2.8, and 2.9, respectively. Probably the value for PPh_3 is not very different, as found for various other complexes.[9] For this reason, in eq 2 is inserted also the reaction of $Fe(CO)_3L$ with CO.

Given eq 2 and assuming the steady-state approximation is valid for the intermediates $Fe(CO)_4$, $Fe(CO)_3$, and $Fe(CO)_3L$, expression 3 is obtained for the ratio $\alpha/(1-\alpha)$.

$$\frac{\alpha}{1-\alpha} = \frac{v_M}{v_D} = \frac{k_2}{k_5}\frac{[Fe(CO)_4]}{[Fe(CO)_3L]} + \frac{k_4}{k_5}\frac{[CO]}{[L]} = \frac{k_2k_{-1}'k_4[CO]^2}{k_1'k_5k_3[L]} + \left[\frac{k_2k_{-1}'}{k_3k_1'} + \frac{k_2k_4}{k_1'k_5}\right][CO] + \frac{k_4}{k_5}\frac{[CO]}{[L]} + \frac{k_2}{k_1'}[L] \tag{3}$$

The values of v_M and v_D correspond to the rates of formation of $Fe(CO)_4L$ and $Fe(CO)_3L_2$, respectively. All the rate constants refer to reaction mechanism 2 and L indicates the phosphine ligand. Expression 3 indicates a parabolic dependence of $\alpha/(1-\alpha)$ on both [CO] and $1/[PPh_3]$ variation. Curve A of Figure 1 fits better than curve B to a parabolic dependence: owing to the low CO pressure value for the measurements of curve B, the CO developed during the reaction changes the CO total pressure. For this reason the intercept of curve B is higher than that of curve A. Both curves are consistent with a parabolic dependence. The coefficients of the parabolic plots give the following very rough values: $k_2k_{-1}'k_4/k_1'k_5k_3 \approx (1\text{-}2) \times 10^2$, $k_4/k_5 \approx 5\text{-}7$, and $k_2k_{-1}'/k_3k_1' + k_2k_4/k_1'k_5$ negligible compared to $k_4/k_5[L]$.

The fact that the ratio $\alpha/(1-\alpha)$ is not zero for zero concentration of CO and for very low concentration of PPh_3 may be due to the development of CO during the reaction 1. The amount given off is sufficient to influence the dissociative step of $Fe(CO)_4$ to $Fe(CO)_3$ and to favor the formation of $Fe(CO)_4PPh_3$.

The formation of the $Fe(CO)_3$ is not unreasonable; in fact other carbonyl complexes[10] undergo step dissociation, and recently experimental evidence of the formation of $Fe(CO)_3$ in the photolysis of $Fe(CO)_5$ in matrix[11] was obtained.

Mechanism 2 also suggests that the formation of $Fe(CO)_3(PPh_3)_2$, observed during the reaction between several carbonyl complexes of Fe and PPh_3, is due to the formation of the intermediate $Fe(CO)_4$ in the first step of the reaction. If this mechanism does indeed occur, then the ratio $\alpha/(1-\alpha)$ should be the same. This has been observed for all the $(CH_2{=}CHX)Fe(CO)_4$ and $Fe_2(CO)_9$ complexes.[1] For $Fe_3(CO)_{12}$, however, this ratio is very different and changes with the concentration of PPh_3. In fact, a different reaction mechanism for this complex was suggested.[12] According to this mechanism $Fe_3(CO)_{12}$ reacts with PPh_3, giving $Fe_3(CO)_{11}PPh_3$, which on further reaction with PPh_3 leads to $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$.

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Registry No. $Fe(CO)_4(CH_2{=}CHPh)$, 12193-57-6; PPh_3, 603-35-0; CO, 630-08-0.

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Contribution from the Laboratorio di Fotochimica e Radiazioni d'Alta Energia del CNR
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Reduction by the Triplet Charge-Transfer State of Tris(bipyridyl)ruthenium(II). Photochemical Reaction between Tris(bipyridyl)ruthenium(II) and Thallium(III)[1]

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Phosphorescent emission from the ^{3}CT state of $Ru(bipy)_3{}^{2+}$ is quenched by Fe^{3+}, Fe^{2+}, and Tl^{3+} ions in aqueous solution with quenching rate constants of 1.9×10^9, 1.6×10^7, and 1.1×10^8 M^{-1} sec^{-1}, respectively at room temperature (*ca.* 20°), $\mu = 0.5$ M. Irradiation of solutions containing $Ru(bipy)_3{}^{2+}$ and Tl^{3+} in the singlet charge-transfer absorption band of $Ru(bipy)_3{}^{2+}$ causes oxidation of the ruthenium(II) complex to $Ru(bipy)_3{}^{3+}$. The limiting quantum yield for the loss of $Ru(bipy)_3{}^{2+}$ at infinite thallium(III) concentration is 2.0 ± 0.4. The rate constant for the photochemical reduction of Tl^{3+} determined from the dependence of the quantum yield upon thallium(III) concentration is the same as the rate constant for the quenching of the $Ru(bipy)_3{}^{2+}$ phosphorescence by thallium(III). Tl^{2+} ions are produced as intermediates in the photochemical reaction and can oxidize $Ru(bipy)_3{}^{2+}$ and reduce $Ru(bipy)_3{}^{3+}$. The quantum yield is unchanged in the presence of methanol. The quenching of the $Ru(bipy)_3{}^{2+}$ phosphorescence cannot take place by an energy-transfer mechanism and electron transfer from ^{3}CT $Ru(bipy)_3{}^{2+}$ to Tl^{3+} is responsible for the phosphorescence quenching and the initial step in the photochemical reaction.

In recent years $Ru(bipy)_3{}^{2+}$ has been widely used in quenching and photosensitization experiments with transition metal complex acceptors. The lowest charge-transfer triplet state (17.1 kK above the ground state[3]) which is involved in these processes emits phosphorescence (λ 620 nm, lifetime 0.65 μsec[4]) even in fluid solution at room temperature and is ex-

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pected to show reducing properties.[5] If the entropy difference between the ground state and the ^{3}CT state is small, the oxidation potential of the ^{3}CT state could be more than 2 V more positive than that of the ground state. The standard reduction potential of $Ru(bipy)_3{}^{3+}$ is +1.26 V and therefore $E°$ for the reduction of $Ru(bipy)_3{}^{3+}$ to ^{3}CT $Ru(bipy)_3{}^{2+}$ may be *ca.* −1 V. ^{3}CT $Ru(bipy)_3{}^{2+}$ is therefore a potential electron donor as well as an energy donor, but evidence of its reducing properties is conflicting.

Chromium(III) complexes are not easily reduced and have electronic excited states which are lower in energy than 17 kK. Quenching of $Ru(bipy)_3{}^{2+}$ phosphorescence by these complexes takes place by energy transfer and sensitized emission is observed for $Cr(CN)_6{}^{3-}$ and *trans*-$Cr(en)_2(NCS)_2{}^+$ quenchers.[6,7] Many cobalt(III) complexes are able to quench ^{3}CT $Ru(bipy)_3{}^{2+}$ but in these cases reduction and decomposition of the acceptor complexes are observed.[5,8-11] There has been some discussion as to whether these reactions take place by a "chemical" (*i.e.*, electron-transfer) or a "physical" (*i.e.*, energy-transfer) mechanism, as the cobalt(III) complexes have low-energy excited states but are also easily reduced. For the chemical mechanism electron transfer from ^{3}CT $Ru(bipy)_3{}^{2+}$ to the cobalt(III) complex, eq 1,

$$^3\text{CT Ru(bipy)}_3{}^{2+} + \text{Co}^{\text{III}}\text{L}_6 \rightarrow \text{Ru(bipy)}_3{}^{3+} + \text{Co}^{\text{II}}\text{L}_6 \qquad (1)$$

is followed by dissociation of the newly formed cobalt(II) complex, eq 2. For the physical mechanism, energy trans-

$$\text{Co}^{\text{II}}\text{L}_6 \rightarrow \text{Co}^{2+} + 6\text{L} \qquad (2)$$

fer, eq 3, results in a ^{3}CT state of cobalt(III) which decom-

$$^3\text{CT Ru(bipy)}_3{}^{2+} + \text{Co}^{\text{III}}\text{L}_6 \rightarrow \text{Ru(bipy)}_3{}^{2+} + {}^3\text{CT Co}^{\text{III}}\text{L}_6 \qquad (3)$$

poses to Co^{2+} and a radical R, eq 4. As the radical R is fre-

$$^3\text{CT Co}^{\text{III}}\text{L}_6 \rightarrow \text{Co}^{2+} + 5\text{L} + \text{R} \qquad (4)$$

quently able to oxidize $Ru(bipy)_3{}^{2+}$ to $Ru(bipy)_3{}^{3+}$, eq 5,

$$\text{R} + \text{Ru(bipy)}_3{}^{2+} \rightarrow \text{Ru(bipy)}_3{}^{3+} + \text{L} \qquad (5)$$

the final products will be the same for both mechanisms. The increase in the Stern–Volmer quenching constants for the series of acceptors fluoro-, chloro-, and bromopentaamminecobalt(III),[5] for which the reduction potentials increase from the fluoro to the bromo complex, is not itself proof that the quenching takes place by electron transfer; as for chromium(III) complexes it has been shown that for quenching by an energy-transfer mechanism the quenching ability increases in the ligand series F < Cl < Br.[7] Endicott, *et al.*, have reported strong evidence in favor of an energy-transfer mechanism for quenching by $Co(NH_3)Br^{2+}$ [10] and Co(HEDTA)X^- (X = Cl, Br, NO_2)[11] complexes.

Clear evidence of the ability of ^{3}CT $Ru(bipy)_3{}^{2+}$ to act as an electron donor can be obtained only with a quenching substrate to which energy transfer cannot occur and with which an electron-transfer reaction is easily observed. This requires that the reduced substrate cannot be readily oxidized by the $Ru(bipy)_3{}^{3+}$ formed in the electron-transfer quenching step. Tl^{3+} probably does not have excited states lower than about 30 kK, and Miller and Prince[12] found that the thermal reduction of Tl^{3+} by $Ru(bipy)_3{}^{2+}$ apparently proceeds by successive one-electron-transfer steps, producing Tl^{2+} as an intermediate. The reaction was also reported to be photosensitive. Participation of the intermediate oxidation state, thallium(II) in one-electron oxidation–reduction reactions of thallium(I) and thallium(III), and the recent determination of the standard one-electron reduction potentials for the couples involving thallium(II)[13] suggested Tl^{3+} as a suitable acceptor with which to attempt to observe direct electron transfer from the ^{3}CT state of $Ru(bipy)_3{}^{2+}$.

Experimental Section

Materials. Tris(2,2′-bipyridyl)ruthenium(II) chloride was prepared from $RuCl_3$. $Ru(bipy)_3{}^{2+}$ was determined spectrophotometrically (ϵ 1.38 × 10^4 at 454 nm). $Ru(bipy)_3{}^{3+}$ solutions were prepared from $Ru(bipy)_3{}^{2+}$ solutions by oxidation with PbO_2 or Cl_2. Solutions prepared by oxidation with Cl_2 in initially neutral solution, followed by acidification and removal of the excess Cl_2 by several cycles of bubbling with N_2 and evacuation gave more reproducible results than those prepared by oxidation with PbO_2. This may have been due to traces of excess lead(IV) in the solutions oxidized with PbO_2. Ruthenium(III) solutions were prepared just before use and the half-life of the reduction of $Ru(bipy)_3{}^{3+}$ by water was long enough in 0.5 *M* perchloric acid for the change in concentration during the photochemical experiments to be negligible.

Thallium(III) solutions were prepared by dissolving thallic oxide in perchloric acid. Thallium(I) solutions were prepared by dissolving thallous carbonate in perchloric acid. Thallium concentrations were determined by titration with potassium iodate. Iron(III) solutions were prepared from the perchlorate salt and standardized by titration with EDTA. Iron(II) solutions were prepared from iron(III) solutions by reduction with zinc amalgam. Acid concentrations and ionic strengths of solutions were adjusted with perchloric acid and sodium perchlorate. All solutions were prepared from water distilled from potassium permanganate.

Techniques. Phosphorescent emission from $Ru(bipy)_3{}^{2+}$ was measured with a Perkin-Elmer MPF-3 fluorescence spectrophotometer. The exciting wavelength was 450 nm and the emission intensity was measured at 610 nm. None of the added ions absorbed significantly at these wavelengths and the emission spectrum in the presence of Fe^{3+}, Fe^{2+}, and Tl^+ was the same as that of $Ru(bipy)_3{}^{2+}$ alone. The exciting light caused significant photoreaction in the solutions containing Tl^{3+} and the emission spectrum could not be measured. Relative emission intensities were determined by comparison with $Ru(bipy)_3{}^{2+}$ solutions of the same ruthenium(II) concentration and the same acidity and ionic strength. The measurements were made on aerated solutions and the solutions containing Fe^{3+}, Fe^{2+}, or Tl^+ were stable in the light from the exciting lamp. Initial intensities were determined for the solutions which contained Tl^{3+}, because of the photoreaction. The emission intensity was followed for *ca.* 30 sec after opening the excitation shutter, and the initial intensity was determined from the extrapolation of this plot to the time of opening of the shutter. The correction was *ca.* 1–2%.

The photochemical light source was a tungsten lamp and the irradiation wavelength (464 nm) was isolated with a Schott interference filter. Light intensities were determined by ferrioxalate actinometry and were *ca.* 10^{-7} *Nhν* min^{-1}. During the irradiations the solutions were stirred by bubbling with nitrogen, which did not appreciably alter the O_2 concentrations because the irradiation times were short (10–15 sec). Absorbed light intensities were calculated from the absorbance of the solutions and did not change by more than 2% during a run. $Ru(bipy)_3(ClO_4)_2$ is only slightly soluble and in perchlorate solutions with an ionic strength of 0.5 *M* the maximum concentration of the complex was limited to *ca.* 7 × 10^{-5} *M*. The extent of photolysis was followed by measuring the fall in ruthenium-

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(II) concentration spectrophotometrically at 450 nm, where the absorption coefficient of the ruthenium(III) complex is only 4% of that of the ruthenium(II) complex. In some experiments the production of $Ru(bipy)_3{}^{3+}$ was followed by the increase in absorbance at 310 nm, where the ruthenium(III) complex has a higher absorption coefficient than the ruthenium(II) complex. Quantum yields were determined from the slope of a plot of $[Ru(bipy)_3{}^{2+}]$ against irradiation time for each run, and allowance was made for the thermal reaction between $Ru(bipy)_3{}^{2+}$ and Tl^{3+}, using a sample of the photolysis solution as a blank with which to monitor the extent of the thermal reaction. From the measurements of the blank solution the change of $[Ru(bipy)_3{}^{2+}]$ with irradiation time was corrected for the thermal reaction. In experiments in which the solutions contained $Ru(bipy)_3{}^{3+}$ the reduction of the complex by water was also monitored, but this reaction was never significant. Irradiations were performed at room temperature (19 ± 2°). Duplicate irradiations were performed for each set of experimental conditions and the quantum yields in general agreed to within *ca.* 8%.

Results

Phosphorescence Quenching. At constant ionic strength (0.5 *M* perchloric acid) Stern–Volmer plots of reciprocal intensity against quencher concentration were linear (Figure 1). Stern–Volmer constants and quenching rate constants for Fe^{3+}, Fe^{2+}, and Tl^{3+} are given in Table I. Quenching rate constants were calculated from the ^3CT $Ru(bipy)_3{}^{2+}$ lifetime in air-saturated solutions, 0.40 μsec.[4] No quenching was observed by 10^{-2} *M* Tl^+.

Photochemical Reaction. a. Stoichiometry. The total stoichiometry of the photochemical reaction was not determined because of the difficulty of analyzing for thallium(I) at concentrations of 10^{-6} *M* in the presence of much larger concentrations of thallium(III) and $Ru(bipy)_3{}^{2+}$. The stoichiometric ratio of ruthenium(II) conversion to ruthenium(III) was determined by measuring the quantum yield for $Ru(bipy)_3{}^{3+}$ production, which was the same as the quantum yield for the loss of $Ru(bipy)_3{}^{2+}$ at the same Tl^{3+} concentration (Table II). At 327.5 nm the ruthenium(II) and ruthenium(III) complexes have the same absorption coefficient, and in one experiment the absorbance at 327.5 nm was measured for various irradiation times. At this wavelength the changes in absorbance of the solution were very small and were only about 5% of those calculated from the absorbance changes at 454 nm, assuming only the loss of $Ru(bipy)_3{}^{2+}$, and effectively an isosbestic point was observed. These results suggest that the photochemical reaction results in the complete conversion of $Ru(bipy)_3{}^{2+}$ to $Ru(bipy)_3{}^{3+}$, with no loss of bipyridyl ligand. In confirmation of this, it was always possible to regenerate completely the initial absorbance due to the $Ru(bipy)_3{}^{2+}$ by reducing the solutions after irradiation by adding a small amount of solid Na_2SO_3.

b. Dependence on Thallium(III). At constant $Ru(bipy)_3{}^{2+}$ concentration (3.9×10^{-5} *M*) in 0.5 *M* perchloric acid ($\mu = 0.5$ *M*) the quantum yield for the loss of ruthenium(II), $\phi_{-Ru^{II}}$, was dependent on the Tl^{3+} concentration, in the range from 10^{-3} to 10^{-2} *M*. A plot of $1/\phi_{-Ru^{II}}$ against $1/[Tl^{3+}]$ is linear (Figure 2) with an intercept at infinite Tl^{3+} which corresponds to a limiting quantum yield of 2.0 ± 0.4. The intercept over slope ratio of Figure 2 is 53 ± 10 M^{-1}.

c. Dependence on Light Intensity. The light intensity could not be varied over a wide range because the correction for the thermal reaction became too large at low light intensities. Over a range of a factor of 5 the quantum yield was independent of light intensity (Table II).

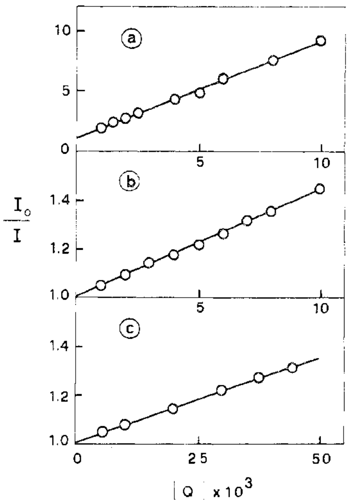

Figure 1. Stern–Volmer quenching plots for the quenching of $Ru(bipy)_3{}^{2+}$ phosphorescence by (a) $Fe_{aq}{}^{3+}$, (b) $Tl_{aq}{}^{3+}$, and (c) $Fe_{aq}{}^{2+}$, in 0.5 *M* acid; $\mu = 0.50$ *M* for (a) and (b) and varied between 0.50 and 0.65 *M* for (c).

Table I. Quenching of $Ru(bipy)_3{}^{2+}$ Phosphorescence ($\mu = 0.5$ *M*, ~20°)

Quenching ion	K_{S-V}, M^{-1}	k_q,[a] M^{-1} sec^{-1}
Fe^{3+}	760 ± 50	$(1.9 \pm 0.2) \times 10^9$
Tl^{3+}	44 ± 5	$(1.1 \pm 0.1) \times 10^8$
Fe^{2+}	6.4 ± 0.7	$(1.6 \pm 0.2) \times 10^7$
Tl^+	<0.5	$<10^6$

[a] Calculated from K_{S-V} using the lifetime for the charge-transfer triplet state of 0.4 μsec in aerated solutions.[4]

Table II. Quantum Yields for Photosensitized Reaction between $Ru(bipy)_3{}^{2+}$ and Tl^{3+} [a]

10^3-$[Tl^{3+}]$, *M*	$\phi_{-Ru^{II}}$	Other data
2.0	0.20 ± 0.02	$\phi_{Ru^{III}} = 0.22 \pm 0.03$
4.0	0.32 ± 0.03	$\phi_{Ru^{III}} = 0.30 \pm 0.05$
6.1	0.53 ± 0.05	$\phi_{Ru^{III}} = 0.53 \pm 0.05$
4.0	0.30 ± 0.03	10^{-2} *M* Tl^+
4.0	0.34 ± 0.03	1 *M* CH_3OH
6.1	0.51 ± 0.05	1 *M* CH_3OH
4.0	0.32 ± 0.03	$I_{abs} = 9.6 \times 10^{-8}$ $Nh\nu$ min^{-1}
4.0	0.30 ± 0.03	$I_{abs} = 7.2 \times 10^{-8}$ $Nh\nu$ min^{-1}
4.0	0.31 ± 0.04	$I_{abs} = 4.7 \times 10^{-8}$ $Nh\nu$ min^{-1}
4.0	0.32 ± 0.04	$I_{abs} = 1.9 \times 10^{-8}$ $Nh\nu$ min^{-1}

[a] $[Ru(bipy)_3{}^{2+}] = 3.9 \times 10^{-5}$ *M*, $[H^+] = 0.50$ *M*, and $\mu = 0.5$ *M*, at 19° and at an absorbed light intensity of 9.6×10^{-8} $Nh\nu$ min^{-1}, except where indicated.

d. Dependence on $Ru(bipy)_3{}^{3+}$. At long irradiation times the quantum yield for the loss of $Ru(bipy)_3{}^{2+}$ fell. This was attributed to the production of $Ru(bipy)_3{}^{3+}$. The concentration of $Ru(bipy)_3{}^{3+}$ produced by the photolysis was never large enough for this species to absorb a significant fraction of the light at 464 nm and the fall in the quantum yield was not due to an inner filter effect or to the photolysis of $Ru(bipy)_3{}^{3+}$ [14] but was due to a secondary back-reaction. The effect of $Ru(bipy)_3{}^{3+}$ on the quantum yield was investigated in solution which contained 3.9×10^{-5} *M* $Ru(bipy)_3{}^{2+}$, 4×10^{-3} *M* Tl^{3+}, and 0.5 *M* H^+, by adding $Ru(bipy)_3{}^{3+}$ in concentrations between 10^{-5} and 10^{-4} *M*. The ratio of the quantum yield in the absence of $Ru(bipy)_3{}^{3+}$ to the quantum yield of the same solutions in the presence of $Ru(bipy)_3{}^{3+}$ is plotted against $[Ru(bipy)_3{}^{3+}]$ in Figure 3. The ratio [Ru(II)]/[Ru(III)] was altered only in this way because the range of ruthenium(II) concentrations was limit-

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[14] We have observed that $Ru(bipy)_3{}^{3+}$ is photoreactive. The observations have not been extensive, but illumination of a solution containing 10^{-3} *M* $Ru(bipy)_3{}^{3+}$ and 10^{-2} *M* Tl^+ by 464-nm light results in the formation of $Ru(bipy)_3{}^{2+}$ and Tl^{3+}.

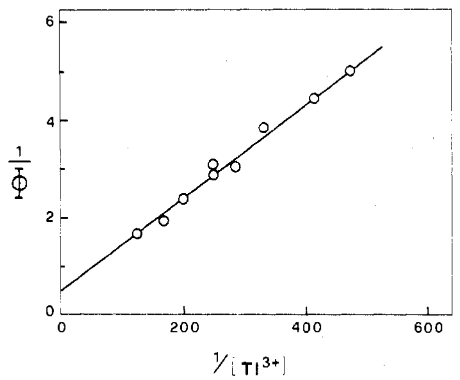

Figure 2. Dependence of the reciprocal quantum yield for the oxidation of ruthenium(II) to ruthenium(III) upon $1/[\mathrm{Tl}^{3+}]$ in 0.5 M $HClO_4$. The line has an intercept of 0.48 ± 0.1 and the limiting quantum yield is 2.0 ± 0.4.

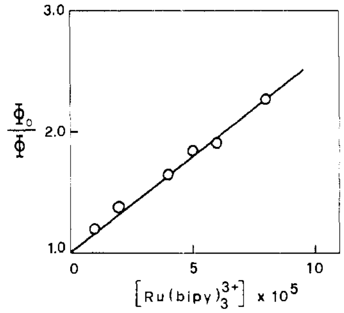

Figure 3. Dependence of the quantum yield for the oxidation of ruthenium(II) to ruthenium(III) upon $[\mathrm{Ru(bipy)_3}^{3+}]$ at constant $[\mathrm{Ru(bipy)_3}^{2+}]$ (3.9×10^{-5} M) and $[\mathrm{Tl}^{3+}]$ (4.1×10^{-3} M) in 0.5 M acid. ϕ_0 is the quantum yield in the absence of ruthenium(III).

ed by the solubility of $\mathrm{Ru(bipy)_3(ClO_4)_2}$ and by the requirements that the concentration of $\mathrm{Ru(bipy)_3}^{2+}$ be high enough for it to absorb the major fraction of the light and for the thermal reaction to be a small fraction of the photochemical reaction.

e. **Effects of Thallium(I) and Methanol.** The addition of the presumed lower oxidation state of thallium produced by the photochemical reaction, Tl^+, to the photolysis solutions made no difference to the quantum yield (Table II). Under the conditions of irradiation the thermal reaction between Tl^+ and $\mathrm{Ru(bipy)_3}^{3+}$ was very slow.

One-electron reductants produce the unstable intermediate oxidation state, Tl^{2+}, from Tl^{3+}, but specific scavengers for Tl^{2+} which did not react with $\mathrm{Ru(bipy)_3}^{2+}$ or $\mathrm{Ru(bipy)_3}^{3+}$ could not be found. Fe^{2+} reacts with Tl^{2+} rapidly ($k = 2.6 \times 10^6$ M^{-1} sec^{-1})[15] but equally rapidly reduces $\mathrm{Ru(bipy)_3}^{3+}$ ($k = 7.2 \times 10^5$ M^{-1} sec^{-1}),[16] and in the presence of 5×10^{-3} M Fe^{2+} the quantum yield was zero. Methanol reacts with Tl^{2+}, in the presence of Tl^{3+} initiates a chain reaction,[17] and is also a well-known scavenger for radicals such as OH. The phosphorescence intensity of the $\mathrm{Ru(bipy)_3}^{2+}$ solutions was not changed in the presence of 1 M methanol, and the quantum yields were also unaltered (Table II).

Discussion

Photochemical Reaction of $\mathrm{Ru(bipy)_3}^{2+}$ and Tl^{3+}. The results are discussed on the basis of the reaction scheme of

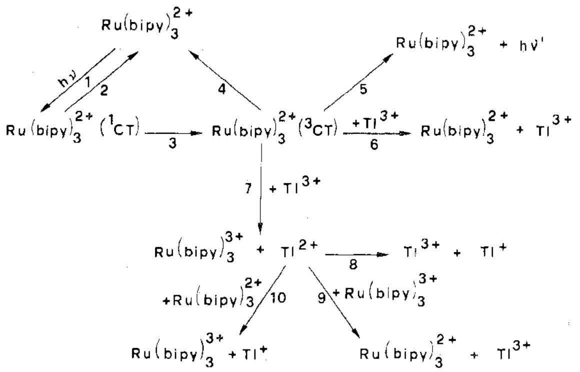

Figure 4. Reaction scheme for the photooxidation of $\mathrm{Ru(bipy)_3}^{2+}$ by Tl^{3+}.

Figure 4, which is based on the known photophysics of $\mathrm{Ru(bipy)_3}^{2+}$ and the oxidation-reduction chemistry of thallium and on the experimental observation that the limiting quantum yield for the disappearance of $\mathrm{Ru(bipy)_3}^{2+}$ is 2.

Irradiation of $\mathrm{Ru(bipy)_3}^{2+}$ in the charge-transfer band leads to the singlet charge-transfer state, ^{1}CT (step 1) which either deactivates to the ground state (step 2) or undergoes intersystem crossing to the triplet charge-transfer state, ^{3}CT (step 3). In the absence of Tl^{3+} the ^{3}CT state deactivates to the ground state by step 4, which includes deactivation due to quenching by dissolved oxygen in aerated solutions, or emits phosphorescence (step 5). When Tl^{3+} ions are present, the ^{3}CT state may be deactivated before emission and the phosphorescence is quenched. In this system a static quenching mechanism[18] is improbable because a complex is unlikely to be formed between two ions for which the charge product is 6+. The lifetime of the ^{1}CT state is very short (*ca.* 10^{-10} sec)[19] and quenching of this state by Tl^{3+} is impossible in experiments in which the concentration of Tl^{3+} was always less than 10^{-2} M. The phosphorescence quenching is accompanied by the conversion of $\mathrm{Ru(bipy)_3}^{2+}$ to $\mathrm{Ru(bipy)_3}^{3+}$ and the most plausible mechanism is one in which electron transfer takes place from the ^{3}CT $\mathrm{Ru(bipy)_3}^{2+}$ to the Tl^{3+} (step 7). In principle other quenching processes are possible, which lead to ground-state $\mathrm{Ru(bipy)_3}^{2+}$ without reaction, and these are represented by step 6. One-electron reducing agents react with Tl^{3+} to give the intermediate oxidation state Tl^{2+}, which can disproportionate (step 8), reduce $\mathrm{Ru(bipy)_3}^{3+}$ (step 9), or oxidize $\mathrm{Ru(bipy)_3}^{2+}$ (step 10).

A steady-state treatment of the reaction scheme of Figure 4 gives eq 6 and 7. I^0 and τ^0 $(=1/(k_4 + k_5))$ are the phosphorescent intensity and the lifetime of the ^{3}CT state in the absence of Tl^{3+}.

$$I^0/I = 1 + \tau^0(k_6 + k_7)[\mathrm{Tl}^{3+}] \qquad (6)$$

$$\phi = \eta_{\mathrm{isc}}\left(\frac{k_7[\mathrm{Tl}^{3+}]}{(k_4 + k_5) + (k_6 + k_7)[\mathrm{Tl}^{3+}]}\right) \times \left(\frac{k_8[\mathrm{Tl}^{2+}] + 2k_{10}[\mathrm{Ru^{II}}]}{k_8[\mathrm{Tl}^{2+}] + k_9[\mathrm{Ru^{III}}] + k_{10}[\mathrm{Ru^{II}}]}\right) \qquad (7)$$

I is the phosphorescent intensity in the presence of Tl^{3+}, ϕ is the quantum yield for the removal of $\mathrm{Ru(bipy)_3}^{2+}$ or the formation of $\mathrm{Ru(bipy)_3}^{3+}$. η_{isc} is the intersystem crossing efficiency for step 3 and is known to be close to unity.[3,20]

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[15] B. Falcinella, P. D. Felgate, and G. S. Laurence, *J. Chem. Soc., Dalton Trans.*, in press.

[16] B. M. Gordon, L. L. Williams, and N. Sutin, *J. Amer. Chem. Soc.*, **83**, 2061 (1961); J. N. Braddock and T. J. Meyer, *ibid.*, **95**, 3158 (1973).

[17] C. E. Burchill and F. G. Hickling, *Can. J. Chem.*, **48**, 2466 (1970).

[18] F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J. Phys. Chem.*, **78**, 1374 (1974).

[19] F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, **91**, 253 (1969).

The normal Stern-Volmer plot (Figure 1) is described by eq 6. For $\eta_{\mathrm{isc}} = 1$ the reciprocal of the quantum yield is given by eq 8. For photolysis experiments in which Ru-

$$1/\phi = \left(\frac{k_6 + k_7}{k_7} + \frac{1}{\tau^0 k_7[\mathrm{Tl}^{3+}]}\right) \times \left(\frac{k_8[\mathrm{Tl}^{2+}] + k_9[\mathrm{Ru^{III}}] + k_{10}[\mathrm{Ru^{II}}]}{k_8[\mathrm{Tl}^{2+}] + 2k_{10}[\mathrm{Ru^{II}}]}\right) \quad (8)$$

$(\mathrm{bipy})_3{}^{3+}$ was initially absent, and for short irradiation times ($\mathrm{Ru^{II}}$ to $\mathrm{Ru^{III}}$ conversion less than 10%) the plot of $1/\phi$ against $1/[\mathrm{Tl}^{3+}]$ (for constant initial $[\mathrm{Ru(bipy)_3}^{2+}]$) was found to be linear (Figure 2). This implies that under these conditions the term

$$\frac{k_8[\mathrm{Tl}^{2+}] + k_9[\mathrm{Ru^{III}}] + k_{10}[\mathrm{Ru^{II}}]}{k_8[\mathrm{Tl}^{2+}] + 2k_{10}[\mathrm{Ru^{II}}]}$$

in eq 8 was constant within the experimental errors. This will only be true if the two terms $k_8[\mathrm{Tl}^{2+}]$ and $k_9[\mathrm{Ru^{III}}]$ are negligible with respect to the term $k_{10}[\mathrm{Ru^{II}}]$. That the terms in the species Tl^{2+} and $\mathrm{Ru(bipy)_3}^{3+}$ are negligible under these conditions is confirmed by the fact that the quantum yield was independent of the light intensity (at least over a small range) and that ϕ decreased in cases where $\mathrm{Ru(bipy)_3}^{3+}$ was added initially or at long irradiation times when the concentration produced by the photolysis became significant. We can also note that the steady-state concentration of Tl^{2+}, calculated from the absorbed light intensity and the value of k_8[13] measured at the same acidity and ionic strength, was less than 10^{-8} *M*. For the usual concentration of $\mathrm{Ru(bipy)_3}^{2+}$ in the photolysis solutions (4×10^{-5} *M*) a value of k_{10} of $5 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ would be large enough for the term $k_8[\mathrm{Tl}^{2+}]$ to be less than about 10% of the term $k_{10} \cdot [\mathrm{Ru^{II}}]$. An effect of this magnitude would be concealed by the experimental errors. The value of k_{10} is expected (see below) to be of the order of $10^6\ M^{-1}\ \mathrm{sec}^{-1}$. As for the term $k_9[\mathrm{Ru^{III}}]$, we have shown (see below) that k_{10} is about twice k_9, so that for short irradiations (less than 10% conversion of $\mathrm{Ru^{II}}$ to $\mathrm{Ru^{III}}$) in the absence of added $\mathrm{Ru^{III}}$, $k_9[\mathrm{Ru^{III}}]$ will be less than 5% of the term $k_{10}[\mathrm{Ru^{II}}]$. As a result, for these experimental conditions eq 8 reduces to eq 9.

$$1/\phi = \left(\frac{k_6 + k_7}{k_7} + \frac{1}{\tau^0 k_7[\mathrm{Tl}^{3+}]}\right)\left(\frac{1}{2}\right) \quad (9)$$

From eq 9 the ratio of the intercept to the slope of Figure 2 should be equal to the Stern-Volmer constant obtained from the quenching experiments. The ratio of the intercept and slope in Figure 2 is $53 \pm 10\ M^{-1}$ and within the experimental error is equal to the Stern-Volmer constant, $44 \pm 5\ M^{-1}$. The intercept of Figure 2 is 0.48 ± 0.10 and from eq 9 should be equal to $0.5(k_6 + k_7)/k_7$. The intercept of 0.5 implies that k_7 is much larger than k_6 and confirms that $k_{10}[\mathrm{Ru^{II}}]$ was much larger than $k_8[\mathrm{Tl}^{2+}]$ and $k_9[\mathrm{Ru^{III}}]$ for the experimental conditions in which the dependence of the quantum yield upon Tl^{3+} was measured. The condition that $k_7 \gg k_6$ means that quenching of $^3\mathrm{CT}$ $\mathrm{Ru(bipy)_3}^{2+}$ by Tl^{3+} occurs overwhelmingly by processes which lead to $\mathrm{Ru(bipy)_3}^{3+}$. From the magnitude of the experimental error, k_6 must be at least 5 times smaller than k_7.

For long irradiation times (25% oxidation of $\mathrm{Ru^{II}}$ or more) and for cases where $\mathrm{Ru(bipy)_3}^{3+}$ was added to the solutions, $k_9[\mathrm{Ru^{III}}]$ was no longer negligible compared with $k_{10}[\mathrm{Ru^{II}}]$ and the quantum yield was reduced. For constant $[\mathrm{Tl}^{3+}]$, eq 10 may be obtained from eq 8, for conditions in which

$$\phi^0/\phi = 1 + k_9[\mathrm{Ru^{III}}]/k_{10}[\mathrm{Ru^{II}}] \quad (10)$$

$k_8[\mathrm{Tl}^{2+}]$ may still be neglected and where $[\mathrm{Ru^{II}}]$ and $[\mathrm{Ru^{III}}]$ do not change significantly during photolysis. Here ϕ^0 is the quantum yield at constant $[\mathrm{Tl}^{3+}]$ in the absence of added $\mathrm{Ru(bipy)_3}^{3+}$, and ϕ is the quantum yield in the presence of $\mathrm{Ru(bipy)_3}^{3+}$. The ratio ϕ^0/ϕ is a linear function of $[\mathrm{Ru(bipy)_3}^{3+}]$ at constant $[\mathrm{Ru(bipy)_3}^{2+}]$, with an intercept of 1 ± 0.1 (Figure 3). From the slope of Figure 3 the ratio k_{10}/k_9 is 1.6 ± 0.1. The ratio confirms that the effect of the $\mathrm{Ru(bipy)_3}^{3+}$ produced by the photolysis will be negligible for experiments in which less than 10% of the initial $[\mathrm{Ru(bipy)_3}^{2+}]$ is oxidized.

Mechanism of the Quenching by Tl^{3+}. The agreement of the experimental results with the expectations of the reaction scheme outlined in Figure 4 does not constitute proof that the sole, or even principal, mechanism by which Tl^{3+} ions quench $^3\mathrm{CT}$ $\mathrm{Ru(bipy)_3}^{2+}$ is electron transfer, but the quenching reactions must lead to the limiting quantum yield of 2 for the oxidation of $\mathrm{Ru(bipy)_3}^{2+}$, either directly or *via* reactive intermediates. A mechanism involving direct energy transfer from the charge-transfer triplet state to Tl^{3+} is unlikely, if not impossible. For a $6\mathrm{d}^{10}$ ion like Tl^{3+} there are of course no d-d transitions and the lowest energy excited state must be a charge-transfer excited state. The absorption spectrum of $\mathrm{Tl_{aq}}^{3+}$ ions has a maximum at *ca.* 200 nm which is attributed to ligand-to-metal charge transfer. In 0.5 *M* acid an appreciable fraction of the thallium(III) is present as TlOH^{2+} which absorbs at slightly longer wavelengths. This absorption is also attributed to a spin-allowed ligand-to-metal charge-transfer transition in the TlOH^{2+} species. The corresponding triplet charge-transfer states will lie at lower energy, but the singlet-triplet separation is not expected to be large. Luminescence from Tl^{3+} in glasses at 77 K has been looked for but has not been observed.[21] We conclude that neither $\mathrm{Tl_{aq}}^{3+}$ nor TlOH^{2+} are expected to have electronically excited states in the energy range of the $^3\mathrm{CT}$ state of $\mathrm{Ru(bipy)_3}^{2+}$.

Even if direct energy transfer were possible, the limiting quantum yield of 2 implies that a reactive intermediate or intermediates capable of oxidizing two $\mathrm{Ru(bipy)_3}^{2+}$ ions must be created as a result of the energy transfer. This would only be possible if the energy transfer produced from Tl^{3+} or TlOH^{2+} a Tl^{2+} ion and an oxidizing radical, which in these systems could only be OH. The minimum energy for the production of Tl^{2+} and OH from $\mathrm{Tl_{aq}}^{3+}$ can be estimated from the standard reduction potentials and is *ca.* 21 kK, well above the triplet charge-transfer energy of $\mathrm{Ru(bipy)_3}^{2+}$.

The observation that 1 *M* methanol did not alter the quantum yield supports the mechanism of quenching by direct electron transfer from the triplet charge-transfer state and shows that a free-radical mechanism is not involved. Methanol reacts with Tl^{2+} to give Tl^{+} and $\mathrm{CH_2OH}$ radicals which

$$\mathrm{CH_3OH + Tl^{2+} \rightarrow Tl^{+} + H^{+} + CH_2OH}$$

in the presence of Tl^{3+} produce formaldehyde and another Tl^{2+} ion.[17] The effect of these reactions is that the addition

$$\mathrm{CH_2OH + Tl^{3+} \rightarrow Tl^{2+} + H^{+} + CH_2O}$$

of methanol to the photolysis solutions should not alter the yield of $\mathrm{Ru(bipy)_3}^{3+}$ produced by the reaction of Tl^{2+} (step 10, Figure 4) because the chain termination reaction will be

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(20) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 2841 (1971).

(21) G. F. Kirkbright, C. G. Saw, and T. S. West, *Analyst (London)*, **94**, 538 (1969); *Talanta*, **16**, 65 (1969).

that between Tl^{2+} and $Ru(bipy)_3^{2+}$. It has recently been shown that $^3CT\ Ru(bipy)_3^{2+}$ can react with methanol in the glass phase at 77 K to give CH_2OH radicals and H atoms.[22]

$$^3CT\ Ru(bipy)_3^{2+} + CH_3OH \rightarrow Ru(bipy)_3^{3+} + H + CH_2OH^-$$

$$H + CH_3OH \rightarrow CH_2OH + H_2$$

These reactions cannot be important in our experiments because 1 *M* methanol did not quench the phosphorescence. The reaction is probably slow at room temperature because the quantum yield in pure methanol glasses at 77 K is less than 0.1 for a bulk methanol concentration of *ca.* 25 *M*.[23–25] In 1 *M* methanol solutions at room temperature this reaction would not be able to compete with the natural lifetime of the triplet charge-transfer state or the quenching by 10^{-2} *M* Tl^{3+}.

The unchanged quantum yield in the presence of methanol is consistent with the production of Tl^{2+} ions but it is not consistent with any reaction scheme which includes OH radicals. If OH radicals were produced as a result of the quenching process and then reacted with $Ru(bipy)_3^{2+}$ (this reaction being necessary if the limiting quantum yield is to be greater than 1), 1 *M* methanol would act as an effective scavenger for OH radicals in competition with 4×10^{-5} *M* $Ru(bipy)_3^{2+}$, because the rate constants for the reactions of OH radicals with CH_3OH and with $Ru(bipy)_3^{2+}$ are $4.8 \times 10^8\ M^{-1}\ sec^{-1}$ [26] and $9 \times 10^9\ M^{-1}\ sec^{-1}$.[27] The effect of this scavenging of the OH radicals would be to lower the quantum yield.

We conclude that step 7 in Figure 4 represents the first definite observation of the quenching of an inorganic donor by an electron-transfer process to a metal ion.

Mechanism of the Quenching by Fe^{3+} and Fe^{2+}. The mechanism of the quenching of the $Ru(bipy)_3^{2+}$ phosphorescence by Fe^{3+} ions with $k_q = 1.9 \times 10^9\ M^{-1}\ sec^{-1}$ has not been established. Spin-allowed energy transfer is possible to the 12.6-kK energy level of Fe_{aq}^{3+} and excitation of Fe^{3+} to this level would not be expected to cause sensitized reaction in the $Ru(bipy)_3^{2+}$-Fe^{3+} system. We have not observed any reaction in these solutions under steady irradiation at 464 nm. If the phosphorescence quenching by Fe^{3+} were due to electron transfer from the triplet charge-transfer state to give Fe^{2+} and $Ru(bipy)_3^{3+}$

$$^3CT\ Ru(bipy)_3^{2+} + Fe^{3+} \rightarrow Ru(bipy)_3^{3+} + Fe^{2+}$$

the fast thermal reaction between Fe^{2+} and $Ru(bipy)_3^{3+}$ would be sufficient to account for the absence of observable photolysis under continuous illumination. The rate constant for the thermal reaction between Fe^{2+} and $Ru(bipy)_3^{3+}$ is $7.2 \times 10^5\ M^{-1}\ sec^{-1}$ [16] and for the light intensities used in our experiments the steady-state concentrations of the Fe^{2+} and $Ru(bipy)_3^{3+}$ ions would be *ca.* 3×10^{-7} *M*. This concentration is only 0.5% of the initial concentration of $Ru(bipy)_3^{2+}$ and the half-life of the thermal reaction after illumination ceased would be 2–3 sec. These two factors would be sufficient to account for the absence of observable photoredox reaction between Fe^{3+} and $^3CT\ Ru(bipy)_3^{2+}$.[28]

The quenching by Fe_{aq}^{2+} is less effective than that by either Fe_{aq}^{3+} or Tl_{aq}^{3+}. The quenching rate constant of $1.8 \times 10^7\ M^{-1}\ sec^{-1}$ is approximately the same as that for quenching by Ni_{aq}^{2+} in the same ionic strength, $7 \times 10^6\ M^{-1}\ sec^{-1}$.[29] An electron-transfer quenching mechanism is not possible in this case, and the quenching must involve energy transfer to low-lying levels of Fe^{2+}. The greater efficiency of the quenching by Fe^{3+} is understandable as the quenching mechanism in this case is electron transfer rather than energy transfer.[28]

Electron-Transfer Reactions of $^3CT\ Ru(bipy)_3^{2+}$. The observation that the triplet charge-transfer state of $Ru(bipy)_3^{2+}$ can act as an efficient electron donor to Tl^{3+} (and also to Fe^{3+}) as well as an energy donor to other acceptors does not establish the relative importance of the two quenching mechanisms in general cases. Energy transfer in the absence of a redox reaction of the acceptor is more readily demonstrated experimentally[6,7] and few systems in which electron transfer might be energetically feasible have been examined. Natarajan and Endicott[10,11] have shown that energy transfer to a triplet charge-transfer state of the acceptor can lead to the same final products as would arise from direct electron transfer from the donor to the acceptor, and only a combination of dynamic photolysis and scavenger studies can establish the quenching mechanism with certainty in such cases. The nature of the acceptor states lying below the energy of the triplet charge-transfer donor state and their intersections with the potential energy surface for the electron-transfer products must be important in determining whether electron transfer or energy transfer takes place. Simplistic contrasts of energy transfer with electron transfer are not particularly useful because energy transfer to or from a charge-transfer state involves charge separation and the process is more akin to that taking place along the reaction coordinate during electron transfer than to processes of energy transfer involving localized (for example, d–d) excited states.

The relative importance of the factors which control the rates of electron-transfer reactions of excited charge-transfer states have not yet been explored. The triplet charge-transfer state of $Ru(bipy)_3^{2+}$ has been expected to prove a more powerful reducing agent than the ground state[5] but the relative reduction potentials are not themselves sufficient to determine the relative rates of electron-transfer reactions of ground and excited states or the relative importance of electron transfer to other processes such as energy transfer, provided that at least the minimum energy required for electron transfer is available from the donor. In general, the mechanism of the electron-transfer reactions (inner or outer sphere) may differ for the ground and excited states, and even for a

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[22] A. K. Breck and J. K. S. Wan, *Int. J. Radiat. Phys. Chem.*, 5, 517 (1973).

[23] The low quantum yield cannot be due to efficient electron transfer from the ^3CT state followed by back-reaction of the H atoms with $Ru(bipy)_3^{3+}$ because at room temperature 1 *M* methanol does not quench the phosphorescence and because although the relative effective concentrations in the bulk of the solution and in the cage are difficult to estimate, the rate constants for the reactions $Ru(bipy)_3^{3+} + H \rightarrow Ru(bipy)_3^{2+} + H^+$ and $CH_3OH + H \rightarrow CH_2OH + H_2$ are $1.7 \times 10^9\ M^{-1}\ sec^{-1}$ [24] and $1.2 \times 10^6\ M^{-1}\ sec^{-1}$ [25] so that solvent methanol will probably compete effectively with $Ru(bipy)_3^{3+}$ for H atoms. If the quantum yield for CH_2OH and H production is due entirely to the inefficiency of the quenching of the triplet charge-transfer state by methanol, we estimate that at 77 K the quenching rate constant is about 10^3–$10^4\ M^{-1}\ sec^{-1}$, and even at room temperature quenching by this reaction in 1 *M* methanol solution would be negligible.

[24] J. E. Martin, E. J. Hart, A. W. Adamson, H. Gafney, and J. Halpern, *J. Amer. Chem. Soc.*, 94, 9238 (1972).

[25] J. H. Baxendale, E. M. Fielden, and J. P. Keene, "Pulse Radiolysis," M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Academic Press, London, 1965, p 207.

[26] G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael, "Pulse Radiolysis," M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Academic Press, London, 1965, p 131.

[27] G. S. Laurence, unpublished observations.

[28] Flash photolysis experiments (C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Amer. Chem. Soc.*, 96, 4710 (1974)) have recently shown that Fe^{3+} quenches $^3CT\ Ru(bipy)_3^{2+}$ by an electron-transfer mechanism, producing Fe^{2+} and $Ru(bipy)_3^{3+}$ which then react thermally to give the original ions.

[29] V. Balzani, unpublished observations.

common outer-sphere mechanism differences in the intrinsic self-exchange barriers in the ground and excited states may be large, reflecting differences in the shapes of the potential energy surfaces in the two states. The intersections of the ground- and excited-state potential surfaces with that for the reaction products may also be so different that effects due to the differences in $\Delta G°$ for the reactions of the two states cannot necessarily be discussed in simple terms for the extrinsic barriers of the Marcus theory[30] of electron-transfer rates.

Tris(bipyridyl)ruthenium complexes are nonlabile and their electron-transfer reactions (such as that between Fe^{2+} and $Ru(bipy)_3{}^{3+}$) are outer sphere. The reaction between Tl^{3+} and $^3CT\ Ru(bipy)_3{}^{2+}$ is also outer sphere, and the rate constant is very much greater than that for the thermal reaction between ground state $Ru(bipy)_3{}^{2+}$ and Tl^{3+}, $1.9 \times 10^{-1}\ M^{-1}\ sec^{-1}$.[12] The standard one-electron reduction potential of Tl^{3+} is + 0.3 V,[13] and if $E°$ for the reduction of $Ru(bipy)_3{}^{3+}$ to $^3CT\ Ru(bipy)_3{}^{2+}$ is *ca.* −1 V, the standard free energy changes for the reactions of the ground and the triplet charge-transfer states will be +22 and −28 kcal mol^{-1}. Such large differences in $\Delta G°$ would be more than sufficient to account for the difference of a factor of 10^9 in the reaction rates, but as we have pointed out above, such an interpretation may be too simplistic. The quenching by Fe^{3+} is also due to an electron-transfer process,[28] and $\Delta G°$ is *ca.* −38 kcal mol^{-1}, again very much more favorable than $\Delta G°$ for the ground-state reaction, +11.5 kcal mol^{-1}. The rate constant for the ground-state reaction can be calculated from the rate of the reverse reaction[16] and is $2.6 \times 10^{-3}\ M^{-1}\ sec^{-1}$. Once again the increase in the rate of the reaction with $^3CT\ Ru(bipy)_3{}^{2+}$ cannot be assigned definitely to the change in the thermodynamic barrier for the electron transfer.

The ratio of the rate constants for the reactions of Tl^{2+} with $Ru(bipy)_3{}^{2+}$ and $Ru(bipy)_3{}^{3+}$ is 1.6. The reactions have almost the same $\Delta G°$ (−21.8 and −22.1 kcal mol^{-1}, respectively, which are the same within the experimental errors in the $E°$ values for the couples involving Tl^{2+})[13] and the near identity of the rate constants is not surprising, as the reactions are outer sphere and the self-exchange rates for Tl^{III}-Tl^{II} and Tl^{II}-Tl^{I} are probably very similar. From the correlation between $\Delta G°$ and $\Delta G^{\ddagger}$ for other outer-sphere electron-transfer reactions of Tl^{2+},[15] for $\Delta G° = -22$ kcal mol^{-1}, k_9 and k_{10} are expected to be of the order of 10^6-$10^7\ M^{-1}\ sec^{-1}$.

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Registry No. $Ru(bipy)_3{}^{2+}$, 15158-62-0; Fe^{3+}, 20074-52-6; Tl^{3+}, 14627-67-9; Fe^{2+}, 15438-31-0; Tl^{+}, 22537-56-0.

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[30] R. A. Marcus, *J. Phys. Chem.*, 67, 853 (1963); 72, 891 (1968).

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Reaction Mechanisms of Metal-Metal Bonded Carbonyls. IX.[1] Reaction of Tri-*n*-butylphosphine with Dodecacarbonyltriruthenium and Tetracarbonyl(tri-*n*-butylphosphine)ruthenium

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Tri-*n*-butylphosphine reacts with dodecacarbonyltriruthenium according to the rate equation $k_{obsd} = k_1 + k_2[PBu_3]$. $\Delta H_2{}^{\ddagger} = 50.43 \pm 0.80$ kJ mol^{-1}, $\Delta S_2{}^{\ddagger} = -115.0 \pm 2.5$ J K^{-1} mol^{-1}, and $10^2 k_2(50°) = 4.56 \pm 0.17$ l. mol^{-1} sec^{-1}. The products of the reaction are the complexes $Ru_3(CO)_9(PBu_3)_3$, $Ru(CO)_4PBu_3$, and *trans*-$Ru(CO)_3(PBu_3)_2$ in ratios that depend on the relative initial concentrations of complex and phosphine, high values of $[Ru_3(CO)_{12}]/[PBu_3]$ leading to more trinuclear product and low values to more mononuclear products. When mainly mononuclear products are formed, the ratio $[Ru(CO)_4PBu_3]/[Ru(CO)_3(PBu_3)_2]$ in the product solutions is 2:1 suggesting that fission of the Ru_3 cluster occurs mainly in $Ru_3(CO)_{11}PBu_3$. The $Ru(CO)_4$ and $Ru(CO)_3PBu_3$ products of this fission show a strong tendency to trimerize rather than to add an additional ligand. The substitution reaction of tri-*n*-butylphosphine with the complex $Ru(CO)_4PBu_3$ proceeds by a dissociative mechanism and is much more rapid than that of $Fe(CO)_4PPh_3$. Reaction under an atmosphere of carbon monoxide shows that carbon monoxide is about 6 times more nucleophilic than tri-*n*-butylphosphine toward the intermediate $Ru(CO)_3PBu_3$.

Introduction

Reactions of dodecacarbonyltriruthenium with simple phosphorus-donor nucleophiles are generally believed[2-4] to proceed in a stepwise manner to form the trisubstituted complexes $Ru_3(CO)_9L_3$ in which one ligand L is attached to each ruthenium atom in the triangular metal cluster. Whether intermediate, less substituted complexes are formed in detectable amounts during the course of the reaction depends on the particular nucleophile employed. Thus with triphenylphosphine no intermediates are detected although the complex $Ru_3(CO)_{11}PPh_3$ has been isolated after reaction of the dodecacarbonyl with triphenylphosphine in hexane.[4] With triphenyl phosphite and ETPB ($P(OCH_2)_3CEt$) ir bands assignable to mono- and disubstituted intermediates are seen to rise and fall in intensity during the reaction, the trisubstituted complex being the final product.[1a]

Reactions with $P(OPh)_3$,[1] PPh_3,[1] $P(OCH_2)_3CEt$,[1] $P(OMe)_3$,[1] $PMePh_2$,[5] PEt_2Ph,[2] PEt_3,[2] and $P(n\text{-}Bu)_3$[1,2] all proceed by

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[1] (a) Part VIII: A. J. Poë and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, in press; (b) A. J. Poë and M. V. Twigg, *J. Organometal. Chem.*, 50, C39 (1973).

[2] J. P. Candlin and A. C. Shortland, *J. Organometal. Chem.*, 16, 289 (1969), and references therein.

[3] M. I. Bruce and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 7, 427 (1968).

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