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Kinetic Study of the Displacement of Water in Diaquo[N,N'-Ethylenebis(Salicylideneiminate)]Cobalt(III) Monocation by Various Nucleophiles

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The water substitution reactions of the monocation $Co(III)(H_2O)_2(salen)^+$ *[salen = N,N'-ethylenebis(salicylideneiminate)] were studied in aqueous solution. The nucleophiles used were pyridine, thiourea, morpholine, aniline, imidazole,* NCO^-, HSO_3^-, $S_2O_3^{2-}$. *The kinetics of mono-substitution reactions were found to be very rapid, with second order rate constants nearly independent of the nature of the incoming ligand.*

A comparison is made with the corresponding reactions of Co(III)–hematoporphyrin and some other macrocyclic complexes.

Introduction

Cobalt complexes of N,N'-ethylenebis(salicylideneiminate) have been extensively studied because of their interesting properties. It is well known that Co(II)(salen) is capable of adding reversibly to molecular oxygen [1]. Many cobalt(III) pentacoordinated species have been isolated [2, 3]. Furthermore, organometallic derivatives with stable cobalt–carbon bonds are known [2].

Electrochemical [4], spectral [5, 6], structural [7] and other physicochemical properties [8, 9] have been investigated. Equilibrium data for axial ligand exchange have been also reported [3, 10].

Surprisingly, not a great deal of work has been reported on the kinetic properties of these complexes. Since the available data are concerned solely with the alkyl transfer processes [11], we proposed that the study of the axial ligand substitution reactions would provide a deeper insight into the behaviour of these complexes.

This paper is concerned with the kinetics of the axial water replacement of $Co(III)(H_2O)_2(salen)^+$ (Fig. 1) with a series of Lewis bases of various nucleophilicities. Such an approach is currently applied to the study of the mechanism of the axial substitution reactions of many macrocyclic complexes [12], including Vit. B_{12} [13] and metalloporphyrins [14, 15]. Kinetic data so obtained were correlated with steric and electronic properties of the ligand environment of the metal atom. One of the problems concerning this matter has been to assess the labilizing influence of progressive degrees of unsaturation in the macrocycle [12]. Examination of this question may give a contribution to the understanding of the influence of the porphyrin ring on the substitution properties of the metal center. Since the complex $Co(III)(H_2O)_2(salen)^+$ possesses a highly unsaturated chelating ring, it appears to be especially appropriate as a system to be used in a 'model approach' to the study of the chemical reactivity of Co–porphyrins.

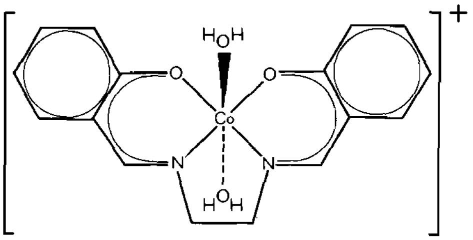

Fig. 1. The complex $Co(III)(H_2O)_2(salen)^+$.

Experimental

Materials

$[Co(III)(H_2O)_2(salen)]NO_3$ was obtained following the original procedure [8] from the corresponding hydroxo–aquo complex in water–methanol solution by acidification with dilute HNO_3. The product was precipitated by excess of $NaNO_3$, and purified by re-precipitation with water from a

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methanolic solution. All other chemicals were reagent grade, the solutions being prepared from a known weight (or volume) of reagent.

Apparatus and Procedure

Kinetic experiments were performed using a stopped-flow Durrum–Gibson model D-130 apparatus, thermostatted at 20.0 ± 0.2 °C. Substitution kinetics were followed in the visible region. A ligand solution of the desired pH and ionic strength was mixed with a cobalt complex solution of the same pH and ionic strength. All kinetics were run under pseudo first order conditions, with excess ligand concentration. In these conditions reaction rates follow the first order expression. The observed rate constants k_{obs}, were determined from the plots of log $(A_t - A_\infty)$ *vs.* time.

Spectra were obtained with a double beam–double wavelength Perkin-Elmer model 356 spectrophotometer.

For pH measurements a Radiometer pH meter type pH M4 equipped with glass and calomel electrodes was used.

Results

Equilibrium Studies

Spectrophotometric titrations of the complex over the range of pH 4.84–13.00 reveal that two pH-dependent equilibria are present:

$$\mathrm{Co(III)(H_2O)_2(salen)^+ \underset{}{\overset{K_1}{\rightleftarrows}} Co(III)(H_2O)(OH)(salen) + H^+} \qquad (1)$$

$$\mathrm{Co(III)(H_2O)(OH)(salen) \overset{K_2}{\rightleftarrows} Co(III)(OH)_2(salen)^- + H^+} \qquad (2)$$

Changes in the spectrum over the range 290–360 nm as the pH was increased indicate that the two equilibria overlap. However, good isosbestic points are observed at 302 and 355 nm for the first part of the change (pH 4.87–7.60), corresponding to pK_1, and at 310 nm for the second part of the change (pH 9.63–13.00), corresponding to pK_2. The pK values were determined using absorbance data at 335 nm, the wavelength of the greatest overall change. The data in the two pH regions corresponding to the reactions 1 and 2 were analyzed independently using an equation of the type:

$$\log \frac{A - A_a}{A_b - A} = \mathrm{pH} + \log K \qquad (3)$$

where A_a is the absorbance at a pH at which the complex is in the protonated form and A_b is the absorbance of the solution at a pH at which the complex is in the deprotonated form. Since the absorbance of the species $\mathrm{Co(III)(H_2O)(OH)(salen)}$ was not experimentally observable because of the second overlapping equilibrium, the data were preliminarily treated by the method of Newton and Arcand [16]. Thus absorbance of this species, obtained as intercept of a plot of A *vs.* $(A - A_a)/[OH^-]$ was used for solving eqn. 3. Plots of pH *vs.* log $(A - A_a)/(A_b - A)$ result in straight lines of slope equal to unity, and intercepts corresponding to the values of $pK_1 = 6.78$ and $pK_2 = 10.52$. These constants were also determined by a potentiometric method. A solution 2×10^{-2} *M* of the complex was titrated with NaOH 0.1 *M*. Typical neutralization curves of a bibasic acid were obtained. The part of the curve corresponding to the first water molecule neutralization and the part corresponding to the second water molecule neutralization have been analyzed independently [17].

Values found are $pK_1 = 6.86$ and $pK_2 = 10.61$ which agree well with the values estimated from spectral studies.

Kinetic Studies

The reactions of $\mathrm{Co(III)(H_2O)_2(salen)^+}$ with pyridine, thiourea, morpholine, aniline, imidazole, NCO^-, HSO_3^-, and $S_2O_3^{2-}$ were followed spectrophotometrically by means of stopped-flow technique at 20.0 ± 0.2 °C in water maintained at 0.1 *M* ionic strength using $NaNO_3$. The reactions were carried out in presence of an excess of ligand (pseudo first order conditions). The initial complex concentration was generally 0.5×10^{-4} *M* and ligand concentrations were varied in the range 1×10^{-3}–1.2×10^{-2} *M*. The pH was adjusted either with acetate buffer (0.05 *M*) or by titrations with dilute NaOH or HNO_3. To ensure that the cobalt complex was predominantly in the form of the diaquo complex the pH was always kept below 5.8. The effect of the pH on the reaction rates was not investigated in great detail. Preliminary experiments using thiourea as ligand at a given constant concentration (0.002 *M*) and a variable acidity of the medium showed that the reaction is pH-independent over the range of pH 3.5–5.8, confirming that in this region the major kinetic path involves the complex in the diaquo form. The results fall in two categories.

When the incoming ligand (L) is pyridine, morpholine, imidazole, or aniline, the stopped-flow kinetic studies indicate the presence of two consecutive processes.

The spectrophotometric titrations show that both the water molecules are replaced by the incoming ligands. These results are in accord with the scheme:

TABLE I. Rate Data for Ligation Reactions of Co(III)-$(H_2O)_2(salen)^+$.[a]

L	10^{-3} k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}
HSO_3^- [b]	5.05 ± 0.08	
$S_2O_3^{2-}$	6.50 ± 0.09	
Pyridine	7.4 ± 0.3	14 ± 2
NCO^-	11.1 ± 0.3	38 ± 3
Thiourea	32.3 ± 0.7	

[a] Data collected at 20.0 ± 0.2 °C and 0.1 *M* ionic strength. Errors are standard deviations. [b] The stoichiometry of the bisulfite reaction is assumed to be: $Co(H_2O)_2(salen)^+ + HSO_3^- \rightarrow Co(H_2O)(SO_3)(salen)^- + H_3O^+$.

$$Co(III)(H_2O)_2(salen)^+ + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(III)(H_2O)(L)(salen)^+ + H_2O \qquad (4)$$

$$Co(III)(H_2O)(L)(salen)^+ + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co(III)(L)_2(salen)^+ + H_2O \qquad (5)$$

where the second process is slower than the first one.

For thiourea, NCO^-, HSO_3^- and $S_2O_3^{2-}$ a single process is observed. Spectrophotometric titrations with ligand concentration not exceeding that used in the kinetic runs (1.2×10^{-2} *M*) indicate that only one of the two aquo ligands is replaced. Therefor, for the latter ligands the kinetic of the first complexation reaction can be studied without any complication arising from the second reaction. This can be done also for pyridine in virtue of the large difference in rates between the reaction 4 and 5 for this ligand.

The plots of pseudo first order rate constants, k_{obs} *vs.* [L] are linear in the range of concentration examined. For thiourea, HSO_3^-, and $S_2O_3^{2-}$ the plots do not have measurable intercept, *viz.*: $k_{obs} = k_1[L]$, whereas equilibrium reactions are observed in the cases of pyridine and NCO^- ligands, *viz.* : $k_{obs} = k_1[L] + k_{-1}$ (Fig. 2).

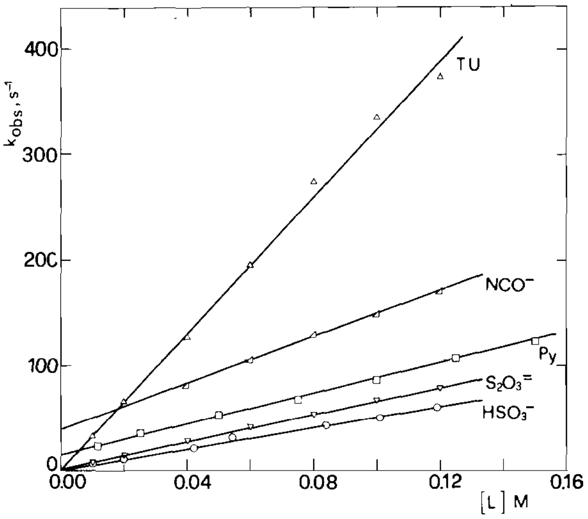

Fig. 2. k_{obs} *vs.* [L] for the reaction of thiourea, NCO^-, pyridine, $S_2O_3^{2-}$, HSO_3^- with $Co(III)(H_2O)_2(salen)^+$ in water at 20.0 ± 0.2 °C, $\mu = 0.1$ *M* ($NaNO_3$). Full lines are calculated from the least-squares parameters given in Table I.

Discussion

The second order rate constants are summarized in Table I. For a wide range of charged and uncharged nucleophiles they vary by approximately a factor of 6. This narrow range of rate constants of reaction with a variety of ligands indicates that the substitution process is dissociative in nature. Of great interest is the extreme lability of the complex under consideration, which demonstrates the strong *cis* effect of the salen ligand, characterized by an extensive electronic delocalization.

Highly unsaturated macrocyclic ligands like corrin and porphyrin ring systems have been shown to strongly enhance the rate of ligand substitution at the metal center. The reaction of Co(III) hematoporphyrin [14, 15] and aquocobalamin [13] are respectively 10^6 and 10^7 times faster than those of the typically inert nitroaquobis(dimethylglyoximato)-Co(III) and iodoaquobis(dimethylglyoximato)Co(III), for which k_1 is of the order of 10^{-4} M^{-1} s^{-1} [18]. Present results show that the reactions for Co(III)-$(H_2O)_2(salen)^+$ are still more rapid, being approximately 10 times faster than those for cobalamin.

The labilizing effect of unsaturated chelating ring systems has been discussed in terms of electronic structure of the complex in which the strong mixing of metal ion and ligand orbitals causes the cobalt ion to lose its d^6 character [14]. However, in the present case the contribution of steric factors must be also taken into consideration.

Structural data for $Co(III)(H_2O)_2(salen)^+$ are not available, but X-ray structural results for some other Co(salen) complexes [7] indicate that significant deviations from planarity occur in the equatorial system in the presence of axial ligands, and that the degree of distortion depends on the bulkiness of these ligands. This suggests that during the substitution process conformational changes of the chelating ring may occur. Thus a large distortion of the transition state, in a dissociative process, may facilitate the rupture of the Co–H_2O bond.

Recently, kinetic studies on the water substitution of Cr(III)$(H_2O)_2$(salen)$^+$ have been reported [19]. It was found that also for this complex the reaction is fast, the k_1 values lying in the range of 0.15–0.53 M^{-1} s^{-1}. However, it is remarkable that the cobalt center is far more strongly affected by this particular ligand environment as compared to the chromium center. In fact, the lability of Co(III)$(H_2O)_2$(salen)$^+$, expressed in terms of second order rate constants, is 10^4 times greater than that of Cr(III)$(H_2O)_2$(salen)$^+$, whereas there is no substantial difference in rates for the anation reactions of Co$(NH_3)_5H_2O^{3+}$ and Cr$(NH_3)_5H_2O^{3+}$ complexes**.

Finally we think that it would be interesting to compare the substitution rate constants reported here with the rate constants of the very rapid electrophilic methyl transfer reactions

$$(CH_3)_2Co(chel')^{o,+} + (H_2O)_2Co(chel'')^+ \longrightarrow$$

$$CH_3Co(chel')H_2O^{+,2+} + CH_3Co(chel'')H_2O \qquad (6)$$

studied in H_2O/THF mixtures at 25 ℃ [11]. Second order rate expressions were followed, supporting a mechanism in which there is a direct transfer of the carbanion in a transition state formed by the bimolecular interactions of the reagents. Furthermore, it was observed that each of the dimethyl complexes used as alkylating agents (chel′ = dpnH or tim) reacts with a given diaquo-complex (chel″ = salen, saloph or Me-salen) at virtually the same rate. For chel″ = salen and chel′ = dpnH and tim the second order rate constants are respectively 17.3 × 10^3 and 13.3 × 10^3 M^{-1} s^{-1}. The coincidence of these values with those for the substitution reactions, together with the scarce influence of the nature of the alkylating agent on the reaction rates, clearly indicate that the methyl transfer reaction is controlled by the Co–H_2O bond rupture. Thus the substitution-limited methyl transfer mechanism postulated in [11] is fully confirmed. Further support to this type of mechanism is also given by our preliminary data, which indicate that the anation reactions of Co(III)$(H_2O)_2$(saloph)$^+$ are 10 times slower than those of the Co(salen). As this complex undergoes the methylation reaction at a rate about 10 times slower than that of the Co(III)$(H_2O)_2$(salen)$^+$, it appears that the trend of the transmethylation rates parallels that of the substitution rates.

References

1 G. McLendon and A. E. Martell, *Coord. Chem. Rev., 19,* 1 (1976).
2 G. Costa, G. Mestroni and L. Stefani, *J. Organomet. Chem., 7,* 493 (1967).
3 G. Tauzher, G. Mestroni, A. Puxeddu, R. Costanzo and G. Costa, *J. Chem. Soc. A,* 2504 (1971).
4 E. Reisenhofer and G. Costa, *Inorg. Chim. Acta, 49,* 121 (1981).
5 R. E. Hester and E. M. Nour, *J. Raman Spectrosc., 11,* 49 (1981).
6 H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni and G. Costa, *J. Organomet. Chem., 11,* 167 (1968).
7 M. Calligaris, G. Nardin and L. Randaccio, *Coord. Chem. Rev., 7,* 385 (1972).
8 A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, E. Reisenhofer, L. Stefani and G. Tauzher, *Inorg. Chim. Acta Rev., 4,* 41 (1970).
9 G. Costa, G. Mestroni and G. Pellizer, *J. Organomet. Chem., 11,* 333 (1968).
10 C. W. Smith, G. W. Van Loon and M. C. Baird, *Can. J. Chem., 54,* 1875 (1976).
11 J. H. Espenson, H. L. Fritz, R. A. Heckman and C. Nicolini, *Inorg. Chem., 15,* 906 (1976).
12 C. K. Poon, *Coord. Chem. Rev., 10,* 1 (1973).
13 D. Thusius, *J. Am. Chem. Soc., 93,* 2629 (1971).
14 E. B. Fleischer, S. Jacobs and L. Mestichelli, *J. Am. Chem. Soc., 90,* 2527 (1968).
15 R. F. Pasternack and G. R. Parr, *Inorg. Chem., 15,* 3087 (1976).
16 T. W. Newton and G. M. Arcand, *J. Am. Chem. Soc., 75,* 2449 (1953).
17 A. Albert and E. P. Serjeant, 'Ionization Constants of Acids and Bases', Wiley, N.Y. (1962).
18 D. N. Hague and J. Halpern, *Inorg. Chem., 6,* 2059 (1967).
19 D. Rajendra Prasad, T. Ramasami, D. Ramaswamy and M. Santappa, *Inorg. Chem., 21,* 850 (1982).
20 E. Campi, J. Ferguson and J. L. Tobe, *Inorg. Chem., 9,* 1781 (1970).
21 N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc., 89,* 272 (1967).
22 F. Basolo and R. Pearson, 'Mechanisms of Inorganic Reactions', Wiley, N.Y., 1967, p. 203.

**There are not many cases where it is possible to compare Cr(III) systems with analogous Co(III) systems. The available data suggest a considerable similarity between the rates of acid hydrolysis reactions [20]. In anation reactions the comparable systems are the pentaminoaquo complexes. The second order rate constant for the reaction of Cr(NH_3)-H_2O^{3+} with NCS^- is 5.0 × 10^{-5} M^{-1} s^{-1} at 29.9 ℃ and μ 0.1 M, and with Cl^- is 7.7 × 10^{-6} M^{-1} s^{-1} at 29.7 ℃ and μ 0.1 M [21]. Rate constants for the anation reactions of Co$(NH_3)_5H_2O^{3+}$ have been calculated from equilibrium constants and rate of reverse reactions. For a variety of nucleophiles, including NCS^- and Cl^-, the values lie in the range 1 × 10^{-7}–1.5 × 10^{-5} M^{-1} s^{-1} at 25 ℃ and μ = 0.5 M [22].