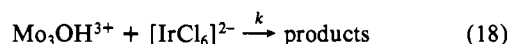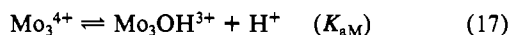oxalate $HC_2O_4^-$, followed by a faster step involving chelation (with displacement of a second H_2O). The three remaining H_2O's of $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ are not readily replaced.[4]

The aquation of NCS^- and monodentate oxalate and chelation of monodentate $HC_2O_4^-$ also proceed via conjugate-base paths. The acid dissociation constant (K_{aMT}) obtained for $[Mo_3O_4NCS(H_2O)_8]^{3+}$ is 0.19 M and the presence of the adjacent negatively charged NCS^- ligands brings about a decrease as compared to K_{aM} (0.42 M). For the monodentate oxalato complex $[Mo_3O_4(C_2O_4H)(H_2O)_8]^{3+}$ the composite term $K_{aMOx}K_{2Ox} = 1.51$ M is obtained, which cannot be compared directly with K_{aMT}. In this case, acid dissociation of the monodentate $C_2O_4H^-$ most likely gives the $[H^+]$ dependence in Figure 8. If this is the case, then the reverse step in (12) corresponding to addition of H_2O will be independent of $[H^+]$.

In an earlier study[13] of the $[IrCl_6]^{2-}$ oxidation of $Mo_3O_4^{4+}$ in 2 M H^+/Li^+ perchlorate (which indicated a rate law first order in both $[IrCl_6^{2-}]$ and $[Mo_3O_4^{4+}]$ (giving second-order rate constants k_{Ir})), it was possible to assign an inner-sphere mechanism. A dominant inverse $[H^+]$ dependence was reported. We are now able to reformulate the reaction as in (17) and (18). At 25 °C

$$Mo_3^{4+} \rightleftharpoons Mo_3OH^{3+} + H^+ \quad (K_{aM}) \qquad (17)$$

$$Mo_3OH^{3+} + [IrCl_6]^{2-} \xrightarrow{k} products \qquad (18)$$

with the exclusion of the two points at lower $[H^+]$ (solutions of $Mo_3O_4^{4+}$ in ClO_4^- are less stable under these conditions), a satisfactory linear plot of k_{Ir}^{-1} against ($K_a + [H^+]$) is obtained by using $K_{aM} = 0.42$ M (average value as determined above). This plot gives $k = 4.5$ M^{-1} s^{-1}, in very good agreement with k_{NCS} (4.8 M^{-1} s^{-1}) and k_{Ox} (3.3 M^{-1} s^{-1}). It appears therefore that the $[IrCl_6]^{2-}$ reaction is inner sphere and could well be substitution controlled.

The dominance of a conjugate-base I_d mechanism for substitution is of interest, because low-d-electron-population mononuclear hexaaqua ions, such as $Ti(III)(3d^1)$,[19] $V(III)(3d^2)$,[20] and

Mo(III)($4d^3$),[21,22] are known to react by an associative interchange (I_a) process. For Mo(IV)($4d^2$) in $Mo_3O_4^{4+}$ metal–metal bonding results in pseudo-eight-coordination at each Mo, and crowding of the Mo site appears to exclude an I_a process. Existing evidence suggests that substitution reactions involving conjugate-base forms proceed by an I_d mechanism.[23]

In the present studies we have no information as to the extent of ion-pair formation preceding the replacement of H_2O by NCS^-, $HC_2O_4^-$, or $[IrCl_6]^{2-}$. The similarity of the $[IrCl_6]^{2-}$ data suggests that there are no large differences between 1- and 2- reactants. Ion pairing is likely to be at the aqua ligand face on each Mo(IV), thus avoiding interactions with negatively charged μ-oxo core ligands. The effective positive charge on each Mo(IV) at 1.33 is small.

Finally, it is of interest that UV–vis absorbance changes corresponding to the formation of the conjugate base of $Mo_3O_4^{4+}$ are small in solutions containing HPTS, which itself absorbs strongly below 300 nm. Even at $[H^+] \sim 0.42$ M, when $[Mo_3^{4+}]$ and $[Mo_3OH^{3+}]$ are equal, changes in the UV–vis absorbance spectrum are barely detectable above 300 nm. Similarly, it is extremely difficult distinguishing between the chloro complexes $Mo_3O_4Cl^{3+}$ and $Mo_3O_4Cl_2^{2+}$[4] and aqua $Mo_3O_4^{4+}$ from UV–vis spectra. Substitution at external (c and d) coordination sites has only a very mild effect on absorbance of the $Mo_3O_4^{4+}$ core. Oxalate and thiocyanate, which give charge-transfer contributions, are somewhat unusual therefore in this context.

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Reductive Quenching of ^2E Cr(bpy)$_3^{3+}$ by Fe^{2+} and Cr(bpy)$_3^{2+}$

Andreja Bakac,* Khurram Zahir, and James H. Espenson*

The reductive quenching of the doublet excited state of Cr(bpy)$_3^{3+}$ by Fe(H$_2$O)$_6^{2+}$ at pH 1 in aqueous perchlorate solutions produces Cr(bpy)$_3^{2+}$; $k = (5.3 \pm 0.3) \times 10^6$ M^{-1} s^{-1} at 25 °C and 1 M ionic strength. Concurrent reduction of ^2E Cr(bpy)$_3^{3+}$ by Cr(bpy)$_3^{2+}$, unrecognized in previous studies, provides a catalytic route for the deactivation of the excited state. This reaction can be eliminated by the addition of Fe(H$_2$O)$_6^{3+}$, which rapidly oxidizes the chromium(II) complex; $k = 9.2 \times 10^8$ M^{-1} s^{-1}. The quenching of ^2E Cr(bpy)$_3^{3+}$ by Cr(bpy)$_3^{2+}$ was demonstrated by the effect of Fe^{2+} on the excited state lifetimes and yields of Cr(bpy)$_3^{2+}$ in experiments with Fe^{2+} as quencher. This required solution of the differential rate equations by numerical integration; the program KINSIM was used and gave the value $k_{Cr} = (5 \pm 3) \times 10^9$ M^{-1} s^{-1}. The indicated quenching reaction was also observed directly.

Introduction

The high reduction potential[1,2] and long lifetime (~ 70 μs)[1-3] of ^2E Cr(bpy)$_3^{3+}$, denoted *Cr(bpy)$_3^{3+}$, as well as its reactivity in energy-transfer reactions,[4-8] have made *Cr(bpy)$_3^{3+}$ one of the

most intensely studied metal-centered excited states in the past decade.

$$*Cr(bpy)_3^{3+} + e^- \rightarrow Cr(bpy)_3^{2+} \quad E° = 1.46 \text{ V}$$

$$*Cr(bpy)_3^{3+} \rightarrow Cr(bpy)_3^{3+} \quad E_{0-0} = 1.7 \text{ eV}$$
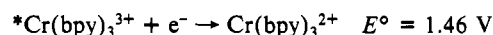
Of all the electron-transfer reactions of *Cr(bpy)$_3^{3+}$ reported to date, that with Fe^{2+} has received the most attention. The initial

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report[9] provided evidence for electron transfer by identifying $Cr(bpy)_3^{2+}$ as a transient product in a (presumably) sulfate medium at 1 M ionic strength (eq 1), $k_1 = 4.1 \times 10^7$ M^{-1} s^{-1}.

$$*Cr(bpy)_3^{3+} + Fe^{2+} \xrightarrow{k_{Fe}} Cr(bpy)_3^{2+} + Fe^{3+} \qquad (1)$$
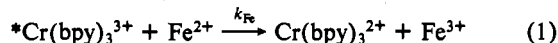
Subsequent electron transfer from $Cr(bpy)_3^{2+}$ ($E^\circ_{3+/2+} = -0.26$ V)[10,11] to Fe^{3+} (eq 2) restores the ground-state reactants, $k_2 = 7.3 \times 10^8$ M^{-1} s^{-1}[9] at 0.2 M ionic strength.

$$Cr(bpy)_3^{2+} + Fe^{3+} \xrightarrow{k_2} Cr(bpy)_3^{3+} + Fe^{2+} \qquad (2)$$
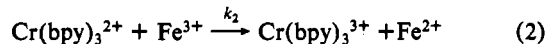
Later studies provided additional kinetic data on reaction 1 at 25 °C in aqueous chloride ($k_{Fe} = 3.7 \times 10^7$ M^{-1} s^{-1}, 1 M HCl)[12] and sulfate solutions (2.8×10^7 M^{-1} s^{-1}, 0.05 M H_2SO_4;[13] 1.6×10^7 M^{-1} s^{-1}, 1 M H_2SO_4[11]), and at 15 °C in chloride (4×10^7 M^{-1} s^{-1}, 1 M HCl)[14] and perchlorate media (7×10^6 M^{-1} s^{-1}, 1 M HClO$_4$).[14] The kinetic studies were extended to the doublet excited states of a series of related polypyridine complexes of Cr(III).[12,13] An excellent correlation between the observed rate constants and the driving force for electron transfer provided strong evidence that electron transfer is the primary step. The other possibility, energy transfer followed by electron transfer from *Fe^{2+} to $Cr(bpy)_3^{3+}$, is considered less favorable in view of the symmetry mismatch between the donor and acceptor orbitals involved[12,13] and the additional reorganizational energy required.

In the course of our recent study[15] of the kinetics and mechanism of the quenching of $*Cr(bpy)_3^{3+}$ by some organochromium and organocobalt complexes (eq 3), we observed unusual kinetic

$$*Cr(bpy)_3^{3+} + R-M^{2+} \rightarrow Cr(bpy)_3^{2+} + R-M^{3+} \qquad (3)$$

dependences on the concentrations of $*Cr(bpy)_3^{3+}$ and the organometallic complexes. The problem was traced to the previously unrecognized quenching (eq 4) of $*Cr(bpy)_3^{3+}$ by the $Cr(bpy)_3^{2+}$ that is produced in the primary quenching step.

$$Cr(bpy)_3^{2+} + *Cr(bpy)_3^{3+} \xrightarrow{k_{Cr}} Cr(bpy)_3^{3+} + Cr(bpy)_3^{2+} \qquad (4)$$
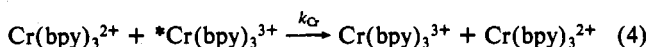
Provided our interpretation is correct, the catalytic loss of $*Cr(bpy)_3^{3+}$ in reaction 4 should also be observed in other electron transfer reactions of $*Cr(bpy)_3^{3+}$. Quenching by Fe^{2+} (eq 1) seems in particular to be a reaction in which $Cr(bpy)_3^{2+}$ would interfere, because of the relatively low value of k_{Fe}, especially in the perchlorate medium. Any contribution from the side reaction of eq 4 should be easily recognized and measured.

This paper reports our results of the complete kinetic study of reactions 1 and 4 in aqueous HClO$_4$. We find in three types of experiments that the quenching by $Cr(bpy)_3^{2+}$ does indeed contribute significantly to the overall rate constant for the loss of $*Cr(bpy)_3^{3+}$. Some experiments were also conducted in chloride and sulfate media, where the effect of quenching by $Cr(bpy)_3^{2+}$ is less striking. The analysis of the data in the presence and absence of Fe^{3+}, a selective scavenger for $Cr(bpy)_3^{2+}$, has enabled us to estimate the value of k_{Cr}.

Experimental Section

Tris(bipyridine)chromium(III) perchlorate was prepared according to the published procedure,[11] and the purity was checked by comparison with the reported UV-visible spectrum.[16] Acidic solutions of Fe^{2+} were
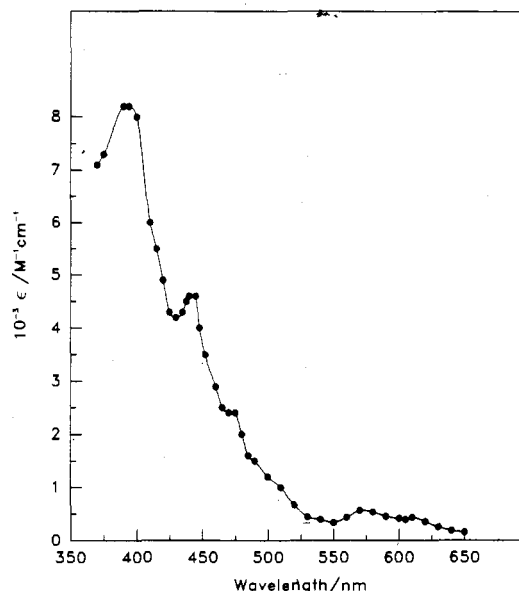

Figure 1. UV-visible spectrum of $*Cr(bpy)_3^{3+}$ at pH 1 in 1 M aqueous perchlorate.

$$10^4[Fe^{2+}]/M$$

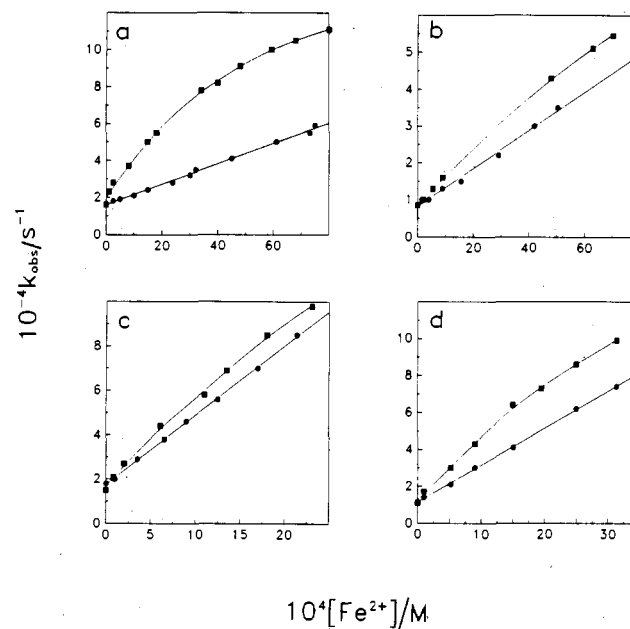**Figure 2.** Plots of k_{obsd} versus the concentration of Fe^{2+} in the absence (squares) and presence (circles) of Fe^{3+} in 0.1 M HClO$_4$ + 0.9 M LiClO$_4$ (a, b), 1 M HCl (c), and 1 M H$_2$SO$_4$ (d). The respective concentrations (μM) of $*Cr(bpy)_3^{3+}$ in the absence and presence of Fe^{3+} are as follows: (a) 40, 40; (b) 5, 5; (c) 30, 6; (d) 30, 9.

prepared from (NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O (99.9%, Aldrich) under argon and treated with Zn/Hg to ensure the complete reduction of the traces of Fe^{3+} present. Solutions of $Cr(bpy)_3^{2+}$ were prepared from Cr^{2+}_{aq} and excess ligand.[17]

The kinetic data were obtained by use of the laser flash photolysis system described earlier.[18] The excitation of $Cr(bpy)_3^{3+}$ was provided by a 600-ns pulse from a Phase-R Model DL-1100 flashlamp pumped dye laser by the use of LD 423 dye. The subsequent optical changes were monitored at the absorption ($\lambda = 445$ nm)[12] or emission ($\lambda = 727$ nm)[11,19] maxima of $*Cr(bpy)_3^{3+}$, or at an absorption maximum of $Cr(bpy)_3^{2+}$ at

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Table I. Summary of the Rate Constants[a] at 25 °C for the Reduction of *Cr(bpy)$_3^{3+}$ by Fe^{2+} in Aqueous Solutions Containing Perchlorate, Chloride, and Sulfate

medium	$10^{-6}k/M^{-1} s^{-1}$	ref
0.1 M HClO$_4$ + 0.1 M LiClO$_4$	4.3	this work
0.1 M HClO$_4$ + 0.9 M LiClO$_4$	5.2	this work
1 M HClO$_4$	7.0[b,c]	14
1 M HCl	31	this work
	37[c]	11
	40[b,c]	14
1 M H$_2$SO$_4$	20	this work
1 M H$_2$SO$_4$	16[c]	13
0.05 M H$_2$SO$_4$	28[c]	12

[a] In the presence of 2.5–21 mM Fe^{3+}; [*Cr(bpy)$_3^{3+}$] = 5–37 μM. [b] At 15 °C. [c] No Fe^{3+} added.

λ = 560 nm.[16] The yields of Cr(bpy)$_3^{2+}$ were calculated from absorbance changes at 560 nm by use of $\Delta\epsilon$ = ($\epsilon_{Cr(II)} - \epsilon_{Cr(III)}$) = 4800 M^{-1} cm^{-1}.[16]

The absorption spectrum of *Cr(bpy)$_3^{3+}$ was determined in the wavelength range 370–650 nm. The concentration of the excited state used in the calculation of the molar absorptivities was determined by use of a 1.7 × 10^{-5} M solution of Ru(bpy)$_3^{2+}$ in 0.1 M NaCl in D$_2$O as an actinometer. The parameters used in the calculation were the intrinsic lifetime of *Ru(bpy)$_3^{2+}$ (τ = 1.0 μs)[20] and the difference in molar absorptivities at 370 nm, $\epsilon_{*Ru(II)} - \epsilon_{Ru(II)}$ = 2.23 × 10^4 M^{-1} cm^{-1}.[21] The spectrum of *Cr(bpy)$_3^{3+}$ obtained is shown in Figure 1.

The rate constant k_2 for the oxidation of Cr(bpy)$_3^{2+}$ by Fe^{3+} was measured in perchlorate media by quenching *Cr(bpy)$_3^{3+}$ by Fe^{2+} in the presence of an excess of Fe^{3+} and monitoring the subsequent disappearance of Cr(bpy)$_3^{2+}$ at 560 nm. The values obtained are: 9.2 × 10^8 M^{-1} s^{-1} (μ = 1.0 M, pH 0), 9.1 × 10^8 (μ = 1.0 M, pH 1), and 1.0 × 10^8 (μ = 0.15 M, pH 1.0).

All the experiments were carried out under an atmosphere of oxygen-free argon at 25 ± 1 °C.

Results

Kinetics. The quenching of *Cr(bpy)$_3^{3+}$ by a large excess of Fe^{2+} is first-order in *Cr(bpy)$_3^{3+}$ (eq 5). For a given initial

$$-d[*Cr(bpy)_3^{3+}]/dt = k_{obsd}[*Cr(bpy)_3^{3+}] \quad (5)$$

concentration of the excited state, the pseudo-first-order rate constants in 1 M HClO$_4$ vary nonlinearly with the concentration of Fe^{2+} (Figure 2). The effect is more pronounced in the series of experiments with a higher initial concentration of *Cr(bpy)$_3^{3+}$. It is our intention to demonstrate that the full description of the system requires the three-term rate law of eq 6, where the term k_0 represents the intrinsic rate constant for the decay of *Cr(bpy)$_3^{3+}$.[22]

$$k_{obsd} = k_0 + k_{Fe}[Fe^{2+}] + k_{Cr}[Cr(bpy)_3^{2+}] \quad (6)$$

Previous work,[9,11–14] as well as the experiments described below, has established that Fe^{2+} reduces *Cr(bpy)$_3^{3+}$ to Cr(bpy)$_3^{2+}$, a much better reductant than Fe^{2+} itself. It seemed reasonable to assume that the reductive quenching of *Cr(bpy)$_3^{3+}$ by Cr(bpy)$_3^{2+}$ might be interfering with the determination of k_{Fe}. Subsequent experiments were performed in the presence of Fe^{3+}, which oxidizes Cr(bpy)$_3^{2+}$ readily (k = 9.1 × 10^8 M^{-1} s^{-1} at μ = 1.0 M) yet does not quench the excited state. The values of k_{obsd} are lower, and the dependence on [Fe^{2+}] is linear in the presence of Fe^{3+} (Figure 2). Under these conditions the disappearance of *Cr(bpy)$_3^{3+}$ is well described by eq 7. The rate constant k_{Fe} is independent of

$$-d[*Cr(bpy)_3^{3+}]/dt = (k_0 + k_{Fe}[Fe^{2+}])[*Cr(bpy)_3^{3+}] \quad (7)$$

the concentration of Fe^{3+} in the range 2.5–20 mM, as expected

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(22) The rate constant k_0 is independent of the concentration of the ground-state complex in 1 M chloride (1.6 × 10^4 s^{-1}) and sulfate (1.1 × 10^4 s^{-1}) media. In 1 M HClO$_4$, however, k_0 increases from 6.3 × 10^3 to 2.3 × 10^4 s^{-1} as [Cr(bpy)$_3^{3+}$] increases from 0.2 × 10^{-4} to 8 × 10^{-4} M.

from a reagent whose sole function is to scavenge Cr(bpy)$_3^{2+}$. In addition, the measured rate constants are no longer dependent on [*Cr(bpy)$_3^{3+}$]$_0$.

The kinetics in the chloride and sulfate solutions are affected by the presence of Fe^{3+} to a much smaller extent than in 1 M perchlorate (Figure 2, Table I).

Yields of Cr(bpy)$_3^{2+}$. In a series of experiments with [*Cr(bpy)$_3^{3+}$] = 40 μM in the absence of Fe^{3+}, the yield of Cr(bpy)$_3^{2+}$ increased with [Fe^{2+}] in qualitative agreement with eq 7. The actual concentrations of Fe^{2+} needed to reach a constant concentration of Cr(bpy)$_3^{2+}$ are, however, higher than predicted by eq 7, again indicating the operation of an additional pathway that does not produce Cr(bpy)$_3^{2+}$. The simulation of the kinetic data by use of the program KINSIM[23] and the rate constants k_0 = 1.6 × 10^4 s^{-1}, k_{Fe} = 5.1 × 10^6 M^{-1} s^{-1}, and k_2 = 9.1 × 10^8 M^{-1} s^{-1} yielded k_{Cr} = (5 ± 3) × 10^9 M^{-1} s^{-1} at 25 °C and 1.0 M ionic strength (HClO$_4$ + LiClO$_4$). The direct measurement of k_{Cr} was attempted by monitoring the luminescence quenching of *Cr(bpy)$_3^{3+}$ by Cr(bpy)$_3^{2+}$ in the presence of an excess of free bipyridine.[17] A rapid quenching of *Cr(bpy)$_3^{3+}$ was indeed observed, but the photochemical decomposition of Cr(bpy)$_3^{2+}$ in the flash rendered the results unreliable for quantitative data.

The UV–visible spectrum of *Cr(bpy)$_3^{3+}$ obtained in this work, Figure 1, shows maxima at 445 and 385 nm, in good agreement with the previously published data.[3,12,14,24,25] The respective molar absorptivities, 4600 and 8300 M^{-1} cm^{-1}, are reasonably close to the published ones with the exception of ref 14, which gives ϵ_{390} = 3.1 × 10^3 M^{-1} cm^{-1}. The rate constant k_2 in 1.0 M perchlorate medium, 9.2 × 10^8 M^{-1} s^{-1}, compares well with values reported previously: 1.0 × 10^9 (1 M HClO$_4$),[14] 1.44 × 10^9 (1 M HCl),[2] and 7.3 × 10^8 (0.2 M sulfate).[2] As expected for these charge types, k_2 is smaller at μ = 0.15 M, 1.0 × 10^8 M^{-1} s^{-1}.

Discussion

The apparent non-first-order kinetic dependence on [Fe^{2+}] in the reduction of *Cr(bpy)$_3^{3+}$ by excess Fe^{2+} is undoubtedly caused by the occurrence of reaction 4. All the observations in this work, as well as our previous results on the quenching of *Cr(bpy)$_3^{3+}$ by the organochromium and organocobalt complexes[15] strongly support this interpretation.

At a constant [Fe^{2+}] the observed rate constants are higher in experiments that produce more Cr(bpy)$_3^{2+}$, i.e. those with higher initial concentrations of *Cr(bpy)$_3^{3+}$ (Figure 2). Similarly, the kinetic contribution from reaction 4 is most obvious at relatively low concentrations of Fe^{2+}. Both observations demonstrate the validity of eq 6, as does the fact that the quenching by Fe^{2+} (eq 1) in HCl and H$_2$SO$_4$ suffers less interference from reaction 4 because k_{Fe} is higher in these media. The scavenging of Cr(bpy)$_3^{2+}$ by Fe^{3+} causes the third term in eq 6 to disappear. The net effect of added Fe^{3+} is a decrease in k_{obsd} for the disappearance of *Cr(bpy)$_3^{3+}$, and a linear dependence of ($k_{obsd} - k_0$) on [Fe^{2+}] (eq 7).

The computer simulation of the reaction scheme based on eq 1, 2, 4 and 6 yields k_{Cr} near the diffusion-controlled limit. The value, (5 ± 3) × 10^9 M^{-1} s^{-1}, is close to that reported for the oxidation of Cr(bpy)$_3^{2+}$ by Ru(bpy)$_3^{3+}$ (k = 2.6 × 10^9 M^{-1} s^{-1}).[9] The rather large error reflects mainly the uncertainties in the concentrations of *Cr(bpy)$_3^{3+}$ and Cr(bpy)$_3^{2+}$.
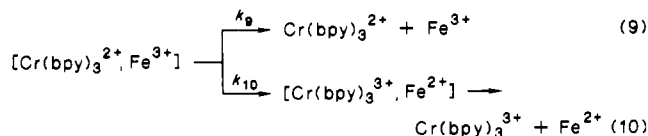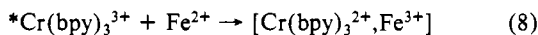
The acceptable fit of the kinetic data in the absence of Fe^{3+} to pseudo-first-order kinetics as in eq 5 is unexpected, since the importance of reaction 4 should increase as the quenching by Fe^{2+} progresses and [Cr(bpy)$_3^{2+}$] builds up. It appears that the adherence to the first-order rate law is fortuitous and can be accounted for by the relative importance of the three terms in eq 6 under different conditions. At the highest and lowest concentrations of Fe^{2+} the majority of the reaction is carried by the $k_{Fe}[Fe^{2+}]$ and k_0 terms, respectively, and pseudo-first-order behavior is expected. In the intermediate cases the increase in the

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importance of the term $k_{Cr}[Cr(bpy)_3^{2+}]$ during the reaction is apparently gradual enough that it does not affect the quality of the pseudo-first-order fits significantly. Indeed, the simulation of the kinetic traces by use of the program KINSIM shows this to be the case.

The low yields of $Cr(bpy)_3^{2+}$ obtained previously[14] in the reduction of $*Cr(bpy)_3^{3+}$ by Fe^{2+} in 1 M $HClO_4$ were rationalized on the basis of eq 8–10. According to this scheme the $Cr(bpy)_3^{2+}$

$$*Cr(bpy)_3^{3+} + Fe^{2+} \rightarrow [Cr(bpy)_3^{2+}, Fe^{3+}] \qquad (8)$$

$$[Cr(bpy)_3^{2+}, Fe^{3+}] \begin{cases} \xrightarrow{k_9} Cr(bpy)_3^{2+} + Fe^{3+} & (9) \\ \xrightarrow{k_{10}} [Cr(bpy)_3^{3+}, Fe^{2+}] \rightarrow \\ \qquad\qquad Cr(bpy)_3^{3+} + Fe^{2+} & (10) \end{cases}$$

and Fe^{3+}, formed by electron transfer, can either escape from the solvent cage (eq 9) or undergo secondary electron transfer within the cage to yield Fe^{2+} and $Cr(bpy)_3^{3+}$ (eq 10). On the basis of the yields of $Cr(bpy)_3^{2+}$ the ratio $k_9/k_{10} \sim 0.2$ was calculated.[14]

Our results indicate that the yield of $Cr(bpy)_3^{2+}$ is nearly quantitative ($\geq 80\%$) provided the concentration of Fe^{2+} used is high enough such that the second term of eq 6 dominates. For example, in an experiment with $[*Cr(bpy)_3^{3+}]_0 = 40$ μM and $[Fe^{2+}] = 0.18$ M, the concentration of $Cr(bpy)_3^{2+}$ produced was 35 μM. We thus conclude that most of the electron transfer events of eq 8 lead to the formation of free $Cr(bpy)_3^{2+}$ and Fe^{3+}, with the secondary electron transfer within the solvent cage playing at best a minor role, i.e. $k_9 \gg k_{10}$. This experimental result agrees well with the values of k_9 ($\sim 10^{10}$ s^{-1}) and k_{10} ($\sim 10^9$ s^{-1}) estimated from the theoretical equations[26] and the measured value of k_2 (k_2

$= k_{10}K_{IP}, K_{IP} \sim 1$).[26,27] The predicted yield of $Cr(bpy)_3^{2+}$ ($k_9/(k_9 + k_{10}) \sim 0.9$) is in good agreement with the observed value (≥ 0.80). We surmise that the low experimental concentrations of Fe^{2+}, as well as the use of the somewhat erroneous spectral data for $*Cr(bpy)_3^{3+}$, are responsible for the low values of k_9/k_{10} reported in ref 14.

The large driving force (1.71 eV) for the net reaction of eq 4, combined with the high self-exchange rate constants for the two reactants, places reaction 4 in the inverted region, yet the reaction is clearly diffusion-controlled. The same observation was made in several other highly exergonic reductions by $Cr(bpy)_3^{2+}$.[9,28] Among the many factors[11,28–31] that could be responsible for the rate constants being higher than predicted, the formation of excited-state $Cr(bpy)_3^{2+}$ (eq 11) and nuclear tunneling[9,11,28] seem

$$*Cr(bpy)_3^{3+} + Cr(bpy)_3^{2+} \rightarrow *Cr(bpy)_3^{2+} + Cr(bpy)_3^{3+} \quad (11)$$

most plausible. The products of reaction 11 are identical with those that would be formed in an energy-transfer process. At present we do not have sufficient experimental evidence that would allow us to distinguish between the possibilities mentioned.

Registry No. $Cr(bpy)_3^{3+}$, 15276-15-0; Fe^{2+}, 15438-31-0; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Cr(bpy)_3^{2+}$, 15276-15-0; $[Cr(bpy)_3](ClO_4)_3$, 23539-86-8; ClO_4^-, 14797-73-0; Cl^-, 16887-00-6; SO_4^{2-}, 14808-79-8.

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Selective Cleavage of the Pt–C(Alkyl) Bond in Alkylarylplatinum(II) Complexes and Mechanism of Cis to Trans Isomerization of the Resulting Solvento Complexes

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Protonolysis of the complexes cis-[Pt(PEt$_3$)$_2$(R)(Me)] (R = Me, Ph, mesityl) by H$^+$A$^-$ (A$^-$ = ClO$_4^-$, BF$_4^-$, *p*-toluenesulfonate) in methanol selectively cleaves the alkyl group, yielding cis-[Pt(PEt$_3$)$_2$(R)(MeOH)]$^+$ and methane. The rates show first-order dependence on complex and on proton concentrations, obeying the simple rate law $k_{obsd} = k_H[H^+]$. Steric hindrance on the Pt–C bond causes a decrease in rate. A mechanism is proposed that involves rate-determining attack of the proton on the Pt–C bond with release of methane in a three-center transition state. The resulting methanol intermediate spontaneously converts to its trans isomer, and for all systems the isomeric equilibrium lies well to the side of the trans form. At 303.16 K for R = Me, $k_i = 6.76 \times 10^{-3}$ s^{-1}, $\Delta H^* = 106 \pm 4$ kJ mol^{-1}, $\Delta S^* = +63 \pm 12$ J K^{-1} mol^{-1}; for R = Ph, $k_i = 11.9 \times 10^{-3}$ s^{-1}, $\Delta H^* = 112 \pm 3$ kJ mol^{-1}, $\Delta S^* = +84 \pm 8$ J K^{-1} mol^{-1}; for R = mesityl, $k_i = 28.8 \times 10^{-3}$ s^{-1}, $\Delta H^* = 106 \pm 3$ kJ mol^{-1}, $\Delta S^* = +75 \pm 8$ J K^{-1} mol^{-1}. Isomerization of cis-[Pt(PEt$_3$)$_2$(Me)(MeOH)]$^+$ in diethyl ether–methanol mixtures undergoes mass law retardation by [MeOH]. The rates of isomerization of cis-[Pt(PEt$_3$)$_2$(Me)(S)]$^+$ (S = a series of hydroxylic solvents) are little influenced by the nature of the solvent. As in the case of the related halide species, the isomerization mechanism involves interconversion of two T-shaped 3-coordinate intermediates that show discriminating ability toward scavenging agents.

Introduction

Studies on the isomerization reactions of square-planar organometallic compounds are of fundamental importance for understanding the chemical reactivity of these species. Indeed, the course of many processes is dictated by the geometry in the square-planar configuration. For example, one reaction scheme postulated for olefin insertion on trans platinum(II) hydrides involves the isomerization of a 4-coordinated *trans*-[Pt(PEt$_3$)$_2$-(H)(C$_2$H$_4$)]$^+$ cation to its cis counterpart followed by migratory

insertion leading to the final monoalkyl complex.[1] Dialkylbis(-phosphine)palladium(II) complexes give strikingly different products in their thermolysis or reactions with CO depending on configuration.[2] For concerted thermal 1,1-reductive elimination

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