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Mechanism of CO_2 and H^+ Reduction by Ni(cyclam)$^+$ in Aqueous Solution. A Pulse and Continuous Radiolysis Study

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The reduction of CO_2 and H^+ by Ni(cyclam)$^+$ in aqueous solution was found to proceed by the reduction of Ni(cyclam)(CO_2)$^+$ or Ni(cyclam)(H)$^{2+}$ by Ni(cyclam)$^+$. At ambient temperature the rate constants for the bimolecular reactions are 1.6×10^8 and 7.2×10^7 M^{-1} s^{-1}, respectively. Continuous γ-radiolysis studies have demonstrated nearly quantitative formation of CO from two Ni(cyclam)$^+$ at pH 5.2 under 1 atm of CO_2 and in the presence of formate. Under the same conditions, but at low CO_2 concentration, the reduction of protons was found to compete with CO_2 reduction.

Introduction

Since the work of Brown et al.[3] and that of Fisher and Eisenberg[4] almost 20 years ago, a remarkable effort has been put forward to study the photo- and electrochemical reduction of protons and/or CO_2 by cobalt(II) and nickel(II) macrocycle complexes. As a result, considerable knowledge now exists on the chemistry and physical properties of many Co^+ and Ni^+ macrocycle complexes in the solid state,[5] in solution,[5−9] and at an electrode.[10−18] However, despite the accumulation of kinetic and thermodynamic information on the binding of protons and CO_2 to the +1 oxidation-state metal centers, little knowledge exists on the mechanism of H_2 and CO evolution from these intermediate species. A notable exception is the work of Fujita et al. who studied the slow reduction of CO_2 by CoL$^+$, where L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, in acetonitrile and found it to proceed by a second-order process involving two CoL$^+$ centers.[11a]

Until recently,[18] the most efficient and selective catalyst for the reduction of CO_2 to CO in acidic (pH 4) aqueous solution was the complex Ni(cyclam)$^{2+}$, where cyclam = 1,4,8,11-tetraazacyclotetradecane.[12a,b] Hydrogen evolution in this system was observed below pH 4.[12b] While equally high current efficiencies were observed earlier,[4] the selectivity displayed toward CO_2 in the presence of protons is a remarkable aspect of Ni(cyclam)$^+$ chemistry. Introducing Ni(cyclam)$^+$ into the photochemical system of Brown et al.[3] has been demonstrated to reduce CO_2 at pH 5 although with low yields for CO formation.[8b]

Electrochemical investigations of the reduction of CO_2 by Ni(cyclam)$^+$ have demonstrated that the active catalyst is absorbed on the surface of the electrode and have suggested

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that homogeneous Ni(cyclam)$^+$ is inactive as a catalyst.[16a] The low CO yields observed during the photochemical reduction of CO_2 by Ni(cyclam)$^+$,[8b] coupled with the importance of the absorbed complex in electrochemical studies,[16a] raise questions concerning the ability of Ni(cyclam)$^+$ to function as a homogeneous catalyst. This is an unfortunate conclusion since the strongly reducing nature of Ni(cyclam)$^+$, $E°(\text{Ni(cyclam)}^{2+/+} = -1.33$ V,[12b] and the low pK_a of Ni(cyclam)(H)$^{2+}$, p$K_a = 1.8$,[19] suggest that Ni(cyclam)$^+$ is an ideal aqueous reducing agent for CO_2.

In previous work, we have characterized the rapid binding of CO_2 and protons by Ni(cyclam)$^+$ using both pulse radiolysis and laser flash photolysis.[19] From that work it is now apparent that the selectivity displayed by Ni(cyclam)$^+$ toward CO_2 over protons at pH 4 is not the result of an intrinsic selectivity. In fact, the reactivity of Ni(cyclam)$^+$ toward CO_2 and protons, and the stabilities of the adducts, Ni(cyclam)(CO_2)$^+$ and Ni(cyclam)(H)$^{2+}$, are quite similar.[19] Rather, the apparent selectivity is primarily due to concentration differences of the two species, i.e., 36 mM CO_2 (1 atm) and 0.1 mM protons (pH 4). In the current work, we report the results of kinetic studies on the decay of Ni(cyclam)$^+$ as a function of proton and CO_2 concentration. Additionally, we have studied gaseous product yields from the continuous γ-radiolysis of aqueous solutions of Ni(cyclam)$^{2+}$. From these results, we propose a mechanism for the catalytic two-electron reduction of protons and CO_2 by Ni(cyclam)$^+$.

Experimental Section

Materials. The compound Ni(cyclam)(ClO_4)$_2$ was prepared according to published procedures[20] and was purified by repeated recrystallization from water and acetone. Sodium formate was reagent grade and was used as received. Water was obtained from a Millipore (Milli-Q) water purification system. Solutions were purged with Ar or saturated with N_2O, CO_2 or Ar/CO_2 mixtures of known composition with 1 atm total pressure. The solubility of CO_2 in water at 1 atm partial pressure was taken to be 36 ± 2 mM at 22 ± 2 °C,[21] i.e., the temperature at which the experiments were performed. In some cases, solutions were degassed by stardard vacuum-line techniques. Solution pH was adjusted with $HClO_4$ (Merck, Suprapur).

Pulse Radiolysis. Pulse radiolysis was performed using the 12 MeV electron linear accelerator at the FRAE-CNR Institute in Bologna. The irradiations were carried out at ambient temperature, 22 ± 2 °C, on samples contained in Spectrosil cells of 2 cm optical path length. Solutions were protected from the analyzing light by means of a shutter and appropriate cutoff filters. The monitoring light source was either a 450 W Xe arc lamp or a 50 W tungsten–halogen lamp, the latter being used when performing long time scale measurements. The bandwidth used throughout the pulse radiolysis experiments was 5 nm. The radiation dose per pulse was monitored by means of a charge collector placed behind the irradiation cell and calibrated with a N_2O-saturated solution containing 0.1 M HCO_2^- and 0.5 mM methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dication; MV^{2+}) using $G\epsilon = 9.66 \times 10^{-4}$ m^2 J^{-1} at 602 nm.[22] G(X) represents the number of moles of species X formed or consumed per joule of energy absorbed by the system.

Table 1. Product G Values Following γ Irradiation[a]

	vacuum-degassed soln			CO$_2$-satd soln	
	$G(H_2)$	$G(CO_2)$	$G(CO)$	$G(H_2)$	$G(CO)$
obsd[b]	0.24	0.26	0.10	0.10	0.24
calcd[c]	0.10	0.34	0.00	0.10	0.00

[a] Conditions: 0.5 mM Ni(cyclam)(ClO_4)$_2$, 0.1 M HCO_2^-, pH 5.2, 22 ± 2 °C and doses = 0.5–1.0 kGy. G values are given in units of μmol J^{-1}. [b] Values measured in this work. [c] Calculation based on the values given in the text, assuming no reaction between Ni(cyclam)$^+$ and protons or CO_2.

Continuous Radiolysis. Continuous radiolyses were carried out at room temperature on 25 mL solutions using a ^{60}Co–Gammacell with a dose rate of ca. 60 Gy min^{-1}. The exact absorbed radiation dose was determined with the Fricke chemical dosimeter assuming $G(Fe^{3+}) = 1.61$ μmol J^{-1}.[23] Solutions were degassed under vacuum or equilibrated with 1 atm of purified CO_2 using standard vacuum-line techniques. The gaseous products were removed from the irradiated sample by means of an automatic Toepler pump, and their total volume was measured in a gas buret. The gas was then analyzed by gas chromatography.

Results

Continuous Radiolysis. The gaseous product yields following continuous γ-irradiation of solutions containing 0.5 mM Ni(cyclam)$^{2+}$ and 0.1 M HCO_2^- at pH 5.2 in vacuum-degassed and CO_2-saturated (1 atm) solutions are given in Table 1.

Pulse Radiolysis. Pulse radiolysis was used to generate e_{aq}^-, $CO_2^{\bullet -}$, and H$^\bullet$, which we have used for the one-electron reduction of Ni(cyclam)$^{2+}$.[19] However, 2-methyl-2-propanol was not used as a hydroxyl radical scavenger due to the reaction of Ni(cyclam)$^+$ with the 2-methyl-2-propanyl radical previously described by Jubran et al., eq 1.[7c] Although we did not study this reaction in detail, we confirmed that Ni(cyclam)$^+$ reacts with 2-methyl-2-propanyl radical and have estimated the rate constant to be 1×10^9 M^{-1} s^{-1}.

$$\text{Ni(cyclam)}^+ + {}^\bullet CH_2C(CH_3)_2OH \rightarrow \text{Ni(cyclam)}^{2+} + CH_2{=}C(CH_3)_2 + OH^- \quad (1)$$

In pulse radiolysis studies using formate as the hydroxyl radical scavenger in the absence of added CO_2, 20–25% of Ni(cyclam)$^+$ formed by the reduction of Ni(cyclam)$^{2+}$ with e_{aq}^- and $CO_2^{\bullet -}$ disappears according to a process which can be approximated to first-order, Figure 1. The value of the observed rate constant, k_{obs}, was independent of [Ni(cyclam)$^{2+}$] over the range 0.1–0.5 mM, but increased linearly with dose, Figure 1 inset. The nature of this reaction will be discussed below.

The decay of the remaining Ni(cyclam)$^+$ absorbance yielded linear plots of $1/(\Delta A - \Delta A_\infty)$ vs time, where ΔA and ΔA_∞ are the absorbance changes observed at time t and infinity after the pulse, Figure S1. A representative fit of the absorbance change data as a function of time is given in Figure 2. Kinetic behavior of this type is consistent with a second-order process. The observed rate constant, k_{obs}, obtained from the absorbance change data, is a function of the second-order rate constant, k, the difference between the molar decadic absorption coefficients of the reagents and products at a specified wavelength, $\Delta\epsilon$, and the optical path length of the sample, l. For an elementary second-order reaction $k_{obs} = k/(\Delta\epsilon l)$. The dimensions of k_{obs}, k,

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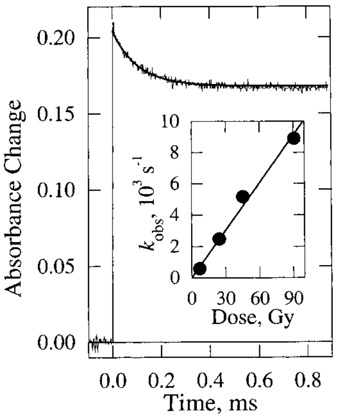

Figure 1. Time dependence of the absorbance monitored at 380 nm for the initial decay of Ni(cyclam)$^+$ following the pulse irradiation of Ar-purged solutions containing 0.5 mM Ni(cyclam)$^{2+}$ and 0.1 M HCO_2^- at pH ~ 7. The dose per pulse was 88.6 Gy, and the optical path length was 2.0 cm. The solid line represents the first-order kinetic fit to the data. Inset: Plot of the observed first-order rate constant, k_{obs}, vs the irradiation dose, under the same conditions as those given above.

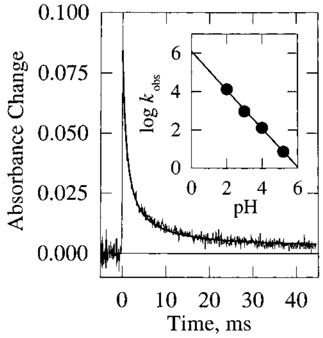

Figure 2. Example of time dependence of absorbance at 380 nm from the pulse irradiation of Ar-purged solutions containing 0.5 mM Ni(cyclam)$^{2+}$ and 0.1 M HCO_2^- at pH 2; dose per pulse = 48.6 Gy; optical path = 2.0 cm. The solid line represents the second-order kinetic fit to the data. Inset: plot of log k_{obs} (extrapolated to zero dose) vs pH. The solid line represents the linear fit to the data based on eq 21.

$\Delta\epsilon$, and l are s^{-1}, M^{-1} s^{-1}, M^{-1} cm^{-1}, and cm, respectively. As will be discussed below, the observed second-order decay is the result of a composite reaction mechanism and, as a result, $k_{obs} \neq k/(\Delta\epsilon l)$ in the present case. Evaluation of the elementary rate constants will be discussed below.

The fit of the second-order model to the data required the presence of a small, i.e., <10%, value for ΔA_∞, indicative of the formation of longer lived products. Unfortunately, we were unable to obtain reliable kinetic or spectral information regarding the nature of these products using the pulse radiolysis technique. However, by irradiating a vacuum-degassed solution containing 0.5 mM Ni(cyclam)$^{2+}$ and 0.1 M HCO_2^- at pH 5.2 with 200 pulses of 50 ns duration and at a repetition rate of 5 Hz, with each pulse delivering a dose of approximately 10 Gy, a differential absorption spectrum could be acquired with a conventional spectrometer ~45 s after the irradiation. The long-lived product exhibited a band at 354 nm, a shoulder at ~400 nm, and a broad weak band at ~620 nm.

In general, the observed rate constant, k_{obs}, was found to be a function of both dose (ca. 20−180 Gy) and pH, Figure S1, inset. The values of k_{obs}, extrapolated to zero dose, were found to be 1.3×10^4, 9.4×10^2, 128, 7.3, and 0.73 s^{-1} at pH 2, 3, 4, 5.2, and ~7, respectively, Figure 2, inset. At pH 2 and 3, the values of k_{obs} were independent of irradiation dose, within experimental error.

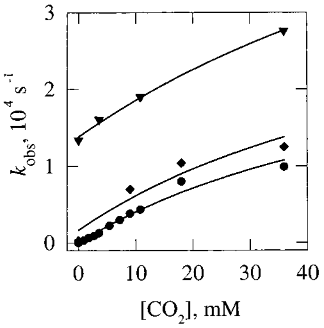

Figure 3. Plot of k_{obs} vs [CO_2] from the pulse irradiation of solutions containing ca. 0.5 mM Ni(cyclam)$^{2+}$ and 0.1 M HCO_2^- at pH 2 (▼), pH 3 (◆), and pH 5.2 (●). Observations were made at 380 nm with an optical path length of 2.0 cm and a dose per pulse of ca. 50 Gy. The solid lines represent the best fits of eq 24 to the data.

The decay of Ni(cyclam)$^+$ is accelerated by the presence of CO_2 but continues to be well represented by the second-order model. The effect of CO_2 concentration on the decay of Ni(cyclam)$^+$ was investigated in the pH range 5.2−2, Figure 3. Investigations of the CO_2 reaction at higher pH was not attempted due to the formation of a species with a visible absorption spectrum similar to that of *cis*-Ni(cyclam)$^{2+}$,[24] which we tentatively attribute to *cis*-[Ni(cyclam)(CO_3)]. The chemistry of the latter species was not investigated. At pH 5.2, the lifetime of Ni(cyclam)$^+$ was identical under 1 atm of H_2 or 1 atm of Ar.

Discussion

In the absence of CO_2, the following reactions and associated *G*-values (in parentheses, μmol J^{-1})[25] are anticipated assuming no reaction between Ni(cyclam)$^+$ and either protons or CO_2.

$$H_2O \rightsquigarrow H^\bullet\ (0.06),\ {}^\bullet OH\ (0.28),\ e_{aq}^-\ (0.27),\ H_2\ (0.045),\ H_2O_2\ (0.07) \quad (2)$$

$$H^\bullet\ (0.06) + HCO_2^- \rightarrow H_2\ (0.06) + CO_2^{\bullet -}\ (0.06) \quad (3)$$

$${}^\bullet OH\ (0.28) + HCO_2^- \rightarrow H_2O + CO_2^{\bullet -}\ (0.28) \quad (4)$$

$$e_{aq}^-\ (0.27) + \mathrm{Ni(cyclam)}^{2+} \rightarrow \mathrm{Ni(cyclam)}^+\ (0.27) \quad (5)$$

$$CO_2^{\bullet -}\ (0.34) + \mathrm{Ni(cyclam)}^{2+} \rightarrow CO_2\ (0.34) + \mathrm{Ni(cyclam)}^+\ (0.34) \quad (6)$$

The yield of Ni(cyclam)$^+$ is therefore expected to be $G = 0.61$, i.e., the sum of eq 5 and 6. However, an initial loss of 20−25% of Ni(cyclam)$^+$ was observed that we attribute to the oxidation of Ni(cyclam)$^+$ by H_2O_2, eq 7. Hydrogen peroxide is

$$2\mathrm{Ni(cyclam)}^+ + H_2O_2 \rightarrow 2\mathrm{Ni(cyclam)}^{2+} + 2OH^- \quad (7)$$

formed radiolytically with $G = 0.07$,[25] eq 2. On the basis of the stoichiometry of eq 7, H_2O_2 produced during the irradiation is capable of consuming ca. 23% of the Ni(cyclam)$^+$ yield, consistent with observation, Figure 1. The ~8-fold excess of

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Ni(cyclam)$^+$over H_2O_2 results in a pseudo-first-order decay of the reduced nickel complex. By converting the dose into [Ni(cyclam)$^+$], assuming $G(\text{Ni(cyclam)}^+) = 0.61$, a bimolecular rate constant was obtained from a plot of k_{obs} vs dose, Figure 1 inset, yielding $k_7 = 8 \times 10^7$ M^{-1} s^{-1}. As a result of the hydrogen peroxide oxidation, eq 7, the yield of Ni(cyclam)$^+$ is reduced to $G = 0.47$.

The mechanism of hydrogen peroxide reduction is of some interest. The multibodied nature of eq 7 implies a composite reaction. However, the initiating reaction cannot be an outer-sphere electron transfer, eq 8, since free hydroxyl radicals would

$$\text{Ni(cyclam)}^+ + H_2O_2 \rightarrow \text{Ni(cyclam)}^{2+} + {}^{\bullet}OH + OH^- \quad (8)$$

react rapidly, $k = 3.2 \times 10^9$ M^{-1} s^{-1},[25] with HCO_2^- forming $CO_2^{\bullet -}$. The latter species is a strong reducing agent, capable of regenerating Ni(cyclam)$^+$, eq 6. The net result would be the catalyzed reduction of H_2O_2 to OH^-, with no net loss of Ni(cyclam)$^+$. In contrast, an inner-sphere reaction provides a mechanism for coordination of the hydroxyl radical to the metal center, eqs 9–11, effectively preventing its release and reaction with HCO_2^-. It is not clear if the hydrogen peroxide adduct,

$$\text{Ni(cyclam)}^+ + H_2O_2 \rightarrow [\text{Ni(cyclam)}(H_2O_2)]^+ \quad (9)$$

$$[\text{Ni(cyclam)}(H_2O_2)]^+ \rightarrow [\text{Ni(cyclam)(OH)}]^{2+} + OH^- \quad (10)$$

$$[\text{Ni(cyclam)(OH)}]^{2+} \rightarrow \text{Ni(cyclam)}^{3+} + OH^- \quad (11)$$

represented here as $[\text{Ni(cyclam)}(H_2O_2)]^+$, is a true intermediate or if hydroxide dissociation, eq 10, is concerted with H_2O_2 coordination, eq 9.[26] In the presence of excess Ni(cyclam)$^+$ the lifetime of Ni(cyclam)$^{3+}$ formed by eq 11 would be limited by the comproportionation reaction, eq 12. As will be discussed

$$\text{Ni(cyclam)}^{3+} + \text{Ni(cyclam)}^+ \rightarrow 2\text{Ni(cyclam)}^{2+} \quad (12)$$

below, the lifetime of the remaining Ni(cyclam)$^+$ is ultimately limited by its reaction with CO_2 produced by the $H^{\bullet}$ and ${}^{\bullet}OH$ scavenging reactions of formate, eqs 3 and 4.

Under CO_2-saturated conditions, the hydrated electron is rapidly scavenged according to eq 13. Therefore, as the

$$e_{aq}^- \ (0.27) + CO_2 \rightarrow CO_2^{\bullet -} \ (0.27) \quad (13)$$

$$CO_2^{\bullet -} \ (0.61) + \text{Ni(cyclam)}^{2+} \rightarrow CO_2 \ (0.61) + \text{Ni(cyclam)}^+ \ (0.61) \quad (14)$$

concentration of CO_2 is increased, eq 5 becomes unimportant relative to eq 13 and eq 14 replaces eq 5. The yield of Ni(cyclam)$^+$, however, remains unchanged.

The product yields following continuous γ-irradiation, Table 1, reveal that in CO_2-saturated solution the yield of H_2 is close to that expected on the basis of the radiolytic yield, eqs 2 and 3. The yield of CO ($G = 0.24$), which cannot be accounted for by radiolytic processes, is equal to half the yield of Ni(cyclam)$^+$ after correcting for the H_2O_2 reaction, eq 7. This is consistent with the fact that the two-electron reduction of CO_2 to CO requires two reducing equivalents, i.e., 2 Ni(cyclam)$^+$.

In the absence of CO_2 there are excess yields of both H_2 and CO and a diminished yield of CO_2, Table 1. The yield of CO ($G = 0.10$) is close to the difference in anticipated radiolytic yield of CO_2 from eqs 3, 4, and 6 ($G = 0.34$), and the observed ($G = 0.26$) CO_2 yield. The yield of H_2 ($G = 0.24$) is in excess of the anticipated yield by $G = 0.13$. The sum of the CO and excess hydrogen yields, $G = 0.23$, is again equal to about half the anticipated Ni(cyclam)$^+$ yield. That is, H_2 evolution competes with CO production under low CO_2 concentration. In other words, at pH 5.2 and in the presence of formate, 97 ± 5% of the reactivity of Ni(cyclam)$^+$ remaining after the hydrogen peroxide reaction, eq 7, is directed toward CO_2 or proton reduction.

In contrast to the reactivity of Ni(cyclam)$^+$ with H_2O_2, discussed above, or N_2O, as reported by Jubran et al.,[7c] the coordination of protons or carbon dioxide to Ni(cyclam)$^+$ does not lead to the spontaneous two-electron reduction of the bound substrate with the concomitant formation of Ni(cyclam)$^{3+}$. This is due to the limited *two-electron* reduction potential of Ni(cyclam)$^{3+}$, $E(\text{Ni(cyclam)}^{3+/+}) = -0.18$ V,[19] which is marginal at best for the two-electron reduction at pH 4 of either protons, $E_4(H^+/H_2) = -0.24$ V, or CO_2, $E_4(CO_2/CO) = -0.34$ V, but is more than sufficient for the two-electron reduction of H_2O_2, $E_4(H_2O_2/H_2O) = 1.53$ V, and N_2O, $E_4(N_2O/N_2) = 1.53$ V.[27]

The absorbance of Ni(cyclam)$^+$, monitored at 380 nm, formed by the pulse irradiation of solutions containing Ni(cyclam)$^{2+}$ and formate under an argon atmosphere, decays with a rate constant of 0.73 s^{-1} (extrapolated to zero dose), at pH ~ 7. On decreasing the pH (pH range 7–2) the observed rate constant increases but remains second-order. In Figure 2 is shown, as an example, the decay of Ni(cyclam)$^+$, monitored at 380 nm, observed after pulse irradiation (dose 48.6 Gy) of a solution containing 0.5 mM Ni(cyclam)$^{2+}$ and 0.1 M HCO_2^- at pH 2. It was impractical to extend this study to lower pH as a consequence of the depletion of Ni(cyclam)$^+$ due to the formation of the hydride, eq 15 ($K_{15} = 62$ M^{-1}), which does not absorb significantly at an accessible wavelength range.[19] A

$$\text{Ni(cyclam)}^+ + H^+ \rightleftharpoons \text{Ni(cyclam)(H)}^{2+} \quad (15)$$

mechanism to account for the second-order decay of Ni(cyclam)$^+$ induced by protons is given by eq 15 followed by eq 16. From this mechanism, assuming that Ni(cyclam)$^+$ is the only absorbing species at 380 nm, the rate law given by eq 17 is derived.

$$\text{Ni(cyclam)(H)}^{2+} + \text{Ni(cyclam)}^+ \rightarrow \text{P(H}^+) \quad (16)$$

$$\frac{dA_{380}}{dt} = \frac{2K_{15}k_{16}[H^+]}{(1 + K_{15}[H^+])\epsilon_{380}l}(A_{380})^2 \quad (17)$$

Integrating eq 17 yields eq 18,

$$\frac{1}{A_{380}} = \frac{1}{A_0} = \frac{2K_{15}k_{16}[H^+]}{(1 + K_{15}[H^+])\epsilon_{380}l}(A_{380})^2 \quad (18)$$

or, on rearranging, eq 19,

$$\frac{1}{A_{380}} = \frac{1}{A_0} = k_{obs}t \quad (19)$$

with the observed rate constant, k_{obs}, being a nonlinear function of the proton concentration, eq 20.

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(26) We thank a reviewer for suggesting this point.

(27) Bratsch, S. G. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1–21.

$$k_{obs} = \frac{2K_{15}k_{16}[H^+]}{(1 + K_{15}[H^+])\epsilon_{380}l} \qquad (20)$$

At high pH, eq 20 reduces to the linear relation, eq 21.

$$\log k_{obs} = \log(2K_{15}k_{16}/\epsilon_{380}l) - pH \qquad (21)$$

The extinction coefficient for $Ni(cyclam)^+$ at 380 nm, ϵ_{380}, optical path length, l, and the equilibrium constant K_{15} have values of 3650 M^{-1} cm^{-1}, 2 cm, and 62 M^{-1}, respectively.[19] A linear fit to the data, Figure 2 inset, yields $k_{16} = (7.2 \pm 2.7) \times 10^7$ M^{-1} s^{-1}.[28]

The CO_2-Induced Decay of $Ni(cyclam)^+$. The presence of a second-order decay over a relatively wide CO_2 concentration range suggests a mechanism of the form observed for the proton reaction, eqs 22 and 23.

$$Ni(cyclam)^+ + CO_2 \rightleftharpoons Ni(cyclam)(CO_2)^+ \qquad (22)$$

$$Ni(cyclam)(CO_2)^+ + Ni(cyclam)^+ \rightarrow P(CO_2) \qquad (23)$$

However, in addition to the CO_2 reactions, the competitive proton reactions of eqs 15 and 16 also need to be considered. Under these conditions, the observed second-order rate constant, k_{obs}, is given by eq 24.

$$k_{obs} = \frac{2K_{15}k_{16}[H^+] + 2K_{22}k_{23}[CO_2]}{(1 + K_{15}[H^+] + K_{22}[CO_2])\epsilon_{380}l} \qquad (24)$$

When $[CO_2] = 0$, eq 24 reduces to eq 20, a situation that cannot be obtained under our conditions since CO_2 is always generated by the reaction of the $CO_2^{\bullet -}$ radical with $Ni(cyclam)^{2+}$ to give $Ni(cyclam)^+$, eq 6.[29] Since the amount of CO_2 will increase with increasing irradiation dose, the rate of $Ni(cyclam)^+$ decay will follow the same trend, accounting for the dose dependence of k_{obs}, Figure S1, inset. The values of k_{obs} reported in Figure 2, inset, were those extrapolated to zero dose. As we have already discussed above, at pH 2 and 3 the values of k_{obs} were independent of irradiation dose. Under these conditions, the amount of CO_2 generated in the system becomes negligible in comparison to the proton concentration.

The rate constants for reaction 23, obtained from the fit of eq 24 to the data shown in Figure 3, are given in Table 2. The value of K_{22} (16 M^{-1}) has been reported previously.[19] The limited data set does not allow us to comment significantly on the apparent increase in k_{23} with decreasing pH. It is likely that the spread of rate constants is due to the accumulation of errors in the parameters of eq 24. The average value of k_{23} is $(1.6 \pm 0.7) \times 10^8$ M^{-1} s^{-1}.

Table 2. Rate Constants Obtained for Reaction 23[a]

pH	k_{23}, M^{-1} s^{-1}
5.2	$(1.08 \pm 0.06) \times 10^8$
3.0	$(1.32 \pm 0.22) \times 10^8$
2.0	$(2.43 \pm 0.07) \times 10^8$

[a] See text for details.

Reduction of the proton or CO_2 substrate requires an additional reducing equivalent. In the current system, the second electron is provided by a second $Ni(cyclam)^+$ which can fill one of two possible roles. First, it may function as an outer-sphere reductant, eq 25,

$$Ni(cyclam)^+ + Ni(cyclam)(S)^{n+} \rightarrow Ni(cyclam)^{2+} + Ni(cyclam)(S)^{n-1} \qquad (25)$$

where S is either a proton or CO_2 and n is 2 or 1, respectively, with the product $Ni(cyclam)(S)^{n-1}$ undergoing facile protonation/decomposition to yield the H_2 or CO product and $Ni(cyclam)^{2+}$. The stoichiometry of the reaction is represented by eqs 26 and 27.[30]

$$Ni(cyclam)(H)^+ + H^+ \rightarrow Ni(cyclam)^{2+} + H_2 \qquad (26)$$

$$Ni(cyclam)(CO_2)^0 + H^+ \rightarrow Ni(cyclam)^{2+} + CO + OH^- \qquad (27)$$

Alternatively, the second $Ni(cyclam)^+$ may act as an inner-sphere reductant, eq 28,

$$Ni(cyclam)^+ + Ni(cyclam)(S)^{n+} \rightarrow Ni_2(cyclam)_2(S)^{(n+1)+} \qquad (28)$$

in which the proton or CO_2 bridges the two Ni(I) complexes. In this case, the stoichiometry of the processes leading to the final products would be represented by eqs 29 and 30.

$$Ni_2(cyclam)_2(H)^{3+} + H^+ \rightarrow 2Ni(cyclam)^{2+} + H_2 \qquad (29)$$

$$Ni_2(cyclam)_2(CO_2)^{2+} + H^+ \rightarrow 2Ni(cyclam)^{2+} + CO + OH^- \qquad (30)$$

Although we are unable to distinguish between these two pathways, reaction 28 is appealing in light of the isolation by Fujita et al. of the species $[LCo(CO_2H)CoL]^{3+}$ which contains a formate bridging group.[11a]

The decay of $Ni(cyclam)^+$ does not result in the clean formation of the $Ni(cyclam)^{2+}$ starting material. Instead, the second-order decay, observed as a change of absorbance, does not return to the baseline. The spectrum of the product, observed ca. 45 s after irradiation, was identical to that obtained by Sauvage and co-workers following continuous electrolysis of $Ni(cyclam)^{2+}$,[12b] by Furenlid et al. after reduction of $Ni(cyclam)^{2+}$ by sodium amalgam in acetonitrile followed by addition of CO,[31] and by ourselves following pulse radiolysis or laser flash photolysis of solutions containing CO.[32] We have previously assigned this spectrum to *RSRS*-$Ni(cyclam)(CO)^+$.[32] The formation of the latter species is presumably the result of a competition between reaction 22 and reaction 31, for which $k_{31} = (2.0 \pm 0.2) \times 10^9$ M^{-1} s^{-1} has been reported.[32] The product of reaction 31 has been suggested to be *RRSS*-$Ni(cyclam)(CO)^+$, which isomerizes to *RSRS*-$Ni(cyclam)(CO)^+$ with $k = 1.8 \pm 0.2$ s^{-1}.[32]

$$Ni(cyclam)^+ + CO \rightarrow Ni(cyclam)(CO)^+ \qquad (31)$$

Conclusions

The binding of protons or CO_2 to $Ni(cyclam)^+$ in aqueous solution is insufficient to drive the two-electron reduction of

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[28] We are grateful to a reviewer for suggesting the use of eq 21 under our experimental conditions rather than eq 20.

[29] At the lowest dose, ca. 25 Gy per pulse, the amount of CO_2 evolved as a result of reaction 6 is ~8.5 μM.

[30] The species $Ni(cyclam)(H)^+$ and $Ni(cyclam)(CO_2)^0$ are, formally, Ni(II) species containing the H^- and CO_2^{2-} ligands, respectively.

[31] Furenlid, L. R.; Renner, M. W.; Szalda, D. J.; Fujita, E. *J. Am. Chem. Soc.* **1991**, *113*, 883−892.

[32] Kelly, C. A.; Mulazzani, Q. G.; Blinn, E. L.; Rodgers, M. A. J. *Inorg. Chem.* **1996**, *35*, 5122−5126.

the substrates with concomitant formation of Ni(cyclam)$^{3+}$. Under the reaction conditions investigated, an additional equivalent of Ni(cyclam)$^{+}$ is required for the reduction of the intermediate Ni(cyclam)(H)$^{2+}$ or Ni(cyclam)(CO$_2$)$^{+}$ adducts. The reactions of Ni(cyclam)$^{+}$ with Ni(cyclam)(H)$^{2+}$ and Ni(cyclam)(CO$_2$)$^{+}$, $k = 7.2 \times 10^7$ and 1.6×10^8 M^{-1} s^{-1}, respectively, proceed at less than the diffusion controlled limit, yet the rate constants differ by only a factor of ~2, suggesting similar driving forces for the two reactions. It is not clear whether the second equivalent of Ni(cyclam)$^{+}$ functions solely as an outer-sphere reducing agent, or if a bridged dinuclear intermediate, [(cyclam)Ni(H)Ni(cyclam)]$^{3+}$ or [(cyclam)Ni(CO$_2$)Ni(cyclam)]$^{2+}$ (or a protonated form thereof), is of importance. From the reduced mononuclear species Ni(cyclam)(H)$^{+}$ and Ni(cyclam)(CO$_2$)^{0} or from the dinuclear intermediates [(cyclam)Ni(H)Ni(cyclam)]$^{3+}$ and [(cyclam)Ni(CO$_2$)Ni(cyclam)]$^{2+}$, nearly quantitative yields of H_2 and CO are obtained.

Previous reports concerning the lack of reactivity of homogeneous Ni(cyclam)$^{+}$ toward CO$_2$ reduction are clearly overstated.[16] The origin of the discrepancy is likely due to more efficient reduction of Ni(cyclam)(CO$_2$)$^{+}$ while adsorbed to the cathode surface relative to the second-order mechanism that we have discovered in homogeneous solution. The low yield observed in the homogeneous photochemical system of Craig et al.[8b] cannot be accounted for by the current work. While we are not able to address specific points of the photochemical system, the low yields cannot be due to inefficient reduction of CO$_2$ by Ni(cyclam)$^{+}$.

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Supporting Information Available: Plots of absorbance and $1/(\Delta A\text{-}\Delta A_\infty)$ vs time and plots of k_{obs} vs dose. This material is available free of charge via the Internet at http://pubs.acs.org.

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