Redox Catalysis of the Formation of $Cr(C_2O_4)_2(H_2O)_2^-$ from $Cr(C_2O_4)(H_2O)_4^+$ in the Vicinity of the Dropping-Mercury Electrode[1]

By DUŠAN I. BUSTIN, JOSEPH E. EARLEY,[2] and DEMETRIOS PETRIDIS

The polarographic limiting diffusion current for the one-electron reduction of $Cr(C_2O_4)(H_2O)_4^+$ is lowered by the presence of oxalate in solution. A mechanism involving formation of $Cr(C_2O_4)_2(H_2O)_2^-$ by a reaction in the diffusion layer is proposed. The relationship of this mechanism to other Cr(III)–Cr(II) reactions is discussed.

The polarographic reduction wave of $Cr(C_2O_4)(H_2O)_4^+$ has been described by Hamm and Davis[3] in connection with studies of the reaction of $Cr(H_2O)_6^{3+}$ with oxalate ion in solution. The half-wave potential of this reduction wave was given as -1.15 v and the wave was ascribed to the Cr(III)–Cr(II) reduction. We have observed that oxalate ion added to the solution causes a decrease of the cathodic current of the $Cr(C_2O_4)(H_2O)_4^+$ reduction. A sufficient explanation of this is a mechanism involving reaction of $Cr(C_2O_4)(H_2O)_4^+$ with $C_2O_4^{2-}$ catalyzed by the Cr(II) species produced at the electrode. This type of mechanism has not previously been reported. It is related to mechanisms reported in chromium–dipyridyl systems[4] but is more similar to systems studied in the bulk as examples of nonbridging ligand effects on the Cr(III)–Cr(II) electron-transfer reaction.[5]

Experimental Section

$Cr(C_2O_4)(H_2O)_4^+$ was prepared by heating appropriate amounts of $Cr(H_2O)_6(ClO_4)_3$ and sodium oxalate in aqueous solution at pH 3–4. This species was separated from other Cr(III) complexes, unreacted Cr(III), and excess oxalate using Dowex 50W-X8 cation-exchange resin. Excess oxalate was rinsed away with water, and the complex was eluted with 0.1 M $HClO_4$. The concentration of the complex in solution was determined spectrophotometrically after oxidation of Cr^{3+} to CrO_4^{2-} by H_2O_2 in alkaline medium.

A Sargent XV polarograph was used for recording current–voltage curves. The capillary employed had a drop time of 3.4 sec and a flow rate of 2.08 mg sec^{-1} (in short circuit with sce and a 64-cm column). A Kalousek polarographic cell was used for measurements at 24°. A water-jacketed cell was used for temperature-dependence studies. All potentials are given $vs.$ the saturated calomel reference electrode.

Ionic strength was maintained at 0.2 M with $NaClO_4$ prepared from Na_2CO_3. Water, triply distilled from a quartz still, and analytical grade reagents were employed. No maximum suppressor was used. All experimental points reported are results of extrapolation of the current to the time of mixing, because a very slow reaction takes place in the body of solution which also lowers the reduction wave.[3]

Results

We were able to confirm the results of Hamm and Davis[3] concerning the half-wave potential and height

of the irreversible reduction wave of $Cr(C_2O_4)(H_2O)_4^+$ at the dme at pH 4–5. If excess oxalate is added to the solution, however, the limiting current is decreased, but the half-wave potential remains constant. The dependence of the height of the wave on the concentration of oxalate added to the solution is shown in Figure 1.

The limiting current of the $Cr(C_2O_4)(H_2O)_4^+$ reduction decreases quite rapidly with concentration of oxalate in the region of low oxalate concentration. At higher oxalate concentration, it maintains a constant value (Figure 1). This indicates that the process determining the current lowering at high oxalate concentrations does not involve oxalate ion, which means that ionic equilibria are fast and are driven to completion at these concentrations.

A temperature change of 28.3° (from 11.2 to 39.5°) elevated the diffusion current of $Cr(C_2O_4)(H_2O)_4^+$ by 48% while Δi increased by 190%. This suggests that a rate process is responsible for the current lowering. Reactions of the depolarizer preceding the electrode reactions proper would be expected to involve rupture or formation of a Cr(III)–O bond; such reactions are too slow to be responsible for the effect observed. The behavior described can, however, be explained by chemical reaction of the reduction product.

Cr(II) is oxidized by excess oxalate.[6] At room temperature, pH 4, $[Cr(II)] = 4.2 \times 10^{-3}$ M, and $[C_2O_4^{2-}] = 3.1 \times 10^{-2}$ M, the reaction was finished in about 1 min. Reaction was followed by recording the time dependence of the anodic current at the dme at potentials of 0.0 and -0.2 v. At a potential of -0.1 v and at more negative potentials, no zero-time anodic current was observed. From this we conclude that chromium-(II) oxalate complexes are not oxidized at dme in that potential region. This is in agreement with the measurements of Pecsok and Lingane.[7]

This result eliminates the possibility that oxalate complexes of Cr(II), formed by the reaction of $Cr(C_2O_4)(H_2O)_4^0$ with excess oxalate, could be oxidized at dme and therefore be responsible for the decrease of reduction current, although this mechanism is observed in the case of the Cr(III)–EDTA complex.[8]

$Cr(C_2O_4)_2(H_2O)_2^{2-}$, however, could react with Cr-

(1) Supported by the U. S. Atomic Energy Commission under Contract AT 40-1-2842.
(2) To whom correspondence may be addressed.
(3) R. E. Hamm and R. E. Davis, *J. Am. Chem. Soc.*, **75**, 3085 (1953).
(4) B. R. Baker and B. D. Mehta, *Inorg. Chem.*, **4**, 848 (1965).
(5) J. B. Hunt and J. E. Earley, *J. Am. Chem. Soc.*, **82**, 5312 (1960).

(6) R. M. Milburn and H. Taube, *J. Phys. Chem.*, **64**, 1776 (1960).
(7) R. L. Pecsok and J. J. Lingane, *J. Am. Chem. Soc.*, **72**, 189 (1950).
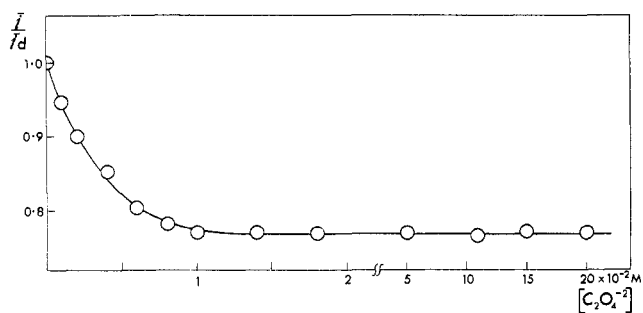(8) N. Tanaka and K. Ebata, *J. Electroanal. Chem.*, **8**, 120 (1964).

Figure 1.—Dependence of reduction current of $Cr(C_2O_4)$-$(H_2O)_4{}^+$ on concentration of oxalate at $24°$; $[Cr(C_2O_4)(H_2O)_4{}^+]$ $= 10^{-3} M$; ionic strength $0.2 M$.

$(C_2O_4)(H_2O)_4{}^+$ forming $Cr(C_2O_4)_2(H_2O)_2{}^-$ which is not electroreducible in the potential region of interest.[3] This reaction would inactivate part of the electroactive $Cr(C_2O_4)(H_2O)_4{}^+$ in the diffusion layer of the dme and thereby account for the decrease of reduction current.

The bulk phase reaction of $Cr(C_2O_4)(H_2O)_4{}^+$ with oxalate was studied in the presence of Cr(II) using polarographic analysis of the system. An oxalate solution was injected into a solution containing $Cr(C_2O_4)$-$(H_2O)_4{}^+$ and $Cr(H_2O)_6{}^{2+}$ in a 4:1 molar ratio. The pH of both solutions was 4.8.

Figure 2 shows the results schematically. The original wave of $Cr(C_2O_4)(H_2O)_4{}^+$ collapses as oxalate is added up to a molar ratio of 1:1. This indicates that reaction of $Cr(C_2O_4)(H_2O)_4{}^+$ with oxalate to form the bix-oxalato species occurs. The increase of the wave of the product $Cr(C_2O_4)_2(H_2O)_2{}^-$ could not be observed $(E_{1/2} = -1.44 \text{ v})$ because this wave coincides with the reduction wave of Cr(II), further complicated by catalyzed proton reduction. When a quantity of oxalate equivalent to the Cr(III) present has been added, however, the three-electron reduction wave of Cr-$(C_2O_4)_2(H_2O)_2{}^-$ can be seen (Figure 2, curve d). If further portions of oxalate are added, the wave of $Cr(C_2O_4)_2(H_2O)_2{}^-$ collapses, probably owing to formation of $Cr(C_2O_4)_2{}^{3-}$, the presence of which, however, has not been proved. Since the concentration of free oxalate in solution is very low during the experiment, decrease of the limiting current of $Cr(C_2O_4)(H_2O)_4{}^+$ is negligible (see Figure 1).

As seen in Figure 2, the anodic wave corresponding to oxidation of Cr^{2+} collapses very slightly after each addition of oxalate. This is probably due to oxidation of Cr^{2+} by oxalate, as described by Milburn and Taube.[6] The ratio of Cr^{2+} lost to the amount of oxalate added, however, is quite low, which indicates that this reaction is much slower than catalyzed formation of $Cr(C_2O_4)_2(H_2O)_2{}^-$. After an equivalent quantity of $C_2O_4{}^{2-}$ has been added, however, Cr^{2+} is rapidly destroyed.

Formation of $Cr(C_2O_4)_2(H_2O)_4{}^-$ from $Cr(C_2O_4)$-$(H_2O)_4{}^+$ is a slow process in the absence of Cr(II). The experiments reported in Figure 2 demonstrate that Cr(II) is an efficient catalyst for this process.[5]

Reduction of $Cr(H_2O)_6{}^{3+}$ in the presence of $C_2O_4{}^{2-}$
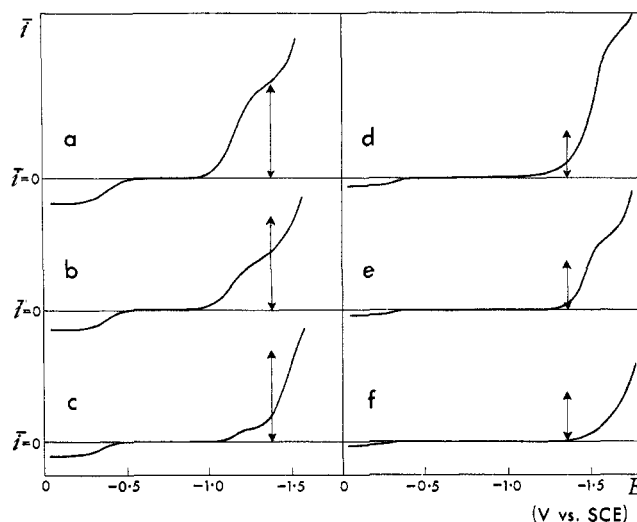
Figure 2.—Polarographic record of titration of $Cr(C_2O_4)$-$(H_2O)_4{}^+$ by oxalate in the presence of Cr^{2+} (schematically). $A = 3.2 \times 10^{-5}$ mole—amount of $Cr(C_2O_4)(H_2O)_4{}^+$ present in solution; 7×10^{-6} mole of Cr^{2+} present in solution: (a) before oxalate addition, (b) $0.5A$ moles of oxalate added, (c) $0.9A$ moles of oxalate added, (d) $1.0A$ moles of oxalate added, (e) $1.5A$ moles of oxalate added, and (f) $2A$ moles of oxalate added. The arrows mean limiting diffusion current of A moles of $Cr(C_2O_4)$-$(H_2O)_4{}^+$ in the same volume of solution.

apparently involves a current lowering similar to the case reported here. However, the reduction is complicated by other effects and was not studied in detail.

Discussion

The following equations summarize the proposed reaction mechanism

$$Cr(C_2O_4)(H_2O)_4{}^+ + e^- \Longrightarrow Cr(C_2O_4)(H_2O)_4{}^0 \qquad (1)$$

$$Cr(C_2O_4)(H_2O)_4{}^0 + C_2O_4{}^{2-} \underset{k_2}{\overset{k_1(K_1)}{\rightleftharpoons}} Cr(C_2O_4)_2(H_2O)_2{}^{2-} + 2H_2O \quad (2)$$

$$Cr(C_2O_4)_2(H_2O)_2{}^{2-} + Cr(C_2O_4)(H_2O)_4{}^+ \underset{k_4}{\overset{k_3(K_2)}{\rightleftharpoons}}$$
$$Cr(C_2O_4)_2(H_2O)_2{}^- + Cr(C_2O_4)(H_2O)_4{}^0 \quad \text{slow} \quad (3)$$
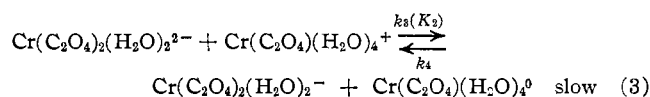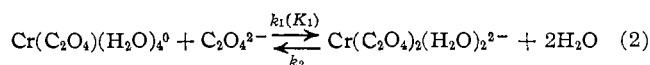
where K_1 and K_2 are formation constants and $\Longrightarrow$ denotes an irreversible electrode reduction.

The proposed reaction sequence can be understood as inactivation of $Cr(C_2O_4)(H_2O)_4{}^+$ by reaction with oxalate, catalyzed by the product of its electrode reduction. $Cr(C_2O_4)_2(H_2O)_2{}^{2-}$ is regenerated by reaction 2.

The following simple treatment of the problem should be understood as a first approximation.

Let us suppose that the inactivation reaction is slow (small current lowering) so that the concentration of the product, $Cr(C_2O_4)_2(H_2O)_2{}^-$, is low. If there is excess free oxalate in solution, it may be assumed that Cr^{2+} formed at the electrode is in the form of Cr-$(C_2O_4)_2(H_2O)_2{}^{2-}$ so that the concentration of Cr-$(C_2O_4)(H_2O)_4{}^0$ is very low. There are mainly two Cr species present in the diffusion layer

$$[Cr(C_2O_4)(H_2O)_4{}^+] + [Cr(C_2O_4)_2(H_2O)_2{}^{2-}] = A \qquad (4)$$
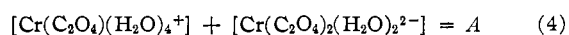
where A is the analytical bulk concentration of Cr-$(C_2O_4)(H_2O)_4{}^+$. If we neglect the backward reaction

(low $\Delta \bar{\imath}$ and hence low $[Cr(C_2O_4)_2(H_2O)_2{}^-]$ and low $[Cr(C_2O_4)(H_2O)_4{}^0]$) we can then write for the rate of the inactivation

$$R_x = \frac{d}{dt}[Cr(C_2O_4)(H_2O)_4{}^+]_x =$$
$$k_3[Cr(C_2O_4)(H_2O)_4{}^+]_x[Cr(C_2O_4)_2(H_2O)_2{}^{2-}]_x \quad (5)$$

The rate is a function of distance (subscript x) from the electrode. Let us suppose that the inactivation reaction is slow enough so that it does not significantly change the concentration gradients in the potential region of the limiting diffusion current. (This assumption will restrict the solution to be valid only for small $\Delta \bar{\imath}$.) Let us take the approximation of linear dependence of concentrations on distance from the electrode in the diffusion layer, with the concentration gradient being A/δ for both reacting components (δ is the thickness of the diffusion layer). It is possible to compute an average reaction rate over the diffusion layer[9]

$$\bar{R} = \frac{1}{\delta}\int_0^\delta R_x dx = \frac{1}{6}k_3A^2 \quad (6)$$

The decrease of current $\Delta \bar{\imath}$ is proportional to the average reaction rate

$$\Delta \bar{\imath} = nF\bar{q}\delta\bar{R} \quad (7)$$

where the mean drop surface area is $\bar{q} = 0.51m^{2/3}t_1{}^{2/3}$ (m being mercury flow rate and t_1 being drop time). The average value of the denominator of eq 25 in ref 10 over the drop time t_1 was used to evaluate δ.

$$\delta = \left(\frac{4}{21}\pi D t_1\right)^{1/2}$$

D is the diffusion coefficient and nF is the charge (in coulombs) exchanged per particle. This coincides with the von Stackelberg concept of the differential thickness of the diffusion layer.[10]

Inserting the Ilkovic equation

$$\bar{\imath}_d = 0.627nFD^{1/2}m^{2/3}t_1{}^{1/6}A$$

and expression 6 into eq 7, one obtains an equation for the current lowering

$$\frac{\Delta \bar{\imath}}{\bar{\imath}_d} = 0.015k_3t_1A \quad (8)$$

Figure 3 shows that a linear dependence holds for low values of $\Delta \bar{\imath}/\bar{\imath}_d$ where the conditions under which eq 8 was derived are fulfilled. From the slope of the linear part of the dependence of $\Delta \bar{\imath}$ on A (Figure 2), the value $k_3 = 1.05 \times 10^3 \ M^{-1} \sec^{-1}$ was computed for 24° and ionic strength 0.2 M.

Equation 8 is formally similar to the equation derived by Brdička[11] and Koutecký[12] for reduction of formaldehyde in unbuffered media, which also has auto-
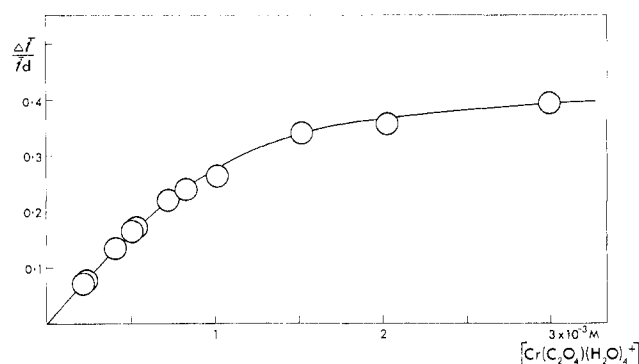

Figure 3.—Dependence of relative current lowering on concentration of $Cr(C_2O_4)(H_2O)_4{}^+$ at 24°; $[C_2O_4{}^{2-}] = 0.1 \ M$; ionic strength 0.2 M.
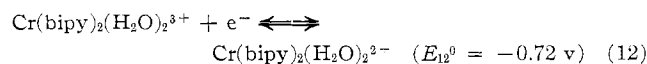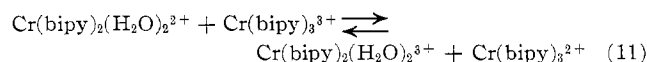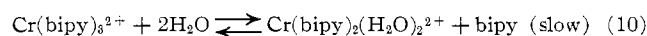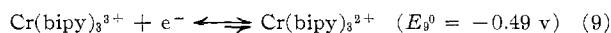
catalytic character. The two systems differ inasmuch as the formaldehyde system is in equilibrium in bulk, the reaction being caused by the decrease of concentration of one equilibrium component, whereas the $Cr(C_2O_4)(H_2O)_4{}^+$–$Cr(C_2O_4)_2(H_2O)_2{}^-$ system is far from equilibrium. Tausch[13] gives the value

$$K = \frac{[Cr(C_2O_4)_2(H_2O)_2{}^-]}{[Cr(C_2O_4)(H_2O)_4{}^+][C_2O_4{}^{2-}]} = 2.56 \times 10^6 \ M^{-1}$$

The high stability of the bis-oxalato Cr(III) complex is responsible for the reaction in the diffusion layer when catalytic concentrations of $Cr(C_2O_4)_2(H_2O)_2{}^{2-}$ are present.

From the dependence of current on free oxalate concentration (Figure 1) the value of K_1 can be estimated. It can be easily derived that the intersection of the limiting tangent to the curve at low $[C_2O_4{}^{2-}]$ and the line corresponding to the limit at high $[C_2O_4{}^{2-}]$ (the region where current does not depend on oxalate concentration) has its abscissa equal to $(1 + K_1A)/K_1$ (A is bulk phase concentration of $Cr(C_2O_4)(H_2O)_4{}^+$). The value of K_1 thus obtained is $(3.6 \pm 1) \times 10^2 \ M^{-1}$; $K_2 = K/K_1 \approx 10^4$ and $k_3 >> k_4$, as assumed.

The reaction described above is an example of the influence of a redox-catalyzed substitution reaction on an electrode reaction. Similar inactivation has been described by Baker and Mehta[4] for the reduction of $Cr(bipy)_3{}^{3+}$ [14]

$$Cr(bipy)_3{}^{3+} + e^- \rightleftharpoons Cr(bipy)_3{}^{2+} \quad (E_9{}^0 = -0.49 \text{ v}) \quad (9)$$

$$Cr(bipy)_3{}^{2+} + 2H_2O \rightleftharpoons Cr(bipy)_2(H_2O)_2{}^{2+} + bipy \text{ (slow)} \quad (10)$$

$$Cr(bipy)_2(H_2O)_2{}^{2+} + Cr(bipy)_3{}^{3+} \rightleftharpoons$$
$$Cr(bipy)_2(H_2O)_2{}^{3+} + Cr(bipy)_3{}^{2+} \quad (11)$$

$$Cr(bipy)_2(H_2O)_2{}^{3+} + e^- \rightleftharpoons$$
$$Cr(bipy)_2(H_2O)_2{}^{2+} \quad (E_{12}{}^0 = -0.72 \text{ v}) \quad (12)$$

where bipy means α,α'-bipyridyl, $\rightleftharpoons$ refers to reversible electrode reaction, and $E_9{}^0$ and $E_{12}{}^0$ are half-wave potentials.

The mechanism proposed for the bipyridyl system is a

(9) The concept of reaction layer as introduced by R. Brdička and K. Wiesner, *Collection Czech. Chem. Commun.*, **12**, 138 (1947), was not used here.

(10) J. Heyrovský and J. Kůta, "Principles of Polarography," Academic Press Inc., New York, N. Y., 1956, pp 80–83.

(11) R. Brdička, *Collection Czech. Chem. Commun.*, **20**, 387 (1955).

(12) J. Koutecký, *ibid.*, **21**, 652 (1956).

(13) W. Tausch, Thesis, Johann Wolfgang Goethe Universität, Frankfurt am Maine, 1961.

(14) A somewhat similar mechanism has been proposed to account for asymmetry of the reduction waves of $CrCl_2{}^+$ and Cr^{3+}: P. J. Elving and B. Zemel, *Can. J. Chem.*, **37**, 247 (1959). However, this effect has also been given an entirely different interpretation: R. Parsons and E. Passeron, *J. Electroanal. Chem.*, **12**, 524 (1966).

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]

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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).