It has been suggested[1] that a twist mechanism should give rise to a very low frequency factor and a corresponding large entropy loss in the transition state because of the expected low probability for distribution of the activation energy into the appropriate vibrational modes. Accordingly, the low frequency factors of $10^{4.16}$ and $10^{-4.8}$ sec^{-1} for racemization of tris(biguanidinium)cobalt(III), $Co(bigH)_3^{3+}$, in aqueous solution and $Co(C_2O_4)_3^{3-}$ in the solid state, respectively, have prompted the assignment of twist mechanisms for these rearrangement processes.[1,22] By way of comparison, the frequency factors for racemization of $Cr(C_2O_4)_3^{3-}$ and $Co(C_2O_4)_3^{3-}$ in aqueous solution, where bond-rupture mechanisms probably operate,[23–25] are $10^{7.2}$ [23] and $10^{14.5}$ sec^{-1},[26] respectively.[26a] It is also known that $Fe(phen)_3^{2+}$ racemizes, in part, by an intramolecular path and that a twisting mechanism apparently operates as the rigid structure of the 1,10-phenanthroline ligand precludes a bond-rupture process.[27] In contrast to the apparent large entropy loss for twisting $Co(bigH)_3^{3+}$ and $Co(C_2O_4)_3^{3-}$, a large entropy gain is associated with the intramolecular racemization of $Fe(phen)_3^{2+}$ ($\Delta S^{\ddagger}_{25°} = 21$ eu). In this latter case it has been suggested[28] that twisting is preceded by excitation of Fe(II) from a low-spin to a high-spin state and consequent expansion of the coordination sphere of the metal ion; the entropy gain was attributed to a greater degree of freedom of the ligands in the excited state. Although an expansion process may cause the magnitude of the frequency factor for twisting a tris chelate of a low-spin d^6 metal ion to be comparable to that expected for a bond-rupture mechanism, no such expansion process is possible for d^0 metal ion complexes. Therefore, the frequency factors for rearrangement of the group III metal β-diketonates listed in Table IV are believed to be indicative of a bond-rupture mechanism. Frequency factors much smaller than those obtained here have been reported by Fortman and Sievers[8] for the rearrangement of other mixed aluminum(III) β-diketonates, but these low values are not believed to be reliable, for reasons given elsewhere.[10]

Acknowledgment.—The support of this research by National Science Foundation Grant GP-9503 is gratefully acknowledged. D. A. C. wishes to thank the National Science Foundation for an undergraduate summer participantship.

(22) C. D. Schmulbach, J. Brady, and F. Dachille, *Inorg. Chem.*, **7**, 287 (1968).
(23) S. T. Spees and A. W. Adamson, *ibid.*, **1**, 531 (1962).
(24) D. R. Llewellyn and A. L. Odell, *Aust. At. Energy Symp., Proc.*, **5**, 623 (1958).
(25) C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Conner, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964).
(26) E. Bushra and C. H. Johnson, *ibid.*, 1937 (1939).
(26a) NOTE ADDED IN PROOF.—Frequency factors in the range $10^{14.7}$–$10^{15.8}$ sec^{-1} have been found recently for the isomerization and racemization of cis and trans isomers of tris(5-methylhexane-2,4-dionato)cobalt(III) [J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970)] and cobalt(III) benzoylacetonate [A. Y. Girgis and R. C. Fay, *ibid.*, **92**, 7061 (1970)] in chlorobenzene solution where bond-rupture mechanisms most probably operate.
(27) F. Basolo, J. C. Hayes, and H. M. Neumann, *ibid.*, **76**, 3807 (1954).
(28) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 315.

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801
AND THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

The Two-Electron Inner-Sphere Reduction of Chloropentaammineplatinum(IV) Ion by Aquochromium(II) Ion

BY JAMES K. BEATTIE*[1] AND FRED BASOLO

Received August 26, 1970

A two-electron inner-sphere reaction is required to account for the stoichiometry and kinetics of the reduction of $Pt(NH_3)_5Cl^{3+}$ by Cr^{2+}. In perchloric acid solutions of pH 0–2 the final chromium(III) products are equivalent amounts of $CrCl^{2+}$ and Cr^{3+}, but at lower acidities appreciable quantities of dimeric $(CrOH)_2^{4+}$ are formed. The rapid and complex absorbance changes observed by stopped-flow spectrophotometry are interpreted as the second-order redox reaction with a rate constant of 5×10^4 M^{-1} sec^{-1} at 25° followed by slower reactions of chromium(III) intermediates. These intermediates have not been completely characterized.

Introduction

The aquochromium(II) ion has been extremely important in the elucidation of oxidation–reduction mechanisms of metal complexes. By exploiting the substitution-inert property of the oxidized Cr(III) product, Taube and Myers[2] were able to demonstrate that the reduction of $Co(NH_3)_5Cl^{2+}$ proceeds by an inner-sphere activated complex accompanied by ligand transfer of the chlorine from cobalt to chromium, producing $CrCl^{2+}$. Subsequently, many other studies[3] have examined the details of the inner-sphere redox mechanism.

Ardon and Plane[4] have shown that various oxidations

(1) To whom correspondence should be addressed at the University of Illinois.
(2) H. Taube and H. Myers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).
(3) For recent reviews see (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, Chapter 6; (b) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1967).
(4) M. Ardon and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3197 (1959).

of Cr^{2+} lead to different Cr(III) products depending on whether one- or two-electron oxidants are used. With typical one-electron oxidants such as Fe^{3+} and Cu^{2+} the Cr(III) product is monomeric Cr^{3+}. With two-electron oxidants such as Tl(III) and O_2 a Cr(III) dimer is obtained, later shown[5] to be a μ-dihydroxo-bridged species, $[Cr(H_2O)_4OH]_2^{4+}$. Their suggestion that the dimer arises from the reaction of Cr^{2+} with a Cr(IV) intermediate is supported by the observation that the Cr^{2+} reduction of Cr(VI) produces two Cr^{3+} and one dimer. The two Cr^{3+} are produced by two successive one-electron reductions of Cr(VI) to Cr(IV) and the Cr(IV) is then reduced by Cr^{2+} to give the dimer. This interpretation is substantially supported by later isotopic tracer studies of Hegedus and Haim.[6]

The stable oxidation states of platinum differ by two electrons. Two-electron transfers between Pt(II) and Pt(IV) are well known in the Pt(II)-catalyzed reactions of Pt(IV) complexes.[7] These are often accompanied by ligand transfer, as in the Pt(II)-catalyzed substitution reaction which apparently involves a bridged activated complex.[8]

$$Pt(NH_3)_5Cl^{3+} + Cl^- + H^+ \xrightarrow[Pt(NH_3)_4^{2+}]{} trans\text{-}Pt(NH_3)_4Cl_2^{2+} + NH_4^+ \quad (1)$$

This article describes an investigation of the Cr^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$. A combination of stoichiometry and kinetic studies under a variety of reaction conditions indicates that a two-electron inner-sphere reaction occurs with transfer of a bridging chloride ligand from platinum to chromium. Subsequent reduction of the chlorochromium(IV) intermediate by Cr^{2+} is apparently rapid, producing chlorochromium(III) intermediates which undergo slower reactions to the final products.

Experimental Section

The preparations of $[Pt(NH_3)_5Cl](ClO_4)_3$, $[Pt(NH_3)_5Cl]Cl_3$, and $[Pt(NH_3)_5Cl]Cl_3 \cdot H_2O$ were described previously.[9] Chromium(II) perchlorate solutions were prepared by zinc amalgam reduction of chromium(III) perchlorate solutions essentially in the manner described by Lingane and Pecsok[10] for chromium(II) chloride and sulfate solutions. Reagent grade sodium dichromate was used instead of potassium dichromate as the starting material for the preparation of the Cr(III) solutions to avoid precipitation of potassium perchlorate.

The Cr(III) products were separated by the usual ion-exchange chromatography technique using Dowex 50-X8 cation-exchange resin. The resin was purified in the first experiments by the method of Dulz[11] and later according to the method of Thompson and Gordon.[12] In the first experiments the $[CrOH]_2^{4+}$ band was eluted with 0.2 M lanthanum perchlorate solution[13] and the eluent was analyzed spectrophotometrically as chromate after complexation of the La with EDTA. Blank experiments indicated that the La did not interfere in the analysis. Later the procedure of Thompson and Gordon[12] was used.

The reaction solutions which were analyzed for the Cr(III) products were prepared by injecting by syringe a solution of the limiting reagent into a stirred solution of the excess reagent. In each case the Pt(IV) solution contained additional reagents ($NaClO_4$, $HClO_4$, and, in experiments with added chloride ion, NaCl) so that the final ionic strength of the mixed solution was 0.1 M. Stirring was achieved by means of a magnetic stirrer, but no systematic investigation was made of the influence of the rate of addition or the efficiency of the mixing. The concentration ranges used in the experiments with excess Cr(II) were $[Cr(II)] = (0.4\text{–}4.0) \times 10^{-3}\ M$ and $[Pt(IV)] = (0.1\text{–}0.5) \times 10^{-3}\ M$; and with excess Pt(IV) they were $[Cr(II)] = (4.4\text{–}9.5) \times 10^{-3}\ M$ and $[Pt(IV)] = (2.5\text{–}4.9) \times 10^{-3}\ M$.

The pH values of the reaction solutions at pH <2 were calculated from the amount of standardized $HClO_4$ added together with a small contribution from the acidity of the Cr(II) solution. At lower acidities the pH was measured before and after the reaction. In these experiments control of the acidity was desired, but suitable buffers with the proper pH range which would not complex the labile chromous ion were unknown. For some of these experiments the Cr(II) solution was prepared so that the Cr(II) concentration was twice the hydrogen ion concentration. In this way the ammonia released by the reaction of Cr(II) with the Pt(IV) complex was just neutralized by the acid added and the pH, adjusted with additional acid in the Pt(IV) solution, remained constant within about 0.1 pH unit.

The rapid-mixing stopped-flow apparatus used for the kinetic studies has been described.[9] The concentration of Cr^{2+} in the reagent solutions used in the kinetic studies was determined directly in the flow apparatus. After calibrating the instrument with water in the observation tube, the Cr(II) solution was allowed to react with a solution of $[Co(NH_3)_5Br]Br_2$. The Co(III) solution was prepared by dissolving a weighed quantity of $[Co(NH_3)_5Br]Br_2$ in a solution of perchloric acid to give a Co(III) concentration slightly greater than the Cr(II) concentration. After reaction the residual concentration of $Co(NH_3)_5Br^{2+}$ was determined by noting the transmittance of the solution at 252.5 nm (ϵ $1.64 \times 10^4\ M^{-1}\ cm^{-1}$).[14] The difference between the initial and final concentrations of Co(III) was taken as the concentration of Cr(II).

Results

Stoichiometry and Product Analyses.—The Pt(II) product of the reaction was identified as $Pt(NH_3)_4^{2+}$ by precipitation of Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, by adding a solution of K_2PtCl_4 to the product mixture. Three experiments were performed with concentrations of $Pt(NH_3)_5Cl^{3+}$ about $3 \times 10^{-2}\ M$ and of Cr(II) about $5 \times 10^{-2}\ M$. Based on a 2:1 Cr(II):Pt(IV) stoichiometry calculated from the limiting Cr(II) concentration the amount of $[Pt(NH_3)_4][PtCl_4]$ isolated was greater than 90% of the theoretical amount expected. Platinum analysis of one sample of the precipitate was satisfactory. *Anal.* Calcd for $[Pt(NH_3)_4][PtCl_4]$: Pt, 65.2. Found: Pt, 64.6.

The Cr(III) products of the reaction were identified under three different sets of reaction conditions: reactions in a slight excess of Pt(IV), reactions in an excess of Cr(II), and reactions with added chloride ion, usually in an excess of Pt(IV).

The results for the reactions with excess Pt(IV) are presented in Figure 1 as a function of pH. The pH values at higher acidities were calculated from the con-

(5) R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).
(6) L. S. Hegedus and A. Haim, *ibid.*, **6**, 664 (1967).
(7) See S. G. Bailey and R. C. Johnson, *ibid.*, **8**, 2596 (1969), and references therein.
(8) F. Basolo, M. L. Morris, and R. G. Pearson, *Discuss. Faraday Soc.*, **29**, 80 (1960).
(9) J. K. Beattie and F. Basolo, *Inorg. Chem.*, **6**, 2069 (1967).
(10) J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **20**, 425 (1948).
(11) G. Dulz, Ph.D. Thesis, Columbia University, 1963.
(12) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 557, 562 (1966).
(13) J. A. Laswick and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3564 (1959).
(14) J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

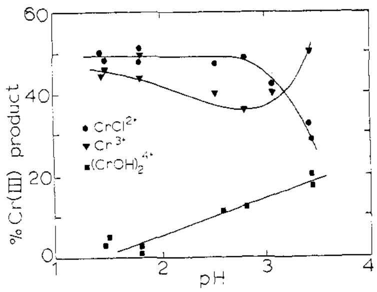
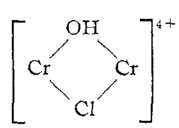


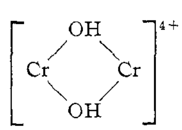
Figure 1.—The pH dependence of the chromium(III) products of the reduction of excess $Pt(NH_3)_5Cl^{3+}$ by Cr^{2+}: ●, $CrCl^{2+}$; ▼, Cr^{3+}; ■, $(CrOH)_2^{4+}$.

centration of acid added; at lower acidities the pH of the solution was measured before and after the Cr^{2+} was added. The pH increased by 0.1–0.2 unit during the reaction. The data are given as per cent of total chromium so that 1 mol of $(CrOH)_2^{4+}$ is reported as 2 mol of chromium. In each case the chromium recovered from the ion-exchange column was 95–100% of the total chromium in the product solution. At pH 1–2 the products are about 50% $CrCl^{2+}$ and 50% Cr^{3+}, with a small amount of $(CrOH)_2^{4+}$. As the pH is increased above pH 3, the proportion of $CrCl^{2+}$ falls rapidly and the amount of $(CrOH)_2^{4+}$ increases, but not so rapidly. The difference is made up by an increase in Cr^{3+}.

In several experiments which are not included in Figure 1 no acid was initially present in the Pt(IV) solution to which Cr^{2+} was added. The only acid present was that in the Cr^{2+} solution itself. The final pH of these product solutions appeared to be determined by the acidity of the chromium(III) product ions. Up to 30% dimeric chromium(III) was observed in these reactions. In one of these experiments the product solution was analyzed for ionic chloride as well as for Cr(III) products. The amount of ionic chloride found was 17% of the total chromium present. Together with the chloride found as $CrCl^{2+}$, this accounts for 90% of the chloride assumed to be released in the reduction of $Pt(NH_3)_5Cl^{3+}$. Since 29% of the chromium was found as $(CrOH)_2^{4+}$, these results indicate that $(CrOH)_2^{4+}$ is a product of the Pt(IV) reduction and not an artifact resulting from the increased pH of the Cr^{2+} solutions. No investigation was made of the possibility that the remaining 10% of the chloride might be incorporated into the dimer, producing



instead of



In a second experiment designed as a blank to confirm that the observation of $(CrOH)_2^{4+}$ is not an artifact of the high pH, a neutral solution of $Co(NH_3)_5OH_2^{3+}$ was reduced by addition of a slightly acidic Cr^{2+} solution. This reaction is known[15] to produce Cr^{3+} in acidic solutions of pH 0–1. No dimeric chromium(III) product was observed by ion-exchange chromatography, further indicating that $(CrOH)_2^{4+}$ is a product of the Cr(II)–Pt(IV) reaction.

The Cr(III) product analysis for reactions in excess Cr^{2+} is more difficult due to the excess Cr^{2+} remaining after the Pt(IV) had been reduced. This was oxidized to Cr(III) by shaking the solution in air for several minutes. Oxidation of Cr^{2+} by oxygen gives $(CrOH)_2^{4+}$.[4] The results are presented in Figure 2. The

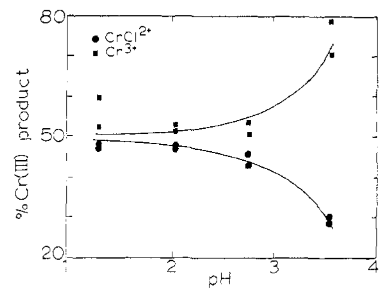


Figure 2.—The pH dependence of the chromium(III) products of the reduction of $Pt(NH_3)_5Cl^{3+}$ by excess Cr^{2+}: ●, $CrCl^{2+}$; ■, Cr^{3+}.

total recovery of Cr(III) from the column was between 84 and 104%, somewhat poorer than for reactions with excess Pt(IV). The proportions of $CrCl^{2+}$ and Cr^{3+} were calculated relative to the amount of $Pt(NH_3)_5Cl^{3+}$ present assuming a 2:1 Cr(II):Pt(IV) stoichiometry.

In some cases the sum of $CrCl^{2+}$ and Cr^{3+} is slightly more than 100%; in no case is it significantly less than 100%. It does not appear that $(CrOH)_2^{4+}$ is a significant product under these conditions although small amounts may be obscured by the $(CrOH)_2^{4+}$ resulting from the air oxidation of excess Cr^{2+}.

At pH 1–2 the products are 50% $CrCl^{2+}$ and 50% Cr^{3+}. As the acidity decreases, the proportion of $CrCl^{2+}$ decreases in a manner similar to the reaction in excess Pt(IV). The amount of Cr^{3+} increases in proportion to the decrease of $CrCl^{2+}$. This is in contrast to the reaction in excess Pt(IV) in which $(CrOH)_2^{4+}$ is an important product at higher pH.

Results for the reaction in the presence of added ionic chloride are presented in Table I. Except for experiments 1 and 2, Cr(II) was the limiting reagent. The results indicate that incorporation of ionic chloride in the Cr(III) product as $CrCl^{2+}$ is an efficient process. With excess chloride ion the Cr(III) product is exclusively $CrCl^{2+}$ (experiments 1–5). Even when the ratio of moles of ionic chloride to moles of Pt(IV) reduced is less than unity, almost all the chloride is incorporated in $CrCl^{2+}$ at pH 1–2 (experiments 6 and 8). The extent of chloride incorporation is reduced as the acid concentration is lowered (experiments 7 and 9).

(15) R. K. Murmann, H. Taube, and F. A. Posey, *J. Amer. Chem. Soc.*, **79**, 262 (1957).

TABLE I
Cr(III) PRODUCT DISTRIBUTION FOR REDUCTION OF $Pt(NH_3)_5Cl^{3+}$ WITH ADDED CHLORIDE ION

Expt	10^3[Pt(IV)], M	10^3[Cr(II)], M	10^3[Cl^-], M	10^2[H^+], M	% Cr recovered	% Cr^a as— $CrCl^{2+}$	Cr^{3+}	$(CrOH)_2^{4+}$
1	2.4	25	93	13	96	96	. . .	. . .
2	3.4	11	44	13	100	96	. . .	4
3	2.9	5.6	38	13	95	95	. . .	. . .
4	3.2	5.6	27	13	96	96	. . .	. . .
5	34	5.8	10	11	92	92	. . .	. . .
6	2.6	5.0	2	36	99	85	12	2
7	2.7	5.0	2	5	96	78	17	1
8	2.6	4.9	1	36	. . .	71	. . .	2
9	2.5	4.4	1	5	99	66	28	5

[a] Calculated from limiting reagent assuming 2:1 Cr(II):Pt(IV) stoichiometry.

Kinetics Observations.—The spectral changes accompanying the reduction are rapid and complex. It was necessary to observe the ultraviolet region of the spectrum in order to obtain sufficiently large absorbance changes at the very low concentrations necessary to keep the reaction half-life longer than the 5-msec minimum of the stopped-flow spectrometer. All of the species involved in the reaction absorb in this region from 230 to 300 nm. Pseudo-first-order conditions were consequently employed in an attempt to analyze the spectral changes observed, but this was only partially successful. The kinetics conditions can be classified as were the stoichiometry experiments as reactions with a pseudo-first-order excess of Cr^{2+}, those with a pseudo-first-order excess of $Pt(NH_3)_5Cl^{3+}$, and reactions with added chloride ion.

Distinctly different spectral changes were observed for the three different classes of reaction conditions. In the presence of excess Cr^{2+} the absorbance rose rapidly to a maximum and then decreased more slowly to the final infinity absorbance, as illustrated for a typical trace in Figure 3a. The slower decrease in absorbance

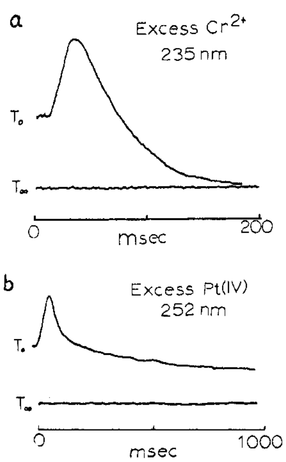


Figure 3.—(a) Absorbance changes observed for the reduction of $Pt(NH_3)_5Cl^{3+}$ by excess Cr^{2+} at 235 nm. Time sweep is 200 msec. (b) Absorbance changes for the reaction in excess $Pt(NH_3)_5Cl^{3+}$ at 252 nm. Time sweep is 1000 msec.

is first order and the rate depends in part on the concentration of Cr^{2+}. The observed rate constants are plotted in Figure 4 together with a line which corresponds to the equation $k_{obsd} = k + k'[Cr^{2+}]$, where $k = 10$ sec^{-1} and $k' = 2 \times 10^4$ M^{-1} sec^{-1}. No large effect of changing the hydrogen ion concentration from 0.1 to 0.001 M was observed, although this point was not examined exhaustively due to the difficulties of using low acid concentrations in the absence of suitable buffers for Cr^{2+}. The rate constant appeared to be independent of wavelength from 235 to 290 nm.

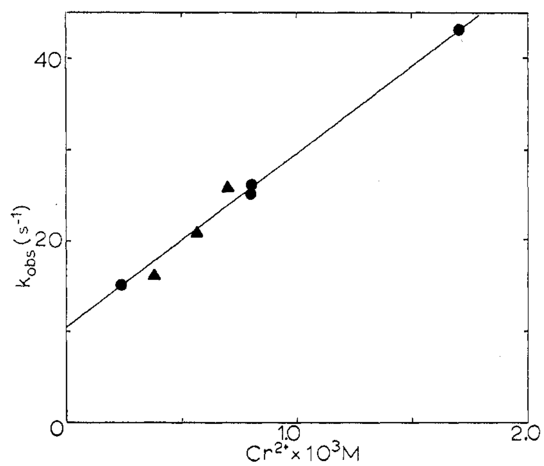


Figure 4.—Dependence on [Cr^{2+}] of the decrease in absorbance observed for the reduction of $Pt(NH_3)_5Cl^{3+}$ by excess Cr^{2+}: ●, [H^+] = 0.05–0.10 M; ▲, [H^+] ≈ 10^{-3} M.

The analysis of the initial rapid increase in absorbance in Cr^{2+} is more difficult due to the presence of the second reaction and the unknown absorbance of the intermediate(s). Preliminary experiments indicated that the observed rate constant had approximately a first-order dependence on the concentration of Cr^{2+}. An analog computer was used to simulate the absorbance changes for two successive first-order reactions with a variable extinction coefficient for the intermediate species. These plots successfully reproduce the observed absorbance changes. Using the measured value for the rate constant of the second reaction, the ratio of the rate constants obtained from the analog computer, and the known concentration of Cr^{2+}, a consistent value of $(5.4 \pm 0.4) \times 10^4$ M^{-1} sec^{-1} for the second-order rate constant of the first reaction was obtained for five experiments over a range of Cr^{2+} concentrations of 4×10^{-4} to 10^{-3} M. No dependence on acid concentration or wavelength was observed in these limited studies although the value of the calculated extinction coefficient of the intermediate(s) varied somewhat with wavelength as would be expected.

Several experiments were performed in the visible region of the spectrum, although the absorbance changes observed were very small. In this region, as in the ultraviolet region, the absorbance increased rapidly and then decreased more slowly with the extent of the decrease strongly wavelength dependent. By measuring the maximum in absorbance as a function of wavelength an approximate spectrum of the intermediate was obtained which displays maxima in the regions 400–425 and about 600 nm. Using the analog computer and the rate constants determined from the observations in the ultraviolet region the extinction coefficient of the intermediate(s) was estimated to be 2–4 times greater than the products at 420 nm.

In the presence of excess $Pt(NH_3)_5Cl^{3+}$ the absorbance changes are more complex, as illustrated in Figure 3b. There is an initial rapid increase in absorbance, followed by a slower decrease, followed by a much slower decrease to the final infinity absorbance. At 235 and 252 nm and 0.05 M H^+ the final slow decrease in absorbance is first order with a rate constant of 4×10^{-2} sec^{-1}, but the rate increases with decreasing acidity and increasing wavelength of observation and apparently represents a complex reaction. The intermediate decrease in absorbance is also a function of overlapping absorbance changes dependent on wavelength and reaction conditions and was not analyzed. An attempt was made to extract an approximate rate constant from the initial rapid increase in absorbance even though neither a stable infinity absorbance nor a known rate of the succeeding reaction was available. By using an estimated infinity absorbance slightly greater than the observed maximum absorbance first-order plots were constructed and rate constants were obtained for absorbance changes at 235 and 252 nm. These are plotted in Figure 5 as

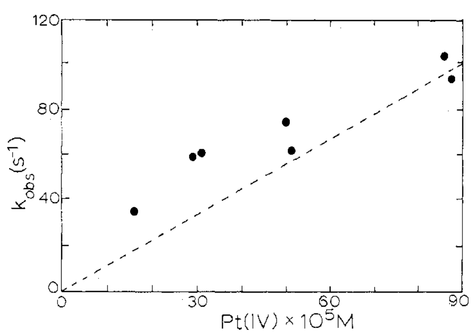


Figure 5.—Dependence on the Pt(IV) concentration of the estimated rate of the initial increase in absorbance for the reduction of excess $Pt(NH_3)_5Cl^{3+}$ by Cr^{2+}.

a function of the concentration of $Pt(NH_3)_5Cl^{3+}$ together with a line with a slope of 11×10^4 M^{-1} sec^{-1} which is twice the rate constant obtained from the studies in excess Cr^{2+}. A definite dependence of the rate on the Pt(IV) concentration is observed, although it is not clearly first order. The deviations from the expected values represented by the line are greatest at the slower rates where the interference from the succeeding reactions is most severe and will lead to overestimation of the rate of the initial absorbance change.

No maximum in absorbance was observed in the presence of low concentrations of ionic chloride of the order of the concentration of Pt(IV) reduced. A single decrease in absorbance with a rate constant of 20–40 sec^{-1} was found whether Cr(II) or Pt(IV) was in excess.

Discussion

Although the reduction of $Pt(NH_3)_5Cl^{3+}$ by Cr^{2+} is clearly a complex reaction and many of our observations must remain unexplained, two conclusions can be drawn from the results reported here. The first is that the redox reaction is probably inner sphere. The observation that the chloride ion of $Pt(NH_3)_5Cl^{3+}$ is completely incorporated in the Cr(III) product at pH 0–2 under conditions of excess Cr(II) and of excess Pt(IV) indicates an inner-sphere mechanism. This conclusion is weakened, however, by the observations that small amounts of added ionic chloride strongly accelerate the reaction and are almost completely incorporated in the Cr(III) products. It is possible that the chloride coordinated to the Pt(IV) reactant is released as ionic chloride in an initial reaction and subsequently incorporated in the chromium product in a later redox process. Additional support for an inner-sphere mechanism is obtained, however, from our observations[16] that the Cr^{2+} reduction of $Pt(NH_3)_6^{4+}$ and $Pt(en)_3^{4+}$, presumably outer-sphere processes, proceed very much more slowly than reduction of $Pt(NH_3)_5Cl^{3+}$, suggesting that chloride is serving as a bridging group.

The second conclusion is that the reaction proceeds by an initial two-electron transfer. This is a consequence of the stoichiometric and kinetics results considered together and requires careful analysis. The kinetics observations in a pseudo-first-order excess of Cr^{2+} indicate two successive first-order reactions. The first reaction is more rapid and depends linearly on the concentration of Cr^{2+}, so that the complete rate law is

$$\frac{-d[Pt(IV)]}{dt} = k_1[Cr^{2+}][Pt(IV)] \qquad (2)$$

with $k_1 = 5 \times 10^4$ M^{-1} sec^{-1}. The second reaction, presumably the reaction of an intermediate produced in the first step, is slower. The rate law contains a term dependent on Cr^{2+} and a term independent of Cr^{2+} (eq 1). Ignoring for the moment the Cr^{2+}-independent term, these two successive reactions might be interpreted as the successive one-electron reductions of Pt(IV) to Pt(II) with a Pt(III) intermediate

$$Pt(IV) + Cr(II) \longrightarrow Pt(III) + Cr(III) \qquad (3)$$

$$Pt(III) + Cr(II) \longrightarrow Pt(II) + Cr(III) \qquad (4)$$

Chloride ion transfer in either reaction 3 or reaction 4 would account for the observed stoichiometry.

This one-electron transfer mechanism is eliminated, however, by the observations made on the stoichiometry and kinetics of the reaction in excess Pt(IV). Although the complex absorbance change cannot be completely analyzed, the first step of the reaction in

(16) J. K. Beattie, unpublished observations.

excess Pt(IV) appears to be the same as that in excess Cr(II). (See below for further discussion on this point.) Because this first step is more rapid than the succeeding reactions, the one-electron mechanism requires that the chromium(III) products of the reaction in excess Pt(IV) be different from those with excess Cr(II). Under conditions of excess Pt(IV), reaction 3 will consume more than half of the limiting amount of Cr(II). If chloride transfer occurs in (3), then more than 50% of the chromium(III) product will be $CrCl^{2+}$. Conversely, if chloride transfer occurs in (4), then less than half of the chromium(III) product will be $CrCl^{2+}$. The observation that the products are equivalent amounts of $CrCl^{2+}$ and Cr^{3+} is inconsistent with the one-electron mechanism.

In a second mechanism which can be eliminated by similar arguments the initial more rapid reaction is identified with a two-electron oxidation from Cr(II) to Cr(IV) with chloride transfer, followed by the slower reaction of Cr(IV) with Cr(II) to produce $CrCl^{2+}$ and Cr^{3+}

$$\mathrm{Cr(II)} + \mathrm{Pt(IV)} \longrightarrow \mathrm{Cr^{IV}Cl} + \mathrm{Pt(II)} \qquad (5)$$

$$\mathrm{Cr^{IV}Cl} + \mathrm{Cr(II)} \longrightarrow \mathrm{CrCl^{2+}} + \mathrm{Cr^{3+}} \qquad (6)$$

This mechanism again accounts for the stoichiometry and kinetics in excess Cr^{2+} but not the results in excess Pt(IV) since the faster initial reaction would here oxidize more than half of the Cr(II) to $Cr^{IV}Cl$. The excess $Cr^{IV}Cl$ might disproportionate or oxidize water to give Cr(III) but in any case would produce more than 50% $CrCl^{2+}$. Disproportionation of Cr(IV) is eliminated by the observation that no Cr(VI) is found; all of the Cr^{2+} is oxidized to Cr(III) products.

To account satisfactorily for both the stoichiometry and kinetics in both excess Cr^{2+} and excess Pt(IV), we suggest that the redox reactions (eq 7 and 8) are complete in the initial stage of the reaction and that the subsequent absorbance changes correspond to reactions of the initially formed chromium(III) products (eq 9 and 10). According to this mechanism reaction 7 is the

$$\mathrm{Cr^{2+}} + \mathrm{Pt(IV)} \xrightarrow{k_1} \mathrm{Cr^{IV}Cl} + \mathrm{Pt(II)} \qquad (7)$$

$$\mathrm{Cr^{IV}Cl} + \mathrm{Cr^{2+}} \xrightarrow{\text{fast}} \mathrm{Cr^{III}{}_2Cl} \qquad (8)$$

$$\mathrm{Cr^{III}{}_2Cl} \longrightarrow \mathrm{Cr^{3+}} + \mathrm{CrCl^{2+}} \qquad (9)$$

$$\mathrm{Cr^{III}{}_2Cl} + \mathrm{Cr^{2+}} \longrightarrow \mathrm{Cr^{3+}} + \mathrm{CrCl^{2+}} + \mathrm{Cr^{2+}} \qquad (10)$$

rate-determining reduction of $Pt(NH_3)_5Cl^{3+}$ directly to $Pt(NH_3)_4^{2+}$ by an inner-sphere two-electron transfer producing a $Cr^{IV}Cl$ species which is rapidly reduced to some dimeric chlorochromium(III) intermediate. The rate of the redox reaction is given by (2) in excess Cr^{2+}, but since two Cr^{2+} are consumed in the sum of (7) and (8), the rate in excess Pt(IV) is

$$\frac{-d[\mathrm{Cr(II)}]}{dt} = 2k_1[\mathrm{Pt(IV)}][\mathrm{Cr(II)}] = k_{\mathrm{obsd}}[\mathrm{Cr(II)}] \qquad (11)$$

This accounts for the observation that the rate of the initial increase in absorbance in excess Pt(IV) is definitely faster than in excess Cr^{2+} although the fit to eq 11 shown in Figure 5 is not very satisfactory due to the complication of the succeeding absorbance changes.

In the presence of excess Cr^{2+} the $Cr^{III}{}_2Cl$ intermediate is hydrolyzed by parallel Cr^{2+}-independent and Cr^{2+}-dependent reactions. The Cr^{2+}-dependent pathway is an example of a Cr^{2+}-catalyzed hydrolysis reaction of which there are many examples, although this appears to be one of the faster reported.[3b] In the absence of excess Cr^{2+} the $Cr^{III}{}_2Cl$ intermediate undergoes a slower hydrolysis reaction to $CrCl^{2+}$ and Cr^{3+}. Under both conditions the final chromium(III) products are equivalent amounts of $CrCl^{2+}$ and Cr^{3+} in agreement with the observations at pH 0–2.

In the presence of ionic chloride the $Cr^{III}{}_2Cl$ intermediate is not observed; presumably a $Cr^{III}{}_2Cl_2$ intermediate is rapidly hydrolyzed to $2CrCl^{2+}$. This and other interpretations of some of the observations must remain speculative. The decrease of the $CrCl^{2+}$ product as the acidity is lowered probably occurs in conjunction with reaction 8 since loss of chloride in (9) seems less probable. The observation of dimeric $(CrOH)_2^{4+}$ lends support to the mechanism involving the Cr(IV) oxidation state, since some two-electron oxidations of Cr^{2+} apparently produce $(CrOH)_2^{4+}$. The relative proportions of the various Cr(III) products are probably a complicated function of the hydrogen ion dependencies of (8)–(10) and will require a study under carefully controlled conditions. We are presently examining the use of aluminum perchlorate solutions as a buffer for these studies.

In summary, it appears that two-electron inner-sphere oxidations of Cr^{2+} can be quite rapid, that the Cr(IV) intermediate produced is very rapidly reduced to Cr(III) by Cr^{2+}, and that the immediate product(s) of the latter reaction undergoes complex hydrolysis reactions to monomeric chromium(III) products.

Acknowledgments.—The authors wish to acknowledge many helpful discussions with Professors R. G. Pearson and G. P. Haight, Jr. This work was supported in part by grants from the National Institutes of Health, GM-07488 and -16168.