relatively slow substitution reaction of Cr(II) followed by an outer-sphere electron transfer which is quite rapid. This mechanism is not the only possible explanation for the current lowering noted in the dipyridyl system. The polarographic reversibility[4,15] of the reduction of $Cr(bipy)_2(H_2O)_2{}^{3+}$ (eq 12) indicates that the oxidation of the corresponding Cr(II) species at the dme is rapid, perhaps rapid enough to compete with the outer-sphere process proposed by Baker and Mehta. In the case of reduction of Cr(III) in the presence of EDTA, Tanaka has proposed that the reoxidation of the Cr(II)–EDTA complex produced at the dme proceeds at the electrode surface, negating the reduction current of $Cr(H_2O)_6{}^{3+}$. From these two systems, it is apparent that, in the case of reversible reactions, the question of whether a specific redox reaction occurs *at* the electrode or in the diffusion layer is open.

In contrast to the two systems discussed above, Cr(II) oxalate complexes are not oxidized at the dme in potential regions studied. This enables one to exclude the possibility of the reaction occurring at the electrode and unambiguously indicates a reaction in the diffusion layer.

(15) A. A. Vlček, *Nature*, **189**, 383 (1961).

The rate-determining step of the oxalate mechanism is the reduction of a Cr(III) species by a more highly complexed Cr(II) complex. We have previously studied this type of reaction in bulk[5] and have attempted to correlate the rate of such reactions with electrochemical parameters.[16]

The special roles played by bis-bidentate Cr(II) complexes in both the bipyridyl and the oxalate systems is interesting. In view of the known proclivity of Cr(II) to form tetragonally distorted complexes, it is reasonable to assume that the *trans* complexes are more stable than the *cis*. The rate of electron transfer between the Cr(II) and the Cr(III) oxalate species is much more rapid than the correponding aquo ion rate; this may well indicate a specific *trans* effect on the electron transfer. Such specific steric effects have been discussed in recent papers from this laboratory[17] and also by Haim, *et al.*[18] It would not be surprising if the involvement of π systems caused different effects in the case of oxalate and dipyridyl complexes of the reductant than in the NH_3 and ethylenediamine complexes of the oxidant studied previously.

(16) J. H. Walsh and J. E. Earley, *Inorg. Chem.*, **3**, 343 (1964).
(17) R. D. Cannon and J. E. Earley, *J. Am. Chem. Soc.*, **88**, 1872 (1966).
(18) D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966).

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The Reduction of Some Platinum(IV) Complexes with Tris(bipyridine)chromium(II) Ion[1a,b]

By JAMES K. BEATTIE[1c] AND FRED BASOLO

The stoichiometry and kinetics of the reduction of several Pt(IV) complexes to Pt(II) by $[Cr(bipy)_3]^{2+}$ have been investigated. In most cases, a second-order rate law is observed and rate constants at 25° are reported. The rate of reduction of the amine complex, $[Pt(en)_3]^{4+}$, is 20 times faster than that of its conjugate base, $[Pt(en)_2(en-H)]^{3+}$. A general parallel of rate constants with polarographic half-wave potentials and with the rates of reduction of analogous Co(III) complexes is noted. These results suggest that the Pt(IV) complexes are reduced by a rate-determining one-electron process *via* Pt(III) intermediates.

Introduction

Studies of the reduction of substitution-inert metal ion complexes with a variety of reducing agents have led to important conclusions regarding the mechanisms of redox reactions.[2] Complexes of Co(III) and Cr(III) have been investigated extensively, and some experi-

(1) (a) Presented in part before the Great Lakes Regional Meeting of the American Chemical Society, Chicago, Ill., June 1966; (b) taken in part from the Ph.D. thesis of J. K. B., Northwestern University, 1967; (c) NSF Coop Fellow, 1964–1966, to whom correspondence should be addressed at the Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill. 61801.
(2) For recent reviews see (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 6; (b) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962); (c) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961); (d) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

ments with Rh(III), Ir(III), and Ru(III) have been reported. Two types of mechanism have emerged from these studies, involving either an inner-sphere or an outer-sphere activated complex. For example, with Cr^{2+} as the reducing agent definite evidence for an inner-sphere mechanism can be obtained[3] for the reduction of $[Co(NH_3)_5Cl]^{2+}$, whereas with $[Cr(bipy)_3]^{2+}$ an outer-sphere mechanism is indicated.[4]

The substitution-inert octahedral complexes of platinum(IV) have not been investigated in reactions with these types of reducing agents. The stable oxidation states of platinum differ by two electrons, whereas

(3) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).
(4) (a) A. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 42 (1960); (b) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

most of the reactions of substitution-inert oxidants studied previously involve only one-electron changes. Accordingly, an investigation of the kinetics and mechanisms of the reduction of Pt(IV) complexes with a variety of reducing agents has been undertaken. This article describes the reduction of some Pt(IV) complexes with $[Cr(bipy)_3]^{2+}$.

Experimental Section

Preparation of Materials.—All of the platinum(IV) compounds used are known complexes prepared by standard procedures. A few new perchlorate salts were isolated. Platinum was analyzed gravimetrically by ignition of the complex to platinum metal. This method is generally unsuitable for perchlorate and nitrate salts which deflagrate on heating. Chloride ion was analyzed by potentiometric titration with standard silver nitrate solution using a combined silver–mercurous sulfate electrode with a Radiometer TTT1 automatic titrator. Coordinated chloride ion was analyzed similarly after reduction of the complex with alkaline hydrazine sulfate, acidification with nitric acid, and filtration to remove metallic platinum. Perchlorate ion was analyzed gravimetrically as tetraphenylarsonium perchlorate.[5] Analyses for H and N were performed by Micro-Tech Laboratories, Skokie, Ill.

The following compounds were prepared according to the references cited with the analytical results. *Anal.* Calcd for $[Pt(en)_3]Cl_4$:[8] Pt, 37.7. Found: Pt, 37.9. Calcd for $[Pt(NH_3)_6]Cl_4 \cdot H_2O$:[7] Pt, 42.7; Cl, 30.8. Found: Pt, 42.6; Cl, 30.6. Calcd for $[Pt(NH_3)_5Cl]Cl_3$:[8] Pt, 46.2; Cl, 25.2. Found: Pt, 45.9; Cl, 25.3. Calcd for $[Pt(NH_3)_5I]_2(CO_3)_3$:[9] Pt, 39.3. Found: Pt, 38.9. Calcd for $[Pt(NH_3)_5OH](NO_3)_3$:[7] N, 23.2; H, 3.11. Found: N, 23.0; H, 3.14. Calcd for *trans*-$[Pt(NH_3)_4ClOH](NO_3)_2$:[10] Cl, 8.1. Found: Cl, 8.3. Calcd for *trans*-$[Pt(en)_2(OH)_2]Cl_2$:[11] Pt, 46.4; Cl, 16.8. Found: Pt, 46.3; Cl, 16.8. K_2PtCl_4 was prepared according to ref 12. The compounds $[Pt(NH_3)_5Cl](NO_3)_3$, *trans*-$[Pt(NH_3)_4Cl_2](NO_3)_2$, and *cis*-$[Pt(NH_3)_4Cl_2]Cl_2$ were prepared previously in this laboratory by R. C. Johnson.

The perchlorate salt of $[Pt(en)_3]^{4+}$ was prepared from the chloride salt by metathesis with silver perchlorate followed by precipitation with concentrated perchloric acid. *Anal.* Calcd for $[Pt(en)_3](ClO_4)_4$: ClO_4, 51.3. Found: ClO_4, 51.3. Recrystallization of $[Pt(NH_3)_5Cl]Cl_3$ from dilute hydrochloric acid gives the monohydrate. *Anal.* Calcd for $[Pt(NH_3)_5Cl]Cl_3 \cdot H_2O$: Pt, 44.3. Found: Pt, 44.1. Precipitation with concentrated hydrochloric acid gives the anhydrous salt. Perchlorate salts of chloro- and bromopentaammineplatinum(IV) were prepared from the respective phosphate salts by solution in dilute perchloric acid and precipitation with concentrated perchloric acid. *Anal.* Calcd for $[Pt(NH_3)_5Cl](ClO_4)_3$: ClO_4, 50.0; Cl, 5.78. Found: ClO_4, 48.5; Cl, 5.38. Calcd for $[Pt(NH_3)_5Br]$$(ClO_4)_3$: ClO_4, 45.5. Found: ClO_4, 46.5. The compound $[Pt(NH_3)_5I]CO_3 \cdot HCO_3$ was obtained by dissolving $[Pt(NH_3)_5I]_2$$(CO_3)_3$ in dilute perchloric acid and precipitating by addition of a concentrated solution of sodium carbonate. *Anal.* Calcd for $[Pt(NH_3)_5I]CO_3 \cdot HCO_3$: Pt, 37.0. Found: Pt, 36.9.

A modification of the method described in the literature[13] was used to prepare $[Cr(bipy)_3](ClO_4)_2$. Solid $Cr(OAc)_2 \cdot H_2O$ (0.9 mmole) was added to a deoxygenated solution of 10 ml of perchloric acid (0.23 M) and 5 ml of methanol containing 2,2′-bipyridine (3 mmoles). After cooling to 0° the resulting black

precipitate was collected on a filter under a nitrogen atmosphere, washed with deoxygenated water and deoxygenated methanol, and dried under vacuum and then over P_2O_5 in a nitrogen atmosphere. The compound was analyzed for perchlorate ion gravimetrically and for chromium spectrophotometrically as chromate after alkaline oxidation with hydrogen peroxide.[14] *Anal.* Calcd for $[Cr(bipy)_3](ClO_4)_2$: Cr, 7.23; ClO_4, 27.7. Found: Cr, 7.26; ClO_4, 27.5.

Concentrated sodium perchlorate stock solutions were prepared by neutralizing reagent grade sodium carbonate or sodium hydroxide with perchloric acid. All other materials used were of the highest quality available.

All solutions involving chromium(II) were carefully deoxygenated by bubbling nitrogen gas through them for at least 30 min. The nitrogen was purified of traces of oxygen by bubbling it through two concentrated (>1 M) solutions of chromous chloride and then through a solution of potassium hydroxide.

Solutions of $[Cr(bipy)_3]^{2+}$ contained at least 2×10^{-3} molar excess bipyridine after mixing. This ensures that at least 90% of the Cr(II) is present as the tris(bipyridine)chromium(II) ion.[4a,15]

Owing to the low solubility and slow rate of solution of $[Cr(bipy)_3](ClO_4)_2$ in perchlorate media, solutions were prepared by deoxygenating a solution of bipyridine and perchloric acid, adding $[Cr(bipy)_3](ClO_4)_2$, and, after this had dissolved, adding an aliquot of concentrated sodium perchlorate solution. From our observations and kinetic experiments reported in the literature the solubility product at 25° can be estimated as less than 6×10^{-6} M^3. In certain experiments employing 2,6-lutidine as a buffer, an aliquot of concentrated lutidine solution was added near the end of the deoxygenation procedure in order to avoid substantial loss of lutidine by transpiration.

Stoichiometry Experiments.—The stoichiometry of the reaction of excess $[Cr(bipy)_3]^{2+}$ with several of the Pt(IV) complexes was examined by potentiometric titration using a platinum foil electrode, a saturated calomel reference electrode, and a Beckman Model G pH meter. A solution of $[Cr(bipy)_3]^{2+}$ was standardized by potentiometric titration of a deoxygenated standard Fe(III) solution. A known volume of this standard Cr(II) solution was added to a deoxygenated solution containing a weighed quantity of a Pt(IV) complex. After a suitable interval the excess Cr(II) was titrated with the standard Fe(III) solution. In two blank experiments a known volume of Cr(II) solution was added to a solution containing $[Pt(en)_2]Cl_2$ but no Pt(IV) oxidant. After several minutes the Cr(II) was titrated with Fe(III), with the results that 97 and 93% of the added Cr(II) were titrated. The low values are attributed to partial air oxidation of the Cr(II) during the experiment. Some of the kinetic experiments also provide information regarding the stoichiometry.

Kinetic Experiments.—A rapid-mixing stopped-flow apparatus constructed by Moore[16] after a design of Sturdevant[17] was used in most experiments. This apparatus was modified for greater sensitivity by increasing the signal to noise ratio for small transmittance changes. Fluctuations in tungsten lamp intensity were reduced by operating the lamp from a bank of four 6-v lead storage batteries. The Beckman DU phototube was replaced by a high gain photomultiplier, EMI 6256B, powered by a John Fluke Model 405B high-voltage power supply. The photomultiplier signal was sent through an offset and RC filter circuit[1b] regulated by a Philbrick PR 30 power supply. The signal was observed on a storage-type oscilloscope and recorded with a Polaroid camera.

The reactions were monitored by observing the decrease in optical density at 562.5 mμ, a maximum[4a] for $[Cr(bipy)_3]^{2+}$. No other reactant or product absorbs appreciably at this wavelength. The initial concentration of Pt(IV) oxidant was calcu-

(5) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1321 (1964).
(6) F. Basolo, J. C. Bailar, and B. R. Tarr, *ibid.*, **72**, 2433 (1950).
(7) J. R. Hall and R. A. Plowman, *Australian J. Chem.*, **8**, 158 (1955).
(8) "Gmelin's Handbuch der Anorganischen Chemie," Verlag Chemie, Berlin, Vol. 68D, 1953, p 484.
(9) I. I. Chernyaev and V. S. Orlova, *Russ. J. Inorg. Chem.*, **6**, 653 (1961).
(10) Reference 8, p 490.
(11) Reference 8, p 507.
(12) G. B. Kaufman and D. O. Cowen, *Inorg. Syn.*, **7**, 239 (1963).
(13) Reference 8, Vol. 52C, 1965, p 14.

(14) C. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).
(15) J. M. Crabtree, D. W. March, J. C. Thomkins, R. J. P. Williams, and W. C. Fernelius, *Proc. Chem. Soc.*, 336 (1961).
(16) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **5**, 1523 (1966).
(17) J. M. Sturdevant in "Rapid Mixing and Sampling Techniques in Biochemistry," B. Chance, *et al.*, Ed., Academic Press Inc., New York, N. Y., 1964, p 89.

lated from the weight of complex used to prepare the reagent solution. The concentration of $[Cr(bipy)_6]^{2+}$ was obtained by direct observation of the optical density of the Cr(II) solution in the flow apparatus just prior to a kinetic run. Despite all precautions, a slight loss in Cr(II) concentration ($(1-2) \times 10^{-6} M$) was observed when a dilute solution ($<10^{-5} M$) was mixed with a deoxygenated solution of the same ionic strength containing no Pt(IV) oxidant. Consequently, the rate constant for the reduction of dissolved O_2 by $[Cr(bipy)_3]^{2+}$ was determined. In order to use larger concentrations of Cr(II), 0.1 M NaCl was used as the medium. Three experiments employing concentrations of Cr(II) in the range $(4.9-8.0) \times 10^{-5} M$ and about $10^{-6} M$ O_2 gave decreases in optical density which resulted in linear plots of log $(D_t - D_\infty)$ against time. Second-order rate constants of $(3.3 \pm 0.3) \times 10^5 M^{-1} sec^{-1}$ were calculated by dividing the observed first-order constant by the Cr(II) concentration. One experiment employed excess O_2. Reaction of an air-saturated 0.1 M NaCl solution with a more concentrated Cr(II) solution resulted in oxidation of $2 \times 10^{-4} M$ Cr(II). Since the concentration of O_2 in this solution is estimated to be 1.2×10^{-4} M from solubility data,[18] this result suggests that the reaction observed is a 2-equiv oxidation–reduction. Reaction of this air-saturated solution with a dilute solution of $[Cr(bipy)_3]^{2+}$ produced a first-order change in optical density with a second-order rate constant calculated to be $5.3 \times 10^5 M^{-1} sec^{-1}$ if a value of $1.0 \times 10^{-4} M$ is used for the concentration of O_2. This is in fair agreement with the value obtained using excess Cr(II).

Most experiments were performed using pseudo-first-order conditions with an excess of platinum(IV) oxidant. Transmittance changes were from 95 to 100%, in which case the observed oscilloscope trace is directly proportional to the concentration change. Second-order conditions were also used, both for the faster reactions and as a check on the stoichiometry. Rapid stopped-flow kinetic experiments using second-order conditions are generally more difficult than with pseudo-first-order conditions because the time axis of the oscilloscope trace is uncertain with respect to the zero time of the reaction. The reactions studied here present a favorable case, however, since only $[Cr(bipy)_3]^{2+}$ absorbs at the wavelength used. By assuming a stoichiometry for the reaction observed, the instantaneous concentration of Pt(IV) oxidant can be calculated from the known initial concentration of Pt(IV) and the observed concentration of $[Cr(bipy)_3]^{2+}$. Thus, for the reactions studied the stoichiometry is

$$Pt(IV) + 2Cr(II) \longrightarrow products \qquad (1)$$
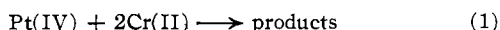
In most cases the observed rate law is

$$-\frac{d[Pt(IV)]}{dt} = -\frac{1}{2}\frac{d[Cr(II)]}{dt} = k[Pt(IV)][Cr(II)] \qquad (2)$$

For pseudo-first-order conditions of excess Pt(IV)

$$-\frac{d[Cr(II)]}{dt} = k_{obsd}[Cr(II)] \qquad (3)$$

$$k_{obsd} = 2k[Pt(IV)] \qquad (4)$$

For second-order conditions, assuming

$$[Pt(IV)] = [Pt(IV)]_0 - \frac{1}{2}([Cr(II)]_0 - [Cr(II)]) \qquad (5)$$

the second-order rate constant k can be obtained from the integrated rate law using the observed time dependence of the concentration of Cr(II).

Results

Stoichiometry and Product Identification.—The stoichiometry of the reduction of $[Pt(en)_3]^{4+}$ was examined directly by potentiometric titration. These experiments require considerably more concentrated solutions than were used in the kinetic studies. Con-

sequently, the ionic strength was not maintained at 0.1 M NaClO$_4$ owing to the low solubility of $[Cr(bipy)_3](ClO_4)_2$. An excess of a standardized solution of $[Cr(bipy)_3]^{2+}$ was added to a solution of $[Pt(en)_3]Cl_4$ (0.02 M) and HClO$_4$ ($4 \times 10^{-5} M$). Titration of the excess Cr(II) indicated 2.3 moles of Cr(II) was oxidized for each mole of Pt(IV). The stability of $[Pt(en)_2]^{2+}$ in the presence of excess $[Cr(bipy)_3]^{2+}$ was established by mixing solutions of the two ions and observing no change in optical density due to the oxidation of $[Cr(bipy)_3]^{2+}$. These results are taken as evidence of a 2Cr(II):Pt(IV) stoichiometry since errors due to extraneous oxidation of Cr(II) would lead to a ratio larger than 2:1.

The stoichiometry of the reduction of $[Pt(NH_3)_6]^{4+}$, $[Pt(NH_3)_5Cl]^{3+}$, $[Pt(NH_3)_5Br]^{3+}$, and $[Pt(NH_3)_5I]^{3+}$ was determined to be 2Cr(II):Pt(IV) from kinetic experiments by observation of the over-all change in optical density and conformance of the optical density changes to a second-order rate law based on this stoichiometry. The stoichiometry of the reduction of trans-$[Pt(NH_3)_4Cl_2]^{2+}$ and trans-$[Pt(NH_3)_4ClOH]^{2+}$ is assumed to be the same.

The Pt(II) ion, $[Pt(en)_2]^{2+}$, was identified as a product of the reduction of $[Pt(en)_3]^{4+}$ by isolating the insoluble Magnus-type salt, $[Pt(en)_2][PtCl_4]$, from the product solution. About 20 ml of a 0.01 M $[Cr(bipy)_3]^{2+}$ solution (0.20 mmole) was added to 10 ml of a 0.02 M solution of $[Pt(en)_3]Cl_4$ (0.20 mmole), producing an immediate color change from the purple of $[Cr(bipy)_3]^{2+}$ to yellow. Several milliliters of a solution of K_2PtCl_4 (0.30 mmole) in HCl was added, and, after cooling in an ice–salt bath, about 33 mg (0.05 mmole) of the pink salt, $[Pt(en)_2][PtCl_4]$, was collected. The composition of the salt was confirmed by Pt analysis. The Pt(II) product collected corresponds to at least 50% of the Pt(IV) reduced, this being a lower limit found by assuming that no Cr(II) was lost due to air oxidation. The solubility of $[Pt(en)_2][PtCl_4]$ in water at 0° was found to be less than 210 mg l.$^{-1}$.

Qualitative evidence for $[Pt(NH_3)_4]^{2+}$ as a Pt(II) product of the reduction of $[Pt(NH_3)_6]^{4+}$ and $[Pt(NH_3)_5Cl]^{3+}$ was obtained by precipitation of a green salt, presumably the insoluble Magnus green salt, $[Pt(NH_3)_4][PtCl_4]$, on addition of a solution of K_2PtCl_4 to the product solutions.

The nature of the chromium oxidation product was not investigated.[4,19,20]

Kinetics.—The kinetics of the reduction of $[Pt(en)_3]^{4+}$ were studied under pseudo-first-order conditions with Pt(IV) in excess in the concentration ranges of $(6-82) \times 10^{-5} M$ Pt(IV) and $(1-2) \times 10^{-5} M$ Cr(II). The observed rate constant for the first-order disappearance of $[Cr(bipy)_3]^{2+}$ was linearly dependent on the Pt(IV) concentration. The second-order rate constants k calculated from eq 6 were found to depend on the pH. Buffer solutions of perchloric acid–

(18) "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 271.

(19) B. R. Baker and B. D. Mehta, *Inorg. Chem.*, **4**, 848 (1965).

(20) R. Murray and G. M. Waind, "Proceedings of the Seventh International Conference on Coordination Chemistry," Almqvist and Wiksell, A.B., Uppsala, Sweden, 1962, p 309.

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bipyridine and perchloric acid–bipyridine–lutidine were used. The measured pH of the product solution effluent from the flow apparatus agreed within 0.1 pH unit with that calculated from the buffer composition using reported pK_a values (bipyridine, 4.44; lutidine, 6.72). There is no evidence that the sterically hindered lutidine was involved in coordination to the labile Cr-(II).

The calculated second-order rate constants could be fitted to a titration-type curve with eq 6 as shown in Figure 1.

$$k = \frac{k_a[\text{H}^+] + k_b K_a}{K_a + [\text{H}^+]} \qquad (6)$$

where $k_a = 7.7 \times 10^3 \ M^{-1} \text{ sec}^{-1}$, $k_b = 4 \times 10^2 \ M^{-1} \text{ sec}^{-1}$, and $pK_a = 5.75$. Within experimental error the rate constants were independent of whether the chloride or perchlorate salt of $[\text{Pt(en)}_3]^{4+}$ was used.
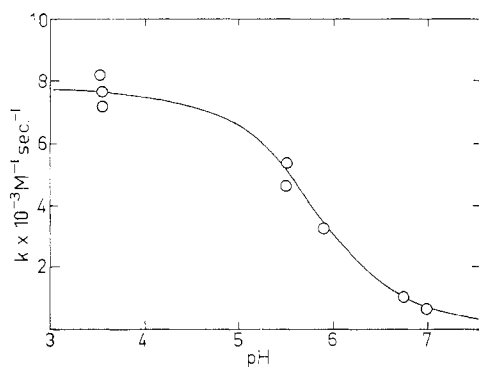

Figure 1.—pH dependence of the $[\text{Pt(en)}_3]^{4+}$–$[\text{Cr(bipy)}_3]^{2+}$ reaction at 25° and $\mu = 0.1$ (NaClO$_4$).

The results of kinetic experiments for the other Pt(IV) complexes are summarized in Table I. The observed decreases in optical density are consistent with a second-order rate law based on a 2Cr(II):Pt(IV) stoichiometry. Both pseudo-first-order and second-order conditions were used for the reduction of $[\text{Pt(NH}_3)_6]^{4+}$ and $[\text{Pt(NH}_3)_5\text{Cl}]^{3+}$ and consistent rate constants obtained over a large concentration range. For $[\text{Pt(NH}_3)_5\text{Br}]^{3+}$, $[\text{Pt(NH}_3)_5\text{I}]^{3+}$, and *trans*-$[\text{Pt(NH}_3)_4\text{Cl}_2]^{2+}$ the extreme rapidity of the reactions restricted the concentration ranges used. The results are fully consistent with a second-order rate law over the ranges observed.

Using a pseudo-first-order excess of *trans*-$[\text{Pt(NH}_3)_4\text{ClOH}]^{2+}$, a rapid decrease in optical density was observed followed by a much slower decrease. The rapid decrease is ascribed to the reduction of an impurity in the Pt(IV) preparation, probably *trans*-$[\text{Pt(NH}_3)_4\text{Cl}_2]^{2+}$.

No acid dependence was observed in the following pH ranges for the rate constants of the three complexes which are reduced more slowly: $[\text{Pt(NH}_3)_6]^{4+}$, pH 3.9–4.4; $[\text{Pt(NH}_3)_5\text{Cl}]^{3+}$, pH 3.9–5.7; $[\text{Pt(NH}_3)_4\text{ClOH}]^{2+}$, pH 4.1–5.5.

Experiments with $[\text{Pt(NH}_3)_6]^{4+}$ and $[\text{Pt(NH}_3)_5\text{Cl}]^{3+}$ in a 0.1 M NaCl medium gave rate constants

Table I

KINETIC RESULTS FOR REDUCTION OF Pt(IV) COMPLEXES BY $[\text{Cr(bipy)}_3]^{2+}$ IN 0.1 M NaClO$_4$ AT 25°

| Oxidant	[oxidant], $M \times 10^5$	[Cr-(bipy)$_3$]$^{2+}$, $M \times 10^5$	k, M^{-1} sec^{-1}	No. of expts
$[\text{Pt(NH}_3)_6]^{4+}$	1.3–113	2.0–3.6	$(7.7 \pm 1) \times 10^2$	3[a]
	4.0	5.9	4.8×10^2	1[b]
$[\text{Pt(NH}_3)_5\text{Cl}]^{3+}$	1.1–9.0	1.0–5.0	$(2.9 \pm 0.3) \times 10^5$	5[a]
	6.4–22.5	0.5–2.9	$(1.2 \pm 0.2) \times 10^5$	7[a,b]
$[\text{Pt(NH}_3)_5\text{Br}]^{3+}$	0.2–0.8	0.3–3.7	$(8 \pm 4) \times 10^6$	5[c]
$[\text{Pt(NH}_3)_5\text{I}]^{3+}$	0.5–2.0	1.0–2.0	$(3 \pm 1) \times 10^6$	3
trans-$[\text{Pt(NH}_3)_4\text{Cl}_2]^{2+}$	0.2–0.9	0.6–1.3	10^7	3
trans-$[\text{Pt(NH}_3)_4\text{ClOH}]^{2+}$	31–57	1–2	$(2.4 \pm 0.4) \times 10^3$	3

[a] Each is the average of four to six observations. [b] A 0.1 M NaCl solution was used in place of 0.1 M NaClO$_4$. [c] Each is the average of two observations.

smaller by about a factor of 2 than those observed in a 0.1 M NaClO$_4$ medium.

Discussion

Both the stoichiometric and kinetic evidence indicate that the observed reactions are net two-electron reductions of octahedral platinum(IV) complexes to square-planar platinum(II) ions. Except for $[\text{Pt(en)}_3]^{4+}$, a simple second-order rate law is observed, first order each in Pt(IV) and Cr(II). Consequently, the reaction mechanisms must involve the unstable oxidation states of either Pt(III) or Cr(IV), but no further information on this question can be obtained directly from the rate law.

The pH-dependent rate law for the reduction of $[\text{Pt(en)}_3]^{4+}$ is readily explained in terms of reduction of both the parent complex and its conjugate base

$$[\text{Pt(en)}_3]^{4+} \xrightleftharpoons{K_a} [\text{Pt(en)}_2(\text{en-H})]^{3+} + \text{H}^+ \qquad (7)$$
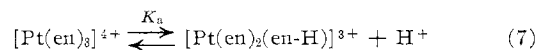
The value of pK_a of 5.75 obtained from the kinetic experiments agrees well with the value of 5.45 reported by Grinberg[21] for different conditions. It is noteworthy that the amido form reacts $^1/_{20}$ as rapidly as the amine form in spite of the reduction in coulombic repulsion between oxidant and reductant. A somewhat smaller decrease in the rate of reduction by [Cr(bipy)$_3$]$^{2+}$ is observed[4a] for $[\text{Co(NH}_3)_5\text{OH}]^{2+}$ compared with $[\text{Co(NH}_3)_5\text{OH}_2]^{3+}$. It is likely that these differences reflect an increased thermodynamic stability of the more slowly reacting complexes. The amido group apparently stabilizes the Pt(IV) oxidation state more effectively than coordinated amine.

Table II summarizes the rate constants for the reduction of the Pt(IV) complexes together with rate constants available for reduction of analogous cobalt(III) complexes by $[\text{Cr(bipy)}_3]^{2+}$. The order of reactivity of the halogenopentaamminecobalt(III) complexes is F < Cl < Br, with no value given for the iodide complex which is presumably too fast to measure. The observed values for the platinum(IV) complexes are Cl < I < Br, but little significance can be attributed to the iodide–bromide inversion, for the reactions are very fast and the rate constants correspondingly inaccurate.

(21) A. A. Grinberg and Kh. I. Gil'dergershel, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 479 (1948).

TABLE II

RATES OF REDUCTION OF Pt(IV) AND Co(III)[a]
COMPLEXES BY [Cr(bipy)₃]²⁺ AT
25° AND μ = 0.1 (NaClO₄)

Complex	k, M⁻¹ sec⁻¹	Complex	k, M⁻¹ sec⁻¹
[Pt(NH₃)₅Cl]³⁺	(2.9 ± 0.3) × 10⁶	[Co(NH₃)₆Cl]²⁺	8 × 10⁵
[Pt(NH₃)₅Br]³⁺	(8 ± 4) × 10⁶	[Co(NH₃)₅Br]²⁺	5 × 10⁶
[Pt(NH₃)₅I]³⁺	(3 ± 1) × 10⁶	[Co(NH₃)₅I]²⁺	...
[Pt(en)₃]⁴⁺	(7.7 ± 1.0) × 10³	[Co(en)₃]³⁺	1.8 × 10²
[Pt(en)₂(en-H)]³⁺	(4 ± 1) × 10²		
[Pt(NH₃)₆]⁴⁺	(7.7 ± 1.0) × 10²	[Co(NH₃)₆]³⁺	6.9 × 10²
trans-[Pt(NH₃)₄Cl₂]²⁺	10⁷		
trans-[Pt(NH₃)₄ClOH]²⁺	(2 ± 1) × 10³		

[a] J. P. Candlin, J. Halpern, and D. Trimm, *J. Am. Chem. Soc.*,
86, 1019 (1964).

The reduction of [Pt(en)₃]⁴⁺ is ten times more rapid
than [Pt(NH₃)₆]⁴⁺, whereas [Co(en)₃]³⁺ is reduced only
one-fourth as rapidly as [Co(NH₃)₆]³⁺. Better orbital
overlap for electron transfer due to the smaller size of
[Co(NH₃)₆]³⁺ was suggested[4a] as a reason for its more
rapid reduction, but other factors must be important
such as solvation energies, specific hydrogen-bond inter-
actions, or differences in the over-all free energy change
of the reaction.

The most striking aspect of the relative rates is the
extraordinary stabilization of the Pt(IV) oxidation state
conferred by hydroxo ligands. The reduction of *trans*-
[Pt(NH₃)₄ClOH]²⁺ is less than ¹/₁₀₀₀ as rapid as that of
trans-[Pt(NH₃)₄Cl₂]²⁺. Preliminary experiments[1b] in-
dicate that the reduction of *trans*-[Pt(en)₂(OH)₂]²⁺ is
considerably slower than that of *trans*-[Pt(NH₃)₄-
ClOH]²⁺ and that [Pt(NH₃)₅OH]³⁺ is reduced much
more slowly than [Pt(NH₃)₅Cl]³⁺. The slow reduction
of the hydroxo complexes is probably again the result
of thermodynamic stabilization of the Pt(IV) oxidation
state but further work with other reducing agents is
necessary before definite conclusions can be drawn.

The wide variations in rate constants for the various
Pt(IV) complexes have a close parallel in the half-wave
potentials for the irreversible polarographic reduction
of the complexes at the dropping-mercury electrode.
The half-wave potentials available in the literature for
some platinum(IV) complexes are presented in Table
III. In addition, the following qualitative order of
half-wave potentials has been reported for [Pr(NH₃)₅-
X]ⁿ⁺ complexes:[22] Br < Cl < NH₃ < OH.

In those cases for which a complete polarographic
study was reported the current–potential curves corre-
spond to an irreversible two-electron reduction. Slight
inflections were noted in the reductions of [Pt(en)₃]⁴⁺
and [Pt(NH₃)₆]⁴⁺, indicating consecutive one-electron
reductions at potentials separated by about 0.1 v,
suggesting a transient Pt(III) intermediate.

The irreversible nature of the polarographic reduc-

(22) J. R. Hall and R. A. Plowman, *Australian J. Chem.*, 8, 158 (1955).

TABLE III

POLAROGRAPHIC HALF-WAVE POTENTIALS FOR
REDUCTION OF PLATINUM(V) COMPLEXES

Complex	$E_{1/2}$ vs. sce, v[a,b]
trans-[Pt(en)₂Cl₂]²⁺	0.08
[Pt(NH₃)₆]⁴⁺	−0.18, −0.28
[Pt(en)₃]⁴⁺	−0.20, −0.30
trans-[Pt(en)₂ClOH]²⁺	−0.22
[Pt(en)₃]⁴⁺ in 1 M NH₄OH	−0.59
trans-[Pt(en)₂(OH)₂]²⁺	−0.82

[a] See ref 22. [b] R. C. Johnson, F. Basolo, and R. G. Pearson,
J. Inorg. Nucl. Chem., 24, 59 (1962).

tions precludes the application of the Marcus[23] theory
using the observed half-wave potentials as E^0 values.
The relative order of the half-wave potentials is about
the same as the relative order of the rate constants for
chemical reduction, with the exception of [Pt(NH₃)₆]⁴⁺,
which is chemically reduced more slowly than one would
predict from the electrochemical results.

The correlation between the half-wave potentials
and rates of chemical reduction as well as the parallel
observed between the rates of reduction of the Co(III)
and Pt(IV) complexes suggests that the rate-determin-
ing step in the reduction of the Pt(IV) complexes is an
outer-sphere, one-electron transfer to generate a Pt(III)
intermediate. A similar correlation between electro-
chemical and chemical reduction has been established
for the Co(III) complexes[24] and extended to reduction
by substitution-inert [Ru(NH₃)₆]²⁺,[25] which must pro-
ceed by an outer-sphere mechanism. Such correla-
tions are predicted by the Marcus theory for outer-
sphere electron-transfer reactions.

The fate of the postulated Pt(III) intermediate is un-
certain. It could react with a second [Cr(bipy)₃]²⁺
in a second rapid step, but other possibilities involving
Cr(IV) or disproportionation cannot be excluded.
No kinetic or spectrophotometric evidence for an inter-
mediate was observed at 562.5 mμ. Identification of the
Cr(III) oxidation product is desirable, but recent work
indicates that the exchange reactions between Cr(II)
and Cr(III) bipyridine complexes are rapid and com-
plex.[19] These reactions must be understood before
interpretation of the results of the Pt(IV) oxidation
would be meaningful.

(23) R. A. Marcus, *Ann. Rev. Phys. Chem.*, 15, 155 (1964).
(24) See footnote *a* of Table II.
(25) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, 86, 1686 (1964).