first order in nitroprusside and hydrogen sulfide ion, $d[A]/dt = k[(NC)_5FeNO^{2-}][HS^-]$, under the experimental conditions used. This rate law indicates that the activated complex for the rate-determining step contains one hydrogen sulfide ion and one nitroprusside ion. The reaction of either hydrogen sulfide or sulfide ion with nitroprusside to form species A is inconsistent with the observed rate law. This is not to say that in more basic solutions sulfide cannot react directly with nitroprusside.

The activation parameters calculated from the data in Table I are $\Delta H_{12}^* = 7.2 \pm 0.3$ kcal/mole and $\Delta S_{12}^* = -24 \pm 1$ eu.

The kinetic curves at constant temperature for the conversion of species A to B ("fading reaction") are independent of the hydrogen sulfide ion, nitrite ion, and hydrogen ion concentrations. Assuming A and B to be the only iron-containing species present, first-order rate constants can be calculated for the conversion of A to B. Typical kinetic data are presented in Table II.

The activation parameters calculated from the data in Table II are $\Delta H_{23}^* = 19.4 \pm 0.5$ kcal/mole and $\Delta S_{23}^* = -3.0 \pm 1.5$ eu.

TABLE II

KINETIC DATA FOR CONVERSION OF A TO B

$\mu = 1.00$ (NaCl), $[(NC)_5FeNO^{2-}]_{\text{initial}} = 1.25 \times 10^{-4}$ *M*

T,[a] °K	$t_{1/2}$, sec	10^2k_{23},[b] sec^{-1}
293.0	81 ± 1	0.85 ± 0.01
303.0	26 ± 1	2.67 ± 0.05
311.0	11 ± 1	6.30 ± 0.50

[a] Temperature to ±0.5°. [b] Average of three runs at several hydrogen sulfide ion concentrations ($[HS^-]_{\text{initial}}$ from 3×10^{-2} to 10^{-1} *M* and pH from 11.5 to 12.8).

Discussion

Species B is identified as the ion $(NC)_5FeNOS^{4-}$ by a comparison of the spectrum of B with the spectrum of an aqueous solution of $Na_4[(NC)_5FeNOS]$ prepared by the reaction of nitroprusside and sulfide in methanol.[1] Analysis of our preparation of this salt shows that the $(NC)_5FeNO_2^{4-}$ ion can be a contaminant of about 10%. However, after the $(NC)_5FeNO_2^{4-}$ has been allowed to aquate, the spectra of the salt in aqueous solution and of B are identical. From the experimental data it is clear that in the rate-determining step for the formation of A a hydrogen sulfide ion reacts with a nitroprusside. This reaction is similar to that occurring in the hydroxide–nitroprusside system. The rate law for the formation of $(NC)_5FeNO_2^{4-}$ is $d[(NC)_5FeNO_2^{4-}]/dt = k_{12,OH^-}[OH^-][(NC)_5FeNO_2]$. At 298°K, k_{12,OH^-} is 0.55 ± 0.01 M^{-1} sec^{-1}, while in the hydrogen sulfide system k_{12,HS^-} is 170 ± 3 M^{-1} sec^{-1}. The larger value for k_{12,HS^-} can be rationalized on the basis of the lower value of ΔH_{12}^* in the hydrogen sulfide system ($\Delta H_{12}^*{}_{OH^-} = 12.6$ kcal/mole and $\Delta H_{12}^*{}_{HS^-} = 7.2$ kcal/mole). Owing to the larger size of hydrogen sulfide ion compared to hydroxide, hydrogen sulfide ion does not have to approach so closely as hydroxide to react with nitroprusside, accounting for the lower value of ΔH_{12}^*. The values of ΔS^* for k_{12,OH^-} and k_{12,HS^-} are -17.5 ± 0.7 and -24 ± 1 eu, which are of the magnitude expected for a reaction between a 1− and a 2− ion.[3]

The question arises as to the nature of species A and its conversion to $(NC)_5FeNOS^{4-}$ (species B). There are a number of possibilities. The hydrogen sulfide ion certainly attacks the nitrosyl group (NO^+) bound to the iron(II) in the diamagnetic nitroprusside ion to form an addition product.[1] The succeeding steps leading to the conversion of species A to the $(NC)_5FeNOS^{4-}$ ion may involve the rearrangement of the –NOSH group followed by the loss of a proton or the rapid addition of a second hydrogen sulfide ion followed by a rate-determining elimination of H_2S. However, our kinetic data give no information concerning the solution of this problem.

The $(NC)_5FeNOS^{4-}$ ion is unstable in solution and after some time the solution further decolorizes. The addition of acid increases the rate of decolorization. If $[H^+] = 10^{-3}$ *M*, the decolorization of the solution containing $(NC)_5FeNOS^{4-}$ at a concentration of 1.25×10^{-4} *M* is complete in less than 1 sec. It appears that at least two species are formed as products. One is $(NC)_5FeH_2O^{3-}$, which is identified from the spectral change in the solution (gradually increasing absorption in the ultraviolet) and the disappearance of this spectral characteristic when excess cyanide is added (formation of ferrocyanide). The second is probably $(H_2O)(NC)_4FeNOS^{3-}$, since the absorbance around 5500 A in the partially decolorized solution can be enhanced by addition of cyanide. Solutions of $(NC)_5FeNOS^{4-}$ allowed to decolorize in the presence of excess cyanide yield clear solutions containing $Fe(CN)_6^{4-}$, whereas in the absence of excess cyanide the "decolorized" solution are yellow. Apparently $(NC)_5FeNOS^{4-}$ can eliminate either CN^- or NOS^- as opposed to the nitroprusside–hydroxide system in which only NO_2^- is eliminated from $(NC)_5FeNO_2^{4-}$. The reaction $(NC)_5FeNOS^{4-} + H_2O \rightarrow (NC)_5FeOH_2^{3-} + NOS^-$ analogous to the reaction $(NC)_5FeNO_2^- + H_2O \rightleftharpoons (NC)_5FeOH_2^{3-} + NO_2^-$ does not attain equilibrium but is apparently irreversible, possibly owing to the instability of the postulated NOS^- species.

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A Kinetic Study of the Formation of the Ferrous–Nitric Oxide Complex

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The rapid substitution of ligands into the inner hydration sphere of metal ions has recently been the subject of intensive investigation.[1] For the divalent transition metal ions especially, a variety of techniques have been used, leading to self-consistent results in regard to the mechanism of substitution. Studies of ferrous ion have, however, been relatively few in number. Thus, the temperature-jump method has been applied to the system

$$Fe^{2+}(aq) + NO(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeNO^{2+}(aq) \qquad (A)$$

in order to obtain the complexation rate constants.

This reaction forms, of course, the basis for the "brown-ring test" familiar to inorganic chemists. It has been investigated from many standpoints, including the thermodynamic and the spectrophotometric.[2-5] The stability constant for reaction A

$$K_1 = \frac{[FeNO^{2+}(aq)]}{[Fe^{2+}(aq)][NO(aq)]}$$

has the approximate value $4.8 \times 10^2\ M^{-1}$ at 25° and an ionic strength of 0.5 *M*. This value has been calculated from the equilibrium quotient[3,6] for the reaction

$$Fe^{2+}(aq) + NO(g) \rightleftharpoons FeNO^{2+}(aq) \qquad (B)$$

using $1.4 \times 10^{-3}\ M\ atm^{-1}$ for the solubility of NO in this medium, which is based upon a crude extrapolation from available salting-out data[6] involving different electrolytes and tenfold lower ionic strengths.

The broad absorption band which gives rise to the characteristic color of solutions of this complex has a maximum at 450 mμ. Since ferrous ion, nitric oxide, and the anions present in the solution do not absorb appreciably at 450 mμ, changes in the concentration of $FeNO^{2+}$ produced by the temperature jump would be directly followed by utilizing light of this wavelength.

Experimental Section

The temperature-jump apparatus has been described in an earlier publication.[7] The nitric oxide was prepared by a method described in "Inorganic Preparations" by Walton.[8] The NO formed is quite pure, the chief impurity being the gaseous compound N_2O, which does not interfere with the kinetic experiments. Other chemicals used were all reagent grade.

Solutions were prepared by diluting 1.35 ml of concentrated H_2SO_4 to 100 ml with fresh, doubly distilled water. To prevent oxidation of ferrous ion, nitrogen was bubbled through the solution for about 15 min. The appropriate amount of ferrous ammonium sulfate was then added. The addition of nitrogen was continued for another 5 min. The nitric oxide was then bubbled into the solution until the intensity of the color remained constant, at which time the air oxidation of NO to NO_2 above the vessel became prominent. After the solution was transferred to the temperature-jump cell, more nitric oxide was passed through, so that the solution was saturated with nitric oxide at 1 atm pressure. The cell was then closed and the temperature jump initiated.

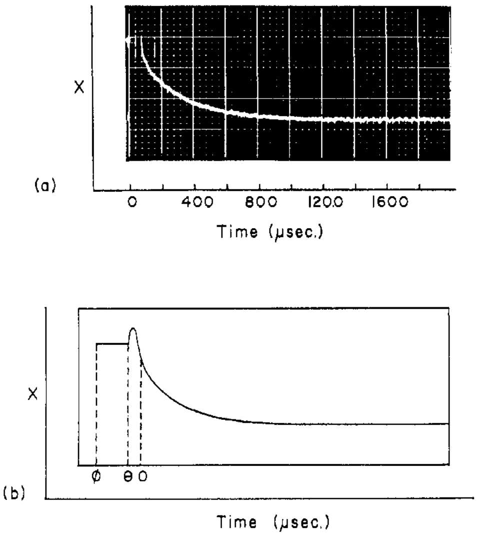

Figure 1.—Temperature-jump effect in the system $Fe^{2+} + NO \rightleftharpoons FeNO^{2+}$. (a) Actual oscillograph of a temperature-jump experiment: $[Fe^{2+}]_0 = 5.3 \times 10^{-3}\ M$, $[NO] = 1.4 \times 10^{-3}\ M$, $\mu = 0.54\ M$, $\tau = 240$ μsec. The horizontal scale is 200 μsec per major division and the vertical scale is in arbitrary units of absorbancy. An increase in *X* value is equivalent to a decrease in light transmission. The effect is complete in the first 600 μsec. However, because the solution is saturated with NO, cavitation occurs, thus accounting for the sharp decrease of the signal during the first 50 μsec. This effect is explained below. (b) Schematic representation of the relaxation effect in (a). From $t = \phi$ (an arbitrary starting point) to $t = \theta$, the point at which the temperature abruptly rises (10° in 2–3 μsec), no change in absorbance occurs. Between $t = \theta$ and $t = 0$, the cavitation is observed, obscuring the chemical relaxation. After $t = 0$, the relaxation effect can be clearly seen. The relaxation time can be measured from $t = 0$ (or any point along the curve after $t = 0$), since the curve is a simple exponential. Therefore, the portion of the effect containing the cavitation can be neglected and no error is introduced into the computation of τ.

Control experiments, consisting of NO in aqueous H_2SO_4 and ferrous ion in the same medium, were tested and found to show no evidence of relaxational effects. In addition, experiments were carried out with perchloric acid in the place of sulfuric acid. These solutions faded rapidly; nevertheless, the results were within 20 to 30% of the sulfate experiments, depending upon the rapidity with which the experiment was performed. Each solution was pulsed for numerous times, with no change in effect observed, for both perchlorate and sulfate.

Individual relaxation times have an error of ±5%. The temperature of this study is 25 ± 1°.

Results

All of the oscillographs showed the cavitation resulting from the dissolved gas in the solution. Figures 1a and 1b show a representative effect, indicating the region of cavitation and showing that its presence does not introduce an error in the calculation of the relaxation times. Since only a single relaxation occurs, the rate constant can be calculated from the equation

$$1/\tau = k_{-1} + k_1([Fe^{2+}] + [NO]) \qquad (1)$$

In order to calculate the free ferrous ion concentration, it is necessary to take into account the NO complexa-

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tion, as well as the minor effects of sulfate and bisulfate complexation, and hydrolysis. For the NO reaction, the above-mentioned K_1 was used. The NO concentration, which is the less significant of the two terms in eq 1, is also fixed by this choice. However, the initial choice of K_1 serves only as a first approximation for the treatment of the data. The graphical analysis provides the kinetically appropriate K_1, which then enables one to recalculate the independent variable, to replot the data, to redetermine the slope, and so on, until the value of K_1 converges.

The plot shown in Figure 2 represents the initial calculation. A second cycle did not show a significant change. The best straight line fitting the data yields the following rate and equilibrium constants: $k_1 = 6.2 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, $k_{-1} = 1.4 \times 10^3\ \text{sec}^{-1}$, and $K_1 = k_1/k_{-1} = 4.5 \times 10^2\ M^{-1}$.

Discussion

The equilibrium constant, K_1, determined directly from the kinetic data is consistent with the best available thermodynamic data. The association rate constant, k_1, is similar to those reported for iron(II) complexes with the neutral ligands 1,10-phenanthroline[9] and 2,2′-bipyridine,[10] which are $8 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ and $2 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, respectively. The dissociation rate constant is characteristic of the specific complex and is therefore of less immediate interest.

In order to relate the association rate constant to a characteristic property of the metal ion, a word of explanation on the mechanism of the reaction is required. The formation of a complex by substitution of a ligand into the inner coordination sphere of the metal ion has been shown to necessitate a minimum of two steps for divalent transition metal ions (and some other ions as well).[11] There is the rapid, diffusion-controlled formation of an ion pair, followed by the rate-determining substitution, as indicated in the generalized reactions

$$M^{z+}(aq) + L^{q-}(aq) \overset{K_0}{\rightleftharpoons} MW,L^{(z-q)+}(aq) \qquad (C)$$

$$MW,L^{(z-q)+}(aq) \overset{k_0}{\rightleftharpoons} ML^{(z-q)+}(aq) + H_2O \qquad (D)$$

where W represents the unsubstituted inner hydration sphere.

For these reactions it can be seen that the experimentally determined second-order rate constant, k_1, is related to the first-order rate constant, k_0, by

$$k_0 = k_1/K_0 \qquad (2)$$

It is possible to approximate K_0 by using an expression derived independently by Fuoss[12] and Eigen[13]

$$K_0 = \frac{4\pi N a^3}{3000} \exp(-U(a)/kT)\ M^{-1} \qquad (3)$$

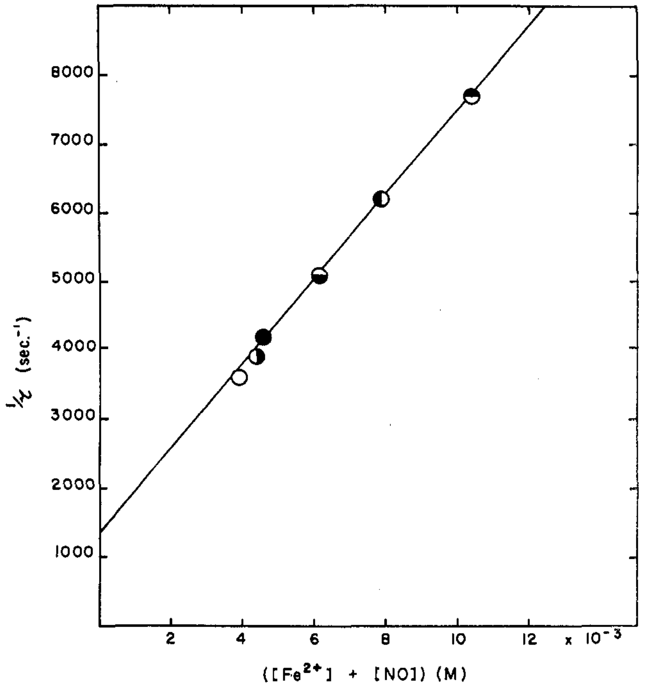

Figure 2.—A plot of $1/\tau$ *vs.* ([Fe^{2+}] + [NO]). The [NO] is the same in each run; that is, $1.4 \times 10^{-3}\ M$. The total stoichiometric concentration of ferrous ion, $[Fe^{2+}]_0$ in each solution is: ○, $4.18 \times 10^{-3}\ M$; ◑, $5.00 \times 10^{-3}\ M$; ◒, $8.00 \times 10^{-3}\ M$; ◐, $1.10 \times 10^{-2}\ M$; ◓, $1.50 \times 10^{-2}\ M$. The salt $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ together with H_2SO_4 was used in these experiments. One run in the perchlorate medium [$Fe(ClO_4)_2$ and $HClO_4$] is shown; namely, ●, $5.3 \times 10^{-3}\ M$.

where $U(a)$ is a potential energy function, N is Avogadro's number, k is Boltzmann's constant, and a is the distance of closest approach. For the reaction between a charged species and a neutral molecule, the interaction potential, $U(a)$, should be small[14] and has been taken as zero. The distance of closest approach, given by the sum of the radii of hexaaquoferrate(II) ion and NO, is 4.2 A.[15,16] From eq 3, $K_0 = 0.185\ M^{-1}$, which leads to a value of $k_0 = 3.3 \times 10^6\ \text{sec}^{-1}$. Now, by using nmr line-broadening techniques, Connick and Swift were able to measure k_0 for Fe^{2+} directly.[17] Their value of $k_0 = 3.2 \times 10^6\ \text{sec}^{-1}$ is in good agreement with the value calculated in this study, considering the gross uncertainties in calculating K_0. The results are therefore consistent with a substitution reaction of iron(II).

If, however, the complex contains monovalent iron and NO^+ as Griffith, *et al.*,[2] contend, but as has been questioned by Jørgensen,[18] an additional step has to be considered. The analysis then involves a much more complicated relationship between k_1 and the various stepwise reaction rate constants. Depending upon the validity of certain simplifying assumptions, then, the value of k_0 can be associated with either the iron(II)

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substitution which is followed by fast electron transfer or a reduction step which is followed by fast iron(I) substitution. A high value for the latter is of course reasonable since the substitution rate is very much dependent on charge (the value[19] for iron(III) is about 2 × 10^4 sec^{-1} and those for monovalent alkali metals[1] are about 10^9 sec^{-1}). It has thus been shown that, should the iron(I) complex exist in solution, it is nevertheless possible for substitution to involve iron(II).

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Resolution of the Oxalatobis(ethylenediamine)chromium(III) Ion

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The oxalatobis(ethylenediamine)chromium(III) ion was first resolved by Werner and Bosshart[2] by the method of preferential crystallization using *d*-[Co-$(en)_2(C_2O_4)$]Br as the seed material. Both Werner and Mathieu[3] found that this particular cation could not be resolved with salts a number of optically active acids.

In 1939 Bushra and Johnson[4] reported a method for obtaining one of the optical antipodes of this ion. These authors found that *d-cis*-dichlorobis(ethylenediamine)chromium(III) chloride reacted with a warm aqueous solution of ammonium oxalate without total racemization to produce some *d*-oxalatobis(ethylenediamine)chromium(III) chloride.

The present investigation was undertaken to find a direct method for the resolution which would avoid the use of substitution reactions on an optically active starting material and would also avoid the use of mixed solvents to precipitate the desired optical forms as used in the method of preferential crystallization.

Experimental Section

Synthesis of the Starting Materials.—Potassium *cis*-dioxalatodiaquochromate(III) dihydrate was prepared according to Werner.[5] *Anal.* Calcd for *cis*-$K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$: Cr, 15.34; $C_2O_4^{2-}$, 51.89. Found: Cr, 15.57; $C_2O_4^{2-}$, 51.67. The solid complex was heated on a steam bath with an excess of dry ethylenediamine for 10 min; the reaction is fairly rapid, and the progress of the reaction can be followed by the color change from gray to dark red. At the end of 10 min the reaction mixture was treated with two 50-ml portions of water and filtered to remove any unreacted starting materials. The dark red, water-insoluble precipitate which remained was washed with acetone and allowed to air dry. *Anal.* Calcd for $[Cr(en)_2(C_2O_4)][Cr(en)(C_2O_4)_2]\cdot 2H_2O$: Cr, 17.75; $C_2O_4^{2-}$, 45.2. Found: Cr, 17.74; $C_2O_4^{2-}$, 45.6. Oxalatobis(ethylenediamine)chromium(III) bromide monohydrate was prepared from the double complex, oxalatobis(ethylenediamine)chromium(III)bis(oxalato)ethylenediaminechromate(III) dihydrate, by grinding the material with an excess of concentrated hydrobromic acid and precipitating the desired product with alcohol. The crude product was collected by filtration, washed with alcohol then acetone followed by ether, and finally air dried. Purification of the complex was by recrystallization from water at 40°. *Anal.* Calcd for $[Cr(en)_2(C_2O_4)]Br\cdot H_2O$: Cr, 14.5; Br, 22.3. Found: Cr, 14.4; Br, 22.2.

Potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was prepared as described by Dwyer, Gyarfas, and Mellor.[6] *Anal.* Calcd for $KCoC_{10}H_{16}N_2O_{10}$: Co, 13.96. Found: Co, 14.1.

Potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was resolved into its optical antipodes as described by Dwyer and Garvan.[7] The optical rotations were in excellent agreement with the literature values. The *cis*-dinitrobis(ethylenediamine)cobalt(III) ion used in the resolution of the potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was prepared as described by Holtzclaw, Sheetz, and McCarty.[8]

Resolution of the Oxalatobis(ethylenediamine)chromium(III) Ion.—A 400-mg (0.0011 mole) sample of the purified racemic complex was quickly dissolved in 12 ml of water at 40°, and 0.94 g (0.003 mole) of solid *l*-potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was added with constant stirring. The dark solution was quickly cooled to 25° and kept at this temperature for 10 min. Crystallization was induced by occasional stirring and scratching of the beaker during this time.

The crystals of oxalatobis(ethylenediamine)chromium(III) ethylenediaminetetraacetatocobaltate(III) monohydrate which had precipitated during this time were filtered off, and the filtrate was immediately cooled in ice. The crystals which had been collected were washed with cold 50–50 alcohol–water, cold alcohol, acetone, and ether and then were air dried. This procedure yielded 0.305 g (81% based on oxalatobis(ethylenediamine)chromium(III) bromide monohydrate) of reddish purple crystals. The specific rotations at the sodium D line and at 5461 A were +350 and −300° for a 0.01% solution. *Anal.* Calcd for *d*-$[Cr(en)_2(C_2O_4)][CoC_{10}H_{12}N_2O_8]\cdot H_2O$: C, 30.76; H, 4.80; N, 13.46. Found: C, 30.88; H, 4.94; N, 13.19. Recrystallization did not appear to raise the optical rotations by an appreciable amount.

The filtrate was kept in ice with stirring and scratching for 5 min after the contents had cooled to 0°. The precipitate was filtered off, washed with cold 50–50 alcohol–water, alcohol, acetone, and ether, and air dried. This procedure yielded 0.205 g (55% based on the racemic complex) of reddish purple crystals whose specific rotations at the sodium D line and 5461 A were +325 and −925° for a 0.01% solution. *Anal.* Calcd for *d*-$[Cr(en)_2(C_2O_4)][CoC_{10}H_{12}N_2O_8]\cdot 4H_2O$: C, 28.31; H, 5.31; N, 12.39. Found: C, 27.99; H, 4.97; N, 12.46.

Nearly all of the excess resolving agent could be recovered in an impure form by the addition of alcohol to the filtrate.

Removal of the resolving agent from the active complex was

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