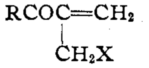
The starting material 1 is conveniently prepared from allene and acetylcobalt tetracarbonyl. A similar insertion reaction was observed for benzoylcobalt tetracarbonyl; 2-benzoyl-π-allyltricarbonylcobalt was obtained in a good yield. Preparation of 2-acyl-π-allyl complexes through a conventional route would

$$CH_3COCo(CO)_4 + C_3H_4 \longrightarrow 1$$

require a very unstable halovinyl ketone



$$\begin{array}{l}RCOC{=}CH_2\\ \quad\;|\\ \quad CH_2X\end{array}$$

as the starting material. Thus the novel insertion reaction provides a new simple route for the preparation of 2-substituted π-allyl derivatives.

Introduction of an electron-attracting acyl group into the π-allyl moiety appears to improve the air stability of π-allylcobalt tricarbonyl system. Further, the 2-acetyl-π-allyl group does not undergo an insertion reaction with isocyanide or CO; the reaction with *tert*-BuNC or PPh_3 merely results in substitution of one of the CO groups. Addition of a large excess of gaseous allene into the benzene solution of 1 at room temperature leads to the effective catalytic polymerization of

$$2 + L \longrightarrow (CH_3COC_3H_4)Co(CO)_2L + CO$$

allene into a regular 1,2 polymer.

Experimental Section

Materials and Instruments.—Dicobalt octacarbonyl[10] and sodium tetracarbonylcobaltate[11] were prepared by the standard methods. Allene (Matheson Co.; purity *ca.* 98.7%) was used without purification. The ^1H nmr spectra were measured by a Jeol JNM 4H-100 instrument using TMS as internal standard. The ir and electronic spectra were obtained by Hitachi Perkin-Elmer 225 and Hitachi EPS-3T instruments. All reactions involving organometallic compounds were carried out under nitrogen.

2-Acetyl-π-allylcobalt Tricarbonyl (1).—Into a tetrahydrofuran solution (40 ml) of sodium tetracarbonylcobaltate freshly prepared from dicobalt octacarbonyl (1.4 g, 4.9 mmol) was added a tetrahydrofuran solution (10 ml) of acetyl chloride (0.75 ml, 8 mmol) at −10° and the mixture was stirred for 2 hr. Then 195 cm^3 of gaseous allene (8.1 mmol at 20°) was slowly introduced by a syringe into the yellowish brown solution at −15° during a 1-hr period. The mixture was allowed to stand overnight at −20°, filtered, and concentrated. Distillation gave an orange liquid (0.66 g, 32%, mp −20°) boiling at 55–56° (1 mm). Ether may be employed equally well as the solvent. *Anal.* Calcd for $C_8H_7O_4Co$: C, 42.49; H, 3.10. Found: C, 42.56; H, 3.14. Ir spectrum (Nujol mull) (cm^{-1}): 3080 (vw), 3000 (w), 2920 (w), 2045 (vs), 1983 (vs), 1668 (s), 1450 (m), 1413 (m), 1360 (s), 1335 (s), 1143 (s), 1005 (m), 975 (m), 960 (m), 940 (w), 808 (w), 770 (w), 660 (m). ^1H nmr spectrum (in the order of the solvent, chemical shifts in δ (ppm) from TMS, multiplicity, area, and assignment throughout this paper): $CDCl_3$, 2.31, singlet, 5H, CH_3 and anti protons; 3.65, singlet, 2H, syn protons.

2-Benzoyl-π-allylcobalt Tricarbonyl.—Addition of an ether solution (10 ml) of benzoyl chloride (0.9 ml, 7.6 mmol) into a stirred ether solution (100 ml) of sodium tetracarbonylcobaltate (1.4 g, 7.2 mmol) at 0° was followed by introduction of gaseous allene (300 cm^3, 12.5 mmol) at −78° in a manner similar to that described above. The reaction mixture was slowly warmed up to room temperature. The raw product obtained on evaporation of the solvent was purified by repeated distillations at 130° (6 mm) on a small scale to give a deep orange liquid (0.1 g, 22%). *Anal.* Calcd for $C_{13}H_9O_4Co$: C, 54.11; H, 3.13. Found: C, 54.04; H, 3.62. Ir spectrum (neat liquid) (cm^{-1}): 3070 (w), 2075 (vs), 2000 (vs), 1650 (s), 1598 (w), 1450 (s), 1355 (s), 1218 (s), 1015 (m), 990 (m), 735 (m), 700 (m), 625 (s). ^1H nmr spectrum (in $CDCl_3$): 2.42, singlet, 2H, anti protons; 3.62, singlet, 2H, syn protons; 7.43–7.74, multiplets, 5H, phenyl protons.

Reactions of 2-Acetyl-π-allylcobalt Tricarbonyl.—(a) Protonation readily occurred simply by dissolution of 1 into concentrated sulfuric acid or 48% fluoroboric acid. The solution was stable in air at room temperature for a few hours. (b) Substitution by triphenylphosphine occurred slowly at room temperature in benzene. The formation of $CH_3COC_3H_4Co(CO)_2(PPh_3)$ was confirmed by the appearance of ir bands at 2000 and 1950 cm^{-1} and also by the ^1H nmr spectrum in CS_2: 1.46, doublet (J_{HP} = 6 Hz), 2H, anti protons; 1.90, singlet, 3H, methyl; 2.92 (J_{HP} = 2.5 Hz), 2H, syn protons; 7.2, broad multiplets, 30H, phenyl protons. (c) Substitution by *tert*-butyl isocyanide occurred slowly at room temperature in benzene to give $CH_3COC_3H_4Co(CO)_2$(*tert*-BuNC). The raw product had ir bands at 2100 cm^{-1} (ν_{NC}), 1995 cm^{-1} (ν_{CO}), and 1950 cm^{-1} (ν_{CO}). The ^1H nmr spectrum (in CS_2) was consistent with the structure: 1.43, singlet, 9H, *tert*-Bu; 1.75, singlet, 2H, anti protons; 2.07, singlet, 3H, CH_3; 2.93, singlet, 2H, syn protons.

Acknowledgment.—Experimental assistance of Mr. K. Nakajima and Mr. K. Osaki is gratefully acknowledged.

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Kinetics and Equilibria of Structural Interconversions. II. Cobalt(II) Bromide–Pyridine–Nitromethane

BY ROBERT D. FARINA AND JAMES H. SWINEHART*[1]

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A kinetic examination of octahedral–tetrahedral equilibrium in the cobalt(II) bromide–pyridine–nitromethane system has been carried out as part of a continuing study of the effects of ligands and solvents on the structural interconversions of cobalt(II) halide complexes in organic solvents.[2] Ligand properties can influence the coordination number of metal ions and much work has been directed toward evaluating their role in affecting the relative stabilities of octahedral and tetrahedral complexes of cobalt(II) halides.[3-5]

Experimental Section

Materials.—$Co(py)_2Br_2$ was the source of cobalt(II) and was prepared from cobalt(II) bromide hexahydrate[6] and pyridine by established techniques.[7] The visible spectrum of $Co(py)_2Br_2$ in nitrobenzene was in agreement with that obtained by other workers.[7] Pyridine and nitromethane were Spectroquality solvents from Allied Chemicals and Matheson Colemen and Bell, respectively. Eastman Chemicals tetraethylammonium perchlorate and tetrabutylammonium bromide were used with the latter salt further purified by recrystallization from ethyl acetate and anhydrous benzene. Both salts were dried under vacuum at 100° for 2 hr before use. The water content of 0.1 M solutions of Et_4NClO_4 and/or Bu_4NBr in pyridine and nitromethane did not exceed 0.01_4 and 0.03_3 M, respectively, as determined by the Karl Fischer method.

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[1] Address correspondence to this author.

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Kinetic Experiments.—The temperature-jump apparatus and technique for measuring the temperature change have been described elsewhere.[2] Concentration changes resulting from temperature perturbations were followed photometrically in the 585–610-nm region. For changes in concentration near equilibrium

$$\frac{d\Delta C}{dt} = -\frac{1}{\tau}\Delta C$$

where ΔC is the concentration difference between that at a given time and the final concentration, and τ is defined as the relaxation time. Recorded τ values are the average of at least two measurements. Solutions of 0.1 M Et_4NClO_4 and/or Bu_4NBr equilibrated at designated temperatures for at least 30 min prior to the applied temperature perturbation. Density corrections were made in determining concentrations.

Equilibrium Experiments.—Equilibrium constants for the reaction

$$^{oct}Co(py)_4Br_2 = {}^{tet}Co(py)_2Br_2 + 2py \qquad K_1 \qquad (1)$$

in pyridine and nitromethane were determined spectrally using thermostated cells (±0.5°) of the Cary Model 14 recording spectrophotometer. The method of determining equilibrium constants for these systems in nitromethane has been previously described.[3] The determination of equilibrium constants in pyridine was somewhat different from that used on the corresponding chloride system.[8] Optical absorptivities at the absorption maxima of $Co(py)_2Br_2$ in pyridine were estimated by heating the solution until no increase in absorbance was observed (approximately 97°). The estimated optical absorptivities at 647 and 597 nm are 525 and 344 M^{-1} cm^{-1} at 25° after density corrections. This assumes no intrinsic temperature dependence of the optical absorptivities. The concentration of the tetrahedral species was obtained from the absorbance at 647 nm where the contribution from the octahedral species is negligible.

Results and Discussion

Equilibrium Results.—The equilibrium data for reaction 1 in nitromethane and pyridine are contained in Tables I and II. The equilibrium constants are 1.4 and 4.7 M^2 in nitromethane and pyridine, respectively, at 25°. The enthalpy changes for reaction 1, ΔH_1, are 11.2 ± 0.6 (nitromethane) and 13.4 ± 1.3 kcal/mol (pyridine).

Table I

Summary of Equilibrium Data in Nitromethane[a]

Temp, °C	[py], M	K, M^2	No. of expts
27	0.49–2.46	1.8 ± 0.1	8
39	0.49–2.42	3.5 ± 0.3	8
48	0.49–2.40	5.8 ± 0.7	8
57	0.61–2.40	8.0 ± 0.4	4

[a] Ionic strength 0.1 (Et_4NClO_4); absorbance measured at 647 nm where $Co(py)_2Br_2$ absorbs; density corrections made at different temperatures.

Table II

Equilibrium Data in Pyridine[a]

A[b]	[py],[c] M	K_{calcd}, M^2	Temp, °C
0.593	11.9	56	63.0
0.349	12.0	29	51.5
0.178	12.2	13	41.0
0.092	12.3	6.9	32.0

[a] Total Co(II) is 4 × 10^{-3} M and μ = 0.1 (Et_4NClO_4) after density corrections. [b] $Co(py)_2Br_2$ absorption at 647 nm; $\epsilon_{Co(py)_2Br_2}$ 525 M^{-1} cm^{-1}. [c] Concentrations corrected at the different temperatures.

Figure 1 shows the spectral changes that occur when bromide and pyridine are added to 10^{-3} M $Co(py)_2Br_2$ in nitromethane. Two absorbing species are present up to 10^{-2} M bromide: $Co(py)_2Br_2$ (597 and 647 nm) and $Co(py)Br_3^-$ (621, 649, and 682 nm). The isosbestic point obtained is illustrated by curves 1 and 2 in Figure 1. When 10^{-2} M pyridine is added with 2 × 10^{-3} M free bromide present, the resulting absorption curve 3 does not pass through the isosbestic point. This suggests formation of the octahedral complex due to displacement of equilibrium 1 to the left. At bromide concentrations exceeding 10^{-2} M $CoBr_4^{2-}$ forms, as evidenced by the appearance of new bands at longer wavelengths corresponding to those reported for the tetrahalide complex in nitromethane.[9] A new isosbestic point (curves 4 and 5) is formed as a result of the equilibrium between $Co(py)Br_3^-$ and $CoBr_4^{2-}$. No appreciable spectral change occurs at $[Br^-] < 0.1$ M indicating that only $CoBr_4^{2-}$ is present.

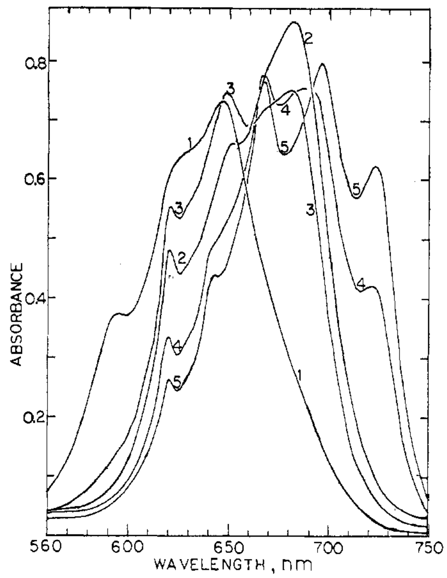

Figure 1.—Absorbance *vs.* wavelength (nm) of solutions of 1.0 × 10^{-3} M $Co(py)_2Br_2$ in nitromethane with (1) no added Br^-, (2) 2.0 × 10^{-3} M Br^-, (3) 2.0 × 10^{-3} M Br^- and 1.0 × 10^{-2} M pyridine, (4) 5.0 × 10^{-2} M Br^-, and (5) 1.0 × 10^{-1} M Br^-. μ = 0.10 (Et_4NClO_4 and/or Et_4NBr), temperature is 8.6°, and path length is 1.0 cm.

Introduction of bromide (4 × 10^{-3} to 5 × 10^{-2} M) to 4 × 10^{-3} M solutions of $Co(py)_2Br_2$ in pyridine increases the intensity of the spectral band at 647 nm while the band at 597 nm disappears. Two new bands appear at 621 and 675 nm which overlap the third band at 647 nm giving rise to the increased absorbance at this wavelength. The spectral changes are probably due to a reaction of the type

$$Co(py)_4Br_2 + Br^- = Co(py)Br_3^- + 3py \qquad (2)$$

The enthalpy change for equilibrium 2 in pyridine was obtained from the temperature dependence of the absorbancies at 675 and 621 nm. The value of ΔH_2 obtained was 13.9 ± 0.3 kcal/mol, which is within experimental error of ΔH_1 in pyridine. Since reaction 2 can be expressed as the sum of reaction 1 and

$$Br^- + Co(py)_2Br_2 = Co(py)Br_3^- + py \qquad (3)$$

then $\Delta H_2 = \Delta H_1 + \Delta H_3$. Consequently, ΔH_3 is small, which is in agreement with observations from the kinetic measurements.

Kinetic Results.—Both conductivity and spectral

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measurements in nitromethane support the equilibrium represented by reaction 1.[3] Although other reaction schemes were tested, the kinetic data derived from measurements made on reaction 1 were consistent with the following mechanism where reaction 4 equilibrates rapidly compared to reaction 5

$$^{oct}Co(py)_4Br_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Co(py)_3Br_2 + py \qquad K_4 \tag{4}$$

$$Co(py)_3Br_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} {}^{tet}Co(py)_2Br_2 + py \qquad K_5 \tag{5}$$

Two relaxations are predicted for this mechanism. Since $^{tet}Co(py)_2Br_2$ is being monitored, only one relaxation is observed and it is in the microsecond range. If $Co(py)_3Br_2$ is present at small concentrations

$$(\tau[py])^{-1} = k_{-5} + k_5K_4[py]^{-2} \tag{6}$$

Figure 2 is a plot of $(\tau[py])^{-1}$ *vs.* $[py]^{-2}$ in nitromethane. At 8.6°, the plot remains linear for pyridine concentrations up to 3.1 M but deviates at larger concentrations. This deviation is consistent with the observation that k_{-5} is smaller in pure pyridine. In nitromethane the values of k_{-5} and k_5K_4 at temperatures accurate to within ±0.10° are (1.7 ± 0.2) × 10^4 M^{-1} sec^{-1}, (7.80 ± 0.5) × 10^3 M sec^{-1} (4.6°); (2.0 ± 0.3) × 10^4, (1.1 ± 0.1) × 10^4 (8.6°); and (2.5 ± 0.2) × 10^4, (2.3 ± 0.3) × 10^4 (13.0°) at μ = 0.1 (Et_4NClO_4). From a plot of ln (k_{-5}/T) *vs.* $1/T$ the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 6.8 ± 0.6 kcal/mol and −15 ± 3 eu, respectively. The consistency of k_5K_4 and k_{-5} was checked using the expression $K_1 = k_5K_4/k_{-5}$ from which the overall equilibrium constant K_1(kinetic) can be determined and compared with K_1(spectral). The values of K_1(spectral) and K_1(kinetic) at various temperatures are 0.36 M^2, 0.43 M^2 (4.6°); 0.47 M^2, 0.48 M^2 (8.6°); and 0.85 M^2, 0.92 M^2 (13.0°), respectively. The effect of the cobalt(II) concentration, as derived from $Co(py)_2Br_2$, on the relaxation time was examined. At 8.6° and 4.0 M pyridine, solutions of 1.0 × 10^{-2} and 6.6 × 10^{-2} M $Co(py)_2Br_2$ gave $10^{-4}/\tau$ values of 7.1 and 7.2 sec^{-1}, respectively. For nitromethane solutions of 1.0 × 10^{-2} M $Co(py)_2Br_2$ and 2.5 M pyridine, $10^{-4}/\tau$ values at various $[H_2O]$ are 5.3 sec^{-1} (0.03 M), 5.2 sec^{-1} (0.65 M), and 5.7 sec^{-1} (1.23 M), respectively.

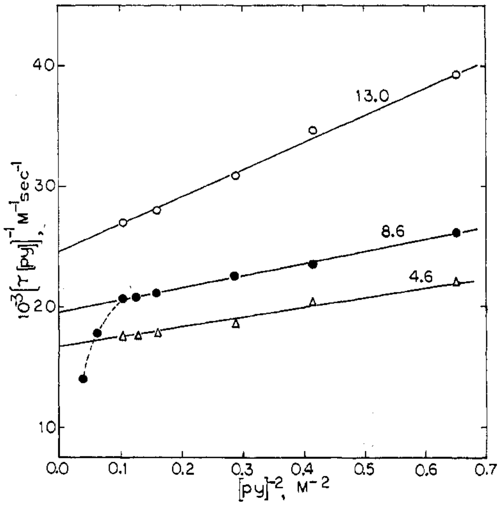

Figure 2.—Plot of $(\tau[py])^{-1}$ *vs.* $[py]^{-2}$ for 1.0 × 10^{-2} M $Co(py)_2Br_2$ in nitromethane–pyridine mixtures at 4.6° (Δ), 8.6° (●), and 13.0° (O). μ = 0.1 (Et_4NClO_4).

Attempts to study equilibrium 2 were unsuccessful. No effort was made to study the equilibrium between $Co(py)Br_3^-$ and $CoBr_4^{2-}$ since solutions containing these species showed no absorbance change when heated. Evidently ΔH for halide addition to tetrahedral cobalt(II) complexes is small as suggested by enthalpy measurements made on the trichloride and tribromide systems in pyridine.

Kinetic measurements made on reaction 1 in pyridine gave the following values of $1/\tau$ at different temperatures: (3.0 ± 0.2) × 10^4 sec^{-1} (13.0°), (3.5 ± 0.1) × 10^4 sec^{-1} (21.5°), (3.9 ± 0.2) × 10^4 sec^{-1} (28.0°), and (4.6 ± 0.2) × 10^4 sec^{-1} (38.5°) at μ = 0.1 (Et_4NClO_4). Equation 6, when rearranged to include K_1, becomes

$$\tau^{-1} = k_{-5}([py] + K_1/[py]) \tag{7}$$

The value of k_{-5} in pyridine at 25° is 2.9 × 10^3 M^{-1} sec^{-1}, a factor of 14 less than in nitromethane assuming the same mechanism is operative. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for k_{-5} are 2.4 ± 0.8 kcal/mol and −35 ± 4 eu. The relaxation time is independent of the cobalt(II) concentration between 0.01 and 0.1 M. Added bromide up to 0.1 M does not influence the relaxation time. Spectral measurements show $Co(py)Br_3^-$ is present in $Co(py)_2Br_2$ solutions containing 0.1 M Br^-. Despite the presence of $Co(py)Br_3^-$ it appears that the relaxation process being measured corresponds to reaction 1. Introduction of 1.1 M water increased the rate constant k_{-5} from 2.2 × 10^3 to 3.1 × 10^3 sec^{-1} at 8.6° and μ = 0.1 (Et_4NClO_4).

The activation parameters of k_{-5} for cobalt(II) bromide and chloride in nitromethane–pyridine [$\Delta H^{\ddagger}$ = 6.8 ± 0.6 (Br^-), 5.4 ± 0.8 kcal/mol (Cl^-); $\Delta S^{\ddagger}$ = −15 ± 3 (Br^-), −18 ± 3 eu (Cl^-)] and in pyridine [$\Delta H^{\ddagger}$ = 2.4 ± 0.8 (Br^-), 2.6 ± 1.0 kcal/mol (Cl^-); $\Delta S^{\ddagger}$ = −35 ± 4 (Br^-) and −34 ± 4 eu (Cl^-)] are similar. A slightly larger reactivity of the chloride complex compared to the corresponding bromide complex was observed in a study of the ligand exchange of some tetrahedral tertiary phosphine complexes of cobalt(II) bromide and chloride in deuteriochloroform.[10] At 25° in our nitromethane study k_{-5} is slightly larger for the chloride complex then the bromide complex. Zumdahl and Drago[11] examined the exchange of 2-picoline (2-methylpyridine) with dichlorobis(2-picoline)cobalt(II) in acetone-d_6. A pentacoordinated activated complex was postulated and the second-order rate constant was about 10^6 M^{-1} sec^{-1} at 25°. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were 4.8 kcal/mol and −15 eu, respectively. The rate constants k_{-5} and activation parameters determined in this study and the cobalt chloride study[2] also suggest the formation of a pentacoordinated activated complex. Howard and Marianelli[12] have investigated the cobalt(II) chloride–pyridine equilibria and the exchange of pyridine with $Co(py)_4Cl_2$ and have found their data to be consistent with the mechanism proposed in reactions 4 and 5 and ref 2.

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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 chloroform[3] 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, $Co(py)_3Br_2$; 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.

Acknowledgment.—The authors acknowledge support of this work through a grant (PRF-2177-A3,5) from the Petroleum Research Fund administered by the American Chemical Society.

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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, $(NC)_5FeNO^{2-} \equiv RNO^{2-}$) 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-}

$$RNO^{2-} + SO_3^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RNO(SO_3)^{4-} \quad Q_1 \qquad (1)$$

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: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. It is suggested from the above studies that the equilibrium

$$RNO(SO_3)^{4-} + M^+ = [RNO(SO_3)]M^{3-} \quad Q_2 \qquad (2)$$

along with (1), must be considered in a description of the system. Another equilibrium study indicates that, besides the 1:1 RNO^{2-}–SO_3^{2-} species, a 1:2 RNO^{2-}–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.[3] An infrared analysis of salts of $(NC)_5FeNO(SO_3)^{4-}$ suggests that the bonding is $(NC)_5FeNOSO_3^{4-}$.[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—$Na_2[(NC)_5FeNO] \cdot 2H_2O$, Na_2SO_3, NaCl, CsCl, and $Na_2C_{10}H_{14}N_2O_8 \cdot 2H_2O$ (disodium salt of ethylenediaminetetraacetic acid, Na_2EDTA)—were reagent grade. Stock solutions were prepared by adding weighed amounts of $Na_2[(NC)_5FeNO] \cdot 2H_2O$ 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[6,8]

$$(NC)_5FeNO^{2-} + 2OH^- = (NC)_5FeNO_2^{4-} + H_2O$$

$$(NC)_5FeNO_2^{4-} + H_2O = (NC)_5FeH_2O^{3-} + NO_2^-$$

$$\left\{\begin{matrix}(NC)_5FeNO_2^{4-}\\(NC)_5FeH_2O^{3-}\end{matrix}\right\} + SO_3^{2-} = (NC)_5FeSO_3^{5-} + \left\{\begin{matrix}NO_2^-\\H_2O\end{matrix}\right\}$$

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 ±0.2°.

Results and Discussion

Equilibrium Measurements.—It has been suggested from previous work[2-4] that equilibria 1 and 2 may be present in aqueous solutions containing RNO^{2-}, SO_3^{2-}, and an inert electrolyte, MCl (where $M^+ \equiv Li^+, Na^+, K^+$, 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_4^{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

$$M^+ + SO_3^{2-} \rightleftharpoons MSO_3^- \quad Q_3 \qquad (3)$$

$$MSO_3^- + RNO^{2-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [RNO(SO_3)]M^{3-} \quad Q_4 \qquad (4)$$

where Q_3 and Q_4 represent the equilibrium concentra-

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