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Autocatalysis by Co(II) in the Reduction of Carbonatocobaltate(III) Complexes by Hydrazine in Aqueous Carbonate–Bicarbonate Solution

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The kinetics of the title reaction have been investigated in aqueous Na_2CO_3–$NaHCO_3$ media at ionic strength 1.0 M. In the pH range 8–10 the experimental rate expression contains two terms representing different reaction pathways. One term is similar to expressions obtained for substitution reactions of cobalt(III)–carbonato complexes and is consistent with a mechanism involving a rate-determining substitution process followed by a fast inner-sphere redox decomposition of the carbonatocobalt(III)–hydrazine complex. The second term in the rate expression involves autocatalysis by Co(II). A mechanism is proposed which involves an outer-sphere electron-transfer step between $Co(CO_3)_3^{3-}$ and a Co(II) complex containing carbonate and hydrazine ligands. Such electron transfer results in substitution of hydrazine onto Co(III) and is followed by fast redox decomposition. The composition of the Co(II)–hydrazine complex is discussed. In solution of pH <7, Co(II) promotes the formation of a Co(III) complex which is more stable toward redox decomposition and which is believed to contain several hydrazine ligands. This complex is not formed when Co(II) is made ineffective by complexing with ethylenediaminetetraacetate.

Introduction

The reduction of tris(carbonato)cobaltate(III) by hydrazine proceeds according to

$$(1 + 3x)\mathrm{Co(III)} + N_2H_4 = (1 + 3x)\mathrm{Co(II)} + N_2 + {}^1/_2(1 - x)(N_2 + 2NH_3)$$

A previous study[2] of this reaction has determined that x varies between 0.86 and 2.02 depending on the relative concentrations of the reactants. This study has also suggested that the reaction proceeds via an intermediate substitution product which then undergoes internal redox decomposition at a slower rate. At that time there was little known about the substitution reactions of tris(carbonato)cobaltate(III) and there was some question as to the nature and stability of the complex in solution. Recent work[3] has indicated that in aqueous sodium bicarbonate solution, carbonatocobaltate(III) complexes are relatively stable and such solutions can be used for mechanistic studies. Kinetics of the substitution reactions of pyridine, ethylenediamine, and other nitrogen donor ligands in these aqueous bicarbonate solutions have been interpreted by assuming that under the reaction conditions different monomeric carbonatocobaltate(III) complexes exist in equilibrium, e.g.

$$Co(CO_3)_3^{3-} + H_3O^+ \rightleftharpoons Co(CO_3)_2(HCO_3)H_2O^{2-}$$

$$Co(CO_3)_2(HCO_3)H_2O^{2-} + H_2O \rightleftharpoons Co(CO_3)_2(H_2O)_2^- + HCO_3^-$$

The incoming ligand was believed to replace a coordinated water molecule in a rate-determining substitution step.

Since the earlier investigation of the hydrazine–tris(carbonato)cobaltate(III) reaction proposed a mechanism involving substitution, it was decided to study this reaction in more detail. The rate of the hydrazine reaction could then be compared to the rate of substitution of ligands which have similar coordinating properties but are not reducing agents. Ligands which are potential reducing agents often undergo substitution reactions with Co(III) complexes more rapidly than nonreducing ligands,[4] although in the substitution of the coordinated water in $Co(CN)_5H_2O^{2-}$ hydrazine reacts at a rate similar to ligands such as pyridine and ammonia.[5]

Also of interest is the nature of the intermediate substitution product itself. The spectrum of this purple cobalt(III) complex[2] suggests that several (more than two) hydrazine molecules are coordinated to the metal. Since the final product of pyridine substitution is *cis*-bis(carbonato)bis(pyridine)-cobaltate(III), one of the objects of the present study is to determine the mechanistic differences between the two reactions which could account for the apparent difference in the substitution products.

Oxidation of hydrazine by metal complexes yields either molecular nitrogen alone or a mixture of molecular nitrogen and ammonia as the ultimate products.[6,7] The stoichiometry is dependent on the reaction mechanism.[8] Reactions may be of the outer-sphere or inner-sphere type, depending on the lability of the complex involved and on its strength as an oxidizing agent, and may involve radical or nonradical mechanisms. The stoichiometry of the hydrazine–tris(carbonato)cobaltate(III) reaction has been investigated in some detail.[2] This paper concentrates on the kinetics of the reaction, attempting to distinguish not between radical or nonradical mechanisms but between outer-sphere and inner-sphere processes.

Experimental Section

Sodium tris(carbonato)cobaltate(III) trihydrate was prepared by the literature procedure[9] and stored in a desiccator over P_2O_5 in the dark. Saturated solutions in 1 M $NaHCO_3$ were prepared and stored as described in ref 3a. The concentration of Co(III) in the stock solution was determined, after addition of KI and acidification with 2 M acetic acid, by titration of the liberated iodine with standard thiosulfate solution.[10] The concentration of Co(III) was in close agreement with the value obtained spectrophotometrically at λ 440 and 635 nm using literature molar absorptivities.[3a] Other solutions were therefore analyzed only by spectrophotometry. The concentration of Co(II) in the stock solution was determined from the absorbances at λ 440 and 635 nm after addition of 30% hydrogen peroxide.[10] After oxidation of the stock solution the absorbance of these wavelengths showed a marked increase indicating the presence of a significant concentration of Co(II).

Solutions of cobalt(II) sulfate, hydrazine sulfate, zinc sulfate, copper(II) sulfate, manganese(II) sulfate, nickel(II) sulfate, sodium bicarbonate, sodium carbonate, disodium ethylenediaminetetraacetate, and sodium chloride were prepared fom analytical grade chemicals. Pyridine was fractionally distilled from barium oxide. All pH measurements were made on a Radiometer Model 26 pH meter calibrated with standard borate and phosphate buffers. The acid dissociation constant of $N_2H_5^+$ at $\mu = 1.0$ was determined by pH titration. The spectra of cobalt(II) sulfate in aqueous carbonate–bicarbonate solution ($\mu = 1.0$) in the presence of hydrazine were measured on a Cary 15 spectrophotometer using 10.0-cm cells. All other spectral measurements and single-wavelength absorbance measurements were made on a Perkin-Elmer Model 402 recording spectrophotometer fitted with a thermostated cell housing. The temperature was maintained at 25.00 ± 0.04 °C, the temperature of the reaction mixture being measured in the cell by a thermistor.

The ionic strength of all reaction mixtures was adjusted to 1.0 M by addition of sodium chloride. An aliquot of 2.5 mL of the reaction mixture minus the hydrazine was pipetted into the spectrophotometer cell and brought to the reaction temperature. The reaction was initiated by syringe addition of 0.1 mL of a solution of hydrazine sulfate also at the reaction temperature. A stream of nitrogen was then

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bubbled through the reaction solution for a few seconds to effect mixing. Initial experiments were carried out on degassed solutions maintained under nitrogen throughout the kinetic measurements. However, the results of these experiments were identical with those in which air was not excluded and consequently most of the reactions reported were studied under the latter conditon. The reactions were studied by repetitive scanning over the wavelength range 350–750 nm and by following the change in absorbance with time at λ 440 nm. In most cases a fivefold expansion of the absorbance scale was necessary due to the low concentration of cobalt(III) complex employed. At these low absorbances, traces of white solid material (probably $CoCO_3$) in some of the reaction mixtures caused the absorbance readings to be high. Consequently all of the stock solutions were filtered through a Millipore filter. In the kinetic experiments the concentrations of the different species were varied within the following analytical concentration ranges: [hydrazine] = $(1.3\text{–}13.0) \times 10^{-3}$ M, [Co(III)] = $(4.0\text{–}9.8) \times 10^{-4}$ M, $[HCO_3^-]$ = 0.154–0.462 M, $[CO_3^{2-}]$ = 0.00–0.246 M, [Co(II)] = $(0.00\text{–}2.4) \times 10^{-3}$ M, [EDTA] = $(0.00\text{–}1.9) \times 10^{-2}$ M, $[Ni^{2+}] = 7.7 \times 10^{-4}$ M, $[Zn^{2+}] = 7.7 \times 10^{-4}$ M, $[Cu^{2+}] = 6.15 \times 10^{-4}$ M, $[Mn^{2+}] = 7.7 \times 10^{-4}$ M. Reaction mixtures at pH <8 were prepared by adding small volumes of 1.0 M HCl to the bicarbonate solutions.

Results

Preliminary spectral scans over the wavelength range 350–750 nm on hydrazine–tris(carbonato)cobaltate(III) reaction mixtures indicated that the overall redox reaction proceeds at a faster rate as the pH increases. At pHs below 7.2 the "purple intermediate" (previously discussed) is formed in a period of minutes and this reacts to give products over a period of hours. In reaction mixtures of higher pH, no intermediate was detected even in the presence of a large excess of hydrazine. In all cases, the spectrum of the final product was that expected for Co(II). The failure to detect an intermediate in solution of pH >7.2 is contrary to evidence presented in ref 2. This apparent evidence may have been the result of an increase in absorbance caused by traces of precipitate, as discussed in the Experimental Section.

Evolution of CO_2 in solutions of low pH (<7.5) caused fluctuations in absorbance measurements and changes in pH. Consequently accurate kinetic measurements were restricted to the pH range 8–10 where the purple complex was not detected. The consumption ratio of $[Co(III)]/[N_2H_4] \geq 2.0$ allowed first-order conditions to be maintained with a smaller excess of N_2H_4 than would be necessary for a reaction of 1:1 stoichiometry. A typical pseudo-first-order plot of ln $(A_t - A_\infty)$ against t is shown in Figure 1A. The initial curvature is a general feature which becomes more pronounced with increasing pH. Addition of EDTA to the reaction mixture results in a much slower reaction and produces a linear rate plot to over 90% completion (Figure 1). The reaction rate is independent of the concentration of EDTA providing that it is in excess of the initial complex concentration. In most of the reaction mixtures to which EDTA was added, the concentration of cobalt(II) not bound to EDTA was $<10^{-14}$ M. Solutions containing only tris(carbonato)cobaltate(III) and EDTA at similar pHs showed no spectral change over a period of several hours.[11] Hence during the oxidation–reduction process direct reaction between EDTA and the Co(III) complex is negligible. The effect of EDTA in straightening the rate plot and slowing the reaction suggested that the rate equation contained two terms, one of which depended on Co(II) produced by the reaction. The effect of Co(II) is suppressed by complexation with EDTA producing a simple pseudo-first-order rate expression. Addition of cobalt(II) sulfate solution to reaction mixtures resulted in large rate increases and decreased initial curvature of the rate plots. In these reactions the rate of the catalyzed reaction is very large compared to that of the uncatalyzed pathway. The dependence of the observed constants on [Co(II)] is shown in Figure 2. Each rate constant in this figure was calculated from the straight part of the rate plot toward the end of the reaction. The maximum initial concentration of Co(II) was approximately 2×10^{-3} M since greater concentrations resulted in precipitation of $CoCO_3$.

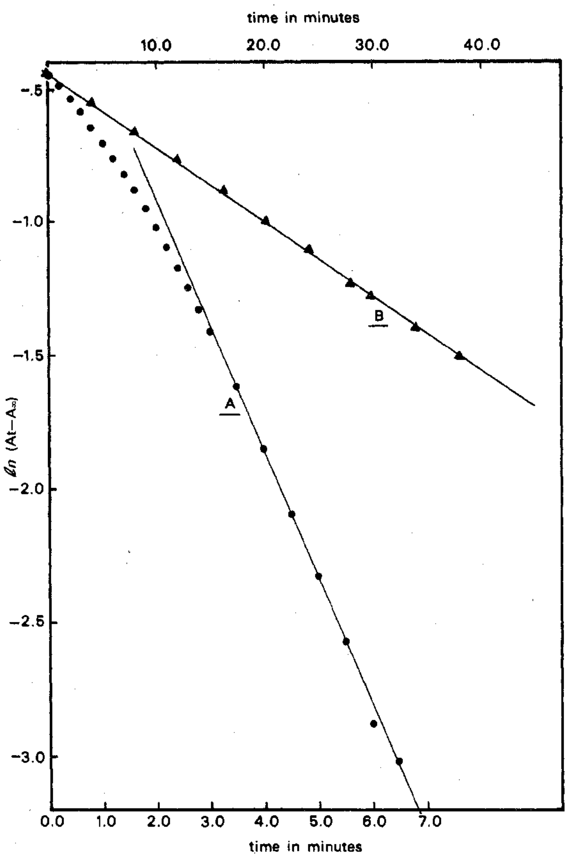

Figure 1. ln $(A_t - A_\infty)$ vs. time at λ 440 nm. A (lower time scale): $[Co(III)]_0 = 8.12 \times 10^{-4}$ M, $[Co(II)]_0 = 2.94 \times 10^{-4}$ M, $[N_2H_4]_0 = 4.23 \times 10^{-3}$ M, $[HCO_3^-] = 0.283$ M, $[CO_3^{2-}] = 0.089$ M, pH 9.07. B (upper scale): same concentrations as A except for presence of [EDTA] = 3.05×10^{-3} M.

In the absence of EDTA, the reaction rate can be described by eq 1. The pseudo-first-order rate constant (k_1) for the

$$-\mathrm{d}[\mathrm{Co(III)}]/\mathrm{d}t = k_1[\mathrm{Co(III)}] + k_2[\mathrm{Co(III)}][\mathrm{Co(II)}] \qquad (1)$$

uncatalyzed pathway and the pseudo-second-order constant (k_2) for the catalyzed reaction are discussed below.

Equation 1 integrates to

$$\frac{\ln(1 + Q[\mathrm{Co(II)}]_0 + QX)}{1 + Q[\mathrm{Co(II)}]_0} - \frac{\ln([\mathrm{Co(III)}]_0 - X)}{[\mathrm{Co(III)}]_0} = (1 + Q[\mathrm{Co(II)}]_0 + [\mathrm{Co(III)}]_0)k_1 t \qquad (2)$$

where $Q = k_2/k_1$ and X is the concentration of complex converted to products at time t. The initial concentration of Co(II), $[Co(II)]_0$, includes the Co(II) present to the extent of approximately 30% of $[Co(CO_3)_3^{3-}]$ in the stock solution as found by analysis.

Rate data in Figure 1 A are replotted in Figure 3 using eq 2. The values of k_1 and k_2 which are consistent with eq 2 are identical (within experimental error) with the values of k_1 and k_2 determined by addition of EDTA and excess Co(II), respectively. The more accurate values were determined by the latter procedures since each reaction pathway is studied independently, and the rate constants were obtained from first-order plots. All of the rate constants discussed below were determined using these procedures.

Uncatalyzed Reaction. The rate constant k_1 (eq 1) is directly proportional to the total hydrazine concentration (at

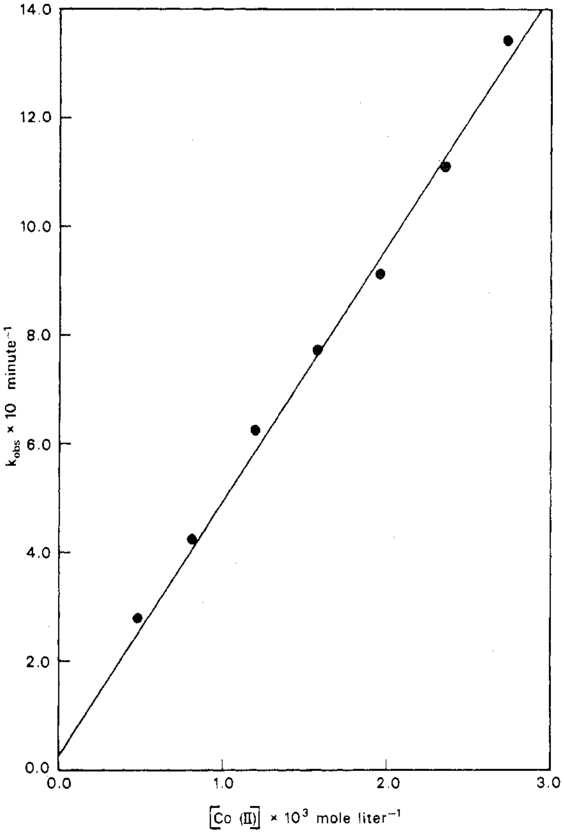

Figure 2. k_{obsd} vs. [Co(II)] (assumed to be $[Co(II)]_0 + [Co(III)]_0$). Rate constants determined from straight part of first-order rate plots after 75% completion of reaction; pH ≃9.10, $[HCO_3^-] = 0.283$ M, $[CO_3^{2-}] = 0.089$ M.

constant $[HCO_3^-]$ and constant pH) and inversely proportional to $[HCO_3^-]$ (at constant $[N_2H_4]_{tot}$ and constant pH). The pH dependence of k_1 (Figure 4) shows the reaction rate passing through a shallow minimum around pH 9.

The rate data are fit by a three-term equation of the general form

$$k_1 = (A[H_3O^+] + B + C[H_3O^+]^{-1})\frac{[N_2H_4]}{[HCO_3^-]} \qquad (3)$$

where

$$[N_2H_4] = \left(\frac{K_A}{K_A + [H_3O^+]}\right)[N_2H_4]_{tot}$$

K_A, the acid dissociation of constant of $N_2H_5^+$, was determined by pH titration to be 4.79×10^{-9} M. The inverse dependence on $[HCO_3^-]$ implies that a carbonate ligand is lost from tris(carbonato)cobaltate(III) in a reversible step prior to the rate-determining step.[12] The three rate constant terms in eq 3 indicate parallel pathways differing in the proton content of the activated complexes.

A rate constant/pH profile such as shown in Figure 4 normally suggests that at least two acid–base equilibria have to be considered.[13] The suggestions of Davies[3] regarding the species present in the Co(III) carbonate–bicarbonate buffer system (eq 4, 5) provide a scheme for interpreting these results,

$$Co(CO_3)_3^{3-} + H_3O^+ \overset{K_1}{\rightleftharpoons} Co(CO_3)_2CO_3H{\cdot}H_2O^{2-} \qquad (4)$$

$$Co(CO_3)_2CO_3H{\cdot}H_2O^{2-} \overset{K_2}{\rightleftharpoons} Co(CO_3)_2(H_2O)_2^- + HCO_3^- \qquad (5)$$

where[3a] $K_1 = (1.31 \pm 0.12) \times 10^9$ M^{-1} and $K_2 < 0.06$ M.

In the reaction with hydrazine only species having lost a carbonate ligand need be considered, vide supra.

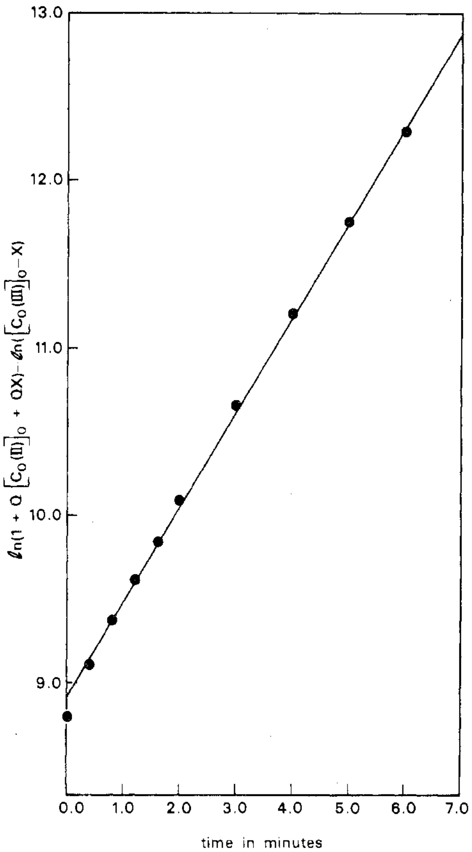

Figure 3. $\ln(1 + Q[Co(II)]_0 + QX) - \ln([Co(III)]_0 - X)$ vs. time (see eq 2). Concentration data given in Figure 1. $Q = 1.9 \times 10^4$, $k_1 = 2.6 \times 10^{-2}$ min^{-1}, $k_2 = 4.9 \times 10^2$ M^{-1} min^{-1}.

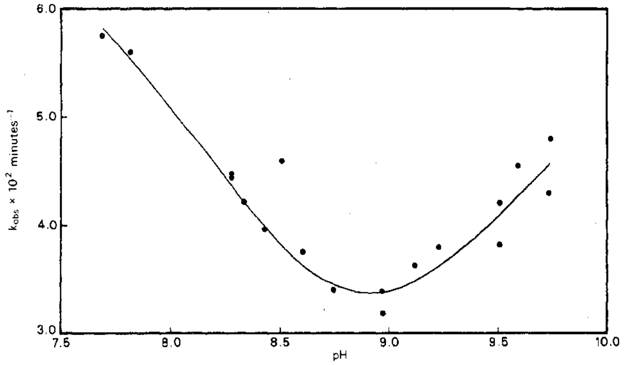

Figure 4. k_{obsd} vs. pH for the uncatalyzed reaction. $[HCO_3^-] = 0.231$ M, [hydrazine] $= 4.23 \times 10^{-3}$ M, $[Co(III)]_0 = 8.22 \times 10^{-4}$ M, [EDTA] $= 3.85 \times 10^{-3}$ M.

The experimental rate expression is consistent with a mechanism involving the equilibria

$$Co(CO_3)_2(H_2O)_2^- + H_2O \overset{K_3}{\rightleftharpoons} Co(CO_3)_2(H_2O)OH^{2-} + H_3O^+ \qquad (6)$$

$$N_2H_5^+ + H_2O \overset{K_A}{\rightleftharpoons} N_2H_4 + H_3O^+ \qquad (7)$$

which lead to the possible rate-determining steps

$$Co(CO_3)_2(H_2O)_2^- + N_2H_5^+ \xrightarrow{k_H} \text{products} \qquad (8)$$

$$Co(CO_3)_2(H_2O)_2^- + N_2H_4 \xrightarrow{k} \text{products} \qquad (9)$$

$$Co(CO_3)_2(H_2O)OH^{2-} + N_2H_5^+ \xrightarrow{k'_H} \text{products} \qquad (10)$$

$$Co(CO_3)_2(H_2O)OH^{2-} + N_2H_4 \xrightarrow{k'} \text{products} \qquad (11)$$

This mechanism generates the equation

$$k_1 = \frac{\left(\frac{k_H K_1 K_2 [H_3O^+]^2}{[HCO_3^-]} + \frac{(kK_A K_1 K_2 + k'_H K_1 K_2 K_3)[H_3O^+]}{[HCO_3^-]} + \frac{k' K_A K_1 K_2 K_3}{[HCO_3^-]}\right) \frac{[N_2H_4]_{tot}}{K_A + [H_3O^+]}}{1 + K_1[H_3O^+] + \frac{K_1 K_2 [H_3O^+]}{[HCO_3^-]} + \frac{K_1 K_2 K_3}{[HCO_3^-]}} \qquad (12)$$

When K_2 is very small, as indicated in ref 3a, the expression reduces to eq 13, which has the general form of eq 3. Equation

$$k_1 = \frac{A[H_3O^+]^2 + B[H_3O^+] + C}{1 + D[H_3O^+]} \frac{[N_2H_4]}{[HCO_3^-]} \qquad (13)$$

13 produces a slightly better fit of the experimental data than does eq 3. A nonlinear least-squares computer calculation yields the following values: $A = (1.7 \pm 0.8) \times 10^{18}$ M^{-2} min^{-1}, $B = (2.4 \pm 1.4) \times 10^9$ M^{-1} min^{-1}, $C = 3.2 \pm 0.4$ min^{-1}, $D = (2.2 \pm 1.2) \times 10^9$ M^{-1}. The value of D (K_1) is in agreement with the literature value of $K_1 = (1.31 \pm 0.12) \times 10^9$ M^{-1}. The solid line in Figure 4 is calculated from the values above. There are other possible equilibria and rate-determining steps which can produce rate expressions similar to eq 3 or 13 and which would be kinetically indistinguishable, e.g., loss of a proton from N_2H_4 rather than from $Co(CO_3)_2(H_2O)_2^-$ or mechanisms involving loss of a proton from $Co(CO_3)_2(H_2O)OH^{2-}$. The mechanism proposed is believed to be the most reasonable in view of the significantly smaller acid dissociation constants of N_2H_4 and $Co(CO_3)_2(H_2O)OH^{2-}$ compared with those for the equilibria given by eq 6 and 7.

The similarity between eq 13 and rate expressions for substitution reactions of carbonate complexes[3a,15,16] and the similarity between the overall rate of the hydrazine reaction and the pyridine substitution reaction[3a] strongly suggest that the reduction of tris(carbonato)cobaltate(III) by hydrazine takes place by an inner-sphere mechanism in which the rate-determining steps (eq 8, 11) are substitution processes, e.g.

$$Co(CO_3)_2(H_2O)_2^- + N_2H_4 \xrightarrow{slow} Co(CO_3)_2(H_2O)(N_2H_4)^- + H_2O$$

Since no substitution products are observed, the monosubstituted product must undergo fast redox decomposition either before or after further substitution.

$$Co(CO_3)_2(H_2O)(N_2H_4)^- \xrightarrow{fast} Co(II) + ({}^1/_2 N_2 + NH_4^+)_{approx}$$

$$Co(CO_3)_2(H_2O)(N_2H_4)^- \xrightarrow[fast]{N_2H_4} Co(CO_3)_2(N_2H_4)_2 \xrightarrow{fast} Co(II) + N_2H_4 + ({}^1/_2 N_2 + NH_4^+)_{approx}$$

A mechanism involving reactions 8–11 requires that both N_2H_4 and $N_2H_5^+$ act as nucleophiles. If it is assumed that reaction between $N_2H_5^+$ and $Co(CO_3)_2(H_2O)OH^{2-}$ (eq 10) makes an insignificant contribution to the reaction rate, the values of the parameters in eq 12 and 13 indicate that $k_H/k = 3 \pm 2$.

There is evidence that $N_2H_5^+$ is an effective nucleophile (e.g., in the inner-sphere reduction of $PtCl_6^{2-}$[14]) and in this case it would be favored by charge effects (eq 8).

According to the scheme proposed, the increase in rate which occurs at higher pHs is the result of reaction of hydrazine with $Co(CO_3)_2(H_2O)(OH)^{2-}$ (eq 11), which represents base catalysis of substitution of a coordinated water molecule.

Autocatalysis Reaction. In order to better understand the effect of Co(II) in catalyzing the reaction between hydrazine and tris(cabonato)cobaltate(III), reaction rates were measured in the presence of other metal ions at comparable concentrations. The results are summarized in Table I. Only the metal cations with redox properties affect the reaction rate. These ions, Mn(II), Cu(II), and Co(II), effect catalysis by different mechanisms. Mn(II) reduces $Co(CO_3)_3^{3-}$, even in the absence of hydrazine, in a very fast reaction which results in the formation of a brown precipitate (probably MnO_2). In reactions in the presence of hydrazine, it is likely that Co(III) oxidizes Mn(II) to a higher oxidation state which is then reduced by hydrazine. In the absence of hydrazine Cu(II) and Co(II) have no effect. Since Cu(II) is not a reducing agent, it must function differently from Co(II). Since reaction of Cu(II) with hydrazine is relatively slow,[16,17] reactions such as

Table I

Metal ion	Rate compared to rate in absence of metal ion
Ni(II)	No increase
Zn(II)	Ca. 10% increase
Cu(II)	Rate increase; Cu(II) ca. 1.5–2 times as effective as Co(II)
Mn(II)	Very fast reaction

$$Cu(II) + N_2H_4 \rightarrow Cu(I) + N_2H_3 + H^+$$

or

$$Cu(II) + Cu^{II}(N_2H_4) \rightarrow 2Cu(I) + N_2H_2 + 2H^+$$

cannot be first steps in the catalysis reaction unless complexation by carbonate significantly affects the reaction rate. The mechanism may involve simultaneous reduction of both Co(III) and Cu(II), e.g.

$$Co(III) + Cu^{II}(N_2H_4) \rightarrow Co(II) + Cu(I) + N_2H_2 + 2H^+$$

Since Cu(II) is not a significantly better catalyst than Co(II), the possibility of catalysis by Cu(II) present in reaction mixtures only as an impurity is eliminated. The reaction pathway for autocatalysis must involve electron transfer between carbonatocobaltate(III) and a cobalt(II) species. This electron-transfer reaction is faster than the rate-determining substitution process which occurs in the uncatalyzed reaction. Since such electron transfer produces no net reaction of Co(III) → Co(II), it must serve as means of promoting the substitution of hydrazine into the coordination sphere of Co(III). In the pH range 8–10, no intermediate substitution product is detected; therefore, subsequent redox decomposition is fast compared with the Co(II)–Co(III) exchange reaction.

The dependence of the observed rate constant k_2 (eq 1) on pH, $[HCO_3^-]$, and $[N_2H_4]$ is shown in Figures 5–7. The plot of rate constant vs. pH resembles a pH titration curve for an acid, $pK_a = 8.6$. This is close to the measured pK_a of 8.3 for $N_2H_5^+$. The rate of reaction of $N_2H_5^+$ is negligibly small compared to that of N_2H_4. Since the pH dependence can be explained by considering only the $N_2H_5^+/N_2H_4$ equilibrium, the reaction rate is not dependent on equilibria involving carbonatocobaltate(III) such as those described by eq 4 and 5.

The hydrazine dependence of k_2, Figure 7, shows that a limiting rate is attained at a hydrazine concentration of 5×10^{-3} M. This is unlike the hydrazine dependence of the uncatalyzed reaction and is undoubtedly related to the nature of the Co(II) species involved in the rate-determining electron-transfer step.

Spectra of cobalt(II) sulfate in aqueous solution and in media similar to reaction mixtures described in this paper are shown in Figure 8. The large spectral change which takes place in going from an aqueous solution to an aqueous bicarbonate–carbonate medium is indicative of formation of a

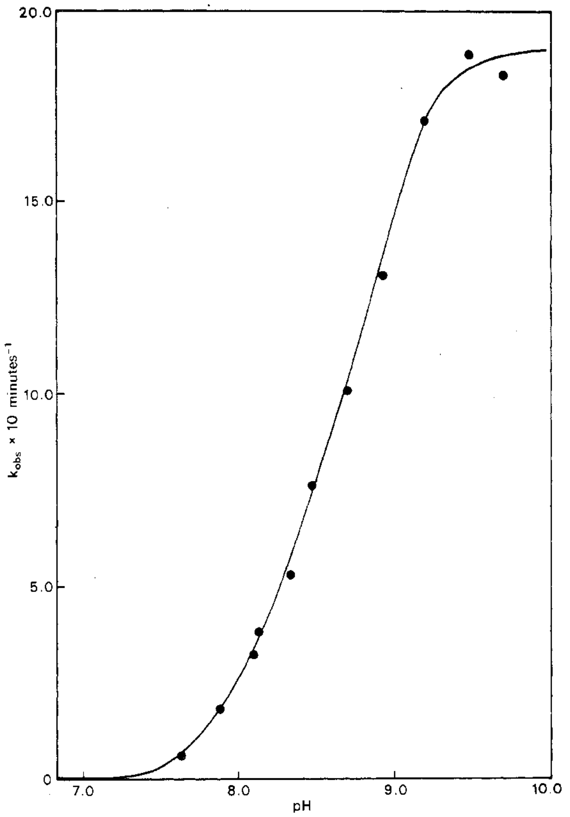

Figure 5. k_{obsd} vs. pH for the catalyzed reaction. [Hydrazine] = 4.23×10^{-3} M, $[HCO_3^-] = 0.231$ M, $[Co(II)]_0 = 2.21 \times 10^{-3}$ M, $[Co(III)]_0 = 8.22 \times 10^{-4}$ M.

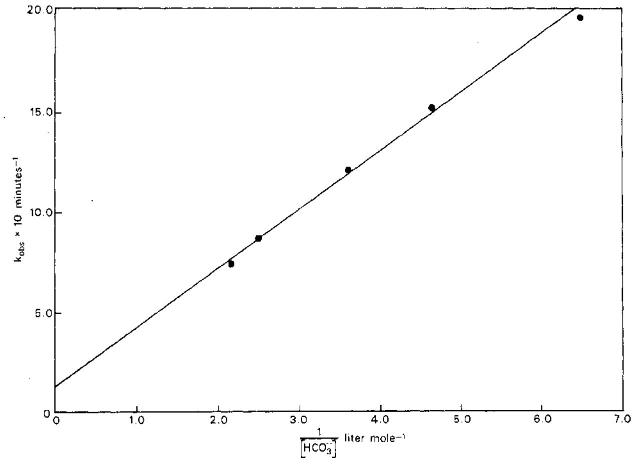

Figure 6. k_{obsd} vs. $1/[HCO_3^-]$ for the uncatalyzed reaction. [Hydrazine] = 4.23×10^{-3} M, $[Co(II)]_0 = 2.21 \times 10^{-3}$ M, $[Co(III)]_0 = 8.22 \times 10^{-4}$ M, pH ~9.10.

carbonato complex. Addition of hydrazine results in further spectral changes as hydrazine complexes are formed. Changes in the spectrum continue as the hydrazine concentration is increased beyond 5×10^{-3} M at which the limiting reaction rate is reached.

The absence of stable isosbestic points over the hydrazine concentration range of the kinetic experiments suggests that several complexes are present, e.g.

$$Co(II) + N_2H_4 \overset{K_1}{\rightleftharpoons} Co^{II}(N_2H_4)$$

$$Co^{II}(N_2H_4) + N_2H_4 \overset{K_2}{\rightleftharpoons} Co^{II}(N_2H_4)_2, \text{ etc.}$$

where Co(II) represents a carbonate species.

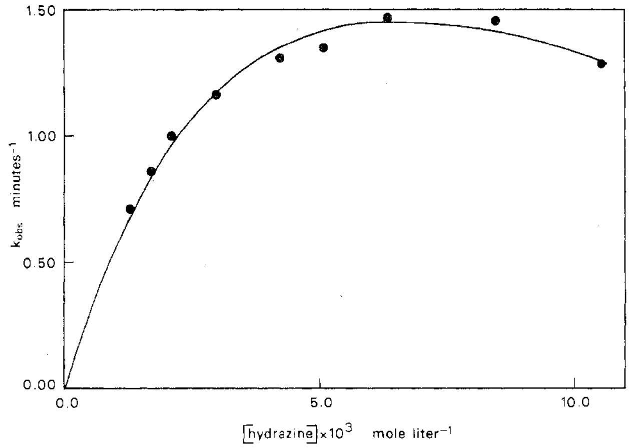

Figure 7. k_{obsd} vs. [hydrazine] for the catalyzed reaction. $[HCO_3^-] = 0.283$ M, $[Co(II)]_0 = 2.21 \times 10^{-3}$ M, $[Co(III)]_0 = 8.22 \times 10^{-4}$ M, pH ~9.22. The solid line passes through calculated values. See text.

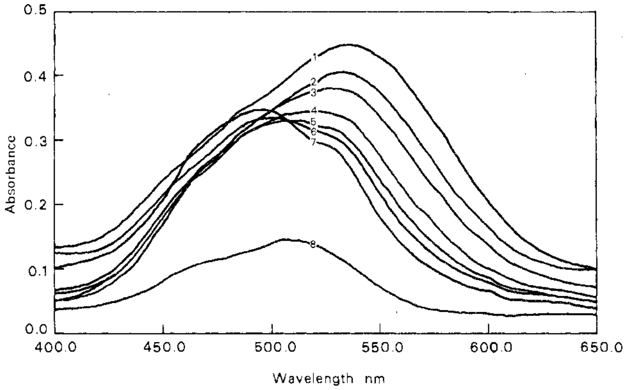

Figure 8. Spectra of cobalt(II) sulfate–hydrazine mixtures in aqueous carbonate–bicarbonate solution. pH ~9.40, $[Co(II)] = 2.5 \times 10^{-3}$ M, $[HCO_3^-] = 0.32$ M, $[CO_3^{2-}] = 0.12$ M, $\mu = 1.0$. $[N_2H_4]$: (1) 0.00; (2) 2.0×10^{-3} M; (3) 4.0×10^{-3} M; (4) 8.0×10^{-3} M; (5) 1.2×10^{-2} M; (6) 2.0×10^{-2} M; (7) 4.0×10^{-2} M. Curve 8 shows the spectrum of $CoSO_4$ (2.5×10^{-3} M in distilled water).

The bicarbonate (or carbonate dependence, which is similar) is probably related to these equilibria since hydrazine competes with carbonate for the metal coordination sites.

It is proposed that the rate-determining step in the catalyzed reaction involves electron transfer between one or more of these carbonato–hydrazine cobalt(II) complexes and tris(carbonato)cobaltate(III). Such reactions would lead to substitution of hydrazine onto Co(III)

$$Co(III) + Co^{II}(N_2H_4) \xrightarrow{k'_1} Co^{III}(N_2H_4) + Co(II)$$

$$Co(III) + Co^{II}(N_2H_4)_2 \xrightarrow{k'_2} Co^{III}(N_2H_4)_2 + Co(II)$$

Assuming this mechanism, the rate constant data in Figure 7 were analyzed by a least-squares program for systems involving multiple equilibria, similar to that described by Maier and Drago.[18] Equilibrium constants K_1 and K_2 and rate constants k'_1 and k'_2 in the above equations are too highly correlated to allow the program to solve for all four unknowns simultaneously. A series of values for K_2 and k'_2 were inserted as constants and best fits determined for K_1 and k'_1. The various possibilities are discussed below.

(a) Assume only the formation of a 1:1 complex; i.e., $K_2 = 0$. Calculated: $K_1 = 1.9 \times 10^5$ M^{-1}, $k'_1 = 5.34 \times 10^2$ M min^{-1}. This value for K_1 is unreasonably large compared to published values of stability constants[19] for Co^{2+} complexes of hydrazine and similar ligands. The assumption of only a 1:1 complex is also inconsistent with the spectral data discussed previously.

(b) Assume formation of both 1:1 and 2:1 complexes with only the 1:1 complex reacting; i.e., $k'_2 = 0$. Better statistical fits are obtained than in (a). The solid line in Figure 7 joins calculated rate constants based on $K_1 = 348.0$ and $K_2 = 300.0$ M^{-1} and $k'_1 = 1.58 \times 10^3$ and $k'_2 = 0.00$ M^{-1} min^{-1}. The differences between experimental and calculated values are well within experimental error. The statistical fit of the data is improved slightly but not significantly by using higher values of K_2. This leads to a situation in which $K_2 \gg K_1$.

(c) Assume formation of 1:1 and 2:1 complexes with both reacting. If the 2:1 complex is assumed to react at a significant rate, the statistical fit is significantly worse than in (b).

Thus a best fit of both spectral and kinetic data is obtained when it is assumed tht Co(II) forms both a 1:1 and 2:1 complex with hydrazine with only the 1:1 complex reacting at a significant rate. This result is consistent with the observation that $Co^{II}EDTA^{2-}$, which also contains two nitrogen and four oxygen donor ligands, does not undergo measurable reaction with $Co(CO_3)_3^{3-}$.

The statistical evidence is not sufficient to differentiate between $K_1 \approx K_2$ and $K_1 < K_2$. Comparison with stability constants measured in aqueous perchlorate solution ($K_1 = 60$, $K_2 = 36$)[20] suggests that the former is more likely.

Irrespective of the relative values of K_1 and K_2, the results are consistent with a mechanism in which the rate-determining step involves an electron-transfer reaction between a monohydrazino–cobalt(II) complex and $Co(CO_3)_3^{3-}$ producing a Co(III) species containing one hydrazine ligand. As in the uncatalyzed reaction, this species undergoes a fast redox decomposition either before or after substitution of a second hydrazine.

Reactions in Solutions of pH <7. Under these conditions reactions were studied semiquantitatively due to evolution of CO_2. The "purple intermediate" described previously was found to be produced only by the autocatalysis reaction. In the presence of EDTA no purple intermediate is formed. When excess Co(II) is added, a higher concentration of intermediate is produced. Once formed this relatively stable complex decomposes over a period of hours. Brown and Higginson proposed that in this complex several hydrazine ligands were coordinated to Co(III). Comparison of its spectrum (λ_{max} 366, 520 nm) with the spectra of carbonatotetrakis(pyridine)cobalt(III) (λ_{max} 378, 530 nm),[21] carbonatotetraamminecobalt(III) (λ_{max} 357, 520 nm),[22] and carbonatobis(ethylenediamine)cobalt(III) (λ_{max} 359, 512 nm)[23] suggests that the purple species is $Co(CO_3)(N_2H_4)_4^+$. If this is true then the slowness of the redox decomposition is not surprising. The stronger ligand field of the hydrazine ligands compared to carbonate should stabilize the Co(III) toward reduction. A first step in the redox decomposition of such a complex may involve the loss of hydrazines thereby producing a more reactive entity. Such a mechanism is believed to operate in the decomposition of tris(oxalato)cobaltate(III).[24]

If Na_2CO_3 is added to a solution of the purple complex (at pH <7) to raise the pH (to approximately 9), the decomposition of the complex takes place within the period of the addition. If the complex is $Co(CO_3)(N_2H_4)_4^+$ as proposed, the addition of carbonate could result in the elimination of hydrazine ligands, perhaps catalyzed by Co(II), leading to a less stable complex, i.e.

$$Co^{III}(CO_3)(N_2H_4)_4 + CO_3^{2-} \rightarrow Co^{III}(CO_3)_2(N_2H_4)_2 + 2N_2H_4$$

$$Co^{III}(CO_3)_2(N_2H_4)_2^- \rightarrow \text{redox products}$$

The formation of this purple complex in the catalyzed reaction is further evidence that the Co(II) catalyzes a substitution process. The reaction of this complex will be a subject of future investigation.

Summary

The oxidation of hydrazine by tris(carbonato)cobaltate(III) is believed to take place by an inner-sphere mechanism involving a rate-determining substitution step. The rate of the reaction is not significantly different from the rate of substitution of pyridine and the rate expression is similar.

It is proposed that the increase in reaction rate in the presence of Co(II) is due to an outer-sphere electron-transfer reaction between tris(carbonato)cobaltate(III) and a hydrazinocobalt(II) complex which catalyzes the substitution reaction.[25] Although catalyses of substitution reactions of Cr(III) complexes by Cr(II) are numerous, similar reactions of cobalt are uncommon. The reasons for this are both thermodynamic and kinetic. Ligand-field stabilization of Co(III) often forbids reduction by Co(II) surrounded by weak-field ligands. Co(III)–Co(II) electron-transfer reactions are generally kinetically slow since an electron in an e_g orbital is involved and also because of the low spin–high spin transition involved.[13] Fast Co(III)–Co(II) exchange reactions occur only when the low spin–high spin energy difference is small. This occurs when the ligands of both complexes are weak field (e.g., H_2O) or very strong field (e.g., phenanthroline).[13,27] In the reactions investigated in this work, the carbonate ligand is of the weak-field type. Tris(carbonato)cobaltate(III) is more labile than most Co(III) complexes and is easier to reduce from both a thermodynamic and kinetic standpoint. The rate of the electron transfer between $Co(CO_3)_3^{3-}$ and the Co(II) species depends on the ligands bound to Co(II). When hydrazine is one of the ligands on the carbonato–cobalt(II) complex, electron transfer is faster than the rate of substitution onto Co(III). With pyridine, the relative rates are reversed since Co(II) has no effect on the overall substitution process. Similarly, the Co(II)–EDTA complex does not take part in electron transfer. Preliminary studies indicate that the substitution reaction between ethylenediamine and tris(carbonato)cobaltate(III) is catalyzed by Co(II).

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Registry No. Hydrazine, 302-01-2; $Co(CO_3)_3^{3-}$, 12602-46-9; EDTA, 60-00-4; $CoSO_4$, 10124-43-3; Co(II), 22541-53-3; Zn(II), 23713-49-7; Cu(II), 15158-11-9; Mn(II), 7439-96-5.

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Cobalt Nitrosyl Complexes in Zeolites A, X, and Y

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Nitrosyl complexes were formed when NO reacted with Co^{2+} ions in zeolites A, X, and Y. In the A-type zeolite the mononitrosyl complex was favored, whereas in the Y-type zeolite only the dinitrosyl complex was formed. Both complexes were formed in the X-type zeolite. The greatest thermal stability occurred in the Y-type zeolite. Infrared and XPS data suggest that there is no appreciable electron transfer between the metal ion and the ligand in either complex, although diffuse-reflectance spectra indicate that the nitrosyl group has a significant effect on the electronic structure of the cobalt ion. The propensity of the Co^{2+} to form the mono- or the dinitrosyl complex is attributed to the position of the cation with respect to the oxide ions of the lattice and the mobility of the cation under the influence of the ligand. These factors may ultimately be related to the charge density in the zeolite.

Introduction

A number of different metal ions in zeolites have been observed to coordinate with nitric oxide, forming nitrosyl complexes. These metal ions include Ag^+, Cu^+, Cu^{2+}, Ni^{2+}, Cr^{2+}, Fe^{2+}, and Co^{2+}.[1-8] Both mono- and dinitrosyl complexes have been observed. In the case of the nickel nitrosyl complex and EPR spectrum provides convincing evidence that electron transfer occurs from the ligand to the metal ion.[3,4] Similar interpretations have been given for the formation of nitrosyl complexes with Cu^{2+}, Fe^{2+}, and Cr^{2+}.[2,5,6] An unusual situation occurs in Ag–Y zeolites where nitric oxide apparently forms a bridge between Ag^+ ions.[1]

In a Y-type zeolite Co^{2+} forms a dinitrosyl complex which has been identified by infrared spectroscopy.[7] The spectra suggest that there is no appreciable electron transfer between the metal ion and the ligand. On the basis of the electron diffraction data of Seff,[8] one may conclude that a mononitrosyl complex is formed in an A-type zeolite. The Co^{2+} ion is coordinated to three oxide ions in the six-membered window and the bent nitrosyl ligand extends into the large cavity.[9]

It was at first believed that the M–N–O angle was approximately 180° in all complexes which had a cationic nitrosyl ligand and that the bond angle was nonlinear for complexes containing an anionic nitrosyl ligand. Additional structural data have shown that in fact there is no correlation between the effective charge on the NO group and the geometry of the molecule.[10] Enemark and Feltham[10] have pointed out that the ultimate geometry assumed by the NO group is dependent not only on the total number of electrons but also upon the nature of the highest occupied molecular orbital.

The present study has been an attempt to understand the role of the zeolite framework in the formation of either mono- or dinitrosyl cobalt complexes. In particular it was of interest to explain why the mononitrosyl complex was favored in the A-type zeolite and the dinitrosyl complex was favored in the Y-type zeolite. In order to evaluate the effect of charge density on this question the formations of the complexes in X- and Y-type zeolites have been compared. Both of these zeolites are of the faujasite structure, but the X zeolite has a smaller silicon to aluminum ratio and, therefore, a greater charge density. The charge density in the A-type zeolite is even greater than in the zeolites of the faujasite structure. An additional purpose of the study was to determine whether the cobalt ion underwent any oxidation or reduction during the formation of the complexes.

Experimental Section

The experiments were performed on cobalt(II) A, X, and Y zeolite samples prepared by ion exchange as described elsewhere.[7] The Co^{2+} exchange levels were 72, 69, and 70% for the A, X, and Y zeolites, respectively. In the preparation of a sample which contained cobalt(III) the $[Co(NH_3)_6]^{3+}$ complex was exchanged into a Y-type zeolite from an aqueous solution. Unless otherwise indicated, all of the zeolites were degassed under vacuum (10^{-5} Torr) to a temperature of 300 °C.

The nitric oxide, obtained from a commerical source, was repeatedly sublimed and frozen using a pentane slush and liquid nitrogen, respectively, in order to remove nitrogen dioxide which was present as a major impurity.

A Cary 14 spectrophotometer with a type-II diffuse-reflectance attachment was used to obtain the spectra in the range from 6000 to 30 000 cm^{-1}. A NaY zeolite, dehydrated under vacuum to 460 °C, was used as the reference material. Spectra were recorded with the zeolite both in the form of a loose powder and as an opaque compressed wafer. In the former case there was less of a problem with contamination of the sample, but larger amounts of material were required and it was more difficult to introduce the nitric oxide uniformly so that direct comparison could be made with the results from infrared and photoelectron spectroscopy.

The infrared spectra were recorded using a Beckman IR-9 spectrophotometer in the transmission mode. The zeolite was in the form of a self-supporting wafer which had a single-beam transmission of approximately 50%. The cell used for the infrared work was similar to that described previously.[11] Slit widths were set so that a minimum resolution of 1.5 cm^{-1} was achieved. The accuracy of the band positions was estimated to be ± 5 cm^{-1}.

A Hewlett-Packard 5950A ESCA spectrometer utilizing monochromatic Al $K\alpha_{1,2}$ x radiation (1486.6 eV) was employed to obtain the photoelectron spectra. The cobalt-exchanged zeolite was pressed into a thin film and placed on a sample plate. The samples were

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