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Pressure Effects on the Equilibration Kinetics of the $RhCl_n(OH_2)_{6-n}^{(n-3)-}$ Species for n = 4, 5, 6 in Acidic Aqueous Solution

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Received August 9, 1977

The rates of equilibration of the $RhCl_6^{3-}$, $RhCl_5(OH_2)^{2-}$, and *cis*-$RhCl_4(OH_2)_2^-$ ions were studied as a function of chloride ion concentration and pressure (1–1500 bar) at 20 °C and μ = 4 M ($HClO_4$). $\Delta V^{\ddagger}_{\text{exptl}}$ values for the aquation of the hexachloro and pentachloro species are 21.5 ± 0.6 and 14.3 ± 0.5 $cm^3\ mol^{-1}$. For the chloride anation of the pentachloro and tetrachloro species $\Delta V^{\ddagger}_{\text{exptl}}$ are 15.7 ± 6.5 and 14.7 ± 1.6 $cm^3\ mol^{-1}$. These results are discussed in terms of a dissociative mechanism.

Introduction

The kinetics[2-6] and thermodynamics[7] of the $RhCl_n(OH_2)_{6-n}^{(n-3)-}$ system in acidic aqueous solution have been extensively investigated. These species are of further interest as potential catalysts for such reactions as the oxidation of ethylene to acetaldehyde.[8] Harris et al.[3,5,9] have studied the kinetics of anation of $Rh(OH_2)_6^{3+}$ by chloride and bromide ions and $RhCl(OH_2)_5^{3+}$ by chloride ion and have interpreted the resulting rate equations in terms of a dissociative (D-type) mechanism. This conclusion is compatible with earlier work[10] on the water exchange of $Rh(OH_2)_6^{3+}$. At the other end of the reaction sequence, chloride exchange with equilibrated mixtures of $RhCl_6^{3-}$ and $RhCl_5(OH_2)^{2-}$, in conjunction with the aquation–anation rate data, indicated the mechanism to also be dissociative.[2] Robb et al.[11] substantiated this assignment by studying the anation of $RhCl_5(OH_2)^{2-}$ by a variety of nucleophiles. Finally, a kinetic study[6] of the steric course of the entire series of aquation–anation reactions of $RhCl_n(OH_2)_{6-n}^{(n-3)-}$ showed them to be controlled by the trans effect of the chloride ligands involving an unsymmetrical five-coordinate intermediate, probably in the form of a square pyramid.

A high-pressure study[12] of the water exchange of $Rh(NH_3)_5OH_2^{2+}$ and earlier work[13] on the aquation of some chloroamminerhodium(III) complexes have been interpreted in terms of an associative mechanism, I_a. However, in view of the above-mentioned findings for the $RhCl_n(OH_2)_{6-n}^{(n-3)-}$ system, this interpretation has been questioned.[9] Therefore, a kinetic pressure study of the $RhCl_n(OH_2)_{6-n}^{(n-3)-}$ complexes, n = 4, 5, 6, was undertaken in an attempt to confirm the mechanistic nature of these reactions and to further study the effectiveness of the volume of activation as a mechanistic tool.

Table I. Pressure Dependencies of the Rates of Aquation and Anation of the $RhCl_6^{3-}$, $RhCl_5(OH_2)^{2-}$, and *cis*-$RhCl_4(OH_2)_2^-$ Ions at 20 °C

P, bar	[$HClO_4$], M	[HCl], M	10^4k_{obsd}, s^{-1}
A. $RhCl_6^{3-}/RhCl_5(OH_2)^{2-}$			
1	1		27.5 ± 0.9
250	1		21.7 ± 0.3
500	1		16.3 ± 0.4
750	1		12.5 ± 0.3
1000	1		9.90 ± 0.34
1500	1		5.98 ± 0.08
1	4		8.83 ± 0.33
250	4		6.77 ± 0.14
500	4		5.89 ± 0.09
750	4		4.30 ± 0.12
1000	4		3.58 ± 0.05
1250	4		2.97 ± 0.12
1500	4		2.28 ± 0.06
1		4	14.0 ± 0.1
250		4	10.6 ± 0.5
500		4	8.97 ± 0.23
750		4	6.81 ± 0.17
1000		4	5.85 ± 0.14
1250		4	5.09 ± 0.12
1500		4	4.32 ± 0.18
B. $RhCl_5(OH_2)^{2-}$/*cis*-$RhCl_4(OH_2)_2^-$			
1	4		4.98 ± 0.09
250	4		4.32 ± 0.02
500	4		3.56 ± 0.05
750	4		3.12 ± 0.10
1000	4		2.55 ± 0.03
1200	4		2.28 ± 0.02
1500	4		2.10 ± 0.05
1	3.8	0.2	6.61 ± 0.16
250	3.8	0.2	6.02 ± 0.15
500	3.8	0.2	5.28 ± 0.12
750	3.8	0.2	4.74 ± 0.08
1000	3.8	0.2	3.73 ± 0.12
1250	3.8	0.2	3.15 ± 0.11
1500	3.8	0.2	3.09 ± 0.03

Experimental Section

The following direct methods for the preparation of $K_3[RhCl_6]$ and $K_2[RhCl_5(OH_2)]$ were found to be more convenient than the established procedures[2,4] and hence are reported in detail.

$K_3[RhCl_6]$ was prepared by dissolving commercial $RhCl_3{\cdot}xH_2O$ (5 g) in boiling concentrated HCl (ca. 45 cm^3) and maintained under reflux for 1 h. The dark red solution was cooled to −20 to −25 °C and left at this temperature for 5 days. Under these conditions the endothermic equilibrium tends to favor the formation of $RhCl_6^{3-}$.[14] Pellets of KOH (5 g) were individually and cautiously added to the vigorously stirred solution which was kept below 20 °C during which time a precipitate formed. The mixture was left overnight at −20 °C, filtered, and washed with ethanol. The complex was finally stirred for 2 h in 250 cm^3 of ether, filtered, and vacuum-dried; yield 7.3 g (89%). For the preparation of $K_2[RhCl_5(OH_2)]$ a solution of $RhCl_3{\cdot}xH_2O$ was heated to boiling with a 3.5-fold excess of KCl in 4 N HCl (after 15 min, a precipitate formed). The mixtue was boiled for a further 10 min, cooled to room temperature, and filtered. The precipitate was thoroughly washed with ethanol and a large quantity of ether to remove any trace amounts of KCl; yield ca. 84%. The purity of both complexes was confirmed by a comparison of the spectral parameters of their solutions with those previously published.[2,6,7]

Reaction rates were obtained from absorption vs. time data measured with a Cary 15 spectrophotometer equipped with a thermostated high-pressure cell.[15] In view of the relatively rapid rate of aquation of $RhCl_6^{3-}$, the reaction solutions (perchloric–hydrochloric acid media of constant ionic strength) were cooled to 5 °C prior to dissolving the complex. After dissolution the mixture was filtered to remove the insoluble $KClO_4$ so formed. Mixing, filtration, and manipulation of the quartz cell and pressurization required about 4 min. A further 3 min was allowed for the system to reach thermal equilibrium at the desired temperature of 20 °C before measurement was begun.

The observed rate constants were calculated from the slopes of the usual log ($A_t - A_\infty$) vs. time plots and are given in Table I as a function of [Cl^-] and pressure. Each value represents the mean of 2–4 individual experiments giving rise to the standard deviations presented in Table I. In a series of preliminary experiments, the aquation reactions of $RhCl_6^{3-}$ at various Cl^- concentrations were reinvestigated. The agreement between the two studies is excellent (T = 20 °C; ref 2: $k_{aq} = 1.27 \times 10^{-4}\ M^{-1}\ s^{-1}$, $k_{an} = 9.8 \times 10^{-4}\ s^{-1}$; this work: $k_{aq} = 1.36 \times 10^{-4}\ M^{-1}\ s^{-1}$, $k_{an} = 8.9 \times 10^{-4}\ s^{-1}$) and reconfirms the first-order dependence on Cl^- concentration.

0020-1669/78/1317-1647$01.00/0

Table II. Rate Constants and Activation Volumes for the Aquation and Anation of $RhCl_6^{3-}$, $RhCl_5(OH_2)^{2-}$, and *cis*-$RhCl_4(OH_2)_2^-$ Ions at 20 °C and $\mu = 4$ M

Substrate	$10^4 k_{aq}$, s^{-1}	$10^5 k_{an}$, M^{-1} s^{-1}	$\Delta V^{\ddagger}_{exptl}$, cm^3 mol^{-1}
$RhCl_6^{3-}$	27.5 ± 0.9^a		24.5 ± 0.3^a
	8.8 ± 0.3		21.5 ± 0.6
$RhCl_5(OH_2)^{2-}$	0.498 ± 0.009		14.3 ± 0.5
		11.3 ± 1.0	15.7 ± 6.5
cis-$RhCl_4(OH_2)_2^-$		8.2 ± 0.7	14.7 ± 1.6

[a] Measured at $\mu = 1$ M.

Results

The equilibration

$$RhCl_6^{3-} \underset{k_{1an}}{\overset{k_{1aq}}{\rightleftharpoons}} RhCl_5(OH_2)^{2-} + Cl^- \qquad (1)$$

was followed at 395 nm which corresponds to the isosbestic point[6] of $RhCl_5(OH_2)^{2-}$ and *cis*-$RhCl_4(OH_2)_2^-$. In the absence of added chloride ion the aquation of $RhCl_6^{3-}$ proceeds to completion[16] so that the pressure dependence of ln k_{obsd} at [HCl] = 0 leads directly to $\Delta V^{\ddagger}_{aq}$ for this reaction. As shown in Table I, k_{aq} is 3 times faster at $[HClO_4] = 1$ M than at $[HClO_4] = 4$ M where $k_{aq} = (8.8 \pm 0.3) \times 10^{-4}$ s^{-1}. It was found necessary to study this system at $\mu = 4$ M in order to shift equilibrium 1 sufficiently toward the hexachloro species; e.g. at 4 M hydrochloric acid the ratio $[RhCl_5(OH_2)^{2-}]/[RhCl_6^{3-}] = 0.52$. The position of the equilibrium results in relatively small absorbance changes during anation which in turn accounts for the larger errors in k_{an}. As $k_{aq} = (9.0 \pm 0.2) \times 10^{-4}$ s^{-1} at $\mu = 4.00$ M with $[HClO_4] = 1$ M and [LiClO] = 3 M, the difference in rate constants is merely due to an ionic strength effect rather than acid catalysis. These findings are in agreement with those of Robb and Harris[2] who found $k_{aq} = (10.5 \pm 0.7) \times 10^{-4}$ s^{-1} at 20 °C and $\mu = 4$ M made up of $HClO_4$ and LiCl.

The isosbestic point in the absorption spectra of *cis*-$RhCl_4(OH_2)_2^-$ and *fac*-$RhCl_3(OH_2)_3$ at 382 nm was used to follow the equilibration

$$RhCl_5(OH_2)^{2-} \underset{k_{2an}}{\overset{k_{2aq}}{\rightleftharpoons}} cis\text{-}RhCl_4(OH_2)_2^- + Cl^- \qquad (2)$$

Previous studies[4,6] have shown these reactions to be stereospecific with no trans species being observed.

Second-order rate constants for both anation reactions were determined using the familiar relationship $k_{obsd} = k_{aq} + k_{an}[Cl^-]$. However, in order to obtain optimum k_{an} values, linear least-squares analyses of the ln k_{obsd} vs. pressure data were made at each $[Cl^-]$, and the calculated k_{obsd} values at each pressure were substituted in the above relationship. The plots of ln k_{aq} vs. pressure proved to be linear, within experimental error, over the pressure range 1–1500 bar. The volumes of activation are collected in Table II.

Discussion

In view of previous experience in inorganic high-pressure studies,[15-17] one can make the following predictions as to the expected sign and general order of magnitude of $\Delta V^{\ddagger}_{exptl}$ for the $RhCl_n(OH_2)_{6-n}^{(n-3)-}$ system. For an associative, A-type mechanism $\Delta V^{\ddagger}_{aq}$ originates from the formation of a Rh–OH_2 bond and should be negative with a minimum value of −18 cm^3 mol^{-1}, the molar volume of bulk water (ignoring the effects of ionic strength). In addition, $\Delta V^{\ddagger}_{aq}$ may be expected to be virtually independent of the substrate to within ca. 3 cm^3 mol^{-1} depending on the charge on the substrate.[17] On the other hand, $\Delta V^{\ddagger}_{an}$ should be definitely sensitive to the charge on the substrate as chloride *ion* is involved as the incoming group, because a triply charged composite ion, for example, would be expected to have a smaller overall partial molar volume than a doubly and singly charged ion together; e.g., the partial molar volumes of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ are respectively 90.5 and 132.9 cm^3 mol^{-1}.[18] The $\Delta V^{\ddagger}_{exptl}$ values in Table II clearly show that these expectations are not fulfilled.

Conversely, a dissociative mechanism demands that $\Delta V^{\ddagger}_{aq}$ be positive as it involves separation of charges with the lengthening of the Rh–Cl bond and the release of electrostricted solvent. Furthermore, $\Delta V^{\ddagger}_{aq}$ should vary with the charge on the substrate, becoming less positive as the charge on the substrate becomes more positive. In the extreme case, when the substrate assumes a positive charge, $n = 0, 1, 2$, $\Delta V^{\ddagger}_{aq}$ would be negative due to the overall increase in electrostriction upon dissociation of a chloride ion and the consequent increase in charge on the complex; e.g. for the aquation of $Co(NH_3)_5Cl^{2+}$, which is known to react via a basically dissociative mechanism,[20,21] $\Delta V^{\ddagger}_{aq} = -10.6 \pm 0.4$ cm^3 mol^{-1}.[21] Since ion-pair formation is not expected to be important in the reaction of two negatively charged species, the anation reactions in this scheme must result in positive $\Delta V^{\ddagger}_{an}$ values with a maximum of +18 cm^3 mol^{-1} corresponding to the complete loss of coordinated water in the limit of a D mechanism. $\Delta V^{\ddagger}_{an}$ should also be essentially insensitive to the charge on the substrate. These conditions are met in every aspect by the experimental results.

The aquation of $RhCl_6^{3-}$ may be compared to the analogous reaction of $Co(CN)_5Cl^{3-}$ for which $\Delta V^{\ddagger}_{aq} = +7.8 \pm 0.4$ cm^3 mol^{-1}.[22] Similarly, the anation of $Co(CN)_5OH_2^{2-}$, for which $\Delta V^{\ddagger}_{an} = +8.4 \pm 1.0$ cm^3 mol^{-1}, may be directly compared to the present $RhCl_6^{3-}/RhCl_5(OH_2)^{2-}$ system. The reactions of pentacyanocobalt(III) complexes have long been considered as classic examples of a dissociative, D-type, mechanism involving a trigonal-bipyramid intermediate.[23] It should be noted that the cobalt complexes were studied at $\mu = 1.0$ M while most of the present study used $\mu = 4.0$ M. However, this can only partially account for the more positive $\Delta V^{\ddagger}_{aq}$ observed here since $\Delta V^{\ddagger}_{aq}$ for $RhCl_6^{3-}$ at $\mu = 4.0$ M is approximately 10% lower than the value at $\mu = 1.0$ M (see Table II).

The difference between $\Delta V^{\ddagger}_{aq}$ for the Co and Rh systems of ca. +16 cm^3 mol^{-1} is surprisingly large and may be indicative of a difference in the geometries of the intermediates involved. The Rh system is thought to involve a square-pyramid intermediate.[6] A limited number of high-pressure studies[24-26] have been made on the interconversion of the geometries of five-coordinate compounds but have only dealt with the solid state. Although some of these studies[25] have shown that a trigonal-bipyramid structure is favored at high pressure, Ferraro et al.[26] have recently indicated that $Ni(CN)_6^{3-}$ is converted to a square-pyramidal geometry under pressure. The inconclusiveness of such work and the anticipated importance of the role of solvation in determining the relative stabilities of these species allow no definite conclusion to be drawn for the present system.

The absolute values of $\Delta V^{\ddagger}_{aq}$ and $\Delta V^{\ddagger}_{an}$, allowing for the effect of ionic strength, for the $RhCl_6^{3-}/RhCl_5(OH_2)^{2-}$ system are remarkably similar to the partial molar volumes of their respective leaving groups, Cl^- and H_2O (21.75 and 18 cm^3 mol^{-1}).[27] This tends to indicate that the leaving groups are virtually fully solvated in the transition state which is in keeping with a dissociative (D) mechanism. Stranks and Vanderhoek[28] stated that a D mechanism should manifest itself in the nonlinearity of ln k_{obsd} vs. pressure plots. However, no curvature was observed for the ln k_{aq} plots (k_{an} values were not sufficiently accurate to allow any definite curvature to be seen). In the present study the ionic strength was maintained at 1.0 and 4.0 M. Therefore, it is readily conceivable that the compressibility of bulk water in such concentrted solutions is significantly different from pure water, such that the transfer of water molecules from the second coordination sphere to the bulk solvent involves negligibly small changes in the overall compressibility of the system.

The persistence of the first-order dependence of k_{an} on chloride concentration over the entire range of chloride ion studied[2,4,6] requires that the rate of water exchange with the substrates be significantly faster than k_{an}.[4] Similar arguments have been used[23] for the anation of $Co(CN)_5(OH_2)^{2-}$ where the results were discussed in terms of the ratio of the competitive rate constants for the water exchange and anation of the proposed $Co(CN)_5^{2-}$ intermediate.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft is gratefully appreciated.

Registry No. $RhCl_6^{3-}$, 21412-00-0; $RhCl_5(OH_2)^{2-}$, 15276-84-3; *cis*-$RhCl_4(OH_2)_2^-$, 15157-53-6; $K_3[RhCl_6]$, 13845-07-3; $K_2[RhCl_5(OH_2)]$, 15306-82-8.

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Kinetics of Oxidation of (Cysteinato-*N*,*S*)bis(ethylenediamine)cobalt(III) and Related Thiolato Complexes to Sulfenatocobalt(III) Complexes

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Received October 27, 1977

The Λ-((*R*)-cysteinato-*N*,*S*)bis(ethylenediamine)cobalt(III) ion is oxidized by hydrogen peroxide to the N,S-bound cysteinesulfenato complex $(en)_2Co[(R)\text{-}NH_2CH(COO)CH_2S(O)]^+$ in a process that is first order in each reactant; $k_{SO} = 0.36\ M^{-1}\ s^{-1}$ at 20.3 °C, pH 5–7, 0.10 M ionic strength. The pH dependence of k_{SO} for the cysteinato species was obtained over the range 0.3–6.9, in which $[(en)_2Co[NH_2CH(COOH)CH_2S]^{2+}]$- and $[H^+][(en)_2Co[NH_2CH(COOH)CH_2S]^{2+}]$-dependent pathways also were observed. For the related complexes $(en)_2Co(NH_2CH_2CH_2S)^{2+}$ and $(en)_2Co[(S)\text{-}NH_2CH(COO)C(CH_3)_2S]^+$, $k_{SO} = 0.85\ M^{-1}\ s^{-1}$ and $0.14\ M^{-1}\ s^{-1}$, respectively. Oxidation of Λ-$(en)_2Co[NH_2CH(COO)CH_2S]^+$ produces a mixture of what is presumed to be the *S* and *R* forms of the chiral (sulfur) sulfenate, with second-order rate constants of formation of $0.27\ M^{-1}\ s^{-1}$ and $0.09\ M^{-1}\ s^{-1}$, respectively. Circular dichroism spectra were obtained and the stability and rate of oxidation to the sulfinato complex was studied for each of the diastereomers. The reactions are interpreted in terms of nucleophilic substitution by coordinated thiolate sulfur on peroxide oxygen. The relative order of reactivity toward hydrogen peroxide of several sulfur-containing nucleophiles is $H_3N^+CH(COO^-)CH_2S^- > (en)_2Co[NH_2(COO)CH_2S]^+ > SO_3^{2-} > (HOCH_2CH_2)_2S > NCS^-$. Thus, cobalt(III)-bound cysteinate, although less reactive than free $H_3N^+CH(COO^-)CH_2S^-$, exhibits considerable nucleophilic reactivity.

Introduction

We have reported previously the generation of sulfur-bound sulfenato (RSO^-) and sulfinato (RSO_2^-) cobalt(III) complexes via oxidation of N,S-coordinated cysteinate.[1] This oxidative process provides a convenient route to nonlabile complexes in which an otherwise highly reactive alkylsulfenate is stabilized through bonding to a metal center. Recently, Jackson, Sargeson, and Whimp have reported[2] the separation of diastereomers in the oxidation of $(en)_2Co[(R)\text{-}NH_2CH(COOH)CH_2S]^{2+}$, including, in particular, a crystallographic determination of the Λ-((*R*)-cysteine-*S*-sulfenato)bis(ethylenediamine)cobalt(III) ion. In addition, Deutsch, Elder, and co-workers[3] have described the oxidative synthesis and structural determination of the bis(ethylenediamine)(2-sulfinatoethylamine-*N*,*S*)cobalt(III) ion.

The oxidation of the cysteinato to cysteinesulfenato species by hydrogen peroxide provides a useful system in which the nucleophilic reactivity of coordinated thiolate can be examined. We report herein a study of the kinetics of oxidation of thiolato and of sulfenato complexes by H_2O_2 and a comparison of their reactivities with that of other sulfur nucleophiles. Principal attention has been focused on reactions of the Λ-((*R*)-cysteinato-*N*,*S*)bis(ethylenediamine)cobalt(III) cation, Λ-$(en)_2CoCyS^+$. Reactions of the related N,S-bound (*S*)-penicillaminato, $(en)_2CoPenS^+$, and cysteaminato (2-aminoethanethiolato), $(en)_2Co(cystS)^{2+}$, species were examined briefly.

Experimental Section

((*R*)-Cysteinato-*N*,*S*)bis(ethylenediamine)cobalt(III) Complexes. $(en)_2Co[(R)\text{-}NH_2CH(COO)CH_2S]ClO_4$ was prepared from L-cystine

0020-1669/78/1317-1649$01.00/0