Thermal and Photochemical Reduction of Aqueous Chlorine by Ruthenium(II) Polypyridyl Complexes

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Studies are reported on the reactions of aqueous chlorine with a series of substitution-inert, one-electron metal-complex reductants, which includes $[Ru(bpy)_3]^{2+}$, $[Ru(4,4'-Me_2bpy)_3]^{2+}$, $[Ru(4,7-Me_2phen)_3]^{2+}$, $[Ru(terpy)_2]^{2+}$, and $[Fe(3,4,7,8-Me_4phen)_3]^{2+}$. The reactions were studied by spectrophotometry at 25 °C in acidic chloride media at $\mu = 0.3$ M. In general the reactions have the stoichiometry $2[ML_3]^{2+} + Cl_2 \rightarrow 2[ML_3]^{3+} + 2Cl^-$. In the case of $[Ru(bpy)_3]^{2+}$, the reaction is quite photosensitive; the thermal reaction is so slow as to be practically immeasurable. The reactions of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and $[Ru(4,7-Me_2phen)_3]^{2+}$ are also highly photosensitive, giving pseudo-first-order rate constants that depend on the monochromator slit width in a stopped−flow instrument; however, the thermal rates are fast enough that they can be obtained by extrapolation of k_{obs} to zero slit width. The reactions of $[Ru(terpy)_2]^{2+}$ and $[Fe(3,4,7,8-Me_4phen)_3]^{2+}$ show no appreciable photosensitivity, allowing direct determination of their thermal rate laws. From the kinetic effects of pH, $[Cl_2]_{tot}$, and $[Cl^-]$ it is evident that all of the thermal rate laws have a first-order dependence on $[ML_3]^{2+}$ and on $[Cl_2]$. The second-order rate constants decrease as $E°$ for the complex increases, consistent with the predictions of Marcus theory for an outer-sphere electron-transfer mechanism. Quantum yields at 460 nm for the reactions of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and $[Ru(4,7-Me_2phen)_3]^{2+}$ exceed 0.1 and show a dependence on $[Cl_2]$ indicative of competition among spontaneous decay of *Ru, nonreactive quenching by Cl_2, and reactive quenching by Cl_2.

Introduction

The halogens are generally regarded as oxidants but only recently have general studies of their aqueous reactions with one-electron reductants emerged. Both I_2 and Br_2 have now been shown to obey Marcus theory in their reactions with outer-sphere reductants, and reasonable estimates have been made of the effective self-exchange rate constants for the X_2/X_2^- redox couples.[1,2] In contrast, the state of knowledge regarding chlorine chemistry is less well established. Part of the reason for this is the relative difficulty of working with chlorine because of its hydrolysis, which limits its study to acidic chloride-containing solutions, and its strength as an oxidant, which can favor complicating side reactions. Further problems arise from the ready conversion of the radical Cl_2^- to $ClOH^-$, which leads to uncertainty regarding the value of $E°$ for the Cl_2/Cl_2^- redox couple.[3]

Studies of the oxidation of metal ions by aqueous chlorine include those of V(III),[4] Ti(III),[5] V(IV),[6,7] V(II),[8] Cr(II),[9,10] Fe(II),[11] and U(IV).[12] For all of these aquo ions an inner-sphere

mechanism is possible. The reaction of V(IV) is unusual in that it shows kinetic inhibition by V(V), suggestive of reversible formation of Cl_2^- in the first step.[7] Unfortunately, the complex effects of $[H^+]$ were not included in the analysis of the V(V) inhibition. The roster of coordination complexes oxidized by chlorine includes *cis*-$[Ru(bpy)_2(NH_3)_2]^{2+}$,[13] $[Fe(phen)_3]^{2+}$,[14,15] $[Ni^{II}(CN)_4]^{2-}$,[16] and $[Pt^{II}(CN)_4]^{2-}$.[17] Only for the first two of these complexes can an outer-sphere mechanism be assigned unambiguously, and of these two the reaction of *cis*-$[Ru(bpy)_2-(NH_3)_2]^{2+}$ is complicated by further oxidation of the NH_3 ligand. The reaction of $[Fe(phen)_3]^{2+}$ would seem to be on firm grounds, but even here there are problems. If an outer-sphere mechanism is assumed, then the rate-limiting step entails the formation of $[Fe(phen)_3]^{3+}$ and Cl_2^- and a reverse rate constant of 6×10^9 M^{-1} s^{-1} can be calculated from the forward rate constant and the $E°$ value of 0.50 V for the $Cl_2(aq)/Cl_2^-$ redox couple (corrected from the value of 0.43 V for $Cl_2(g)/Cl_2^-$).[18a] In contrast, a pulse-radiolysis study of this reaction indicates a reverse rate constant less than 1×10^7 M^{-1} s^{-1}.[18b] This disagreement could arise because of an error in the value of $E°$, an error in the presumed mechanism, or experimental errors in either of the rate constant measurements. While we are not yet able to address all of these possibilities, the present paper describes the reactions of a series of coordination complexes that define the broad features of outer-sphere reactions of Cl_2.

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A potential complication in any study of chlorine chemistry is the hydrolysis of chlorine, as in

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad K_h = 8.87 \times 10^{-4} \ M^2 \tag{1}$$
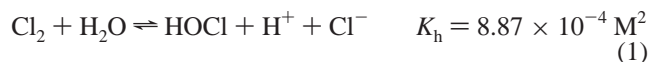
This reaction is rapid on the time scale of the reactions reported in the present paper, and it yields two highly reactive oxidants: Cl_2 and HOCl. The equilibrium favors HOCl except when there are substantial amounts of Cl^- and H^+ in solution. As a consequence, when the reactivity of molecular Cl_2 is of interest, the reactions are best studied in acidic Cl^--containing media, and under such conditions it is appropriate to express the composition of the solutions in terms of the total chlorine concentration as $[Cl_2]_{tot} = [Cl_2] + [HOCl]$. When experiments are performed as a function of $[H^+]$ and $[Cl^-]$, the reactivities of the two molecular species can be assessed.

Experimental Section

Reagents and Solutions. Distilled deionized water was obtained by passage of deionized water through a Barnstead pretreatment cartridge and subsequent distillation in a Barnstead Fi-stream all-glass still. Trifluoromethanesulfonic acid (HCF_3SO_3) was from 3M, and sodium trifluoromethanesulfonate (sodium triflate) was prepared by neutralization of concentrated HCF_3SO_3 with sodium carbonate. The solution was heated to boiling in order to remove any dissolved CO_2 gas, and crystalline product was obtained by slow cooling. The salt was further recrystallized from water and dried in a desiccator. Sodium chloride (Fisher) was recrystallized from water. The concentrations of HCl and HCF_3SO_3 were determined by titration with standardized NaOH. Stock solutions of NaOCl were prepared by bubbling Matheson high-purity Cl_2 gas through 0.6 M NaOH solution until the solution was saturated. This solution was then diluted with an additional volume of NaOH to raise the pH to 12 and stored at ca. ~5 °C in polyethlene bottles that had been aged by previous exposure to a hypochlorite solution. The concentration of NaOCl was determined spectrophotometrically at 292 nm ($\epsilon = 350 \ M^{-1} \ cm^{-1}$),[19] which was further confirmed by an iodometric method.[20] 4,4'-Dimethylbipyridine (Aldrich) (=4,4'-Me$_2$bpy), 4,7-dimethylphenanthroline (Aldrich) (=4,7-Me$_2$phen), 2,2':6',2''-terpyridine (Aldrich) (=terpy), 3,4,7,8-tetramethylphenanthroline (Aldrich) (=3,4,7,8-Me$_4$phen), $RuCl_3 \cdot 3H_2O$ (Aldrich), [Ru(bpy)$_3$]Cl$_2$·6H$_2$O (Aldrich), FeSO$_4$ (Baker Chemical Co.), Fe(NH$_4$)(SO$_4$)$_2$·12H$_2$O (Fisher), and K$_2$C$_2$O$_4$ (Fisher) were used without further purification.

All the solutions were prepared in deionized distilled water. Solutions of Cl_2 and for actinometry were prepared just prior to each experiment. For the preparation of Cl_2 solutions, appropriate volumes of HCl, HCF_3SO_3, NaCF$_3$SO$_3$, NaCl, water, and NaOCl were added to a 10 mL volumetric flask and drawn immediately into an airtight glass syringe to minimize the loss of Cl_2 gas by volatility. At high acidity, the solution from the syringe was injected into a quartz cell with a Teflon lid and the Cl_2 content was measured spectrophotometrically at 325 nm ($\epsilon = 70 \ M^{-1} \ cm^{-1}$).[21] At pH > 1 and low chloride concentration, the HOCl content was determined from the absorbance at 254 nm ($\epsilon = 59 \ M^{-1} \ cm^{-1}$)[22] and $[Cl_2]_{tot}$ was taken as the initial hypochlorite concentration. The remaining solution was used for the kinetic studies. The actual Cl_2 concentration for each run was measured at the beginning of the experiment and used for the calculation. Measurement of the Cl_2 content of the same solution at the end of the

experiment indicated that loss of Cl_2 during the reaction of this technique was 2−3%. For the oxidation of [Ru(terpy)$_2$]$^{2+}$ with chlorine, reaction solutions were prepared directly into a quartz cell by adding appropriate volumes of HCl, NaCl, H$_2$O, NaCF$_3$SO$_3$, complex, and finally NaOCl. Experiments with [Ru(4,4'-Me$_2$bpy)$_3$]$^{2+}$ and [Ru(4,7-Me$_2$phen)$_3$]$^{2+}$ under deaerated conditions were performed by purging all solutions with argon gas.

General Synthesis of Ru(II) Complexes. Although Lin et al. reported that [Ru^{II}(4,4'-diphenyl-2,2'-bipyridine)$_3$]$^{2+}$ could be synthesized by refluxing $RuCl_3$ with the ligand in DMF for 3 h,[23] Creaser et al. subsequently found that 60 h reflux times were required for the preparation of [Ru^{II}(4,4'-dimethyl-2,2'-bipyridine)$_3$]$^{2+}$, and even then chromatography was required to obtain a pure product.[24] More recently, Matsumara-Inoue et al. have reported that the reflux time could be reduced to 20 min by using a modified microwave oven for heating and ethylene glycol as a solvent instead of DMF.[25] We have found that the combination of heating with a conventional heating mantle and refluxing in ethylene glycol provides a pure product in good yield in under 4 h. The products are isolated as the BF_4^- salts rather than the more usual ClO_4^- salts in order to avoid the explosion hazards posed by these compounds. In this synthesis, ethylene glycol serves as both a high-boiling solvent and a reductant. In a related synthesis with water as the solvent, hypophosphite is used as an extrinsic reductant.[26]

(a) [Ru(4,4'-Me$_2$bpy)$_3$](BF$_4$)$_2$·2H$_2$O. Amounts of 0.26 g of RuCl$_3$·3H$_2$O (1 mmol) and 0.56 g of 4,4'-Me$_2$bpy (3 mmol) were dissolved in 20 mL of ethylene glycol and refluxed for 4 h. The solution was then allowed to cool to room temperature and filtered to remove any insoluble impurities. A saturated solution of sodium tetrafluoroborate was then added dropwise into the filtrate until an orange precipitate formed. The product was filtered, washed with cold water and diethyl ether, and dried in a vacuum desiccator. Yield was 88%. The product was further purified by recrystallization from water. ^{1}H NMR (D$_2$O, δ vs DSS): 8.3 (2H, s), 7.6 (2H, d), 7.2 (2H, d) and 2.5 (6H (CH$_3$), s). Anal. Calcd for [Ru(4,4'-Me$_2$bpy)$_3$](BF$_4$)$_2$·2H$_2$O: C, 50.08; H, 4.67; N, 9.73. Found: C, 49.68; H, 4.53; N, 9.69.

(b) [Ru(4,7-Me$_2$phen)$_3$](BF$_4$)$_2$·2H$_2$O. This complex was prepared following the above procedure using 4,7-dimethylphenanthroline as ligand. ^{1}H NMR (D$_2$O, δ vs DSS): 8.25 (2H, s), 7.83 (2H, d), 7.3 (2H, d), and 2.74 (6H (CH$_3$), s). Anal. Calcd for [Ru(4,7-Me$_2$phen)$_3$](BF$_4$)$_2$·2H$_2$O: C, 53.92; H, 4.31; N, 8.98. Found: C, 54.35; H, 4.16; N, 9.10.

(c) [Ru(terpy)$_2$](BF$_4$)$_2$·H$_2$O. This complex was synthesized in good yield by analogy to [Ru(4,4'-Me$_2$bpy)$_3$]$^{2+}$. ^{1}H NMR (DMSO, δ vs TMS): 9.09 (2H, d), 8.83 (2H, d), 8.56 (1H, t), 8.05 (2H, dt), 7.46 (2H, d), and 7.26 (2H, dt). Anal. Calcd for [Ru(terpy)$_2$](BF$_4$)$_2$·H$_2$O: C, 47.59; H, 2.93; N, 11.10. Found: C, 47.60; H, 3.07; N, 11.07.

Synthesis of [Fe(3,4,7,8-Me$_4$phen)$_3$](BF$_4$)$_2$·2H$_2$O. This complex was synthesized following the reported method[23] using 3,4,7,8-tetramethylphenanthroline as ligand. An amount of 0.36 g 3,4,7,8-tetramethylphenanthroline (1.5 mmol) was added gradually to 0.14 g of ferrous sulfate (0.5 mmol) dissolved in 10 mL of water, and the solution was continuously stirred for 30 min. The solution was then filtered, and a saturated solution of sodium tetrafluoroborate was added to the filtrate dropwise to form a reddish-orange precipitate. The product was recrystallized from warm water. Yield before recrystallization was 94%. ^{1}H NMR (DMSO, δ vs TMS): 8.47 (2H, s), 7.28 (2H, s), 2.77 (6H (CH$_3$), s), and 2.18 (6H (CH$_3$), s). Anal. Calcd for [Fe(3,4,7,8-Me$_4$phen)$_3$](BF$_4$)$_2$·2H$_2$O: C, 59.17; H, 5.38; N, 8.62. Found: C, 59.65; H, 5.24; N, 8.69.

Methods. UV−vis spectra were recorded on HP-8452A and HP-8453 diode array spectrophotometers equipped with thermostated water baths to maintain the temperature at 25.0 ± 0.1 °C. A Corning pH meter, model 130, with a Mettler semimicrocombination glass electrode

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was used for pH measurements. Standard electrochemical measurements were carried out with 0.3 N H_2SO_4 as supporting electrolyte at 25.0 ± 0.1 °C using a thermostated water bath. Cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV) were recorded with a BAS-100 electrochemical analyzer employing a conventional three-electrode cell with a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode. Some experiments were also conducted using a gold working electrode. Potential values are expressed relative to NHE by adding 0.197 V as $E°$ for the Ag/AgCl couple.

Kinetic studies of the reactions of $[Ru(bpy)_3]^{2+}$ and $[Ru(terpy)_2]^{2+}$ were monitored on the HP-8452A and HP-8453 spectrophotometers, respectively, mentioned above with use of stoppered 1 cm quartz cuvettes. Kinetic studies of the reactions of $[Ru(4,4'-Me_2bpy)_3]^{2+}$, $[Ru(4,7-Me_2phen)_3]^{2+}$, and $[Fe(3,4,7,8-Me_4phen)_3]^{2+}$ were performed on a Hi-Tech Scientific model SF-51 stopped−flow apparatus with a SU-40 spectrophotometer unit in the 1.0 cm path length configuration. The temperature was maintained at 25 °C with a C-400 circulatory water bath. Reactions were initiated by mixing equal volumes of the two reactants, both of which were maintained at 0.3 M ionic strength. An OLIS 4300S system was used for data acquisition and analysis. Reactions were monitored at 460 nm for $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and $[Ru(4,7-Me_2phen)_3]^{2+}$, 473 nm for $[Ru(terpy)_2]^{2+}$ ($\epsilon_{473} = 705$ M^{-1} cm^{-1} for $[Ru(terpy)_2]^{3+}$), 452 nm for $[Ru(bpy)_3]^{2+}$, and 500 nm for $[Fe(3,4,7,8-Me_4phen)_3]^{2+}$. All reactions were performed with a large excess of chlorine over reductant in acidic Cl^--containing media, and under these conditions the kinetic traces showed excellent pseudo-first-order behavior.

Actinometry. Kinetic studies of the photosensitive reactions of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and $[Ru(4,7-Me_2phen)_3]^{2+}$ with chlorine were performed at 460 nm on the Hi-Tech stopped−flow instrument, which illuminates the sample with a monochromatic beam of light. Accordingly, ferrioxalate actinometry[27] was used to calibrate the instrument as a function of slit width at 460 nm. All the experiments were carried out in a dark room. A 4×10^{-3} M ferric oxalate solution was irradiated for 10 min in the spectrophotometric cell of volume 0.040 mL at each slit width. The irradiated solution was then collected, mixed with 3 equiv of 1,10-phenanthroline solution, and diluted with water to 10 mL in a volumetric flask. The yield of $[Fe(phen)_3]^{2+}$ was measured at 510 nm in a 1.0 cm quartz cell. Parallel blank experiments were conducted to correct for dark reactions. The quantum yield of the ferrioxalate actinometer at 460 nm was taken as 1.0. Table S-1 of Supporting Information shows the value of light intensity at different slit widths.

Results

Preliminary Study: Reaction of $[Ru(bpy)_3]^{2+}$ with Chlorine. In preliminary studies we investigated the reaction of $[Ru(bpy)_3]^{2+}$ with a large excess of chlorine in acidic media at high concentrations of Cl^- to minimize the disproportionation of Cl_2. These experiments revealed the reaction to be slow and highly photosensitive. Because of the slowness of the reaction, kinetic measurements were performed with conventional mixing and reactions were monitored for only a fraction of the first half-life. A typical experiment was run under the following conditions: $[Cl_2]_{tot} = 1$ mM, $[Ru(II)]_0 = 0.062$ mM, $[Cl^-] = 0.1$ M, pH = 2.02 (HClO$_4$), and 25 °C. In 1200 s only a 0.127 absorbance change ($A_0 = 0.91$) was noted with the following spectrophotometer settings: a 20 s cycle time and a 0.2 s integration time. If pseudo-first-order kinetics are assumed, this absorbance loss corresponds to a rate constant, k_{obs}, of 1.6×10^{-4} s^{-1}. Increasing the light exposure of the sample 4-fold by decreasing the cycle time to 5 s led to an increase in k_{obs} (2.0×10^{-4} s^{-1}), and a further decrease in cycle time to 1 s gave a k_{obs} value of 4.8×10^{-4} s^{-1}. Returning to a cycle time of 20 s

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Table 1. UV−Visible and Electrochemical Properties of Ruthenium and Iron Complexes^a

complexes	λ_{max}, nm ($10^{-4}\epsilon$, M^{-1} cm^{-1})	$E°$, V vs NHE	electrochem method^b
$[Ru(4,4'-Me_2bpy)_3]^{2+}$	460, 1.43^c	1.10^c	CV
	(460, 1.45)	(1.079)^f	CV, OSWV
$[Ru(4,7-Me_2phen)_3]^{2+}$	445, 2.53^c	1.09^c	CV
	(446, 2.48)	(1.086)^f	CV, OSWV
$[Ru(terpy)_2]^{2+}$	473, 1.62^c	1.25^d	EST
	(473, 1.72)	(1.26)^g	CV, OSWV
$[Fe(3,4,7,8-Me_4phen)_3]^{2+}$	500, 1.38^e	0.85^e	potentiometric titration
	(500, 1.47)	(0.86)^h	OSWV

^{a} Parenthetical values are from this work, with electrochemical measurements performed in 0.3 N H_2SO_4. ^{b} CV = cyclic voltammetry; OSWV = Osteryoung square wave voltammetry; EST = estimated from CV data in CH_3CN by application of a solvent correction. ^{c} Reference 23. ^{d} Reference 38. ^{e} Reference 39. ^{f} [Ru(II)] = 0.5 mM. ^{g} [Ru(II)] = 1.0 mM. ^{h} [Fe(II)] = 0.12 mM.

and placing a 420 nm optical cutoff filter between the source and the sample reduced k_{obs} to 9.7×10^{-5} s^{-1}. These results demonstrate that the observed reaction rates were enhanced by photochemistry arising from the spectrophotometer beam. Because of the slowness of the reaction and these photochemical difficulties, further studies were conducted with related metal complex reductants that were expected to have larger thermal rate constants or to be less photosensitive.

Reactant Electrochemical and UV−Vis Properties. The electrochemical properties of all the complexes were characterized by voltammetry with a glassy carbon working electrode in 0.3 N H_2SO_4 medium as shown in Table 1. The CV of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ showed a quasireversible wave with $E_{1/2} = 1.08$ V vs NHE and $\Delta E_{p/p} = 75$ mV at a sweep rate of 50 mV/s. Under similar conditions $[Ru(4,7-Me_2phen)_3]^{2+}$ showed a quasi-reversible wave with $E_{1/2} = 1.09$ V and $\Delta E_{p/p} = 86$ mV. Osteryoung square wave voltammetric measurements yielded $E_p = 1.08$ and 1.085 V for $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and $[Ru(4,7-Me_2phen)_3]^{2+}$, respectively. These values are in good agreement with the reported[23] ones. Cyclic voltammetric measurements on $[Ru(terpy)_2]^{2+}$ yielded a reversible wave with $E_{1/2} = 1.26$ V and $\Delta E_{p/p} \approx 60$ mV. OSWV experiments on $[Ru(4,4'-Me_2bpy)_3]^{2+}$, $[Ru(4,7-Me_2bpy)_3]^{2+}$, and $[Ru(terpy)_2]^{2+}$ using a gold working electrode confirmed the results obtained with a carbon working electrode. Because of the very low solubility of the $[Fe(3,4,7,8-Me_4phen)_3]^{2+}$ complex in aqueous media, the cyclic voltammetric method failed to produce well-defined waves. However, the more sensitive OSWV method showed $E_p = 0.86$ V. All of these processes are assigned as one-electron oxidations on the basis of the well-known chemistry of these complexes and, in the case of the Ru(II) systems, on the basis of the observed values of $\Delta E_{p/p}$.

Solutions of the four M(II) complexes have strong absorptions in the visible region. As is shown in Table 1, these spectral features are in good agreement with prior reports.

Stoichiometry and Product Characterization. The stoichiometry of the reaction between $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and chlorine was examined in detail. With the complex in excess over chlorine, consumption ratios were determined at varying concentrations of both the reactants adopting the following conditions: $[Ru(II)]_0 = 0.5-0.1$ mM, $[Cl^-] = 0.3$ M, $[H^+] = 0.3$ M, and $[Cl_2]_{tot,0} = 0.04-0.2$ mM at 25 °C. Parallel blank experiments showed that no decomposition of the complex occurred under these conditions. The residual concentration of ruthenium(II) was determined by spectrophotometry at 460 nm,

which led to a $(1.93 \pm 0.29){:}1$ stoichiometric ratio for the consumption of ruthenium(II) to the total chlorine (shown in Table S-2 of Supporting Information).

Two sets of experiments were performed to characterize the ruthenium-containing product by UV–vis spectrophotometry. In the first set of experiments Ru(II) was oxidized by chlorine adopting the above conditions with $[\text{Ru(II)}]_0 = 0.1$ mM and $[\text{Cl}_2]_{\text{tot}} = 0.1$ mM. In the second set of experiments Ru(II) was oxidized by peroxydisulfate. The UV–vis spectra of both solutions were identical, showing strong peaks at 302 and 312 nm and a small peak at 442 nm. A 98% yield of Ru(III) was calculated for the reaction with chlorine by comparing the absorbance at 312 nm with that of Ru(III) obtained by peroxydisulfate oxidation. Further information was gathered by sparging the product solution with nitrogen gas to remove excess Cl_2 and then adding Na_2SO_3, which reduced Ru(III) back to Ru(II). Spectrophotometric analysis of this solution indicated that the recovery of $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{2+}$ was $96 \pm 4\%$.

Further confirmation of the reaction product was achieved by ^1H NMR spectroscopy. A 1 mM $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{2+}$ sample was oxidized by excess chlorine under the same conditions as for the consumption ratio experiments, and then unreacted chlorine was removed by sparging with nitrogen gas. The resulting Ru(III) solution was then reduced back to Ru(II) by adding a sufficient amount of Na_2SO_3 solution and taken to dryness by rotary evaporation. The ^1H NMR spectrum of this material in D_2O was identical to that of the starting complex, further indicating that $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{3+}$ is the reaction product.

On the basis of the above results, the overall reaction is

$$2[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{2+} + \text{Cl}_2 \rightleftharpoons$$
$$2[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{3+} + 2\text{Cl}^- \quad (2)$$
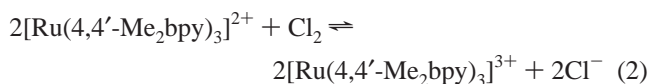
Stability of the product, $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{3+}$, was checked spectrophotometrically at 312 nm by oxidizing 4×10^{-5} M $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{2+}$ in 0.3 N H_2SO_4 with PbO_2. After 5.5 h only 3% of the $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{3+}$ decomposed.

Kinetics: Reaction of $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{2+}$ with Chlorine. This reaction is highly photosensitive, its rate increasing with the optical slit width of the stopped–flow spectrophotometer. A similar slit width dependence has previously been reported for intramolecular electron transfer in some Fe/Co dinuclear complexes.[28] The kinetic conditions adopted were $[\text{Cl}_2]_{\text{tot}} = 1.0$–11.9 mM, $[\text{Ru(II)}]_0 = 0.02$–0.03 mM, $[\text{Cl}^-] = 0.3$–0.1 M, pH = 0.5–1.52, $\mu = 0.3$ M (NaCF$_3$SO$_3$), and 25 °C. For each set of conditions the value of k_{obs} was determined as a function of incident light intensity by changing the slit value of the stopped–flow spectrophotometer. As is shown in Figure 1, there is a linear relationship between the pseudo-first-order rate constant, k_{obs}, and $I_0\epsilon$, where $I_0 =$ incident light intensity and $\epsilon =$ molar extinction coefficient of the complex. According to standard photochemical theory,[29] the slope in such a plot is related to the reactive quantum yield, ϕ_c, through

$$k_{\text{obs}} = k_o{}^{\text{th}} + 2.303 I_0 \phi_c \epsilon \quad (3)$$

Values of the thermal pseudo-first-order rate constants, $k_o{}^{\text{th}}$, were obtained as the intercepts of these plots and are shown in Table S-3 of Supporting Information. At $[\text{H}^+] = 0.3$ M and
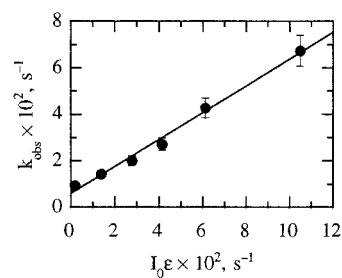

Figure 1. Plot of first-order rate constants against $I_0\epsilon$ for the oxidation of $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{2+}$ with chlorine at $[\text{Cl}_2] = 6.43$ mM, $[\text{Cl}^-] = 0.3$ M, $[\text{H}^+] = 0.3$ M, $\mu = 0.3$ M, $[\text{Ru(II)}] = 0.02$ mM, and 25 °C. I_0 = light intensity and ϵ = molar extinction coefficient of $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{2+}$.

constant $[\text{Cl}^-]$ (0.3 M), the plot of $k_o{}^{\text{th}}$ vs $[\text{Cl}_2]_{\text{tot}}$ is linear with an intercept very close to zero, indicating a first-order rate dependence on $[\text{Cl}_2]_{\text{tot}}$. On the other hand, at constant $[\text{Cl}_2]_{\text{tot}}$ the values of $k_o{}^{\text{th}}$ are independent of $[\text{Cl}^-]$ and pH over the range studied. The rather limited range of $[\text{Cl}^-]$ studied is imposed by the precipitation of Ru(II) as its $\text{CF}_3\text{SO}_3{}^-$ salt at $[\text{Cl}^-] <$ 0.1 M and $\mu = 0.3$ M. Hydrolysis of Cl_2 as in eq 1 occurs with $K_h = 8.87 \times 10^{-4}$ M^2 at $\mu = 0.3$ M as interpolated from the data of Wang et al.[30] Thus, under the present conditions, hydrolysis of Cl_2 occurs only to a minor degree, so $[\text{Cl}_2] \approx [\text{Cl}_2]_{\text{tot}}$ and the minor component of HOCl is relatively unreactive. Blank studies with chloride-free HOCl solution, prepared according to the method as described by Cady,[31] indicate that HOCl is indeed quite unreactive with $[\text{Ru(4,4'-Me}_2\text{bpy)}_3]^{2+}$. These results indicate that the thermal rate law is

$$k_o{}^{\text{th}} = 2k^{\text{th}}[\text{Cl}_2] \quad (4)$$

The data in Table S-3 of Supporting Information lead to a value of 0.48 ± 0.03 M^{-1} s^{-1} for k^{th}.

To obtain accurate photochemical data, experiments were performed at low $[\text{Ru(II)}]_0$ to maintain absorbances less than 0.1. This requirement for low absorbances is imposed by the need to maintain effectively constant light intensity throughout the path length of the cell and to comply with the approximations made in deriving the relationship between k_{obs} and I_0 (eq 3).[29] Moreover, to eliminate potential complications from oxygen quenching, these experiments were performed in degassed solutions. The results are shown in Table S-4 of Supporting Information and demonstrate that the value of ϕ_c is significantly dependent on $[\text{Cl}_2]_{\text{tot}}$. Less exact experiments at higher concentrations of Ru(II) indicate that ϕ_c is independent of $[\text{H}^+]$ and $[\text{Cl}^-]$. Since Cl_2 is the predominant form of chlorine under these conditions, the dependence on $[\text{Cl}_2]_{\text{tot}}$ can be attributed to a dependence on $[\text{Cl}_2]$. As is shown in Figure 2,, a plot of $1/\phi_c$ as a function of $1/[\text{Cl}_2]$ is linear with a slope b of $(3.06 \pm 0.25) \times 10^{-3}$ M and an intercept m of 3.23 ± 0.13, or $\phi_c = [\text{Cl}_2]/(m + b[\text{Cl}_2])$.

From the above, the overall rate law is

$$-\frac{d[\text{Ru(II)}]}{dt} = \left\{ \frac{2.303 I_0 \epsilon [\text{Cl}_2]}{m + b[\text{Cl}_2]} + 2k^{\text{th}}[\text{Cl}_2] \right\}[\text{Ru(II)}] \quad (5)$$

The first term of the above equation is related to the excited-state reactivity and the second term to the ground-state reactivity of the complex.

(28) Malin, J. M.; Ryan, D. A.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1978**, *100*, 2097–2102.

(29) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970; p 12.

(30) Wang, T. X.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 1050–1055.

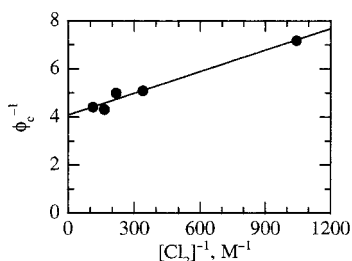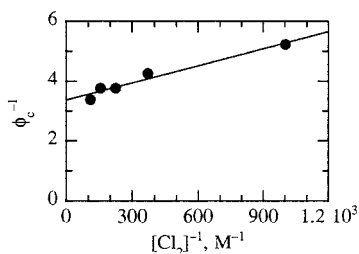(31) Cady, G. H. *Inorg. Synth.* **1957**, *5*, 156–165.

Figure 2. Plot of ϕ_c^{-1} vs $[Cl_2]^{-1}$ with intercept = 3.23 ± 0.13 and slope = $(3.06 \pm 0.25) \times 10^{-3}$ M for the reaction of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ with chlorine in deaerated solution. ϕ_c ($=2k_p\phi[Cl_2]/(k_{nr} + (k_p + k_q)[Cl_2])$) is obtained from the slope of the plot of k_{obs} vs $I_0\epsilon$. $[Cl_2]_{tot} = 0.95-9.0$ mM, $[H^+] = 0.3$ M, $[Cl^-] = 0.3$ M, $[Ru(4,4'-Me_2bpy)_3^{2+}]_0 = 6.5 \times 10^{-6}$ M, 25 °C.

Figure 3. Plot of ϕ_c^{-1} vs $[Cl_2]^{-1}$ with intercept = 3.36 ± 0.11 and slope = $(1.95 \pm 0.22) \times 10^{-3}$ M for the reaction of $[Ru(4,7-Me_2phen)_3]^{2+}$ with chlorine in deaerated solution. $[H^+] = 0.3$ M, $[Cl^-] = 0.3$ M, $[Ru(II)]_0 = 4.5 \times 10^{-6}$ M, 25 °C. ϕ_c ($=2k_p\phi[Cl_2]/(k_{nr} + (k_p + k_q)[Cl_2])$) is obtained from the slope of the plot of k_{obs} vs $I_0\epsilon$.

A study of the temperature dependence of the kinetics of this reaction was conducted in the range 15.5−49 °C. These measurements at constant chlorine concentration (Table S-3) reveal that the value of kth increases with temperature; the value of ϕ_c remains almost constant. The Eyring activation parameters for k^{th} are $\Delta S^\ddagger = (-33 \pm 15.6)$ J K^{-1} mol^{-1} and $\Delta H^\ddagger = (65.0 \pm 4.76)$ kJ mol^{-1}.

Reaction of [Ru(4,7-Me₂phen)₃]²⁺ with Chlorine. This reaction shows qualitative features quite similar to that of $[Ru(4,4'-Me_2bpy)_3]^{2+}$. Accordingly, it was studied under similar conditions, monitoring the loss of Ru(II) at 460 nm, which is the same wavelength as was used in the study of $[Ru(4,4'-Me_2bpy)_3]^{2+}$. Kinetic studies were performed under the following conditions: $[Cl_2]_{tot} = 1.0-9.5$ mM, $[Ru(II)]_0 = 0.02$ mM, $[Cl^-] = 0.3$ M, $[H^+] = 0.3-0.03$ M, $\mu = 0.3$ M (NaCF$_3$SO$_3$), and 25 °C. Under these conditions the values of k_{obs} were sensitive to the incident light intensity as in eq 3. Values of k_o^{th} were obtained from intercepts of linear plots of k_{obs} vs $I_0\epsilon$ and are shown in Table S-5 of Supporting Information ($\epsilon_{460} = 2.21 \times 10^4$ M^{-1} cm^{-1} for Ru(II)). These kinetic data reveal that the thermal reaction rate law is first-order with respect to $[Cl_2]_{tot}$ and independent of $[H^+]$ as in eq 4. Some experiments at various chlorine concentrations were carried out under anaerobic conditions, and the corresponding values shown parenthetically in Table S-5 indicate no oxygen dependence. The second-order rate constant for the thermal process (k^{th}) obtained from Table S-5 is 5.32 ± 0.50 M^{-1} s^{-1}.

Photochemical data were obtained under anaerobic conditions at low $[Ru(II)]_0$, the conditions being $[Ru(II)]_0 = 4.5$ μM, $[H^+] = 0.3$ M, $[Cl^-] = 0.3$ M, and $[Cl_2]_{tot} = 1.0-9.1$ mM. Here also, the plot of k_{obs} vs $I_0\epsilon$ is linear, and the values of the intercept ($2k^{th}[Cl_2]$) and the slope ($2.303\phi_c$) for each experiment are shown in Table S-6 of Supporting Information. The plot of ϕ_c^{-1} vs $[Cl_2]^{-1}$ is linear (Figure 3), with intercept and

slope values of 3.36 ± 0.11 and $(1.95 \pm 0.27) \times 10^{-3}$ M, respectively.

Reaction of [Ru(terpy)₂]²⁺ with Chlorine. This reaction differs significantly from those of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and $[Ru(4,7-Me_2phen)_3]^{2+}$ in that it is much slower and displays negligible photosensitivity. Kinetic studies were characterized by the loss of absorbance due to Ru(II); the traces gave no evidence for kinetic inhibition by the Ru(III) product. Photochemical tests included placing a 455 nm glass cutoff filter between the source and the sample, changing the instrument cycle time, and changing the instrument integration time. These tests, performed with $[Cl_2]_{tot} = 20$ mM and $\mu = 0.3$ M at 25 °C, revealed no perceptible photosensitivity. Nevertheless, all further experiments were conducted using the 455 nm glass filter as a precaution. The overall form of the rate law was determined from values of k_{obs} under the conditions $[Cl_2]_{tot} = 5.0-50.0$ mM, $[Ru(II)]_0 = 0.03$ mM, $[Cl^-] = 0.1-0.3$ M, $[H^+] = 0.05-0.3$ M, $\mu = 0.3$ M (NaCF$_3$SO$_3$), and 25 °C. The dependence of k_{obs} on $[Cl_2]_{tot}$ was studied at $[H^+] = 0.3$ M and showed a clear first-order dependence on $[Cl_2]_{tot}$. The upper limit to $[Cl_2]$ in these experiments was set by the solubility of Cl$_2$ (0.057 M atm^{-1}).[32] Pseudo-first-order rate constants are independent of $[H^+]$ and $[Cl^-]$ as shown in Table S-7 of Supporting Information. Thus, the overall rate law for this reaction is

$$-d[Ru(II)]/dt = 2k^{th}[Ru(II)][Cl_2] \qquad (6)$$

where $k_{obs} = 2k^{th}[Cl_2]$ under large excess of chlorine. From the data shown in Table S-7, the second-order rate constant k^{th} is $(1.28 \pm 0.09) \times 10^{-2}$ M^{-1} s^{-1}.

Because of the slowness of these reactions, the decomposition of the Ru(III) product conceivably could be a complication. As a test of the stability of Ru(III), a 0.2 mM solution of $[Ru(terpy)_2]^{3+}$ in 0.1 N H$_2$SO$_4$ was prepared by the oxidation of Ru(II) with PbO$_2$. Under these conditions it has a half-life of ~7000 s. This value is ~10 times longer than the half-life of the fastest chlorine reactions and indicates that decomposition of Ru(III) has a negligible effect on the reaction.

Reaction of [Fe(3,4,7,8-Me₄phen)₃]²⁺ with Chlorine. This rapid reaction was studied with $[Cl_2]_{tot} = 0.4-5.0$ mM, $[Fe(II)]_0 = 0.02$ mM, $[Cl^-] = 0.3-0.1$ M, pH = 0.5−1.3, $\mu = 0.3$ M (Na$_2$SO$_4$), and 25 °C. Kinetic data gathered in Table S-8 of Supporting Information reveal that the rate law is first-order with respect to $[Cl_2]_{tot}$ and independent of $[H^+]$ and $[Cl^-]$. The general rate law for the reaction is

$$-d[Fe(II)]/dt = 2k^{th}[Fe(II)][Cl_2] \qquad (7)$$

The value of kth, the second-order rate constant obtained from Table S-8, is $(6.28 \pm 0.27) \times 10^2$ M^{-1} s^{-1}.

Discussion

The reactions of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and $[Ru(4,7-Me_2phen)_3]^{2+}$ with chlorine are photosensitive, whereas the reactions of $[Ru(terpy)_2]^{2+}$ and $[Fe(3,4,7,8-Me_4phen)_3]^{2+}$ are independent of light intensity. A plausible general reaction mechanism, considering thermal as well as photochemical processes, is given
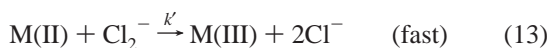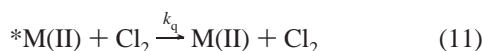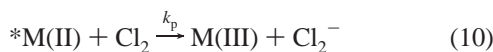
(32) Young, C. L. *Sulfur Dioxide, Chlorine, Fluorine, and Chlorine Dioxide*; Solubility Data Series; Pergamon Press: Elmsford, NY, 1983; Vol. 12, p 346.

Table 2. Second-Order Rate Constants (k^{th}, M^{-1} s^{-1}) for the Reduction of Chlorine by Various Complexes and Their Potential Values

reductant	$E°$, V	k^{th}, M^{-1} s^{-1}	$k_r/k_r(ref)^a$
$[Ru(4,4'-Me_2bpy)_3]^{2+ b}$	1.079	0.48	
$[Ru(4,7-Me_2phen)_3]^{2+ b}$	1.086	5.32	14.55
$[Ru(terpy)_2]^{2+ b}$	1.26	1.28×10^{-2}	30.80
$[Fe(3,4,7,8-Me_4phen)_3]^{2+ b}$	0.86	6.28×10^2	0.26
$[Fe(phen)_3]^{2+ c}$	1.06	2.4	2.38
$[Ru(bpy)_2(NH_3)_2]^{2+ d}$	0.86	1.1×10^3	0.45

^{a} $k_r(ref)$ refers to k_r for $[Ru(4,4'-Me_2bpy)_3]^{2+}$. ^{b} This work. ^{c} Reference 15. ^{d} Reference 13.

by reactions 8–13:

$$M(II) + h\nu \rightarrow {}^*M(II) \qquad \phi \qquad (8)$$

$$^*M(II) \xrightarrow{k_{nr}} M(II) \qquad (9)$$

$$^*M(II) + Cl_2 \xrightarrow{k_p} M(III) + Cl_2^- \qquad (10)$$

$$^*M(II) + Cl_2 \xrightarrow{k_q} M(II) + Cl_2 \qquad (11)$$

$$M(II) + Cl_2 \underset{}{\overset{k^{th}, k_r, K_{et}}{\rightleftharpoons}} M(III) + Cl_2^- \qquad (12)$$

$$M(II) + Cl_2^- \xrightarrow{k'} M(III) + 2Cl^- \quad \text{(fast)} \qquad (13)$$

ϕ is the quantum yield for formation of the lowest-energy excited state of Ru(II). k_{nr}, k_p, and k_q are the rate constants associated with nonradiative, electron transfer, and energy-transfer quenching processes of lowest energy excited-state Ru(II) complexes with chlorine. Reaction 12 is indicated as a reversible process to facilitate discussion, but the reverse process k_r is not significant under the conditions of our experiments and is neglected in the following derivation. The assumption that k' is fast is supported by its value (1.6×10^9 M^{-1} s^{-1}) for the related reductant $[Ru(bpy)_3]^{2+}$.[33] If the steady-state approximation is made for the concentrations of Cl_2^- and $^*Ru(II)$, the overall rate law is

$$-\frac{d[Ru(II)]}{dt} = \left\{ \frac{2k_p 2.303 I_0 \phi \epsilon [Cl_2]}{k_{nr} + (k_p + k_q)[Cl_2]} + 2k^{th}[Cl_2] \right\}[Ru(II)] \qquad (14)$$

In the cases of $[Ru(terpy)_2]^{2+}$ and $[Fe(3,4,7,8-Me_4phen)_3]^{2+}$ the excited-state lifetimes in water at 25 °C are extremely short, so the photochemical term in the rate law can be neglected. For these two reductants the rate law is simply

$$k_{obs} = 2k^{th}[Cl_2] \qquad (15)$$

In view of the stoichiometry, rate law, and known substitution-inert character of the various complex reductants investigated in this study, it is reasonable to assign an outer-sphere electron-transfer mechanism to the kth step for all of them. A similar mechanism has been assigned in the literature reports on the reactions of chlorine with $[Fe(phen)_3]^{2+}$ and $[Ru(bpy)_2(NH_3)_2]^{2+}$.[13–15] Accordingly, Table 2 collects the values of kth for these reactions along with the corresponding $E°$ values pertaining to the reductants. As is shown in Figure 4, there is a linear relationship between log k^{th} and $E°$ for these reactions,

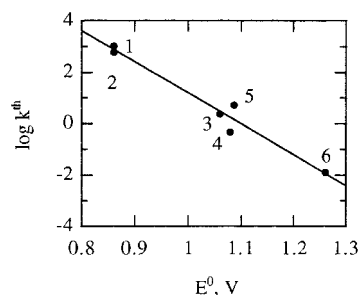**Figure 4.** Plot of log k^{th} vs $E°$ with intercept = 13.31 and slope = -12.10 for the reduction of chlorine with the ruthenium(II) and iron(II) complexes shown in Table 2: (1) $[Ru(bpy)_2(NH_3)_2]^{2+}$; (2) $[Fe(3,4,7,8-Me_4phen)_3]^{2+}$; (3) $[Fe(phen)_3]^{2+}$; (4) $[Ru(4,4'-Me_2bpy)_3]^{2+}$; (5) $[Ru(4,7-Me_2phen)_3]^{2+}$; (6) $[Ru(terpy)_2]^{2+}$.

which lends further support to the concept that they all have the same mechanism. Considerable uncertainty attends the value of $E°$ for the Cl_2/Cl_2^- redox couple, and hence, it is not currently possible to calculate reliable values for the equilibrium constants, K_{et}, in step 12 of the mechanism. Present estimates place $E°$ for the Cl_2/Cl_2^- couple in the range 0.5–0.7 V,[34] which suggests that the equilibrium constants are less than unity and that the values of k_r are greater than their corresponding values of kth. From these data it is also possible to calculate the ratios of the reverse rate constants (k_r). These ratios are shown in Table 2, taking the value of k_r for the reaction of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ as a standard. They span a range from 0.26 to 31 and thus provide clear evidence that the values of k_r are sensitive to the nature of the metal complex. It is to be expected that such sensitivity would not be shown if the values of k_r were at the diffusion-controlled limit. Moreover, the lack of kinetic inhibition by M(III) in these reactions suggests that k_r is considerably smaller than k'. It thus appears that the values of kth are governed by an electron-transfer activated process and hence that Marcus theory should be applicable.

In the Introduction, questions were raised relating to the reaction of $[Fe(phen)_3]^{2+}$ with Cl_2. The LFER (linear free energy relationship) in Figure 4 indicates that the rate constant for this reaction follows the trend given by the other reductants, which suggests that both the rate constant and its mechanistic assignment are correct. This suggests either that the rate constant for the reaction of Cl_2^- with $[Fe(phen)_3]^{3+}$ is incorrect or that the value of $E°$ for the Cl_2/Cl_2^- redox couple is considerably greater than 0.5 V.

From the data in Table 2 it is evident that the value of k_r is largest for the reaction of $[Ru(terpy)_2]^{3+}$. Since this rate constant can be no greater than the diffusion-controlled value, its upper limit is about 2×10^{10} M^{-1} s^{-1}. From the relationship $K_{et} = k^{th}/k_r$ and the measured value of kth, a lower limit of 6.4×10^{-13} can thus be calculated for K_{et}. From the $E°$ value for the $[Ru(terpy)_2]^{3+/2+}$ couple this equilibrium constant leads to a lower limit of 0.54 V for the Cl_2/Cl_2^- reduction potential. The lack of kinetic inhibition by Ru(III) suggests that k_r is well below the diffusion limit and thus that the $E°$ value for the Cl_2/Cl_2^- couple is significantly greater than 0.54 V.

A full test of the values of kth in terms of the cross-relationship of Marcus theory ($k_{12} = (k_{11}k_{22}K_{et}f)^{1/2}$) is not currently possible because accurate values of K_{et} are not available as described above. Another complication is that the self-exchange rate constant for the Cl_2/Cl_2^- redox couple is not known reliably.[35] According to the cross relationship, a plot of log k^{th} vs $E°$ as in

(33) Mulazzani, Q. G.; Venturi, M.; Bolletta, F.; Balzani, V. *Inorg. Chim. Acta* **1986**, *113*, L1–L2.

(34) Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69–138.
(35) Stanbury, D. M. In *Electron-Transfer Reactions*; Isied, S., Ed.; American Chemical Society: Washington, DC, 1997; pp 165–182.
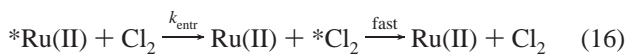
Figure 4 should describe a smooth curve for a homologous series of reductants having similar self-exchange rate constants and ionic charges. The slope of such a curve should lie in the range of -8.45 for reactions with K_{et} near 1 to -16.9 for highly endothermic reactions having k_r at the diffusion-controlled limit. Figure 4 shows that the plot of $\log k^{th}$ vs $E°$ for such a homologous series of reductants is indeed a smooth curve; its slope is -12.1, consistent with the cross relationship at a moderate degree of endothermicity.
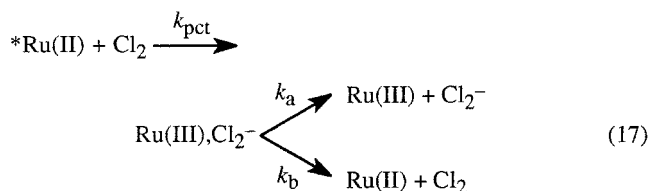
Evaluation of the photochemical parameters for the reactions of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and $[Ru(4,7-Me_2phen)_3]^{2+}$ can be achieved by noting that eq 14 is equivalent to eq 5 where ϕ_c corresponds to $2k_p\phi[Cl_2]/(k_{nr} + (k_p + k_q)[Cl_2])$. A plot of ϕ_c^{-1} vs $[Cl_2]^{-1}$ corresponds to an intercept of $(k_p + k_q)/(2k_p\phi)$ and a slope of $k_{nr}/(2k_p\phi)$. Molecular oxygen, if present in the medium, would quench the Ru(II) excited states, yielding singlet oxygen as a significant product.[23,36] No reports on the reactions of singlet oxygen, with either the ruthenium species or chlorine present in the medium, are available. To avoid these potential complications, photochemical studies were conducted under anaerobic conditions. We assume that the quantum yield of formation of the lowest excited state of Ru(II) is unity. The reported value of the nonreactive rate constant (k_{nr}) for $[Ru(4,4'-Me_2bpy)_3]^{2+}$ is $(2.9 \pm 0.09) \times 10^6$ s^{-1} [24] and that for $[Ru(4,7-Me_2phen)_3]^{2+}$ is $(5.76 \pm 0.13) \times 10^5$ s^{-1}.[23] By use of these rate constants, the plots of ϕ_c^{-1} vs $[Cl_2]^{-1}$ yield the following results: for $[Ru(4,4'-Me_2bpy)_3]^{2+}$, $k_p = (4.7 \pm 0.4) \times 10^8$ M^{-1} s^{-1} and $k_q = (2.57 \pm 0.28) \times 10^9$ M^{-1} s^{-1}; for $[Ru(4,7-Me_2phen)_3]^{2+}$, $k_p = (1.47 \pm 0.17) \times 10^8$ M^{-1} s^{-1} and $k_q = (8.4 \pm 1.2) \times 10^8$ M^{-1} s^{-1}.

These values of k_p are much larger than their corresponding thermal electron-transfer rate constants. A large increase is to be expected, since the $E°$ values for the Ru(III)/*Ru(II) couples are much more favorable, being in the range of -1.0 V.[23] Indeed, these photochemical reactions might be sufficiently exothermic to lie in the inverted region.
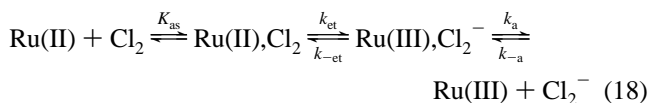
Of the various mechanisms that might be considered to account for the derived values of k_q, collisional energy transfer and back-electron transfer merit careful consideration. Collisional energy transfer is a possibility because the lowest excited state of Cl_2 ($^3\Pi_{2u}$) lies at 17160 cm^{-1},[37] which is comparable to the energy of *Ru(II); this mechanism would also comply with the requirements of spin conservation. This energy-transfer mechanism is represented by

$$*Ru(II) + Cl_2 \xrightarrow{k_{entr}} Ru(II) + *Cl_2 \xrightarrow{fast} Ru(II) + Cl_2 \quad (16)$$

Back-electron transfer arises from the following scheme:

$$*Ru(II) + Cl_2 \xrightarrow{k_{pct}}$$

$$Ru(III),Cl_2^- \begin{array}{c} \nearrow^{k_a} Ru(III) + Cl_2^- \\ \searrow_{k_b} Ru(II) + Cl_2 \end{array} \quad (17)$$

These schemes lead to $k_p = k_{pct}k_a/(k_a + k_b)$, $k_q = k_{entr} + k_{pct}k_b/(k_a + k_b)$ and $k_q = k_{entr} + k_p k_b/k_a$. The detailed mechanism for the thermal process in eq 12 is given by

$$Ru(II) + Cl_2 \underset{}{\overset{K_{as}}{\rightleftharpoons}} Ru(II),Cl_2 \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} Ru(III),Cl_2^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}}$$

$$Ru(III) + Cl_2^- \quad (18)$$

It is clear that electron transfer is the rate-limiting step for k^{th}

and k_r in eq 12 for $[Ru(4,4'-Me_2bpy)_3]^{n+}$, and hence, $k^{th} = K_{as}k_{et}$ and $k_r = k_{-a}k_{-et}/k_a$. This also leads to an equivalence of k_b with k_{-et}. From the k_r ratios given in Table 2 it is evident that k_r is a factor of 30.8 slower than for the $[Ru(terpy)_2]^{n+}$ system, for which a diffusion-controlled upper limit of 1×10^{10} M^{-1} s^{-1} would apply. Thus, for $[Ru(4,4'-Me_2bpy)_3]^{n+}$ k_r has an upper limit of 3.3×10^8 M^{-1} s^{-1}. With reasonable estimates of the ionic radii of Ru(III) and Cl_2^-, one can estimate a value of 4.2 M^{-1} for k_{-a}/k_a. If one assumes a diffusion-controlled rate constant of 1×10^{10} M^{-1} s^{-1} for the association of these two ions, the derived value of k_a is 2.4×10^9 s^{-1}. When combined with the above upper limit to k_r, this estimate for k_{-a}/k_a leads to 7.7×10^7 s^{-1} as an upper limit to k_{-et} (k_b). The ratio k_a/k_b thus exceeds 31, implying that back-electron transfer is insignificant relative to cage escape. When these estimates for k_a and k_b are combined with the experimental value for k_p, the result is an upper limit of 1.5×10^7 M^{-1} s^{-1} for $k_p k_b/k_a$. Since the value for k_q is 2.6×10^9 M^{-1} s^{-1}, over 99% of the nonreactive quenching must occur through collisional energy transfer.

Note that the LFER in Figure 4 implies that the reactions of chlorine with $[Ru(terpy)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ should have similar thermal rate constants, since the complexes have almost identical $E°$ values. With this assumption, a simple calculation shows that the rate of the thermal reaction of $[Ru(bpy)_3]^{2+}$ should be considerably slower than the rates obtained in the preliminary study, which confirms that the observed rates were due principally to the photochemical effects of the spectrophotometer beam.

Conclusions

A number of observations from the present study should be highlighted. Among these, this study appears to be the first report of photochemical quenching by aqueous chlorine. This quenching takes place through both reactive and nonreactive pathways, both of which are explicable within the framework of general chlorine chemistry. This study also presents sufficient data to support a general mechanism and LFER for the rates of thermal electron transfer to chlorine. Although these results establish a lower limit to $E°$ for the Cl_2/Cl_2^- couple, further work is required in order to obtain a firm value for this important parameter.

Supporting Information Available: A table relating slit width to light intensity, tables of pseudo-first-order rate constants for all reactions studied, tables of quantum yields and k_o^{th} for the reactions of $[Ru(4,4'-Me_2bpy)_3]^{2+}$ and $[Ru(4,7-Me_2phen)_3]^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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