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Flash Photolysis and Pulse Radiolysis of the Co(sep)$^{3+}$–X$^-$ (sep = Sepulchrate; X = I, Br) Systems in Aqueous Solution

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The Co(sep)$^{3+}$ complex (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) in aqueous solution forms ion pairs with the I$^-$ and Br$^-$ anions, which exhibit a relatively intense charge-transfer absorption. In deoxygenated aqueous solution no net reaction is obtained upon continuous light excitation in the ion-pair charge-transfer bands, but formation of transient species is observed in flash photolysis experiments. For the Co(sep)$^{3+}$–I$^-$ system, I$_2^-$ ions are formed that decay in the 50-μs time scale to give I$_3^-$. The latter species disappears in a time scale of seconds, leading the system back to the preexcitation conditions. For the Co(sep)$^{3+}$–Br$^-$ system, only formation of the Br$_2^-$ transient is observed, followed by regeneration of the preexcitation conditions in the 20-μs time scale. In order to elucidate the kinetic aspects of the transient formation and disappearance, pulse radiolysis experiments on the Co(sep)$^{3+}$–I$^-$ and Co(sep)$^{3+}$–Br$^-$ systems have been carried out. The rate constants of the reactions of Co(sep)$^{2+}$ with I$_2^-$, I$_3^-$, and Br$_2^-$ have been measured, and a complete picture of the redox processes that follow flash photolysis and pulse radiolysis excitations has been obtained.

Introduction

Co(sep)$^{3+}$ (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) is the prototype of a very interesting class of molecules recently synthetized by Sargeson and co-workers.[2] As discussed in detail elsewhere,[3] this cage complex may be viewed as a perturbed version of Co(NH$_3$)$_6^{3+}$, in the sense that it maintains the spectroscopic properties of Co(NH$_3$)$_6^{3+}$ that are related to the presence of six nitrogen atoms in the first coordination sphere but exhibits a completely different behavior upon photochemical,[4] electrochemical,[2] or radiolytic[5] reduction because the six nitrogen atoms are linked together by covalent bonds and none of them can leave the coordination sphere of the reduced metal ion. Because of this peculiar property, Co(sep)$^{3+}$ has been used as a relay[6–9] and also as a photosensitizer[5] for hydrogen generation from water in sacrificial cycles.

In a recent paper[4] the photochemical behavior of the Co(sep)$^{3+}$–I$^-$ system in continuous irradiation experiments has been described. At natural pH in oxygen-saturated solutions, a photoassisted oxidation of I$^-$ to I$_2$ by O$_2$ was obtained, whereas in deoxygenated solutions no net reaction was observed. These results were interpreted on the basis of the formation of Co(sep)$^{2+}$ and I in the primary photochemical process, followed by reactions involving Co(sep)$^{2+}$ and transient species deriving from the I radical. In order to elucidate the intimate kinetic mechanism of such processes, we have now performed a flash phtolysis and pulse radiolysis investigation on the Co(sep)$^{3+}$–I$^-$ system and on the analogous Co(sep)$^{3+}$–Br$^-$ system. Formation of the I$_2^-$, I$_3^-$, and Br$_2^-$ transients has been observed, and the kinetics of their disappearance has been followed. A complete picture of the processes that follow flash photolysis and pulse radiolysis excitations has been obtained.

Experimental Section

The preparation and purification of Co(sep)Cl$_3$ has been described elsewhere.[2,4] KI and KBr were of reagent grade. All experiments were carried out in aqueous solution at natural pH at room temperature (~20 °C). The solutions were prepared by using tridistilled water and were degassed by bubbling N$_2$ or Argon. The absorption spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometer. Continuous irradiation experiments with 254- or 313-nm light were performed as previously described.[4]

Flash photolysis experiments were carried out with an Applied Photophysics apparatus (pulse duration ≃ 25 μs). Pyrex cells were used to avoid absorption by free X$^-$ ions.

Pulse radiolysis experiments with optical absorption detection were performed with the 12 MeV linear accelerator of the CNR-FRAE Institute.[10] Pulses of 20–100 ns duration were used. The radiolysis of diluted aqueous solutions generates the following species:

$$\mathrm{H_2O} \rightsquigarrow e_{aq}^- \ (2.8),\ \mathrm{OH}\ (2.8),\ \mathrm{H}\ (0.6) \qquad (1)$$

The numbers in parentheses represent the *G* values for the indicated species (*G*(X) = number of molecules of species X formed per 100 eV of energy absorbed by the solution).

Computer analysis of the decay of transient absorptions was performed by numerical integration of the differential equations describing the reaction mechanism, using a program based on that of Hindmarsh,[11] and a Gould Sel Computer 27/32.

Results

Continuous Photolysis. The formation of ion pairs between Co(sep)$^{3+}$ and I$^-$ in aqueous solution with the appearance of a new band at 295 nm has been previously reported.[4] We have found that a similar behavior is exhibited by the Co(sep)$^{3+}$–Br$^-$ system, where a new band appears with maximum at 270 nm. Continuous irradiation with 254- or 313-nm light of an aqueous solution containing 5.0 mM Co(sep)$^{3+}$ and 0.1 M Br$^-$ at natural pH did not cause any spectral change, even after very long irradiation times. An upper limit for the quantum yield of Co(sep)$^{3+}$ disappearance is estimated to be $\leq 10^{-6}$, as in the case of the previously studied Co(sep)$^{3+}$–I$^-$ system. While the latter system was photosensitive in air-saturated or oxygen-saturated solutions,[4] no net reaction could be observed in oxygen-saturated solution of Co(sep)$^{3+}$–Br$^-$.

Flash Photolysis. Flash excitation of aqueous solutions containing 1.0 mM Co(sep)$^{3+}$ and 0.1 M I$^-$ caused the formation of a transient with a weak absorption maximum at about 750 nm and a stronger absorption in the 500–380-nm region, increasing in intensity with decreasing wavelength. For λ < 380 nm meaningful measurements could not be performed because of experimental limitations due to the sensitivity of the equipment used and the intense absorption of the Co(sep)$^{3+}$ complex. The decay of such a transient was observed to occur in the 50-μs time scale, with complete disappearance of the absorption at 750 nm (Figure 1a). At 385 nm the decay occurred with the same rate, leaving a residual absorption (Figure 1a) which only disappeared in a time scale of seconds (Figure 1b). For solutions containing

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[1] (a) Instituto Superior Tecnico. (b) Istituto Chimico "G. Ciamician". (c) Istituto FRAE-CNR.

[2] (a) Creaser, I. I.; Geue, R. J.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016. (b) Creaser, I. I.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Springborg, J. *J. Am. Chem. Soc.* **1977**, *99*, 3181.

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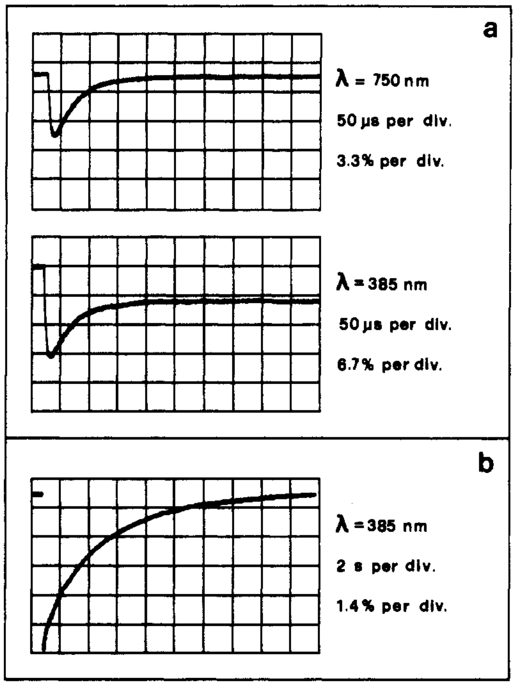

Figure 1. Oscilloscopic traces from flash photolysis of an aqueous solution containing 0.1 M KI and 1.0 mM $Co(sep)^{3+}$. Optical path = 10 cm.

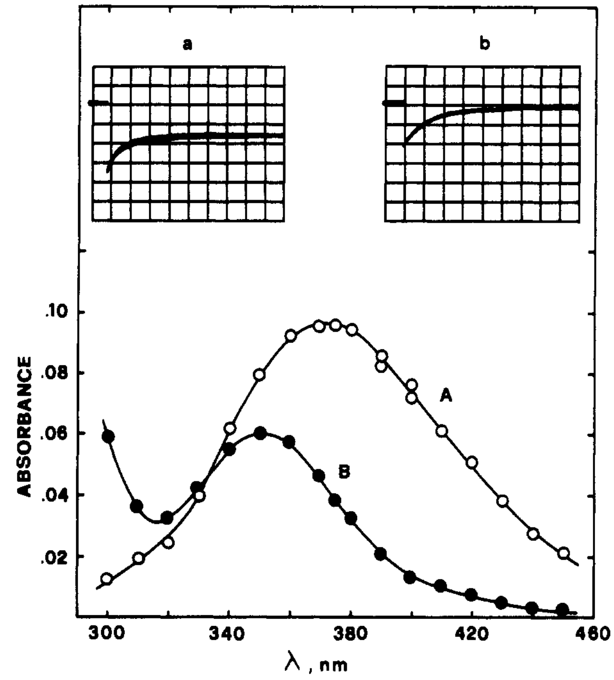

Figure 2. Transient spectra, measured immediately (○) or 450 μs (●) after the pulse, from the pulse radiolysis of an aqueous solution containing 0.1 M KI and 0.1 mM $Co(sep)^{3+}$. Optical path = 2 cm. Dose/pulse = 17 Gy. Insets: (a) 375 nm, 50 μs/division, 5.62% absorption/division; (b) 350 nm, 2 s/division, 5.38% absorption/division.

1.0 mM $Co(sep)^{3+}$ and 0.1 M Br^-, a transient absorption at $\lambda <$ 450 nm was observed, which completely disappeared in the 20-μs time scale.

Pulse Radiolysis. Pulse radiolysis of aqueous solutions containing 0.1 mM $Co(sep)^{3+}$ and 0.1 M I^- caused the appearance of the well-known[12] I_2^- absorption spectrum (Figure 2, curve A) during the pulse. This absorption disappeared in the 50-μs time scale (Figure 2, inset a), to yield the I_3^- absorption spectrum (Figure 2, curve B), which then disappeared in a time scale of seconds (Figure 2, inset b). The rate of decay of this long-lived transient was found to decrease with decreasing intensity of the analyzing light (xenon 450 W), indicating that a photochemical process was superimposed on the thermal decay. This was confirmed by experiments with intermittent analyzing light (Figure 3).

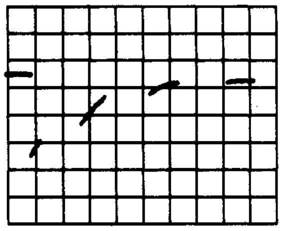

Figure 3. Decay of the long-lived transient (I_3^-) obtained from the pulse radiolysis of an aqueous solution containing 0.1 M KI and 0.1 mM $Co(sep)^{3+}$ monitored with intermittent analyzing light. Optical path = 2 cm. Dose/pulse = 23 Gy, 2 s/division, 5.10% absorption/division.

For the $Co(sep)^{3+}$–Br^- system under the same experimental conditions, an absorption spectrum identical with that of the Br_2^- species (λ_{max} = 360 nm)[12] was observed immediately after the pulse. Such an absorption disappeared completely in the 20-μs time scale (vide infra).

Discussion

As we have seen above, the first transient observed upon flash photolysis of $Co(sep)^{3+}$–I^- shows an absorption maximum at 750 nm and an increasing absorption from 500 to 380 nm, which can be identified with the spectrum of I_2^-,[12] as expected because of the charge-transfer nature of the light-excitation process[4]

$$Co(sep)^{3+}\text{–}I^- \xrightleftharpoons[k_a]{h\nu\ (I^- \to Co^{3+})} Co(sep)^{2+}\text{–}I \qquad (2)$$

which is expected to be followed by cage recombination (k_a in eq 2) and by reactions 3–5:

$$Co(sep)^{2+}\text{–}I \xrightarrow{k_b} Co(sep)^{2+} + I \qquad (3)$$

$$I + I^- \xrightarrow{k_c} I_2^- \qquad (4)$$

$$Co(sep)^{2+}\text{–}I + I^- \xrightarrow{k_d} Co(sep)^{2+} + I_2^- \qquad (5)$$

(For the small amounts of species in which two I^- ions are associated with $Co(sep)^{3+}$, reactions 4 and 5 would be intramolecular rather than intermolecular, with the same results.) According to these reactions $Co(sep)^{2+}$ and I_2^- are formed in a 1:1 ratio. $Co(sep)^{2+}$ is a moderately strong reductant ($E°$ for $Co(sep)^{3+/2+}$ = –0.30 V)[2,14] and I_2^- is a strong oxidant ($E°$ for $I_2^-/2I^-$ = +1.06 V).[13]

The flash photolysis (Figure 1) results show that when the I_2^- transient disappears, the 750-nm band goes to zero, but a residual absorption remains in the 380–450-nm region. On the basis of known spectra[12] and of the results obtained in the pulse radiolysis experiments, it seems reasonable to consider that the disappearance of I_2^- in the flash experiments is accompanied by the generation of I_3^-, according to the well-known reactions[13,15]

$$2I_2^- \xrightarrow{k_e} I_2 + 2I^- \quad \Delta G° = -0.44 \text{ eV} \qquad (6)$$

$$2I_2^- \xrightarrow{k_f} I_3^- + I^- \quad \Delta G° = -0.61 \text{ eV} \qquad (7)$$

whose products are related by the equilibrium[16,17]

$$I_2 + I^- \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} I_3^- \quad K_8 = 768 \text{ M}^{-1} \qquad (8)$$

Analysis of the decay of the first flash photolysis transient (Figure

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[12] Hug, G. L. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1981**, *No. 69.*

[13] Nord, G.; Pedersen, B.; Floryan-Lovborg, E.; Pagsberg, P. *Inorg. Chem.* **1982**, *21*, 2327.

[14] All the potentials quoted refer to NHE.

[15] Ross, A. B.; Neta, P. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1979**, *No. 65.*

[16] Woodruff, W. H.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2578.

[17] This equilibrium constant corresponds to $\Delta G°$ = –0.17 eV.

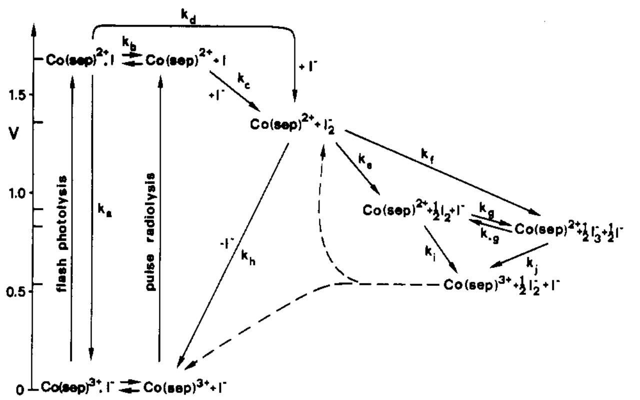

Figure 4. Schematic representation of the energetics of the reactions that follow flash photolysis or pulse radiolysis excitation of the Co(sep)$^{3+}$–I$^-$ system.

1) shows, however, that the absorbance decrease does not follow the second-order behavior expected on the basis of reactions 6 and 7; rather, this decay is closer to first order. As we will see later, this can be accounted for on the basis of the simultaneous occurrence of reaction 9. Leaving aside for the moment the

$$I_2^- + Co(sep)^{2+} \xrightarrow{k_h} 2I^- + Co(sep)^{3+} \quad \Delta G^\circ = -1.36 \text{ eV} \quad (9)$$

quantitative aspects of the problem (vide infra), we will now consider the fate of the I_2 and I_3^- species formed in reactions 6 and 7. Both these species can play the role of one-electron oxidants (E° for I_2/I_2^- and I_3^-/I_2^- + I^- are +0.17[13] and 0.00 V,[18] respectively), so that reactions 10 and 11 are expected to occur.

$$I_2 + Co(sep)^{2+} \xrightarrow{k_i} I_2^- + Co(sep)^{3+} \quad \Delta G^\circ = -0.47 \text{ eV} \quad (10)$$

$$I_3^- + Co(sep)^{2+} \xrightarrow{k_j} I_2^- + I^- + Co(sep)^{3+} \quad \Delta G^\circ = -0.30 \text{ eV} \quad (11)$$

Since the association constant of equilibrium 8 is $K_8 = 768$ M^{-1}, under our experimental conditions (I^- = 0.10 M) the concentration of I_3^- is about 10^2 times larger than that of I_2. Thus, reaction 11 is less exergonic but favored by the higher reactant concentration (and also by a more favorable work term). It should be noted that both reactions 10 and 11 produce the very strong oxidant I_2^-, which will rapidly oxidize Co(sep)$^{2+}$ via reaction 9. Because of their smaller exergonicity, reactions 10 and 11 are much slower than reaction 9. The I_3^- transient, in fact, disappears in a time scale of seconds (Figure 2). The complete sequence of reactions described above, which accounts for the flash photolysis results, is shown schematically in Figure 4.

For the Co(sep)$^{3+}$–Br$^-$ system, the flash photolysis results show that the Br_2^- species is formed, as expected, because of the occurrence of reactions analogous to reactions 2–5. The disappearance of Br_2^- does not leave any residual absorbance at $\lambda >$ 380 nm. Since Br_3^- does not appreciably absorb in this spectral range,[19] we cannot say whether or not this species is formed.

A quantitative analysis of the transient signals obtained in the flash photolysis experiments was not performed because (i) the relatively long duration ($\simeq$25 μs) of the light excitation pulse masked a large part of the decay of the first transient and (ii) the photocatalyzed nature of the decay of the second transient. In pulse radiolysis experiments, the hydrated electrons and OH radicals produced in a 1:1 stoichiometric ratio by water radiolysis (eq 1) react very rapidly with Co(sep)$^{3+}$ and X$^-$, respectively:

$$Co(sep)^{3+} + e_{aq}^- \rightarrow Co(sep)^{2+} \quad (12)^5$$

$$OH + X^- \rightarrow OH^- + X \quad (13)^{20,21}$$

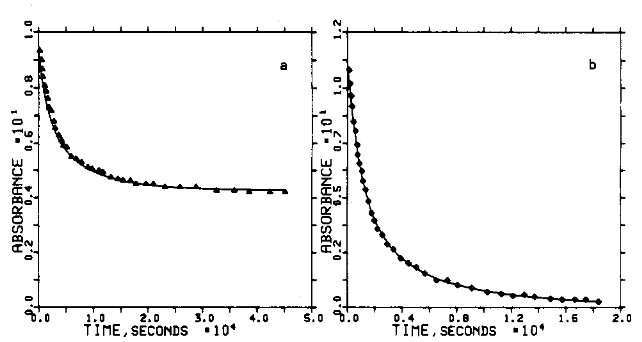

Figure 5. (a) Decay of absorbance at 375 nm from the pulse radiolysis of an aqueous solution containing 0.1 M KI and 0.1 mM Co(sep)$^{3+}$. Optical path = 2 cm. $\epsilon_{I_2^-}$ = 9400 M^{-1} cm^{-1}. $\epsilon_{I_3^-}$ = 17 600 M^{-1} cm^{-1}. (b) Decay of absorbance at 360 nm from the pulse radiolysis of an aqueous solution containing 0.1 M KBr and 0.1 mM Co(sep)$^{3+}$. Optical path = 2 cm. $\epsilon_{Br_2^-}$ = 9900 M^{-1} cm^{-1}. Solid lines represent the calculated curve from the computer analysis (see text).

Because of these reactions, equivalent concentrations of Co(sep)$^{2+}$ and X are produced as happens in the flash photolysis experiments, but in a higher concentration and in a much shorter time scale. For the Co(sep)$^{3+}$–I$^-$ system, the I_2^- transient was found to decay with mixed-order kinetics, as expected by the competition of reactions 6 (or 7) and 9. Although both reactions are second order, their reactants have equal concentrations only at $t = 0$. With increasing time the concentration of I_2^- tends to become lower than that of Co(sep)$^{2+}$, so that reaction 9 tends to assume a pseudo-first-order character and becomes the predominant pathway for I_2^- disappearance. This is the reason why in the flash photolysis experiments, where only the tail of the I_2^- disappearance can be followed because of the relative long light pulse, the decay of the first transient occurs with kinetics close to first order. As mentioned above, in the pulse radiolysis experiments the decay of I_2^- was observed quite clearly since the beginning and was found to follow mixed first–second-order kinetics. With the known rate constants ($k_e + k_f$) = 4.5 × 10^9 M^{-1} s^{-1} for reactions 6 and 7[15], a best-fitting procedure (Figure 5a) led to k_h = 5.0 × 10^9 M^{-1} s^{-1} for reaction 9. For the analogous reaction between I_2^- and Ru(NH$_3$)$_5$(py)$^{2+}$, a preliminary value of 2.3 × 10^9 M^{-1} s^{-1} has been recently reported.[22]

After the disappearance of I_2^- (i.e., in a time scale longer than milliseconds), Co(sep)$^{2+}$ and I_3^- must be present in the system in a 2:1 concentration ratio. According to the known value of the equilibrium constants of reaction 8, under our experimental conditions (I^- = 0.1 M) the $[I_3^-]/[I_2]$ ratio is about 100. Thus, as mentioned before, reaction 11 is expected to prevail over the slightly more exergonic reaction 10. The rate of I_3^- decay was found to depend on the intensity of the analyzing light. The smallest value obtained for k_j under our "best" experimental conditions (i.e., using the lowest analyzing light intensity that gave meaningful signals) was 1 × 10^5 M^{-1} s^{-1} on the assumption that reaction 11 is followed by the faster reaction 9. Such a value is about twice that reported by Rudgewick-Brown and Cannon.[24] Both values may be affected by the presence of the photocatalyzed reaction, which causes the disappearance of I_3^- (see also Figure 3). The nature of this photocatalyzed decay has not been investigated in detail. However we have found that the photoinduced disappearance of I_3^- is almost negligible when I_3^- is obtained in the absence of Co(sep)$^{2+}$. Ford's hypothesis[23] that light displaces equilibrium 8 to the left-hand side is consistent with this observation, implying that a reductant has to be present to scavenge I_2^-.

For the analogous Co(sep)$^{3+}$–Br$^-$ system, with the known[15] rate constant for the Br_2^- dismutation reaction (k = 1.8 × 10^9 M^{-1}

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[18] Obtained from the potential of the I_2/I_2^- couple[13] and the ΔG° value of equilibrium 8.[17]

[19] Gilbert, F. L.; Goldstein, R. R.; Lowry, T. M. *J. Chem. Soc.* **1931**, 1092.

[20] Farhataziz; Ross, A. B. *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)* **1977**, *No. 59*.

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[22] See footnote 17 in ref 23.

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[24] Rudgewick-Brown, N.; Cannon, R. *J. Chem. Soc., Dalton Trans.* **1984**, 479.

s^{-1}), a best-fitting procedure (Figure 5b) leads to $k = 1.4 \times 10^{10}$ M^{-1} s^{-1} for the reaction between Br_2^- and $Co(sep)^{2+}$. It follows that more than 80% of the Br_2^- disappears via $Co(sep)^{2+}$ oxidation. This, together with the less accessible Br_3^- absorption, precluded an investigation of the reaction between Br_3^- and $Co(sep)^{2+}$.

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Registry No. $Co(sep)^{3+}$, 72496-77-6; I^-, 20461-54-5; Br^-, 24959-67-9; I_2^-, 12190-71-5; I_3^-, 14900-04-0; Br_2^-, 12595-70-9.

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Volume Profiles for the Base Hydrolysis of a Series of Monoalkyl-Substituted Chloropentaamminecobalt(III) Complexes in Aqueous Solution

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Volumes of activation ($\Delta V^{\ddagger}_{\text{exptl}}$) for the base hydrolysis reactions of a series of complexes of the type $Co(NH_3)_4(NH_2X)Cl^{2+}$ (X: cis, CH_3; trans, CH_3; trans, C_2H_5; cis, n-C_3H_7; trans, n-C_3H_7; trans, n-C_4H_9; trans, i-C_4H_9) were determined from the pressure dependencies of the hydrolysis rate constants and have values between 26.4 and 29.9 cm^3 mol^{-1} at 25 °C. These data combined with dilatometrically determined overall reaction volumes ($\Delta \bar{V}_{\text{BH}}$) enable the construction of reaction volume profiles for the base hydrolysis process. Volume equation calculations reveal that the partial molar volume of the five-coordinate species $Co(NH_3)_3(NH_2)(NH_2X)^{2+}$ increases linearly with the partial molar volume of NH_2X and almost equals the partial molar volume of the $Co(NH_3)_4(NH_2X)OH^{2+}$ species. These results underline the validity of the S_N1CB mechanism and demonstrate the additivity properties of the partial molar volumes of five- and six-coordinate species of similar charge.

Introduction

Base hydrolysis reactions of pentaamminecobalt(III) complexes are generally accepted to proceed according to a S_N1CB mechanism in which a five-coordinate intermediate, $Co(NH_3)_4NH_2^{2+}$, is formed from the conjugate base species, which rapidly reacts with water or any other competing nucleophile to produce the hydrolysis products.[2-7] Such reactions are orders of magnitude faster than the corresponding aquation or ligand substitution processes and are, therefore, of general interest. However, there is still controversy over the question of a discrete reduced coordination number intermediate and the nature of the hydrolysis mechanism.[7,8] It has been proposed that an E2 mechanism is operative in which abstraction of an amine proton and loss of the leaving group are concerted processes; i.e., no six-coordinate conjugate base species are formed[9,10] (see Discussion). Subsequently, Sargeson and co-workers[11,12] have in detailed studies once again confirmed the applicability of the S_N1CB mechanism.

We have studied the base hydrolysis reactions of pentaamminecobalt(III) complexes in a different way by constructing reaction volume profiles from partial molar volume and volume of activation data.[13] This has enabled us to estimate the partial molar volume of the suggested five-coordinate intermediate and to demonstrate that its value is independent of the nature (size and charge) of the leaving group. Furthermore, the difference between the overall reaction volume for base hydrolysis and the volume of activation represents the volume change for the final step in this mechanism in which $Co(NH_3)_4NH_2^{2+}$ reacts with water to produce $Co(NH_3)_5OH^{2+}$ and was also found to be independent of the nature of the leaving group.[13] These observations further supported the operation of the S_N1CB mechanism.

Our ability to estimate the partial molar volume of a five-coordinate intermediate[13] has contributed to solving the longstanding discrepancy concerning the partial molar volume of such species.[14-19] In the present study we have investigated the base hydrolysis reactions of a series of monoalkyl-substituted chloropentaamminecobalt(III) complexes[20] to determine the effect of ligand size on the partial molar volume of the five-coordinate intermediate. The reported volume profiles enable interesting comparisons with similar data for related base hydrolysis and aquation reactions.

Experimental Section

The following complexes were prepared by Piriz Mac-Coll[1b] and supplied by Prof. S. Balt (Free University of Amsterdam, The Netherlands), originating from their earlier investigation:[20] *cis*-$[Co(NH_3)_4(CH_3NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(CH_3NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(C_2H_5NH_2)Cl](ClO_4)_2$; *cis*-$[Co(NH_3)_4(n\text{-}C_3H_7NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(n\text{-}C_3H_7NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(n\text{-}C_4H_9NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(i\text{-}C_4H_9NH_2)Cl](ClO_4)_2$. UV–vis, IR, and ^1H NMR spectral data have been reported before.[20]

In the dilatometric studies (base hydrolysis and subsequent neutralization) a Carlsberg dilatometer was used and the procedures have been

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(2) Nordmeyer, F. R. *Inorg. Chem.* **1969**, *8*, 2780.
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