# Kinetic and Thermodynamic Studies of the Reactions of Sulfite Ion with Picramide, N-Methylpicramide, and N,N-Dimethylpicramide in Aqueous Solution

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The kinetics of the reactions between sulfite ion and picramide, N-methylpicramide, and N,N-dimethylpicramide, to form 1:1  $\sigma$ -complexes in aqueous solutions of constant ionic strength 0.14 M, have been investigated using a stopped-flow spectrophotometer. Specific rate constants for the formation and decomposition of these three complexes at 25.0 °C are 5.7  $\pm$  0.2 × 10<sup>4</sup>  $M^{-1}$  s<sup>-1</sup> and 7  $\pm$  1 s<sup>-1</sup>, 1.4  $\pm$  0.1 × 10<sup>4</sup>  $M^{-1}$  s<sup>-1</sup> and 0.20  $\pm$  0.02 s<sup>-1</sup>, and 4.1  $\pm$  0.2 × 10<sup>3</sup>  $M^{-1}$  s<sup>-1</sup> and 0.14  $\pm$  0.04 s<sup>-1</sup>, respectively. Enthalpies and entropies of activation characterizing the formation of the 1:1  $\sigma$ -complexes have been determined. Equilibrium constants, determined spectrophotometrically at a number of temperatures, have been used to calculate the enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) changes associated with 1:1 and 2:1  $\sigma$ -complex formation. These values are compared with corresponding ones for complex formation of sulfite ion with 1,3,5-trinitrobenzene and 2,4,6-trinitrobenzaldehyde. The extent of solvation of the  $\sigma$ -complexes is considered to play a primary role in determining the observed trends in the enthalpies and entropies of reaction.

On a étudié à l'aide d'un spectrophotomètre à débit interrompu la cinétique des réactions entre l'ion sulfite et la picramide, la *N*-méthylpicramide et la *N*,*N*-diméthylpicramide; ces réactions conduisent à des complexes- $\sigma$  1:1 dans des solutions aqueuses de force ionique constante 0.14 *M*. Les constantes spécifiques de vitesse pour la formation et la décomposition de ces troix complexes à 25.0 °C sont respectivement égales à 5.7  $\pm$  0.2  $\times$  10<sup>-4</sup>  $M^{-1}$  s<sup>-1</sup> et 7  $\pm$  1 s<sup>-1</sup>, 14  $\pm$  0.1  $\times$  10<sup>4</sup>  $M^{-1}$  s<sup>-1</sup> et 0.20  $\pm$  0.02 s<sup>-1</sup>, 4.1  $\pm$  0.2  $\times$  10<sup>3</sup>  $M^{-1}$  s<sup>-1</sup> et 0.14  $\pm$  0.04 s<sup>-1</sup>. On a déterminé les enthalpies d'activation caractérisant la formation des complexes- $\sigma$  1:1. Les constantes d'équilibre, déterminées spectrophotométriquement à différentes températures, ont été utilisées afin de calculer les changements d'enthalpie ( $\Delta H^0$ ) et d'entropie ( $\Delta S^0$ ) associés à la formation des complexes- $\sigma$  1:1 et 2:1. Ces valeurs sont comparées à celles obtenues lors de la formation des complexes de l'ion sulfite avec le trinitro-1,3,5 benzène et le trinitro-2,4,6 benzaldé-hyde. On considère que le degré de solvatation des complexes- $\sigma$  joue un rôle important dans la détermination des tendances observées dans les enthalpies et les entropies de réaction.

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#### Introduction

The formation of colored species as a result of the reactions of aqueous sodium sulfite solutions with nitroaromatic compounds has been known for some time (1). Early studies of the 1,3,5-trinitrobenzene - sulfite ion interaction were concerned with ascertaining the nature, the composition(s), and spectral properties of the colored species and determining the equilibrium constants and thermodynamic parameters associated with their formation (2-5). Proton magnetic resonance studies of the reactions of sulfite ion with a number of 1-X-2,4,6-trinitrobenzenes  ${X = H, OH, OCH_3, NH_2, NHCH_3, N(CH_3)_2,}$  $NHC_6H_5$ , and  $NCH_3(C_6H_5)$  in water and aqueous dimethylsulfoxide solutions clearly established the colored species as  $\sigma$ -complexes

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(5-8). The complexes of 1:1 stoichiometry were found to have structure 1 whereas those of 2:1 stoichiometry were found to have structure 2.



 $NHCH_3$ ,  $N(CH_3)_2$ ,  $NH(C_6H_5)$ ,  $NCH_3(C_6H_5)$ 

For  $X \neq H$ , there was no evidence for the existence of either 1:1 or 2:1  $\sigma$ -complexes containing the sulfite ion bonded at the C-1 position. Recent studies have shown that  $\sigma$ -complexes with structures **3** and **4** exist when X = CHO(9).



As part of a series of kinetic and equilibrium studies of the reactions of nitroaromatic compounds and bases (9–11) we have investigated the reactions of sulfite ion with picramide, *N*-methylpicramide, and *N*,*N*-dimethylpicramide. We have determined the specific rate constants and activation parameters for the formation of the 1:1  $\sigma$ -complexes as well as the thermodynamic parameters associated with 1:1 and 2:1  $\sigma$ -complex formation in these systems.

#### Experimental

Reagents

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Sodium sulfite and potassium nitrate were both A.R. grade reagents (Fisher Scientific) and were used as received. Picramide (K & K Laboratories) was recrystallized from absolute ethanol and dried to constant weight in vacuo over phosphorus(V) pentoxide, melting point, 192-195 °C (12). N-Methylpicramide was prepared by adding an excess of methylamine in ethanol to a 5% solution of picryl chloride in ethanol and evaporating the resulting solution to dryness. The solution formed by extraction of the residue with acetone was filtered to remove the insoluble methylammonium chloride and evaporated to dryness. The resulting solid was recrystallized to constant melting point from absolute alcohol. After drying in vacuo over phosphorus(V) pentoxide, the product had a melting point 114-115 °C (13). N,N-Dimethylpicramide was prepared in exactly the same manner as N-methylpicramide but using dimethylamine as the base. The product, after repeated recrystallization from absolute ethanol and drying to constant weight in vacuo over phosphorus(V) pentoxide, had a melting point of 138 °C (13). All other reagents used were A.R. grade or better.

Doubly distilled and deionized water was boiled for approximately 30 min to remove dissolved gases, then allowed to cool to room temperature and stored under a nitrogen atmosphere.

Stock solutions of picramide, N-methylpicramide, and N,N-dimethylpicramide ( $\sim 2 \times 10^{-2} M$ ) were prepared by dissolving a weighed amount of the dried compound in a known volume of acetone. Solutions used in the kinetics and equilibrium studies were freshly prepared prior to use by appropriate dilution (usually 0.10 to 100 ml) of an aliquot of the stock solution with 0.14 M aqueous potassium nitrate solution.

Sodium sulfite and potassium nitrate stock solutions were prepared by dissolving weighed quantities of each reagent in known volumes of water. Both stock solutions were always prepared immediately prior to use. The composition of the stock sodium sulfite solution was determined by iodimetric titration (14). Sodium sulfite solutions used in the kinetic and equilibrium studies were prepared by dilution of the stock solution with 0.14 *M* potassium nitrate solution. The p*H* values of the stock solutions and the solutions used in the equilibrium and kinetic studies were checked with a p*H* meter, and if required adjusted to p*H* 9.00 by the addition of  $2 \times 10^{-3} M$  sodium hydroxide. The amount of base added was generally so small that neither the concentration nor the ionic strength of the solution was affected by this procedure.

#### Instruments

Kinetic measurements were carried out on a Durrum-Gibson stopped-flow spectrophotometer.<sup>2</sup> A closed circuit temperature control system utilizing an Ultra Kryomat TK30D constant temperature bath kept the temperature in the valve-block, drive syringes, and observation cell constant to within ±0.1 °C. Temperaturejump or conventional stopped-flow cells of 2.0 cm path length were used. Minimum "dead times" of the two cells were 10 and 2 ms, respectively. For most of the kinetic runs the normal mode of operation of the stopped-flow spectrophotometer was modified so as to yield an oscilloscope trace of absorbance as a function of time rather than % transmittance as a function of time (15). Standard solutions of potassium permanganate, whose absorbances at several different wavelengths had been determined on the Cary 14, were used to establish that the input signal to the vertical axis of the storage oscilloscope was directly related to absorbance over the range 0 to 0.10 absorbance units. One advantage of this method of operation was that, over the range indicated, absorbances could be determined accurately at very low noise to signal ratios.

In the equilibrium studies optical measurements were carried out on a Beckman DU and a Cary 14 recording spectrophotometer using matched silica cells of 1.0 cm path length. In both cases the temperature in the cells was maintained constant to  $\pm 0.1$  °C by circulating water from a constant temperature bath through a specially designed cell holder in the spectrophotometer.

Measurements of pH were carried out with an EIL Model 23A pH meter. Calibration of the pH meter with standard buffer solutions of pH 7.40  $\pm$  0.02 and pH 10.00  $\pm$  0.02 at 25 °C was performed prior to each measurement.

#### Procedures

#### Kinetic Studies

Solutions containing the nitroaromatic compound at approximately  $2 \times 10^{-5} M$  and sodium sulfite were prepared immediately prior to the kinetic run by dilution of known volumes of the corresponding stock solutions with 0.14 M potassium nitrate solution. Prior to each run the drive syringes were rinsed three times with the appropriate solution, filled to capacity and allowed to stand 20 min to reach thermal equilibrium with the bath. In the course of the kinetic measurements the concentration of the nitroaromatic compound was generally kept constant, and therefore only the sodium sulfite solutions

<sup>2</sup>Durrum Instrument Corporation, Palo Alto, Calif.

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were changed. Each time this was done the appropriate drive syringe was flushed thoroughly with the new sodium sulfite solution before being filled for the kinetic run.

Kinetic runs were monitored by following changes in absorbance at a number of wavelengths. Traces on the storage oscilloscope of absorbance vs. time were recorded photographically when at least two consecutive runs gave identical traces. The kinetic curves were then transferred from the photographs to centimeter graph paper. Absorbances at different times, taken from the graph paper, were used to construct plots of  $\ln (A_{\infty} - A_i)$  vs. time  $(A_{\infty}$  and  $A_i$  refer to absorbances at times infinity and t, respectively). The slopes of these plots yielded pseudo first-order rate constants  $k_{obs}$ . Within experimental error  $k_{obs}$  values, calculated using absorbance data collected at a number of different wavelengths, were equal.

Equilibrium Studies

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A 1.0-cm cell containing 3.00 ml of 0.14 M potassium nitrate solution was placed in the thermostatted cell compartment of the spectrophotometer and allowed to come to thermal equilibrium with the compartment. Stock solutions of sodium sulfite and the nitroaromatic compound were added by means of Micrometer syringes,<sup>3</sup> the solution thoroughly mixed, and the values of absorbance measured at a number of preselected wavelengths. Absorbances were always checked as a function of time to ensure that equilibrium absorbance values were being measured. (Fading reactions can occur in these systems particularly at high temperatures and at high sulfite ion concentrations.)

## Treatment of Data Obtained in the Equilibrium Studies

For the systems under investigation both 1:1 and 2:1  $\sigma$ -complexes are formed in aqueous solution (5). The formation reactions can be written as follows:

[1] Nitroaromatic + SO<sub>3</sub><sup>2-</sup> 
$$\rightleftharpoons$$
 1:1  $\sigma$ -Complex (C)  
 $K_2$ 

[2] 
$$C + SO_3^{2-} \rightleftharpoons 2:1 \sigma$$
-Complex (D)

The equilibrium expressions associated with the formation of  ${\bf C}$  and  ${\bf D}$  are

$$[3] K_{1} = \frac{[C]}{[N][S]} = \frac{[C]}{\{[N]_{0} - [C] - [D]\}\{[S]_{0} - [C] - 2[D]\}}$$
  
and  
$$[4] K_{2} = \frac{[D]}{[C][S]} = \frac{[D]}{[C]\{[S]_{0} - [C] - 2[D]\}}$$

where [C], [D], [N], and [S] represent the equilibrium concentrations of 1:1  $\sigma$ -complex, 2:1  $\sigma$ -complex, uncomplexed nitroaromatic, and uncomplexed sulfite ion, respectively. [N]<sub>0</sub> and [S]<sub>0</sub> represent the total concentrations of nitroaromatic compound and sodium sulfite in solution.

The experimental approach best suited to obtaining the most reliable values of  $K_1$ ,  $K_2$ , and the molar extinction coefficients  $\varepsilon_c$  and  $\varepsilon_p$  is dictated by the magnitudes of  $K_1$  and  $K_2$ , the ratio of  $K_2$  to  $K_1$ , and the absorp-

<sup>3</sup>Roger Gilmont Instruments, Inc., Great Neck, N.Y.

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tion characteristics of the nitroaromatic compound and the 1:1 and 2:1  $\sigma$ -complexes that it forms. Because the procedures used in the study of the three systems were different they are briefly outlined.

#### (i) Picramide (P) – Sulfite Ion System

For this system  $K_1$  is large, the ratio  $K_2$  to  $K_1$  is very small, and only C absorbs at 480 nm.

A series of solutions were prepared containing a fixed concentration of picramide ( $\sim 1 \times 10^{-5} M$ ) and a range of sodium sulfite concentrations such that the ratio [C]/[N] was always greater than 100. The absorbance (A) of each solution was measured at 480 nm and this value of A used in an iterative procedure, based on eq. 5 to calculate the best values of both  $K_1$  and  $\varepsilon_c$ .

$$[5] \qquad \qquad \epsilon_{\rm C} = \frac{A}{[{\rm N}]_0} \left(1 + \frac{[{\rm N}]}{[{\rm C}]}\right)$$

Alternatively K and  $\varepsilon_c$  could be obtained from Benesi-Hildebrand type plots of  $[N]_0/A vs. 1/[S]_0$  (16). The above process was repeated using solutions of different initial concentrations of picramide. In all cases the range of sodium sulfite concentrations was chosen so as to keep the maximum conversion of 1:1  $\sigma$ -complex to 2:1  $\sigma$ -complex at less than 0.2% (e.g., the maximum  $[SO_3^{2-}]_0$ was  $4.9 \times 10^{-3} M$  at T = 50.1 °C).

Attempts to operate at high  $[N]_0$  to  $[S]_0$  ratios in order to effect a complete conversion of sulfite ion to the 1:1  $\sigma$ -complex were unsuccessful due to the low solubility of picramide in aqueous solution.

### (ii) N-Methylpicramide (NMP) - Sulfite Ion System

For this system both  $K_1$  and  $K_2$  are large and the ratio of  $K_2$  to  $K_1$  is ~0.02. N-Methylpicramide and both  $\sigma$ -complexes absorb at 480 nm.

In solutions of constant NMP concentration ( $\sim 1 \times 10^{-4} M$ ) there was no observable effect on the visible absorption spectrum when the sulfite ion concentration was increased from 0.10 to 0.50 *M*. Therefore the molar extinction coefficient of the 2:1  $\sigma$ -complex ( $\varepsilon_D$ ) was determined by measuring the absorbances at different wavelengths of a series of solutions of fixed sodium sulfite concentration (0.50 *M*) and varying NMP concentrations over the range 7  $\times 10^{-5}$  to 3  $\times 10^{-4} M$ .

To measure  $\varepsilon_c$ , the absorbances at 480 nm were measured for a series of solutions containing a fixed NMP concentration (~6 × 10<sup>-5</sup> M) and varying sodium sulfite concentrations in the range 1 × 10<sup>-5</sup> to 2 × 10<sup>-4</sup> M. Under these reaction conditions the measured absorbance (A) is the sum of the absorbances due to C ( $A_c$ ) and unreacted NMP { $A_{NMP} = \varepsilon_{NMP}[NMP]$ }. The value of  $A_c$  was calculated and plotted against [S]. Based on the equilibrium expressions [3] and [4] it can be shown that the maximum absorbance in such a plot is related to  $K_1$ ,  $K_2$ , [N]<sub>0</sub>, and  $\varepsilon_c$  as follows:

$$\varepsilon_{\rm C} = \frac{(A_{\rm C})_{\rm max}}{X_{\rm max}[{\rm N}]_0}$$

where

[6]

] 
$$X_{\text{max}} = \frac{\sqrt{K_1/K_2}}{2 + \sqrt{K_1/K_2}} = \frac{[C]_{\text{max}}}{[N]_0}$$

In order to determine  $K_2$ , absorbances at 480 nm were determined for a series of solutions containing different

[12]

NMP concentrations ( $\sim 1 \times 10^{-4} M$ ) and sodium sulfite concentrations over the range  $1 \times 10^{-3}$  to  $3 \times 10^{-2}$  M. The concentration of NMP was chosen to give a range of absorbance values from 0.10 to 0.50.  $K_2$  was calculated using the expression

[8] 
$$\frac{1}{A - \{[C] + [D]\}\varepsilon_{D}}$$
$$= \frac{1}{[N]_{0}(\varepsilon_{C} - \varepsilon_{D})} \{K_{2}[S] + 1\}$$

Under the experimental conditions  $[C] + [D] \simeq [N]_0$ and  $[S] = [S]_0 - [N]_0$ . An iterative procedure using a "least-squares" computer program was utilized to obtain the best values of  $K_2$  consistent with the known  $\varepsilon_c$  and  $\varepsilon_p$ values and the measured values of A.

In order to determine  $K_1$ , absorbances at 480 nm were measured for a series of solutions containing NMP  $(5 \times 10^{-5} \text{ to } 1.1 \times 10^{-4} \text{ } M)$  and various sulfite ion concentrations over the range  $5 \times 10^{-5}$  to  $1.5 \times 10^{-4}$  M. Under these reaction conditions the measured absorbance (A) is due to absorbance by both C and unreacted NMP, i.e.,

$$[9] A_{\rm C} = A - \varepsilon_{\rm N}[{\rm N}]$$

An approximate value of [C] was obtained from the relation  $[C] = A/\varepsilon_{C}$ 

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while the [D] was calculated using the expression

[11] [D] = 
$$\frac{K_2[C][S]_0 - K_2[C]^2}{2K_2[C] + 1}$$

and approximate values of [N] and [S] evaluated. Equations 9, 10, and 11 were then used iteratively to obtain the best values of  $\varepsilon_c$ ,  $A_c$ , [N], [C], and [D].  $K_1$  was then calculated using eq. 3.

(iii) N,N-Dimethylpicramide (DMP) -- Sulfite Ion System For this system  $K_1$  and  $K_2$  are both large and the ratio  $K_2/K_1$  is > 2 over the temperature range 0 to 50 °C. As a

result all three species DMP, C, and D are present in appreciable amounts over most of the workable sodium sulfite and DMP concentration ranges.

The molar extinction coefficients of DMP at 350, 420, and 490 nm were measured in aqueous solutions of constant ionic strength 0.14 M (KNO<sub>3</sub>).

The molar extinction coefficients of D at 350, 420, and 490 nm were obtained from absorbance measurements on solutions containing a range of DMP concentrations  $(3 \times 10^{-5} \text{ to } 1.4 \times 10^{-4} \text{ M})$  and 0.10 M in sulfite ion. There was no observable effect on the recorded absorbances in the visible region when the sulfite ion concentration was increased beyond 0.10 M.

Molar extinctions of C at 350, 420, and 490 nm were obtained from stopped-flow traces of % transmittance vs. time for solutions containing  $\sim 1 \times 10^{-5} M$  DMP and  $2 \times 10^{-2}$  M sodium sulfite. The sulfite concentration was sufficiently large that, in the absence of reaction to form D, all the added DMP would be converted to C. Experimentally the rate of the reaction  $DMP + SO_3^{2-} \rightarrow C$  is very much faster than the conversion of C to D. As a result the absorbance value at infinite time recorded for the first reaction taking place in solution could be attributed exclusively to absorbance by C. Because of the method of determining  $\varepsilon_c$  the error limits on  $\varepsilon_c$  are higher than the error limits on  $\varepsilon_N$  and  $\varepsilon_D$  at the same wavelength.

Absorbance measurements at 350, 420, and 490 nm were then carried out on solutions of varying sodium sulfite and DMP concentration. At a given wavelength the absorbance A is given by the expression

$$A = \varepsilon_{\rm N}[{\rm N}] + \{{\rm C}]\varepsilon_{\rm C} + [{\rm D}]\varepsilon_{\rm D}$$

With three absorbance values at three wavelengths and known values of  $E_N,\,\epsilon_C,\,and\,\epsilon_D$  at these wavelengths, the three quantities [N], [C], and [D] could be calculated.  $K_1$  and  $K_2$  were then evaluated using eqs. 3 and 4.

#### **Results and Discussion**

Kinetics of  $\sigma$ -Complex Formation

Under the conditions employed in our studies, sulfite ion reacts reversibly with the nitroaromatic compounds (N) being discussed to form 1:1 and 2:1  $\sigma$ -complexes according to eqs. 1 and 2. In all the systems the reaction to form the 2:1  $\sigma$ -complex (D) was very slow compared to the reaction leading to the formation of the 1:1  $\sigma$ -complex (C). As a result reliable values of  $A_{\infty}$  could be obtained even at very high sulfite ion concentrations where the 2:1  $\sigma$ -complex D would be the predominant species at equilibrium. Over the entire range of sulfite ion concentrations employed, plots of  $\ln (A_{\infty} - A_{i}) vs$ . time were linear to at least 90% completion of the reaction.

For the reversible formation of C according to eq. 1, studied under conditions such that  $[SO_3^{2^-}]_0 \gg [N]_0$ ,  $k_{obs}$  is related to the specific rate constants  $k_{\rm f}$  and  $k_{\rm b}$  as follows:

13] 
$$k_{obs} = k_f [SO_3^{2^-}]_0 + k_b$$

where  $K_1 = k_f/k_b$ . In all systems values of  $k_{obs}$ were independent of  $[N]_0$  and  $k_{obs}$  vs.  $[SO_3^{2}]_0$ plots were linear over the entire range of sodium sulfite concentrations used in the experiments. Values of  $k_{\rm f}$ , obtained from the slopes of the  $k_{\rm obs}$ vs.  $[SO_3^{2}]_0$  plots, are presented for the three systems in Tables 1, 2, and 3. In all cases the intercepts of the  $k_{obs}$  vs.  $[SO_3^{2^-}]_0$  plots were small. As a result  $k_b$  could not be determined in this way with a high degree of accuracy. The largest values of  $k_{\rm b}$  were observed in the picramide-sulfite system. For purposes of comparison  $k_{obs}$  values, obtained from the intercepts and values of  $k_{\rm f}/K_1$  for this system, are given in Table 1. Clearly the ratio  $k_f/K_1$  yields a much more reliable value of  $k_{\rm b}$ . In the N-methylpicramide - sulfite and N,N-dimethylpicramide - sul-

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TABLE 1. Specific rate constants for the formation  $(k_t)$ and decomposition  $(k_b)$  of the 1:1 picramide – sulfite ion  $\sigma$ -complex in aqueous solutions of constant ionic strength 0.14 M (KNO<sub>3</sub>)<sup>a</sup>

T(°C)	$k_{\rm f} \times 10^{-4}  (M^{-1}  {\rm s}^{-1})$	$k_{\rm b}$ (s <sup>-1</sup> )	$k_{\rm f}/K({\rm s}^{-1})$
1.6	2.0±0.1	0±1	1.2±0.2
6.7	$2.5 \pm 0.2$	$1 \pm 1$	$1.8 \pm 0.2$
13.7	$3.5\pm0.2$	$3\pm1$	$3.0\pm0.3$
21.5	$5.1 \pm 0.3$	$5 \pm 1$	$5.3\pm0.5$
28.8	$6.9 \pm 0.4$	8±2	$8.5 \pm 1.0$
35.5	$8.7 \pm 0.4$	$12 \pm 2$	$13.0\pm1.0$

<sup>e</sup>Error limits on  $k_1$  and  $k_b$  are based on the errors associated with the "least-squares" slopes and intercepts of the  $k_{obs} vs. [SO_3^{2-}]_0$  plots.

TABLE 2. Specific rate constants for the formation  $(k_f)$ and decomposition  $(k_b)$  of the 1:1 *N*-methylpicramide – sulfite ion  $\sigma$ -complex in aqueous solutions of constant ionic strength 0.14 *M* (KNO<sub>3</sub>)<sup>a</sup>

T(°C)	$k_{\rm f} \times 10^{-4}  (M^{-1} {\rm s}^{-1})$	$k_{\rm b}(=k_{\rm f}/K_1)~({\rm s}^{-1})$
9.5	0.69+0.03	$0.06 \pm 0.01$
20.4	$1.06 \pm 0.05$	$0.13 \pm 0.02$
29.5	$1.7\pm0.1$	$0.28 \pm 0.03$
39.4	$2.6 \pm 0.2$	$0.63 \pm 0.06$
49.1	$3.8 \pm 0.2$	$1.4 \pm 0.1$

<sup>a</sup>Errors in  $k_f$  based on the errors associated with the "least-squares" slopes of plots of  $k_{ob}$ , vs.  $[SO_3^{2-}]_0$ .

TABLE 3. Specific rate constants for the formation  $(k_t)$ and decomposition  $(k_b)$  of the 1:1 N,N-dimethylpicramide – sulfite ion  $\sigma$ -complex in aqueous solutions of constant ionic strength 0.14 M (KNO<sub>3</sub>)<sup>a</sup>

	$(h_{1}, h_{2}, h_{3}) = \frac{1}{2} (M - 1 - 1)$	= = =		
$\underline{I(\mathbf{U})}$	$\kappa_{\rm f} \times 10^{-5} (M \times 1)$	$\frac{\kappa_{\rm b}(=\kappa_{\rm f}/\kappa_1)({\rm s}^{-1})}{$		
9.7	$2.2 \pm 0.1$	$0.04 \pm 0.01$		
19.7	$3.4 \pm 0.2$	$0.10 \pm 0.02$		
30.8	$5.2 \pm 0.3$	$0.20 \pm 0.04$		
39.5	$7.3 \pm 0.3$	0.45±0.10		
49.7	$10.3 \pm 0.5$	$0.90 \pm 0.20$		

<sup>e</sup>Error limits on  $k_f$  are based on the errors associated with the "least-squares" slopes of the  $k_{obs} vs. [SO_3^{2-}]_0$  plots.

fite systems  $k_b$  values were so small they could not be accurately obtained from the intercepts. Therefore Tables 2 and 3 list only values of  $k_f/K_1$  for these systems.

Values of  $\Delta H_1^{\dagger}$  and  $\Delta S_1^{\dagger}$  obtained from plots of log  $k_f vs. 1/T$  are tabulated in Table 4. Errors in  $\Delta H_1^{\dagger}$  and  $\Delta S_1^{\dagger}$  are based on the errors in the "least-squares" slopes and intercepts of these plots.

Values of  $k_f$  at 25.0 °C decrease by a factor of four in going from the picramide-sulfite system to the *N*-methylpicramide – sulfite system and decrease by a factor of four again in going from the N-methylpicramide to the N,N-dimethylpicramide – sulfite system. Trends in  $k_b$  are far less regular;  $k_b$  decreases by a factor of 35 in going from the picramide-sulfite system to the N-methylpicramide – sulfite system whereas  $k_b$  for the N-methylpicramide – sulfite system is only slightly smaller than  $k_b$  for the N,N-dimethylpicramide – sulfite system.

Specific rate constants for the formation and decomposition at 25.0 °C of the 1,3,5-trinitrobenzene – sulfite ion complex are  $3.54 \times 10^4$  $M^{-1}$  s<sup>-1</sup> and 125 ± 10 s<sup>-1</sup>, respectively (17). In the 2,4,6-trinitrobenzaldehyde - sulfite ion system values of  $k_{\rm f}$  and  $k_{\rm b}$  at 25.0 °C are approximately  $9 \times 10^4 M^{-1} \, {\rm s}^{-1}$  and  $8 \, {\rm s}^{-1}$ , respectively.<sup>4</sup> Over the range of X groups studied the effect of X is much greater on  $k_{\rm b}$  than on  $k_{\rm f}$ . The primary role of X in determining the stability of the 1:1  $\sigma$ -complex may be related more to the extent to which the group X influences the solvation of the 1:1  $\sigma$ -complex than to its electronic properties. Unfortunately the  $\Delta H^{\pm}$  and  $\Delta S^{\pm}$  values for the formation and decomposition of a wide range of 1-X-2,4,6-trinitrobenzene - sulfite ion complexes, necessary in order to support or refute this suggestion, are not yet available. In the case of the picramide-sulfite and N-methylpicramide - sulfite reactions there are no clear trends in the  $\Delta H_1^{\dagger}$  and  $\Delta S_1^{\dagger}$  values.  $\Delta S_1^{\dagger}$  is significantly more negative for the *N*,*N*-dimethylpicramide - sulfite ion reaction. This observation is consistent with the argument (presented later) that this complex is more strongly solvated than the other 1:1  $\sigma$ -complexes in this series.

## Thermodynamics of $\sigma$ -Complex Formation

Equilibrium constants for the formation of the 1:1 sulfite ion – picramide  $\sigma$ -complex and molar extinction coefficients of this complex at a number of temperatures are listed in Table 5. Values of  $\varepsilon_{\rm C}$  at 480 nm increase slightly over the temperature range studied, possibly as a result of some broadening of the absorption band as the temperature is increased. Studies carried out at sulfite ion concentrations greater than 4.9 ×  $10^{-3}$  M yielded a molar extinction coefficient ( $\varepsilon_{\rm D}$ ) for the 2:1 species at 421 nm of 2.80 ± 0.03 ×  $10^4$   $M^{-1}$  cm<sup>-1</sup>. Values of the equilibrium constant for 2:1  $\sigma$ -complex formation ( $K_2$ ) were found to decrease from 20  $M^{-1}$  at 9.7 °C to 2.6  $M^{-1}$  at 50.1 °C.

<sup>4</sup>A. R. Norris and N. Marendic. Unpublished results.

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TABLE 4. Thermodynamic and kinetic parameters associated with 1:1 sulfite ion  $\sigma$ -complex formation with picramide (P), N-methylpicramide (NMP), and N,N-dimethylpicramide (DMP) in aqueous solutions of ionic strength 0.14 M (KNO<sub>3</sub>)

Compound	$K (at 25.0 \ ^{\circ}C) (M^{-1})$	∆H <sup>o</sup> (kcal mol <sup>-1</sup> ) <sup>a</sup>	$\Delta S^{0}$ (cal deg <sup>-1</sup> mol <sup>-1</sup> )	$k_{\rm f}$ (at 25.0 °C) $(M^{-1} {\rm s}^{-1})^b$	k <sub>b</sub> (at 25.0 °С) (s <sup>-1</sup> )	$\Delta H_1^{\pm}$ (kcal mol <sup>-1</sup> ) <sup>c</sup>	$\Delta S_1^{\pm} $ (cal deg <sup>-1</sup> mol <sup>-1</sup> ) <sup>c</sup>
P	$8.6 \pm 0.4 \times 10^{3}$	$-4.3 \pm 0.1$	$3.5 \pm 0.4$	$5.7 \pm 0.2 \times 10^4$	7 <u>+</u> 1	$6.8 \pm 0.1$	$-14.0\pm0.6$
NMP	$6.8 \pm 0.4 \times 10^{4}$	$-6.1 \pm 0.2$	$1.5 \pm 0.6$	$1.4 \pm 0.1 \times 10^{4}$	$0.20 \pm 0.02$	$7.3 \pm 0.2$	$-14.7 \pm 0.6$
DMP	$3.0 \pm 0.3 \times 10^{4}$	$-7.4 \pm 0.4$	$-4.0\pm0.1$	$4.1 \pm 0.2 \times 10^{3}$	$0.14 \pm 0.04$	6.4±0.1	$-20.4\pm0.6$

<sup>e</sup>Errors in  $\Delta H^0$  based on errors in the "least-squares" slopes of the log  $K_1$  vs. 1/T plots. <sup>b</sup>Errors in  $k_1$  based on errors associated with  $\Delta H_1^{\pm}$  and  $\Delta S_1^{\pm}$ . <sup>c</sup>Errors in  $\Delta H_1^{\pm}$  and  $\Delta S_1^{\pm}$  based on errors in the "least-squares" slopes and intercepts (at 1/T equal to 0) of the log  $k_1$  vs. 1/T.

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TABLE 5. Picramide - sulfite ion interaction in aqueous solutions of constant ionic strength 0.14 M (KNO<sub>3</sub>), pH 9.00. Equilibrium constants for  $1:1 \sigma$ -complex formation and molar extinction coefficients of the 1:1  $\sigma$ -complex at 480 nm<sup>4</sup>

 T(°C)	$\epsilon \times 10^{-4} (M^{-1} \mathrm{cm}^{-1})^b$	$K_1 \times 10^3 (M^{-1})$
9.7 19.7 31.3 40.4	$\begin{array}{c} 1.09 \pm 0.02 \\ 1.13 \pm 0.02 \\ 1.18 \pm 0.02 \\ 1.19 \pm 0.02 \end{array}$	$ \begin{array}{r} 12.7 \pm 0.3 \\ 10.2 \pm 0.7 \\ 7.5 \pm 0.3 \\ 6.2 \pm 0.2 \end{array} $
50.1	$1.20 \pm 0.02$	$4.9 \pm 0.2$

<sup>a</sup>Errors in  $K_1$  and  $\varepsilon$  are based on the observed range of experimental values of  $K_1$  and  $\varepsilon$  calculated using different initial picramide and sodium sulfite concentrations. <sup>b</sup>The absorption maximum for the 1:1  $\sigma$ -complex appears at 424 nm. At this wavelength  $\varepsilon$  is calculated to be 2.73  $\pm$  0.02  $\times$  10<sup>4</sup>  $M^{-1}$  cm<sup>-1</sup> at all temperatures.

The equilibrium constants for 1:1 and 2:1 sulfite ion – N-methylpicramide  $\sigma$ -complex formation, and the molar extinction coefficients at 480 nm of N-methylpicramide and the two complexes at a number of temperatures are presented in Table 6. At 480 nm values of  $\varepsilon_{\rm C}$  for the Nmethylpicramide - sulfite ion complex are somewhat lower than  $\varepsilon_{\rm C}$  values for the picramide – sulfite ion complex.

In Table 7 are listed the molar extinction coefficients at several different wavelengths of N,N-dimethylpicramide and its 1:1 and 2:1  $\sigma$ -complexes with sulfite ion. The values of  $\varepsilon_{N}$ ,  $\varepsilon_{\rm C}$ , and  $\varepsilon_{\rm D}$  were, within experimental error, independent of temperature. Table 8 contains the equilibrium constants for the formation of C and D in the N,N-dimethylpicramide – sulfite ion system over a range of temperatures.

In general Crampton's values of  $K_1$  and  $K_2$ , at  $20 \pm 2 \,^{\circ}\text{C}$  and  $\mu = 0.14 \, M \,(\text{Na}_2\text{SO}_4),^5$  agree reasonably well with our values of  $K_1$  and  $K_2$  at 20.0 °C and  $\mu = 0.14 M (\text{KNO}_3)$ . We find that  $K_1$ , for formation of the N,N-dimethylpicramide - sulfite ion complex, is less however than  $K_1$  for the formation of the N-methylpicramide – sulfite ion complex, whereas Crampton reports equal values of  $K_1$  for these two systems.

Equilibrium constants for formation of the 1:1 and 2:1 sulfite ion  $\sigma$ -complexes show that at 20.0 °C  $K_1$  varies in the order

<sup>5</sup>Crampton's values for  $K_2$  at  $\mu = 0$  and  $T = 20 \pm 2$  °C were used in conjunction with his reported relationship (5)

$$\log_{10} (K_2)_{\mu} = \frac{\sqrt{\mu}}{1 + 1.2\sqrt{\mu}} (4.06) + \log_{10} (K_2)_{\mu=0}$$

to calculate values of  $K_2$  at  $\mu = 0.14 M$  and  $T = 20 \pm 2^{\circ}$ C.

TNT < TNA < TNB < P < TNBA < DMP < NMPwhile  $K_2$ , at 20.0 °C and  $\mu = 0.14 M$ , varies in the order

For the formation of 1:1 hydroxide ion  $\sigma$ -complexes at 25.0 °C  $K_1$  varies in the order

(TNT, TNA, TNB, and TNBA are 2.4.6-trinitrotoluene, 2,4,6-trinitroanisole, 1,3,5-trinitrobenzene, and 2,4,6-trinitrobenzaldehyde respectively).

A consideration of the  $K_1$  values in the light of the  $k_{\rm f}$  and  $k_{\rm b}$  values (Table 4) indicates that the increased stabilities of the 1:1 N,N-dimethylpicramide - sulfite ion and N-methylpicramide sulfite ion complexes compared to the 1:1 picramide - sulfite ion complex are more the result of lower rates of decomposition of the former 1:1  $\sigma$ -complexes rather than, as suggested by Crampton (5), more favorable  $k_{\rm f}$  values for formation of the former  $1:1 \sigma$ -complexes.

Values of  $\Delta H^0$  and  $\Delta S^0$  for 1:1  $\sigma$ -complex formation in the picramide-, N-methylpicramide -, and N,N-dimethylpicramide - sulfite ion systems are presented in Table 5. In the 1,3,5-trinitrobenzene – sulfite ion system  $\Delta H^0$  and  $\Delta S^0$ values for 1:1 o-complex formation are reported to be  $-4.0 \pm 0.1 \text{ kcal mol}^{-1}$  and  $-2.3 \pm 0.5$ cal deg<sup>-1</sup> mol<sup>-1</sup>, respectively (4). In the 2,4,6trinitrobenzaldehyde – sulfite ion system  $\Delta H^0$ and  $\Delta S^0$  are  $-2.41 \pm 0.16 \text{ kcal mol}^{-1}$  and  $11.4 \pm 1.1$  cal deg<sup>-1</sup> mol<sup>-1</sup>, respectively (9).

For the process of  $1:1 \sigma$ -complex formation we can consider, to a first approximation, that  $\Delta H^0$  represents the sum of the enthalpy change associated with formation of the C-SO<sub>3</sub><sup>-</sup> bond  $(\Delta H_a)$ , the enthalpy change associated with desolvation of sulfite ion in going from free sulfite in solution to sulfite bonded to carbon  $(\Delta H_{\rm h})$ , and the enthalpy change associated with solvation of the negatively charged  $\sigma$ -complex ( $\Delta H_c$ ). In the same way  $\Delta S^0$  is the sum of the entropy change associated with the sulfite ion and the nitroaromatic compound coming together to form the complex  $(\Delta S_a)$ , the entropy change associated with desolvation of sulfite ion in going from free sulfite to sulfite in the complex  $(\Delta S_{\rm b})$  and the entropy change associated with solvation of the negatively charged complex  $(\Delta S_{\rm c})$ . For a series of comparably solvated nitro-

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TABLE 6. N-Methylpicramide – sulfite ion interaction in aqueous solutions of constant ionic strength 0.14 M (KNO<sub>3</sub>), pH = 9.00. Equilibrium constants for 1:1 and 2:1 σ-complex formation and molar extinction coefficients of N-methylpicramide and the two σ-complexes C and D at 480 nm

<i>T</i> (°C)	$\epsilon_{\rm N} \times 10^{-2}$ ( $M^{-1}$ cm <sup>-1</sup> )	$\epsilon_{\rm c} \times 10^{-3}$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\epsilon_{\rm D}  imes 10^{-2}$ ( $M^{-1}  {\rm cm}^{-1}$ )	$K_1 \times 10^{-4} (M^{-1})$	$K_2 \times 10^{-2} (M^{-1})$
20.1	$4.4 \pm 0.1$	9.0±0.3	$1.3 \pm 0.1$	7.9+0.8	$18 \pm 2$
29.9	$4.4\pm0.1$	$9.2\pm0.3$	$1.3 \pm 0.1$	$5.8 \pm 0.6$	$10 \pm 1$
39.0	$4.4 \pm 0.1$	$9.0\pm0.3$	$1.3 \pm 0.1$	$4.2\pm0.4$	$6.0\pm0.6$
48.1	$4.4 \pm 0.1$	$8.8\pm0.3$	$1.3 \pm 0.1$	$3.2\pm0.3$	$3.5\pm0.4$

TABLE 7. N,N-Dimethylpicramide – sulfite ion interaction in aqueous solutions of constant ionic strength 0.14 M (KNO<sub>3</sub>), pH = 9.00. Molar extinction coefficients of N,N-dimethylpicramide (DMP) and the 1:1 and 2:1  $\sigma$ -complexes C and D

		$\epsilon \times 10^{-3} (M^{-1} cm)$	m <sup>-1</sup> )
Compound	350 nm	420 nm	490 nm
DMP 1:1 σ-complex (C) 2:1 σ-complex (D)	9.4 $\pm$ 0.2 5.0 $\pm$ 0.2 4.3 $\pm$ 0.1	$ \begin{array}{r} 6.4 \pm 0.1 \\ 20 \pm 2 \\ 20.0 \pm 0.5 \end{array} $	$0.33 \pm 0.01 \\ 8.0 \pm 1.0 \\ 0.285 \pm 0.005$

TABLE 8. N,N-Dimethylpicramide – sulfite interaction in aqueous solutions of constant ionic strength 0.14 M (KNO<sub>3</sub>), pH = 9.00. Equilibrium constants for formation of the 1:1 and 2:1 sulfite ion – N,N-dimethylpicramide  $\sigma$ -complexes C and D

T(°C)	$K_1 \times 10^{-4} (M^{-1})$	$K_2 \times 10^{-4} (M^{-1})$
11.8	$4.8 \pm 0.4$	7.0+1.0
20.5	$3.8 \pm 0.4$	$3.8 \pm 0.7$
30.7	$2.4\pm0.2$	$1.8 \pm 0.3$
40.6	$1.6\pm0.2$	$0.80 \pm 0.10$
49.2	$1.1 \pm 0.1$	$0.35 \pm 0.05$

aromatic compounds forming a series of structurally similar 1:1  $\sigma$ -complexes,  $\Delta H_1$ ,  $\Delta H_2$ ,  $\Delta S_1$ , and  $\Delta S_2$  should each remain reasonably constant. Trends in  $\Delta H^0$  and  $\Delta S^0$  should therefore mainly reflect trends in the overall solvation of the 1:1  $\sigma$ -complex with a greater degree of solvation of the complex implying more negative values of both  $\Delta H^0$  and  $\Delta S^0$ .

For the 1:1 1-X-2,4,6-trinitrobenzene – sulfite ion  $\sigma$ -complexes in which X = CHO, NH<sub>2</sub>, NHCH<sub>3</sub>, and N(CH<sub>3</sub>)<sub>2</sub>, more negative  $\Delta H^0$ values are in fact associated with more negative  $\Delta S^0$  values. For the four X groups mentioned a reasonably linear  $\Delta H^0$  vs.  $\Delta S^0$  plot is obtained (18). For the 2:1 1-X-2,4,6-trinitrobenzene – sulfite ion  $\sigma$ -complexes, where X = NH<sub>2</sub>, NHCH<sub>3</sub>, N(CH<sub>3</sub>)<sub>2</sub>, and CHO, more negative values of  $\Delta H^0$  (-9, -11, -14, and -8.53 kcal mol<sup>-1</sup>, respectively) are also accompanied by more negative  $\Delta S^0$  values (-12, -22, -28, and -21.8 cal deg<sup>-1</sup> mol<sup>-1</sup>, respectively). However, a plot of  $\Delta H^0$  vs.  $\Delta S^0$  is not linear in this case. A complicating factor in 2:1  $\sigma$ -complex formation is the steric strain associated with addition of the second sulfite ion. This steric strain would be expected to be least in the picramide-sulfite 2:1  $\sigma$ -complex and it is for this system that the  $\Delta H^0$  term is accompanied by a higher than expected  $\Delta S^0$  term.

In the picramide – and N-methylpicramide – sulfite  $\sigma$ -complexes a smaller degree of solvation might be required as a result of intramolecular N-O<sup>-</sup>.....H-N bonding serving to compensate, in part, the partial negative charge on the oxygens of the ortho nitro groups in the complex. Trends in the  $\Delta S^0$  values associated with the formation of the picramide-sulfite, N-methylpicramide - sulfite, and 1,3,5-trinitrobenzene sulfite complexes are certainly in accord with this idea. The  $\Delta S^0$  value is highest in the picramide complex (two hydrogen bonds) and becomes progressively more negative the greater the requirement for solvation of the nitro groups by water. That factors other than hydrogen bonding are important is seen by comparing

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 $\Delta S^0$  data in the N-methylpicramide – and 2,4,6trinitrobenzaldehyde – sulfite systems. Both substrates have a single hydrogen available for hydrogen bonding but both  $\Delta S^0$  and  $\Delta H^0$  for the latter system are far more positive. This may arise because of some degree of delocalization of negative charge onto the aldehyde group in the complex which thereby renders solvation of the nitro groups less extensive.<sup>6</sup> Alternatively 2,4,6trinitrobenzaldehyde may be more strongly solvated in its initial state. Extensive heats of solvation data for these nitroaromatic compounds in water would be needed in order to solve this problem.

Financial support by the National Research Council of Canada is gratefully acknowledged.

 $P < NMP \sim TNB < TNBA < DMP < TNA < TNT$ and (based on  $\varepsilon_D$ ) is

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P < NMP < DMP < TNB < TNA

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<sup>&</sup>lt;sup>6</sup>If the magnitudes of  $\varepsilon(\lambda_{max})$  reflect the degree to which the nitro groups ortho to X are rotated out of the plane of the ring in the complex, and solvation of the nitro groups is more extensive the greater their degree of rotation out of the plane, then the order of solvation of the nitro groups (based on  $\varepsilon_c$ ) is