$(NH_3)_5NO_2]Br_2$, and 20% $[Co(NH_3)_5HSO_4]Br_2$. The dried solid was submitted to Dr. Geoffrey E. Dolbear of Stanford University, who kindly converted the water to CO_2 and mass spectrometrically determined the O^{18} content.

Results

The pseudo-first-order rate constants ($k = -\mathrm{d}\ \ln [Co(NH_3)_5NO_2^{2+}]/\mathrm{d}T$) were obtained from linear plots of the logarithm of the $Co(NH_3)_5NO_2^{2+}$ concentration *vs.* time. In most experiments, the rate was followed for at least 2 half-lives. The values of k are given in Table I as a function of the concentration of sulfuric acid. At sulfuric acid concentrations from 0.94 to 55.74%, k is, within the precision of the data, constant. The average value, $(6 \pm 2) \times 10^{-7}$ sec^{-1}, is about 50 times larger than the rate constant extrapolated from the 70–100° data of Lalor[7] for the same reaction in dilute acid solutions. For sulfuric acid concentrations above 57%, k may be calculated, within the precision of the data, from the relation $k = (4 \pm 2) \times 10^{-11}h_0$ sec^{-1}, where h_0 is the antilog of $-H_0$, the Hammett acidity function.[8] We conclude that in the concentrated acid solutions a reaction path which is first-order in hydrogen ion activity predominates.[7]

TABLE I

RATE CONSTANTS FOR AQUATION OF $Co(NH_3)_5NO_2^{2+}$ IN SULFURIC ACID SOLUTIONS

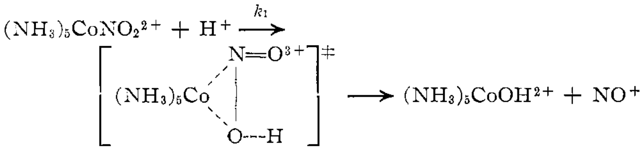
Wt % H_2SO_4	k, sec^{-1}	Temp, °C	Wt % H_2SO_4	k, sec^{-1}	Temp, °C
0.94	8.1×10^{-7}	25	55.74	7.6×10^{-7}	25
5.43	6.2×10^{-7}	25	59.78	2.6×10^{-6}	31
9.79	9.4×10^{-7}	25	64.82	1.1×10^{-5}	31
18.15	4.1×10^{-7}	25	70.07	4.5×10^{-5}	31
33.71	4.3×10^{-7}	25	75.74	1.8×10^{-4}	31
45.20	5.1×10^{-7}	25	79.32	7.7×10^{-4}	31
50.51	5.9×10^{-7}	25	85.27	3.0×10^{-3}	31

Isotopic analysis of three different samples of $[Co(NH_3)_5H_2O]Br_3$, isolated from the reaction of $[Co(NH_3)_5NO_2]SO_4$ with *ca.* 90% sulfuric acid containing about 4% oxygen-18, showed that the coordinated water contained about 0.2% O^{18}, essentially the fraction present in normal oxygen samples. We therefore conclude that the oxygen of the coordinated water molecule came principally from the coordinated NO_2^- ion.

Discussion

The mechanism for the conversion of the nitro complex to the aquo complex in concentrated sulfuric acid solutions must account for the first-order dependence on hydrogen ion activity and the fact that one of the NO_2^- oxygen atoms ends up in the coordinated water molecule.

We suggest the rate-determining step



The proton may be considered as assisting the displacement of the nitrosyl ion. This step would be followed by a rapid protonation of the hydroxy intermediate

$$Co(NH_3)_5OH^{2+} + H^+ \longrightarrow Co(NH_3)_5H_2O^{3+}$$

In dilute sulfuric acid solutions, the aquo complex is the final product. In concentrated sulfuric acid solutions, the aquo complex is converted at a finite rate to the bisulfato complex.[1]

Pearson, *et al.*,[9] have studied the reverse reaction in weakly acidic solution; they found that the nitrosation of $Co(NH_3)_5H_2O^{3+}$ yields the nitrito complex as an intermediate. In our studies there was no evidence for the formation of this species. Indeed, when a sample of nitrito complex was dissolved in 70% sulfuric acid, the initial solution contained only the aquo complex and a smaller amount of nitro complex (the latter presumably was present as an impurity in the nitrito complex). However, we cannot rule out the possibility of a nitrito intermediate. Possibly in *strongly* acid solutions the nitro complex undergoes an acid-catalyzed isomerization to the nitrito complex, which then is rapidly converted to the aquo complex

$$Co(NH_3)_5NO_2^{2+} \xrightarrow[\text{slow}]{(H^+)} Co(NH_3)_5ONO^{2+} \xrightarrow[\text{fast}]{+H^+} Co(NH_3)_5OH^{2+} + NO^+$$

One bit of evidence against such a mechanism is the fact that in *dilute* solutions the nitrito–nitro conversion is retarded, rather than accelerated, by the presence of acid.[10]

Murmann and Taube[11] observed that the conversion of the aquo complex to the nitrito complex in weakly acidic solutions proceeds without breaking the cobalt–oxygen bond and that the nitrito–nitro conversion proceeds without exchange of oxygen atoms with the solvent. These findings are consistent with either of the above mechanisms and make the results of our isotopic study appear quite reasonable.

Acknowledgments.—We wish to thank Dr. Geoffrey E. Dolbear and Professor Henry Taube for determining the O^{18} contents of our $[Co(NH_3)_5H_2O]Br_3$ samples. This research was partly supported by the U. S. Atomic Energy Commission.

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Chloride Exchange of the Hexachlororhenium(IV) Ion[1]

BY JUDITH A. CASEY AND R. KENT MURMANN

Received September 23, 1966

Previous studies have characterized the hexachlororhenium(IV) ion, $ReCl_6^{2-}$, as a very stable species.

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(1) From a dissertation submitted by J. A. Casey to the Graduate Faculty of the University of Missouri in partial fulfillment of the requirements for the Ph.D. degree.

Maun and Davidson[2] reported that acidic solutions (at least 4 M HCl) of potassium hexachlororhenium(IV) are quite resistant to both oxidation and reduction, whereas other forms of rhenium(IV), notably those containing rhenium–oxygen bonds, are quite readily oxidized. This difference in reactivities was thus attributed to the presence or absence of rhenium–oxygen bonds.

The radiochlorine exchange of hexachlororhenium(IV) has been studied[3] in systems having 0.2–2 M HCl at 26°. No exchange was observed for times as long as 648 hr.

Rates of bromide isotope exchange of $ReBr_6^{2-}$ were reported by Schmidt and Herr.[4] Observed rates were in the range 6.60×10^{-6} to 12.3×10^{-6} M sec^{-1} for solutions 0.01 M in complex and from 5 to 8 M in hydrobromic acid. These reactions were carried out at 75°. No exchange law was derived but it was stated that above 4 M HBr the rate increases linearly with HBr and complex concentration. An activation energy of 29.4 kcal/mole was determined.

Since potassium hexachlororhenium(IV) is the starting material for preparation of many other complex ions and is also a potential product of reduction of perrhenate in strong hydrochloric acid solutions, it was of interest to extend the region of study of the hexachlororhenium(IV)—chloride ion exchange reaction.

Experimental Section

Preparation of Potassium Hexachlororhenium(IV).—The complex salt was prepared by the method of Watt and Thompson.[5] Special care was taken to assure purity and prevent hydrolysis. *Anal.* Calcd for K_2ReCl_6: Re, 39.0; Cl, 44.6. Found: Re, 39.2; Cl, 44.5.

Preparation of the Labeled Complex, $K_2Re^*Cl_6$.—The complex containing Cl^{36} was prepared by treatment of a freshly prepared sample of rhenium dioxide with concentrated hydrochloric acid containing HCl^{36}. One gram of K_2ReCl_6 was added to 20 ml of 2 M NaOH in a large centrifuge tube. The resulting mixture was centrifuged, the solution decanted, and the black precipitate of ReO_2 washed with cold water. The solid was immediately added to 25 ml of concentrated HCl containing 0.3 ml of HCl^{36} solution. The resulting yellow-brown solution was heated for 24 hr at just below boiling. A stoichiometric amount of potassium chloride was dissolved in the hot solution which was then allowed to cool slowly to room temperature. The final green crystalline product was collected on a filter, washed with concentrated HCl and ethanol, and dried over $CaSO_4$; yield, 0.64 g, 64% of theory.

Chemicals.—Perrhenic acid was obtained from S. W. Shattuck Chemical Co. as a solution containing 1 g of rhenium/ml and was used without further purification.

The Cl^{36} hydrochloric acid was generously supplied by Dr. W. R. Fleming and had a specific activity of 0.0074 mcurie (±10%) of Cl^{36}/ml.

Toluenesulfonic acid was Fisher Certified reagent and was recrystallized from water before use. All other chemicals were reagent grade and were used without further purification. Water was distilled, deionized, and redistilled from alkaline permanganate solution.

Exchange Experiments.—In a typical run, a total of 0.0005 mole of $K_2ReCl_6 + K_2ReCl^{36}{}_6$ was dissolved in the desired concentration of HCl giving a total volume of 50 ml. The resulting solution was poured into a reaction flask maintained at 90 ± 0.5° by a refluxing mixture of the proper proportions of allyl alcohol and ethanol. Nitrogen was then passed through the solution after first bubbling through a chromium(II) perchlorate solution and then through 90° hydrochloric acid of the same concentration as the solvent. At appropriate intervals, over a period of 1.5–3 half-lives, approximately 6 ml of solution was withdrawn from the flask and quickly cooled to ≈18°. A 5.00-ml sample was pipetted onto an excess of solid cesium chloride and after precipitation was centrifuged and washed with 5 ml of methanol. With another 5-ml portion of methanol it was transferred to the micro filter apparatus, washed again with methanol, and dried over $CaSO_4$. The final sample was evenly distributed over a defined area.

Sample activities were determined with a Technical Associates Decade Scaler, Model DS-5B. Counting was long enough to give a standard deviation of 1% of the count or better.

Treatment of Data.—The slope of a graph of ln $[(x - x_\infty)/(x_0 - x_\infty)]$ *vs.* time was determined by a linear least-squares computer program.[6] Rates of exchange were calculated from the usual exchange rate law: $R = k(6ab)/(6a + b)$, where k is the slope in the above graph, a is concentration of complex, and b is concentration of chloride ion.

Results

Preliminary experiments at room temperature in 7 M HCl showed no exchange for times as long as 384 hr. These experiments indicated that the separation technique did not induce exchange, that exchange was very slow, and that the reproducibility of the activity measurements was ±2%.

When the temperature was increased to 50°, exchange was observed and appeared to be light catalyzed: $t_{1/2} = 500$ hr in 7 M HCl in light; $t_{1/2} = 1405$ hr in 7 M HCl in the dark. However, as shown later, this apparent exchange was due to a loss of $ReCl_6^{2-}$ as it was oxidized to $[ReCl_4(OH)_2]^-$ which exchanges Cl^- rapidly under these conditions.[7]

Increasing the temperature to 90° reduced the half-times of exchange to convenient levels. At this temperature a nonlinearity in the plots of log $[(x - x_\infty)/(x_0 - x_\infty)]$ *vs.* time was noted, suggesting that chemical reaction was taking place. Inspection of visible spectra of solutions and the infrared spectra of precipitated Cs_2ReCl_6 showed that a slow oxidation of rhenium to the +5 oxidation state was occurring with formation of the species $[ReCl_4(OH)_2]^-$, previously reported,[8] or $[ReCl_4O(OH_2)]^-$ as formulated by Cotton,[9] or $[ReOCl_5]^{2-}$ by Wilkinson.[10] This reaction was avoided by careful exclusion of atmospheric oxygen as described in the Experimental Section. When this precaution was taken, the visible spectrum was constant throughout a run and in agreement with that reported in the literature[1,11] for K_2ReCl_6 in hydrochloric acid solutions and various fused-salt systems.

Irradiation of the reaction mixture under a nitrogen

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atmosphere with a tungsten lamp showed that the previously noted effect of light was due primarily to catalysis of the oxidation reaction. However, the experiments reported here were conducted in the dark.

Complex Dependence.—Concentration of potassium hexachlororhenium(IV) was varied from 0.002 to 0.03 *M* keeping hydrochloric acid concentration constant at 8.55 *m*. The results are presented in Table I.

TABLE I
EFFECT OF HEXACHLORORHENIUM(IV) CONCENTRATION ON THE CHLORIDE ION EXCHANGE[a]

[$ReCl_6^{2-}$], M	10^7R, M sec^{-1} [b]	$10^5k'$, sec^{-1} [b,c]
0.002	0.781 ± 0.025	3.90 ± 0.12
0.010	3.37 ± 0.05	3.37 ± 0.05
0.015	5.17 ± 0.07	3.45 ± 0.05
0.020	6.84 ± 0.07	3.42 ± 0.04
0.030	10.54 ± 0.07	3.51 ± 0.02

[a] At $m_{H^+} = m_{Cl^-} = 8.55$ and 90°. [b] Deviations represent 1 standard deviation. [c] k' defined as $R = k'[ReCl_6^{2-}]$.

Effect of Hydrogen Ion and Chloride Ion.—Three different sets of experiments were performed in an attempt to determine the dependence of the rate on hydrogen ion and chloride ion. (1) The hydrochloric acid concentration was varied. (2) The chloride concentration was varied with lithium chloride keeping hydrogen ion constant. (3) The hydrogen ion concentration was varied keeping chloride ion and the ionic strength constant using lithium chloride. The results are given in Table II.

TABLE II
EFFECT OF HYDROGEN ION AND CHLORIDE ION ON THE $ReCl_6^{2-}$ CHLORIDE EXCHANGE REACTION[a]

Run	m_{H^+} [b]	m_{Cl^-} [b]	μ(LiCl)	10^7R, M sec^{-1} [c]
10	4.47	4.47	4.47	3.82 ± 0.05
11	5.47	5.47	5.47	3.00 ± 0.08
12	7.16	7.16	7.16	3.38 ± 0.08
13	8.11	8.11	8.11	3.47 ± 0.09
14	8.55	8.55	8.55	3.53 ± 0.21[d]
15	9.91	9.91	9.91	4.80 ± 0.08
16	11.7	11.7	11.7	6.80 ± 0.18
17	4.36	5.58	5.58	2.53 ± 0.04
18	4.36	6.86	6.86	2.09 ± 0.07
19	4.36	8.25	8.25	2.11 ± 0.07
20	4.36	9.75	9.75	2.03 ± 0.03
21	4.36	11.4	11.4	4.38 ± 0.14
22	5.58	11.4	11.4	4.25 ± 0.05
23	6.86	11.4	11.4	5.80 ± 0.20
24	8.25	11.4	11.4	7.57 ± 0.24
25	9.75	11.4	11.4	7.75 ± 0.06
26	11.4	11.4	11.4	6.91 ± 0.36

[a] At 0.01 *M* K_2ReCl_6 and 90°. [b] Concentrations given are molalities. [c] Deviations represent 1 standard deviation. Although the standard deviation of the slope was usually better than ±3%, duplicate runs generally agreed to ±5%. [d] Unweighted average of values for $0.01k'$ from Table I. Deviation is the standard deviation from the mean; the relatively high value is attributed to the run at 0.002 *M* $ReCl_6^{2-}$, which is probably more in error than indicated by its deviation.

Effect of Foreign Ions.—An attempt was made to determine whether Li^+ had a specific effect using *p*-toluenesulfonate ion. The problem of solubility of the complex in this medium was a limiting factor. Two runs were carried out at 90° and 0.01 *M* K_2ReCl_6: (1) $m_{H^+} = m_{Cl^-} = 5.06$, [$p$-$CH_3C_6H_4SO_3^-$] = [$Li^+$] = 1 *M*, $\mu = 6.1$, $R = (3.06 \pm 0.17) \times 10^{-7}$ *M* sec^{-1}; (2) $m_{H^+} = m_{Cl^-} = 4.72$, [$p$-$CH_3C_6H_4SO_3^-$] = [$Li^+$] = 2 *M*, $\mu = 6.7$, $R = (5.61 \pm 0.04) \times 10^{-7}$ *M* sec^{-1}.

Temperature Dependence.—The temperature was varied from 64.5 to 99.0°. The results are given in Table III. The slope of a plot of ln *R vs.* $1/T$ was determined by a linear least-squares analysis by the computer. The activation energy was found to be 26.0 ± 1.2 kcal/mole. All estimates of error represent 1 standard deviation.

TABLE III
EFFECT OF TEMPERATURE ON THE $ReCl_6^{2-}$ CHLORIDE EXCHANGE REACTION[a]

Temp, °C	10^7R, M sec^{-1} [b]
64.5	0.383 ± 0.042
78.0	1.82 ± 0.06
90.0	6.91 ± 0.36
99.0	12.40 ± 0.12

[a] At 0.01 *M* K_2ReCl_6; $m_{H^+} = m_{Cl^-} = 11.4$. [b] Deviations represent 1 standard deviation.

Discussion

The difficulty encountered in interpreting kinetic data in high ionic strength aqueous media is well documented.[12] In the present study, the hydrolysis tendency of $ReCl_6^{2-}$ is great and both H^+ and Cl^- must be in high concentration to prevent complications due to presence of $ReCl_5OH^{2-}$ and other species. This necessitates working in the range 4–11 *m* H^+ and Cl^-, and in the lower concentration range trace amounts of hydrolytic species must be present. If equilibrium of it with $ReCl_6^{2-}$ is rapid (at 90°) the observed rate of exchange will reflect the contribution of these species and this is thought to be the reason for the relatively high value for run 10. The high concentrations required to reduce the problem of hydrolysis introduce the further problem of drastic changes in solution properties with H^+ and Cl^- changes. The observed kinetics will reflect these changes.

Quantitative evaluation of the rate law must consider at least these four factors: [$ReCl_6^{2-}$], [H^+], [Cl^-], and μ. The over-all rate has been shown to be first order in [$ReCl_6^{2-}$]. Runs 11–16 and 21–26 show a definite catalysis of exchange by H^+, but the order with respect to [H^+] is not an integer even at constant ionic strength using Li^+Cl^-. Over 6 *m* Cl^- the over-all rate appears to be independent of Cl^- until μ is extremely high (runs 17–21) which may reflect only medium changes. The presence of the large *p*-toluenesulfonate ion in 1 or 2 *M* concentration does not modify the rate significantly. Attempts to obtain a rate constant using the observed rates and rate laws containing concentration terms in H^+ and Cl^- to the powers 0, ±1, and ±2 and the incorporation of various functions of ionic strength were not highly successful. The best

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fit was obtained using the rate expression $R = k[\text{ReCl}_6{}^{2-}][\text{H}^+]$. Using this equation all of the data gave a value of $k = (0.659 \pm 0.221) \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$, having a range of $(0.413\text{–}1.188) \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$.

Rate laws using the activities of the various species present[13-17] did not provide a better fit to the data than the use of concentrations.

In view of the lack of a quantitative fit to a single rate law, no positive conclusions can be reached concerning the mechanism of reaction.

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Formation Constant, Enthalpy, and Entropy Values for the Association of Nickel(II) Ion with Glycinate, Alanate, and Phenylalanate Ions at 10, 25, and 40°[1a]

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Received November 2, 1966

Previous studies[2-5] dealing with metal ion–amino acid interaction with Cu^{2+} ion are extended in this work to include interaction with Ni^{2+} ion. The effects of changes of temperature and ligand have been investigated in this study of the nickel(II)–glycine, –alanine, and –phenylalanine systems at 10, 25, and 40°. Values for constants for the association of Ni^{2+} ion with the anions of glycine[6-9] and alanine[7] appear in the literature but no data for the nickel(II) phenylalanine system are available. Apparently no previous calorimetric studies of enthalpy changes associated with the formation of nickel complexes of these three amino acids have been made.

Experimental Section

Materials.—Solutions of NaOH and HClO_4 were prepared from reagent grade chemicals obtained from the J. T. Baker Chemical Co. and standardized using recognized analytical procedures. Stock nickel(II) perchlorate solutions were prepared by dissolving reagent grade nickel perchlorate (The G. Frederick Smith Chemical Co.) in distilled water and determining the metal formality by dimethylglyoxime gravimetric analysis. Stock ligand solutions were prepared by dissolving weighed quantities of glycine (Matheson Coleman and Bell) and alanine and phenylalanine (East Organic Chemicals) in water without further purification. Titration of the carboxyl group of the amino acid in the presence of HCOOH[10] shows these reagents to be 99.7, 99.9, and 99.2% pure, respectively. Buffer solutions were prepared both as discussed by Bates[11] and from packaged powders formulated according to National Bureau of Standards specifications by Beckman Instruments, Inc. The measured pH values of buffer solutions prepared to maintain a given pH value by the two methods were identical within ±0.002 pH unit.

Apparatus.—The submarine isothermal calorimeter operating in a well-stirred, constant-temperature water bath controlled to ±0.005° at 10, 25, and 40° has been described.[3] Temperature differences of 0.0002° were detectable using a Wheatstone bridge assembly, power supply, and timing device described previously.[2,3] A 200-ml round-bottom flask, modified with five 0.75-in. diameter necks spaced about the main neck, served as the container for metal–ligand solutions during titrations for the determination of stepwise constants for the association of metal ion with ligand anion. This container was immersed in a 10-l. water bath whose temperature was controlled to ±0.02°. Hydrogen ion activity values were determined by means of a Beckman Model 76 expanded-scale pH meter for calorimetric runs and by means of a Leeds and Northrup 7664-A1 pH meter whose output was expanded on a Leeds and Northrup Speedomax H 177181 recorder for titration studies.

Association Constants.—Titrations to determine values for the thermodynamic equilibrium constants, K_1 and K_2, for the reactions represented by eq 1 and 2, respectively, were carried out under a nitrogen atmosphere.[3]

$$\text{M}^{2+} + \text{L}^- \rightleftharpoons \text{ML}^+ \qquad (1)$$

$$\text{ML}^+ + \text{L}^- \rightleftharpoons \text{ML}_2 \qquad (2)$$

M^{2+} represents the metal ion, L^- represents the anion of the appropriate amino acid, and ML^+ and ML_2 represent the species resulting from the stepwise association of ligand and metal ions. The calculation methods of Block and McIntyre[12] were used. Activity coefficient values for singly and doubly charged ions, γ_1 and γ_2, were calculated by means of equations derived from the data of Crouthamel and Martin[13] and Harned and Owen[14] as previously described.[2,3] Values of γ_1 and γ_2 calculated by this method agree well with those of Kielland.[15] Values for the thermodynamic equilibrium constants, K_{D_1} and K_{D_2}, for the reactions represented by eq 3 and 4, respectively, are those reported from this laboratory.[2,3]

$$\text{H}_2\text{L}^+ \rightleftharpoons \text{H}^+ + \text{HL} \qquad (3)$$

$$\text{HL} \rightleftharpoons \text{H}^+ + \text{L}^- \qquad (4)$$

Calorimetric Determinations.—Two types of calorimetric runs, type y and type z, were performed to measure enthalpy values. These runs measured the heats evolved when alkaline solutions of a ligand were mixed with solutions of nickel(II) ions. The formality ratios of ligand to metal ion in the final mixed solutions were 2:1 for y runs and 1:1 for z runs.

An equation representing the concentration of the species ML^+, as a function of K_{D_1}, K_{D_2}, K_1, K_2, γ_1, γ_2, and the hydrogen ion activity, and an equation for the heat measured during a

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(1) (a) Supported in part by Public Health Research Grant AM-02170 from the National Institute of Arthritis and Metabolic Diseases; (b) to whom inquiries concerning this article should be sent.

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