

The equilibrium constants K_1 for cobalt bromide and chloride systems are 3.1 and 9.6 M^2 in nitromethane-pyridine, and 11.4 and 6.1 M^2 in pyridine at 38°. It has been suggested that the dissociation of the octahedral chloride complex into the tetrahedral species and free base should be less than that of the corresponding bromide complex in inert solvents.¹³ Such is the case in chloroform⁸ and pyridine as indicated above. However in nitromethane the trend is reversed. Evidently the greater polarizability of the bromide ion which is believed to favor the tetrahedral complex relative to the octahedral form in the solid state and inert solvents is offset by opposing factors in nitromethane.

An interesting and important aspect of this work is the detection of the five-coordinate intermediate, $\text{Co}(\text{py})_3\text{Br}_2$; such intermediates have received considerable attention in studies of substitution reactions of octahedral complexes. Of special interest are the rate constants k_4 and k_{-4} , which can give information about the kinetic characteristics of the intermediate with respect to the six-coordinate complex.

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The Reactions of Pentacyanonitrosylferrate(III) with Bases. VI. Sulfite. The Boedeker Reaction

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When solutions of pentacyanonitrosylferrate(III) (nitroprusside, $(\text{NC})_5\text{FeNO}^{2-} \equiv \text{RNO}^{2-}$) and sulfite (SO_3^{2-}) are mixed, a deep red coloration develops. The coloration results from what is commonly called the Boedeker reaction,¹ and the species giving rise to the red coloration, λ_{max} 475 nm, results from the addition of SO_3^{2-} to the NO moiety of RNO^{2-}



The effect of "inert" electrolytes on the equilibrium properties of (1) has been investigated.²⁻⁴ A specific cation effect is observed with effectiveness of color intensifications: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. It is suggested from the above studies that the equilibrium



along with (1), must be considered in a description of the system. Another equilibrium study indicates

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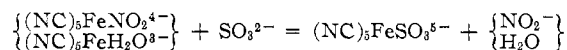
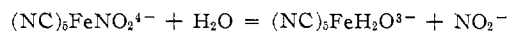
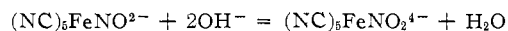
(4) A. G. Fogg, A. D. Jones, and W. Moser, *ibid.*, **28**, 2427 (1966).

that, besides the 1:1 $\text{RNO}^{2-}-\text{SO}_3^{2-}$ species, a 1:2 $\text{RNO}^{2-}-\text{SO}_3^{2-}$ species is present.⁵ Preliminary kinetic data measured by the temperature-jump relaxation technique have been published.⁶ The equilibrium properties in aqueous solution with organic additives have been qualitatively investigated.⁸ An infrared analysis of salts of $(\text{NC})_5\text{FeNO}(\text{SO}_3)^{4-}$ suggests that the bonding is $(\text{NC})_5\text{FeNOSO}_3^{4-}$.⁷

This study deals with the measurement of the thermodynamic and activation parameters for the Boedeker reaction in aqueous solution.

Experimental Section

Chemicals and Solutions.—All chemicals— $\text{Na}_2[(\text{NC})_5\text{FeNO}] \cdot 2\text{H}_2\text{O}$, Na_2SO_3 , NaCl , CsCl , and $\text{Na}_2\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ (disodium salt of ethylenediaminetetraacetic acid, Na_2EDTA)—were reagent grade. Stock solutions were prepared by adding weighed amounts of $\text{Na}_2[(\text{NC})_5\text{FeNO}] \cdot 2\text{H}_2\text{O}$ and NaCl (or CsCl) and Na_2SO_3 , NaCl (or CsCl), and Na_2EDTA into doubly distilled water. Na_2EDTA was added to solutions containing SO_3^{2-} to complex heavy-metal ions which catalyze the oxidation of sulfite.³ The solutions used in the kinetic and equilibrium experiments were prepared immediately before use from thermostated stock solutions. It was noted in the equilibrium measurements that the absorbance of the solutions in the 475–500-nm range decreased slowly with time. This was due to some combination of the reactions^{9,8}



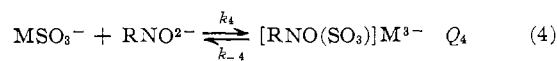
Therefore absorbance measurements were taken as soon after mixture as possible, and, when necessary, the initial absorbance was determined by extrapolation to zero time.

Instruments.—Absorbance measurements were carried out with a Cary 14 recording spectrophotometer (Applied Physics Corp.). Kinetic experiments employed a stopped-flow apparatus (Messanlagen Studiengesellschaft, GmbH, Goettingen, Germany). The instruments were thermostated to $\pm 0.2^\circ$.

Results and Discussion

Equilibrium Measurements.—It has been suggested from previous work²⁻⁴ that equilibria 1 and 2 may be present in aqueous solutions containing RNO^{2-} , SO_3^{2-} , and an inert electrolyte, MCl (where $\text{M}^+ \equiv \text{Li}^+$, Na^+ , K^+ , etc.). However, at the concentrations of Na^+ used in these experiments, 1.00 M , it is reasonable to assume that some ion pairing between Na^+ and SO_3^{2-} , and perhaps RNO^{2-} , takes place prior to complex formation between nitroprusside and sulfite. For example, the equilibrium constant extrapolated to zero ionic strength for ion-pair formation between Na^+ and SO_3^{2-} is 5.⁹ Due to the larger size of RNO^{2-} it seems reasonable that the equilibrium constant for ion-pair formation would be somewhat smaller than that of SO_3^{2-} .

If the equilibria present in aqueous solutions containing RNO^{2-} , SO_3^{2-} , and M^+ (as MCl) are



where Q_3 and Q_4 represent the equilibrium concentra-

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(7) A. G. Fogg, A. H. Norbury, and W. Moser, *J. Inorg. Nucl. Chem.*, **28**, 2753 (1966).

(8) "Gmelin's Handbuch der anorganische Chemie," Iron 59B, Verlag Chemie, GmbH, Berlin, 1938, p 903.

(9) L. G. Sillén and A. E. Martell, Eds., "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964, p 235.

tion quotients for equilibria 3 and 4 and if the assumptions are made that (i) the $[\text{SO}_3^{2-}]$ is in excess over the initial concentration of RNO^{2-} , $[\text{RNO}^{2-}]_t$, (ii) ΔA is the total absorbance minus the absorbance due to free RNO^{2-} , and (iii) ϵ is the extinction coefficient of $[\text{RNO}(\text{SO}_3)]\text{M}^{2-}$ and the amount of sulfite present in the $[\text{RNO}(\text{SO}_3)]\text{M}^{2-}$ ion is small compared to $[\text{SO}_3^{2-}]$ and $[\text{NaSO}_3^-]$ (this will be shown to be correct), the following relationship can be derived

$$\frac{1}{[\text{SO}_3^{2-}]} = \frac{\epsilon Q_4 Q_3 [\text{Na}^+]}{1 + Q_3 [\text{Na}^+]} \frac{[\text{RNO}^{2-}]_t}{\Delta A} - \frac{Q_4 Q_3 [\text{Na}^+]}{1 + Q_3 [\text{Na}^+]} \quad (5)$$

Table I contains data for the testing of eq 5 at 475

$t, ^\circ\text{C}$	$1/[\text{SO}_3^{2-}]^b$ M^{-1}	$(1/\Delta A)_{475 \text{ nm}}^{c,d}$	$(1/\Delta A)_{500 \text{ nm}}^{c,d}$
10	6.66	13.66	11.96
	5.00	10.50	9.28
		10.42	9.24
	3.33	7.13	6.47
	2.50	5.77	5.15
25	6.66	15.65	14.22
	5.00	12.18	10.87
	2.50	6.63	5.89
40	6.66	19.16	17.06
	5.00	14.56	13.02
	2.50	7.68	6.83

^a $[\text{RNO}^{2-}]_t = 1.0 \times 10^{-3} M$, $[\text{Na}^+] = 1.00 M$. ^b Hydrolysis of SO_3^{2-} at $[\text{SO}_3^{2-}]$ used is small and was neglected. ^c Absorbancies corrected to a 1-cm cell. ^d Average of two measurements.

and 500 nm, and Figure 1 presents that data graphically. Data at $[\text{RNO}^{2-}]_t$ less than $1.0 \times 10^{-3} M$ gave plots having slopes proportional to $[\text{RNO}^{2-}]_t$ as predicted by eq 5. Table II presents values of $Q_4 Q_3$.

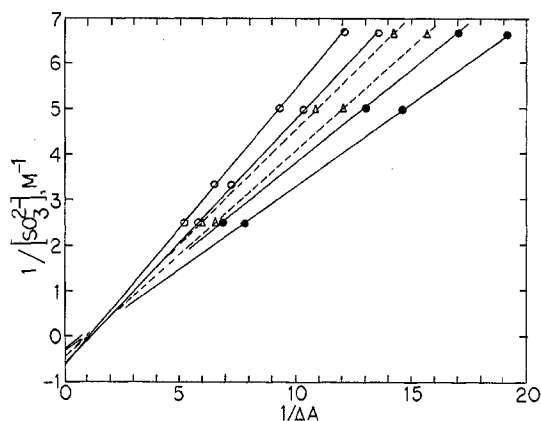


Figure 1.—Plot of $1/[\text{SO}_3^{2-}]$ vs. $1/\Delta A$ at 10° (○), 25° (△), and 40° (●). $[\text{Na}^+] = 1.00 M$ and $[\text{RNO}^{2-}]_t = 1.0 \times 10^{-3} M$.

$[\text{Na}^+]/(1 + Q_3[\text{Na}^+])$ and $\epsilon Q_4 Q_3 [\text{Na}^+]/(1 + Q_3[\text{Na}^+])$, obtained from the intercept at $1/\Delta A = 0$ and the slope, respectively, at 475 and 500 nm and the three temperatures investigated, 10, 25, and 40° . An extinction coefficient, ϵ , recorded in Table II, column 5, can be calculated from the data. The value of ϵ varies slightly with temperature. The extinction coefficients recorded here are smaller than the value of $3100 M^{-1} \text{ cm}^{-1}$ recorded for the $\text{K}^+-\text{RNO}^{2-}-\text{SO}_3^{2-}$ system.³ From the values of the extinction coefficients it can be

TABLE II
DATA OBTAINED FROM FIGURE 1 AND EQ 5^a

$t, ^\circ\text{C}$	λ, nm	$Q_4 Q_3 [\text{Na}^+]/(1 + Q_3 [\text{Na}^+]), M^{-1}$	$10^{-2} \epsilon Q_4 Q_3 [\text{Na}^+]/(1 + Q_3 [\text{Na}^+]), M^{-2} \text{ cm}^{-1}$	$\epsilon, M^{-1} \text{ cm}^{-1}$
10	475	0.65	6.11	940
	500	0.62	5.37	865
25	475	0.45	5.00	1110
	500	0.45	4.52	1005
40	475	0.29	4.06	1400
	500	0.29	3.64	1260

^a $[\text{Na}^+] = 1.00 M$.

shown that one of the restrictions imposed on the use of eq 5 is satisfied, *i.e.*, the amount of sulfite present in the $[\text{RNO}(\text{SO}_3)]\text{M}^{2-}$ ion is small compared to $[\text{SO}_3^{2-}]$ and $[\text{MSO}_3^-]$.

The temperature dependence of $Q_4 Q_3 [\text{Na}^+]/(1 + Q_3 [\text{Na}^+])$ gives values for the enthalpy and entropy change of $-4.6 \pm 0.4 \text{ kcal/mol}$ and $-17 \pm 2 \text{ eu}$, respectively. The thermodynamic parameters are meaningful only if $Q_3 [\text{Na}^+] > 1$, so that $Q_4 Q_3 [\text{Na}^+]/(1 + Q_3 [\text{Na}^+]) \approx Q_4$, or if $1 > Q_3 [\text{Na}^+]$, so that $Q_4 Q_3 [\text{Na}^+]/(1 + Q_3 [\text{Na}^+]) \approx Q_4 Q_3 [\text{Na}^+]$. As the ionic strength increases, the equilibrium concentration quotient Q_3 will decrease from 5 (assuming the same value for the $\text{Na}^+-\text{SO}_4^{2-}$ system) at zero ionic strength to something of the order of 0.1⁹ for the conditions used in this work. Thus the latter assumption appears to be correct, $1 > Q_3 [\text{Na}^+]$. Data obtained under Kinetic Measurements also suggest that this assumption is correct.

The value of $Q_4 Q_3 [\text{Na}^+]$ at 25° of $0.45 M^{-1}$ determined in this work can be compared with the value of $Q_1 Q_2$ of 0.13 determined by other workers at an unspecified temperature using a technique involving the variation of the absorbance of the complex with the concentration of added electrolyte.

Kinetic Measurements.—If equilibria 3 and 4 are operative, the possibilities exist that equilibria 3 and 4 equilibrate in the same time range, (3) equilibrates more rapidly than (4), or *vice versa*. As predicted from the equilibrium experiments, the measured relaxation process corresponds to a decrease in the concentration of $[\text{RNO}(\text{SO}_3)]\text{M}^{2-}$ with increasing temperature. Between 450 and 650 nm only one relaxation process is observed. A very small increase in absorbance occurs before the measured decrease. This effect is seen with solutions containing only $(\text{NC})_5\text{FeNO}^{2-}$ and Na^+ and is not attributable to the chemical system of interest. The observation of only one relaxation process supports the view³ that the 1:2 $\text{RNO}^{2-}-\text{SO}_3^{2-}$ complex⁵ is not present in these solutions. Observation of one relaxation process suggests that either equilibrium 3 equilibrates rapidly compared to (4) or *vice versa*. It is likely that (3) equilibrates more rapidly than (4). This supposition is based on the fact that complexation reactions involving Na^+ occur at a time very much shorter than that observed in the experiments.¹⁰ Thus the reciprocal of one of the possible relaxation times, $1/\tau$, is represented by the equation

$$\frac{1}{\tau} = k_4 \left\{ \frac{[\text{RNO}^{2-}][\text{Na}^+] + [\text{SO}_3^{2-}]}{1 + Q_3([\text{Na}^+] + [\text{SO}_3^{2-}])} + [\text{NaSO}_3^-] \right\} + k_{-4} \quad (6)$$

The data for the temperature jump studies are summarized in Table III for both the $\text{RNO}^{2-}\text{--SO}_3^{2-}\text{--Na}^+$ and $\text{RNO}^{2-}\text{--SO}_3^{2-}\text{--Cs}^+$ systems. At constant $[\text{Na}^+]$, $1/\tau$ is independent of the concentrations and combinations of concentrations of RNO^{2-} , SO_3^{2-} , NaSO_3^- , and $[\text{RNO}(\text{SO}_3)]\text{Na}^{\delta-}$ (although not shown in Table III,

TABLE III
TEMPERATURE-JUMP DATA

$t, ^\circ\text{C}$	$[\text{RNO}^{2-}], M$	$[\text{SO}_3^{2-}], M$	$10^{-3}/\tau, \text{sec}^{-1}$	λ, nm
[Na ⁺] = 1.00 M				
35.0	1.0×10^{-3}	0.40	1.63	475
	1.0×10^{-3}	0.25	1.65	
	1.0×10^{-3}	0.10	1.65	
25.0	1.0×10^{-3}	0.40	0.99	
	0.05	0.01	0.96	
	0.10	0.01	1.02	
	0.40	0.01	0.99	
	0.10	0.01	0.87	
	0.10	0.01	0.99	
	0.10	0.01	0.95	
	0.10	0.01	0.98	
	0.10	0.01	0.99	
	0.10	0.01	0.99	
10.0	1.0×10^{-3}	0.10	0.33	475
	1.0×10^{-3}	0.25	0.38	
	1.0×10^{-3}	0.40	0.33	
[Cs ⁺] = 0.96 M, [Na ⁺] = 0.04 M				
32.9	0.01	0.01	0.320	
23.2	0.01	0.01	0.347	
			0.142	
			0.149	
7.7	0.01	0.01	0.0365	
			0.0356	
			0.0379	

^a Average of two measurements.

this is also true for the Cs^+ case). Considering eq 6, $1/\tau$ then approximates k_{-4} . The values of k_{-4} at 25° and $[\text{M}^+] = 1.0 M$ are $9.8 \times 10^2 \text{ sec}^{-1}$ (Na^+) and $1.8 \times 10^2 \text{ sec}^{-1}$ (Cs^+). The activation parameters have been measured for $1/\tau$ ($\sim k_{-4}$) at $1.0 M \text{ Na}^+$ and at $0.96 M \text{ Cs}^+$ and $0.04 M \text{ Na}^+$. In the former case ΔH^\ddagger and ΔS^\ddagger are $10.4 \pm 0.9 \text{ kcal/mol}$ and $-10 \pm 3 \text{ eu}$ and in the latter case $14.5 \pm 0.6 \text{ kcal/mol}$ and $0 \pm 2 \text{ eu}$.

If the correct mechanism is indeed the one formulated as equilibria 1 and 2, where (1) equilibrates slowly compared to (2) for the reasons given previously and in ref 10, then the reciprocal of the relaxation time, $1/\tau$, equals

$$k_1([\text{RNO}^{2-}] + [\text{SO}_3^{2-}]) + k_{-1} \left\{ \frac{1 + Q_2([\text{M}^+] + [\text{RNO}(\text{SO}_3)^{4-}])}{1 + Q_2[\text{RNO}(\text{SO}_3)^{4-}]} \right\}$$

If $1/\tau$ is independent of $[\text{RNO}^{2-}]$ and $[\text{SO}_3^{2-}]$ and consequently of the concentration of the complex $\text{RNO}(\text{SO}_3)^{4-}$, then $1/\tau$ may be approximated by $k_{-1} \cdot (1 + Q_2[\text{M}^+])$, and the rate constants and associated activation parameters are associated with this quantity.

Stopped-flow experiments were carried out to see if the formation of the complex could be observed. The formation of complex from nitroprusside and sulfite at $[\text{Na}^+] = 1.00 M$ occurred with a bimolecular rate constant greater than $1 \times 10^3 M^{-1} \text{ sec}^{-1}$ at 1° . If, under Equilibrium Measurements, $Q_4 Q_3 [\text{Na}^+] / (1 + Q_3 [\text{Na}^+])$ is approximated by Q_4 , then $k_4 = k_{-4} Q_4 = 160 M^{-1} \text{ sec}^{-1}$ from values of $k_{-4} = 190 \text{ sec}^{-1}$ and $Q_4 = 0.84 M^{-1}$ at 1° . This value is well below the lower limit set on the rate constant for the formation of the complex, $1 \times 10^3 M^{-1} \text{ sec}^{-1}$. However, when $Q_4 Q_3 [\text{Na}^+] / (1 + Q_3 [\text{Na}^+]) \approx Q_4 Q_3 [\text{Na}^+] = 0.84 M^{-1}$,

then $k_4 = 160/Q_3$. It has been shown that Q_3 decreases with increasing ionic strength and can be as low as $0.1 M^{-1}$.⁹ Thus k_4 can be of the order of or larger than $10^3 M^{-1} \text{ sec}^{-1}$, and it appears that $Q_4 Q_3 [\text{Na}^+] / (1 + Q_3 [\text{Na}^+]) \approx Q_4 Q_3 [\text{Na}^+]$.

The dependence of τ on $[\text{Na}^+]$ at 25° has been investigated from 0.20 to 1.00 M. The value of $1/\tau$ is found to vary from $1.4 \times 10^3 \text{ sec}^{-1}$ ($[\text{Na}^+] = 0.20 M$) to $0.98 \times 10^3 \text{ sec}^{-1}$ ($[\text{Na}^+] = 1.00 M$).

Table IV is a summary of kinetic data for the forma-

TABLE IV
SUMMARY OF KINETIC DATA FOR THE
REACTIONS $\text{RNO}^{2-} + \text{B}^{n-} \rightarrow \text{RNO}(\text{B})^{(2+n)-}$

B^{n-}	k^a	$\Delta H^\ddagger,$ kcal/mol	$\Delta S^\ddagger,$ eu	Ref
SO_3^{2-}	450^b	5.8 ^c	-27 ^c	e
OH^-	0.55 ^d	12.6	-18	f
S^{2-}	170^d	7.2	-24	g

^a $\mu = 1.00$ (Na^+), temperature 298°K . ^b Units: $M^{-2} \text{ sec}^{-1}$. ^c The values of ΔH^\ddagger and ΔS^\ddagger recorded are based on assumptions outlined in the section Results and Discussion: Kinetic Measurements. ^d Units: $M^{-1} \text{ sec}^{-1}$. ^e This work. ^f J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966). ^g P. A. Rock and J. H. Swinehart, *ibid.*, **5**, 1078 (1966).

tion of various adducts of RNO^{2-} :¹¹ $\text{RNO}^{2-} + \text{B}^{n-} \rightarrow \text{RNO}(\text{B})^{(2+n)-}$. The large negative values for the entropies of activation in all cases are consistent with the values expected for reactions between negatively charged ions, RNO^{2-} and B^{n-} . The enthalpy change for $k_4 Q_3$ can be calculated from the enthalpy changes for k_{-4} (10.4 kcal/mol) and $Q_4 Q_3$ (-4.6 kcal/mol) to be 5.8 kcal/mol (Table IV). If the enthalpy change for Q_3 is assumed to be 1.1 kcal/mol (using $\text{Na}^+\text{--SO}_4^{2-}$ data),⁹ then the enthalpy of activation for k_4 is 4.7 kcal/mol. This value is substantially smaller than the values measured for the $\text{RNO}^{2-}\text{--OH}^-$ and $\text{RNO}^{2-}\text{--S}^{2-}$ reactions and may reflect the fact that sulfite attacks at the oxygen end of the NO moiety while OH^- and S^{2-} attack at the nitrogen.

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(11) The nomenclature $\text{RNO}(\text{B})^{(2+n)-}$ does not mean B is necessarily attached to the oxygen of the NO moiety.

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Trialkyl Phosphite-Boron Tribromide Coordination Compounds

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The system trialkyl(aryl) phosphite-boron trichloride has been investigated by Gerrard, *et al.*¹⁻⁴ These

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