq. (9b).

$$\log k_2 = \log k_2^0 + \frac{2.04\sqrt{\mu}}{1+1.20\sqrt{\mu}}. \tag{9b}$$

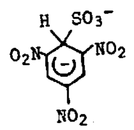
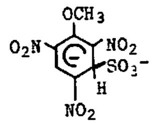
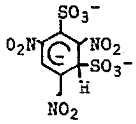
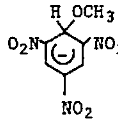
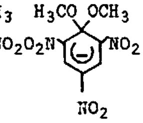
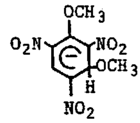
The prediction was verified semiquantitatively for the present case as shown in Fig. 6: the slope of the straight line was 2.3.

For the reverse reaction the electrostatic effect due to ionic strength on k_{-2} would be expected to be quite slight or negligible because the reaction is unimolecular[16]. However, in the present case, k_{-2} increased with increasing ionic strength. No successful account can be taken as yet, though it may be suggested that a more strict treatment with more experimental data should be necessary, including the consideration for the non-electrostatic effects on the activity coefficient of ionic species.

Energetic consideration

Strauss has suggested that anionic sulphite, as doubly charged, should have a much greater solvation requirement than methoxide or cyanide ion so that the steric hindrance to attack at a ring-substituted position will be severe[5]. However, the steric term was found to be not so important. The value of $\Delta S^{\ddagger}$ for sulphite attack at a non-substituted position is much the same as that at a substituted one, in the reaction of picrylchloride with sulphite ion[15]. The same can be said for the methoxide attack to TNA. Kinetic and thermodynamic parameters are summarized in Table 3 together with the results obtained from other workers. There appear some similarities for the sulphite

Table 3 Kinetic and thermodynamic parameters for σ-complex formation reactions at 25.0°C

	 (IV)[a]	 (V)[b]	 (VI)[b,e]	 (I)[c]	 (II)[d]	 (III)[d]
$\overrightarrow{k}$ (l mole^{-1} sec^{-1})	$(3.70\pm0.02)\times10^4$	$(6.69\pm0.24)\times10^3$	$57.6\ \pm5.1$	7.05×10^3	17.3	950
$\overleftarrow{k}$ (sec^{-1})	$115\ \pm\ 9$	$32.0\pm\ 2.3$	$41.4\ \pm1.3$	305	1.03×10^{-3}	350
K (l mole^{-1})	$322\ \pm45$	$209\ \pm24$	1.39 ± 0.14[f]	23.1	1.70×10^4	2.71
$\overrightarrow{\Delta H^{\ddagger}}$ (kcal mole^{-1})	$7.5\pm\ 0.8$	$9.1\pm\ 0.7$	$16.1\ \pm2.1$	10.2 ± 0.8	12.9 ± 1.0	10.4 ± 1.0
$\overleftarrow{\Delta H^{\ddagger}}$ (kcal mole^{-1})	$11.4\pm\ 1.0$	$14.1\pm\ 2.1$	$16.8\ \pm4.0$	9.2 ± 0.8	18.4 ± 1.0	8.2 ± 0.5
$\overrightarrow{\Delta S^{\ddagger}}$ (e. u.)	$-12.6\pm\ 1.8$	$-10.8\pm\ 2.0$	$3.3\ \pm2.2$	-6.7 ± 2.7	-9.4 ± 3.4	-10.8 ± 3.4
$\overleftarrow{\Delta S^{\ddagger}}$ (e. u.)	$-11.4\pm\ 3.4$	$-4.6\pm\ 4.1$	$4.8\ \pm3.5$	-16.3 ± 2.7	-4.8 ± 3.4	-19.3 ± 1.7
ΔH° (kcal mole^{-1})	$-3.9\pm\ 1.8$	$-5.0\pm\ 2.8$	$-0.7\ \pm6.1$[f]	1.0 ± 1.6	-5.5 ± 2.0	2.2 ± 1.5
ΔS° (e. u.)	$-1.2\pm\ 5.2$	$-6.2\pm\ 6.1$	$1.5\ \pm5.7$[f]	9.6 ± 5.4	-4.6 ± 4.0	8.5 ± 5.1

a) Reference 9, b) This work, c) Reference 7b, d) Reference 7a, e) At ionic strength $\mu=0.30$, f) Equilibrium constant K was determined by a static method but ΔH° and ΔS° were calculated from activation parameters.

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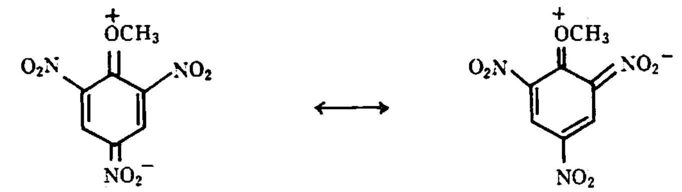
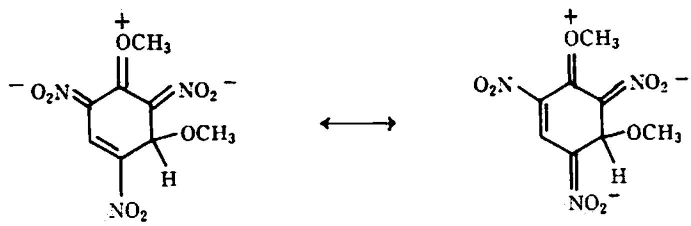
attack on the one hand and for methoxide attack on the other, at the unsubstituted positions of TNB and TNA. The rate constant $\overrightarrow{k}$ and the equilibrium constant K for 1,3-complex formation from TNA are somewhat smaller than those from TNB. Bernasconi has first discussed the reasons for the difference between the reactivities to form (II) and (III)[7]. The main factor attributed by him is considerable ground state stabilization through resonance involving the methoxy group in TNA, and in complex (III).





However, such resonance stabilization is not expected in either TNB or (II). Along these accounts the higher $\overrightarrow{\Delta H}^{\neq}$ for (III) and (V) compared with (I) and (IV) respectively, might be attributed to the loss of part of the resonance stabilization in proceeding from TNA to the complexes: the resonance stabilization would not be conserved so much as expected by Bernasconi's postulate.

The smaller values of $\overrightarrow{k}$ and K for the formation of (VI) are reasonable, considering the negative charge carried by picrylsulphonate ion. The higher $\overrightarrow{\Delta H}^{\neq}$, $\overleftarrow{\Delta H}^{\neq}$, $\overrightarrow{\Delta S}^{\neq}$ and $\overleftarrow{\Delta S}^{\neq}$ compared with those of other complexes suggest that the considerable desolvation is accompanied with the activation process. Further considerations should be met with the data extrapolated to zero ionic strength and with the results for other charged substrates.

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