helically chiral molecular propellers and rearrange by means of concerted rotations of the substituents on the central atom strongly suggests that such behavior should be considered in studies of other stereochemically equivalent systems such as guanidinium ions.

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Reaction of e_{aq}^- into Excited States of Ru(bpy)$_3^{2+}$ [1]

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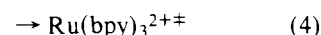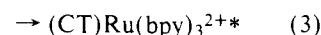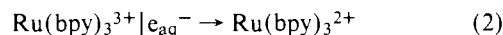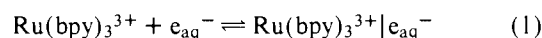
Abstract: In the reaction of e_{aq}^- with Ru(bpy)$_3^{3+}$ it was found that 38% of e_{aq}^- yields (CT)Ru(bpy)$_3^{2+*}$, the well-known, luminescent lowest charge transfer state of Ru(bpy)$_3^{2+}$. More than 55% of e_{aq}^- (that is, almost all of the remainder) yields another excited state or a coordinated radical complex, which is longer lived than (CT)Ru(bpy)$_3^{2+*}$ and does not convert to it. A very small fraction of e_{aq}^- (<7%) is transferred directly to the ground state. While (CT)Ru(bpy)$_3^{2+*}$ decays to the ground state both by first-order conversion and through quenching by Ru(bpy)$_3^{3+}$, the other product decays to Ru(bpy)$_3^{2+}$ almost solely (under our conditions) through a reaction with Ru(bpy)$_3^{3+}$. The lack of a significant direct reaction to the ground state is rationalized as an example of the slow electron transfers to be expected for highly exergonic reactions in the "inverted" region of the Marcus theory. H atoms, Cd⁺, and Ru(bpy)$_3^+$ were found to react with Ru(bpy)$_3^{3+}$ to yield the divalent ground state directly.

Introduction

The reduction of Ru(bpy)$_3^{3+}$ (bpy = 2,2-bipyridine) by several reductants yields the lowest charge transfer state of Ru(bpy)$_3^{2+}$ (denoted (CT)Ru(bpy)$_3^{2+*}$).[2] This was shown to be the case for reduction of Ru(bpy)$_3^{3+}$ by OH⁻ ions,[3] by hydrazine,[4] and by various products of electrochemical reduction of Ru(bpy)$_3^{2+}$.[5] In all of these reactions chemiluminescence was observed, the spectrum of which was similar to the emission spectra obtained on excitation of Ru(bpy)$_3^{2+}$ by light to its lowest charge transfer state.[6] However, in most of these systems it is improbable that the chemiluminescence is a result of simple electron transfer from the reductant to Ru(bpy)$_3^{3+}$ since the thermodynamics of such a simple transfer are either unfavorable or marginally favorable. Recently, Martin et al.[7] have demonstrated that a relatively efficient chemiluminescence results when Ru(bpy)$_3^{3+}$ is reduced

by aquated electrons, e_{aq}^- Since by nature of the reductant the most probable mechanism is a direct electron transfer to Ru(bpy)$_3^{3+}$ we considered it to be of some interest to study this reaction in detail.

Once an e_{aq}^- encounters Ru(bpy)$_3^{3+}$ and a precursor complex is formed[8] (reaction 1) the transferred electron might then find itself after vibrational relaxation in any of the following possible states:

$$Ru(bpy)_3^{3+} + e_{aq}^- \rightleftharpoons Ru(bpy)_3^{3+}|e_{aq}^- \qquad (1)$$

$$Ru(bpy)_3^{3+}|e_{aq}^- \rightarrow Ru(bpy)_3^{2+} \qquad (2)$$

$$\rightarrow (CT)Ru(bpy)_3^{2+*} \qquad (3)$$

$$\rightarrow Ru(bpy)_3^{2+\ddagger} \qquad (4)$$

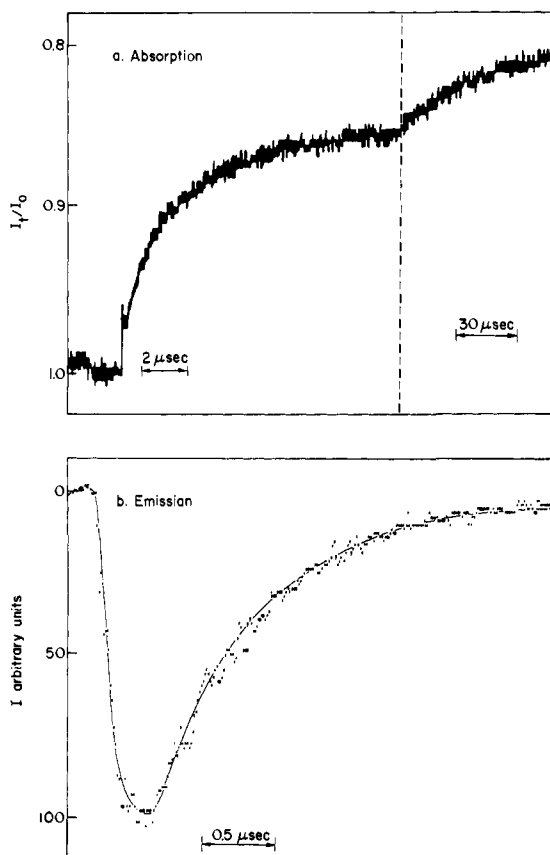Namely, either the ground state (reaction 2) or the lowest charge transfer state (reaction 3) or some other product such

Figure 1. Typical Biomation output in (a) absorption mode at 455 nm; (b) emission mode at 600 nm. Conditions: 10^{-4} M $Ru(bpy)_3^{3+}$, pH 4.6 (acetate buffer), 0.5 M t-BuOH, $\mu = 1.5$, Ar saturated, 2-ns pulse width. Dashed line indicates time scale switching. Solid line in (b) shows the nonlinear least-squares fit of the two consecutive exponentials.

as another excited state or coordinated radical (reaction 4) would be produced. The well-known absorption characteristics of $Ru(bpy)_3^{2+}$ and the detailed information available on the emission characteristics of $(CT)Ru(bpy)_3^{2+*}$ [6,9] make it possible to determine both the yields and the rate constants of reactions 1–4. This is the principal aim of the present study.

Evidence that any excited state accessible by light excitation ($\lambda \gtrsim 250$ nm) collapses very rapidly and with an efficiency of unity to the lowest excited CT state has been presented.[6b] It seems therefore unlikely that reaction 4 could be observed with our pulse radiolysis technique, if $Ru(bpy)_3^{2+\mp}$ corresponds to any of these higher optically excited states. Nonetheless, evidence will be presented here that products other than $(CT)Ru(bpy)_3^{2+*}$, and which are longer lived, are accessible on electron transfer. On the other hand, we find that only a negligible amount of the electrons are transferred from e_{aq}^- directly to the ground state (reaction 2) while the large majority of the products get to the ground state via the other intermediate states (reaction 5 and 6 and other pathways to be discussed).

$$(CT)Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} \ (+ \ h\nu \sim 4\%) \qquad (5)$$

$$Ru(bpy)_3^{2+\mp} \rightarrow Ru(bpy)_3^{2+} \qquad (6)$$
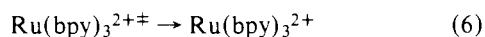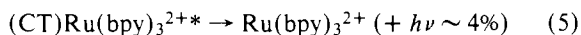
Rationalization for this behavior is obviously needed and excess exothermicity for reaction to the ground state is a possibility.[10]

Experimental Section

The computer-controlled kinetic spectrophotometric pulse radiolysis system has been described previously.[11] Electron pulses of ∼2 ns width produced ∼5 × 10^{-6} M of e_{aq}^- in 1-cm length cells. In a few experi-

ments in which excitation of $Ru(bpy)_3^{2+}$ by Čerenkov light was examined, 20-ns pulses were employed with correspondingly higher yield of radicals. The data were digitized on a Biomation 8100 transient recorder at a sampling rate of 10 ns per channel for first 2/3 of its 2000 channels and 0.1 μ per channel for the remainder of the channels (cf. Figure 1a). In all experiments the solutions were irradiated with a single pulse and then discarded. When spectra or yields were compared, the experiments were performed on the same day with exactly the same optical geometry, the same photomultiplier tube (Hamamatsu R818 or EMI 9781R), and the same gain and slit width. This is particularly important for the emission yields and spectra experiments. The rise time of the electronic setup was less than 20 ns. The yield of e_{aq}^- was measured at 600 nm taking $\epsilon_{600} = 1.25 \times 10^4$ M^{-1} cm^{-1}, and for dosimetry purposes $G_{e_{aq}^-} = 2.7$, $G_H = 0.6$, and $G_{OH} = 2.7$ molecules/100 eV were assumed. Data acquisition and kinetic analysis were done on a Sigma 5 computer.

$Ru(bpy)_3Cl_2$ (G. Fredrick Smith) was twice recrystallized from water. Oxidation to the trivalent state was carried out with PbO_2 in 1–0.1 N H_2SO_4 Ar-saturated solution that was filtered out under an Ar atmosphere a few minutes before irradiation. These solutions were then transfered to Ar- (or N_2O-) saturated solutions containing the other reagents of the desired final solution. This technique was sufficiently rapid for experiments in the very acid range, but turned out to be too slow for the higher pH range (typically pH 4.6 ± 0.1). Owing to the relatively short lifetime of $Ru(bpy)_3^{3+}$ in this pH range,[12] a few percent of $Ru(bpy)_3^{2+}$ was thermally produced and rendered the experiment extremely difficult. These small amounts of $Ru(bpy)_3^{2+}$ could not seriously affect the kinetic analysis or the emission yields but, owing to the high absorptivity of $Ru(bpy)_3^{2+}$, would absorb a large fraction of the analytical light when the absorption of $Ru(bpy)_3^{2+}$ was being monitored. In order to overcome this problem a flow system using motor-driven syringes was constructed to mix the acidic solution (10^{-1}–10^{-3} NH_2SO_4) of $Ru(bpy)_3^{3+}$ with the sodium acetate buffer solution (containing the other desired components of the final solutions). The "dead time" between the mixing point and complete filling of the irradiation cell was 3 s, and the time lapse between the end of the filling to the Linac pulse was 3–30 s. Using this flow system the amount of $Ru(bpy)_3^{2+}$ produced by the thermal reaction was reduced to a negligible level as was evident from the level of the analytical light. The mixed solution were collected and analyzed, after complete reduction, for $Ru(bpy)_3^{2+}$ (ϵ_{455} 1.4 × 10^4 M^{-1} cm^{-1}) and the pH was measured. The calculated pH and $[Ru(bpy)_3^{2+}]$ agreed to within 0.1 pH units or 5%, respectively, with the experimentally measured ones, indicating that the other constituents of the irradiated solutions are also very close to their calculated values. For experiments in this pH range 2–20 mM total concentration of acetate buffer was used. The ionic strength of the irradiated solutions was adjusted to 1.5 M using Na_2SO_4. Unless otherwise stated all chemicals used were of highest purity commercially available and were used without further purification. All solutions were prepared from triply distilled water. Deaeration was achieved by bubbling the desired gas for at least 10 min using either the syringe technique or a specially designed vessel for the $Ru(bpy)_3^{3+}$ parent solutions that allows manipulation of the solution under Ar atmosphere. The temperature of the irradiated solutions was 24 ± 1 °C.

Results and Discussion

Rate of Reaction with e_{aq}^-. The rate of disappearance of e_{aq}^- in Ar-saturated $Ru(bpy)_3^{3+}$ solutions (at pH 4.6, containing 0.5 M *tert*-butyl alcohol as an OH radical scavenger) was measured by following the decay of its absorption at 600 nm. Concomitant with the decay of e_{aq}^-, formation of an emission could also be observed at 600 nm.[13] A typical trace showing the time dependence of the emitted light is displayed in Figure 1b. This emission cannot be attributed to excitation of residual $Ru(bpy)_3^{2+}$ by Čerenkov light since its time of formation is much longer than the 2-ns pulse width and since the intensity is much stronger than the intensity of emission obtained by Čerenkov excitation of 10^{-4} M $Ru(bpy)_3^{2+}$ in otherwise similar conditions (see below and Table I). Furthermore, the rate of the formation of the emission was linearly dependent on $[Ru(bpy)_3^{3+}]$, in line with our interpretation that this formation represents the rate of reaction 1 rapidly followed by reaction 3. Further verification of the rate of the reaction of
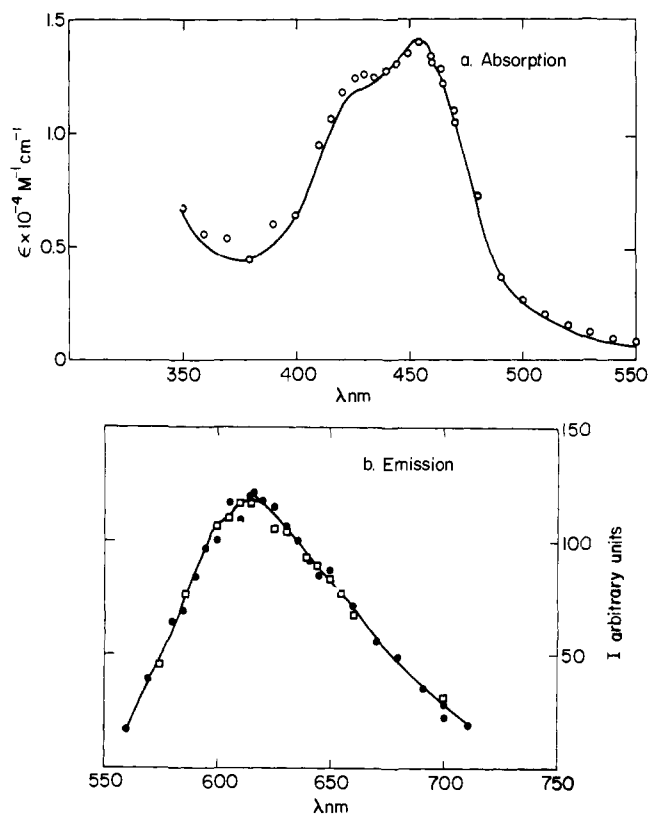
Figure 2. Absorption spectrum of $Ru(bpy)_3^{2+}$ and emission spectra of $(CT)Ru(bpy)_3^{2+*}$ obtained by pulse radiolysis. (a) Absorption (O) pulse radiolysis (2-ns pulse) of 10^{-4} M $Ru(bpy)_3^{3+}$, 0.5 M *tert*-butyl alcohol, pH 4.6 (2 mM acetate buffer), Ar saturated at $\mu = 1.5$ M. Taken 7 μs after the pulse. Solid line is spectrum of $Ru(bpy)_3^{2+}$ taken on a Cary 14 spectrometer. Both normalized at 455 nm. (b) Emission ($\bullet$) pulse radiolysis of the same solutions as above. ($\square$) Čerenkov excitation of similar solutions except for 10^{-4} M $Ru(bpy)_3^{2+}$ and N_2O saturated. Both normalized at 615 nm.

e_{aq}^- with $Ru(bpy)_3^{3+}$ comes from the formation of the absorption of the excited states of $Ru(bpy)_3^{2+}$. This absorption, peaking at 365 nm, is shown below to be attributable to the various intermediates involved. It was formed with a rate similar both to the decay of e_{aq}^- and the formation of the emitting state.

In order to account for the small distortion of the observed rate of formation of the emission by its rate of decay (or vice versa) a nonlinear least-squares curve fitting was employed. Consecutive exponential kinetics, including reactions 1, 5, and 7, were assumed in this procedure. The two parameters to be fit were then k_1 and $(k_5 + k_7[Ru(bpy)_3^{3+}])$. Such a fit is shown in Figure 1b. The observed rate constants thus obtained were linearly dependent on $[Ru(bpy)_3^{3+}]$ and from this dependence $k_1 = (4.8 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1} is obtained. Similarly from the rate of the formation of the 365-nm absorption we get $k_1 = (5.6 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}. From the decay of the e_{aq}^- absorption at 600 nm we get $k_1 = (5.3 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1} assuming simple pseudo-first-order disappearance. The close agreement in these values is considered to indicate that these rate constants correspond to the same reaction, the reaction of e_{aq}^- with $Ru(bpy)_3^{3+}$. The precursor complex is not expected to have any appreciable lifetime on this time scale; we therefore conclude that $k_1 (\simeq k_2 + k_3 + k_4) = 5.2 \pm 0.5 \times 10^{10}$ M^{-1} s^{-1}.

$$(CT)Ru(bpy)_3^{2+*} + Ru(bpy)_3^{3+} \rightarrow Ru(bpy)_3^{2+} + Ru(bpy)_3^{3+} \quad (7)$$
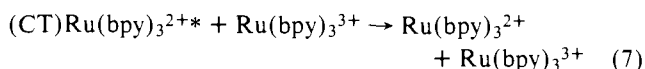
Identity of the Emitting State. Martin et al.[7] have suggested that the emitting state produced by the reaction of e_{aq}^- with
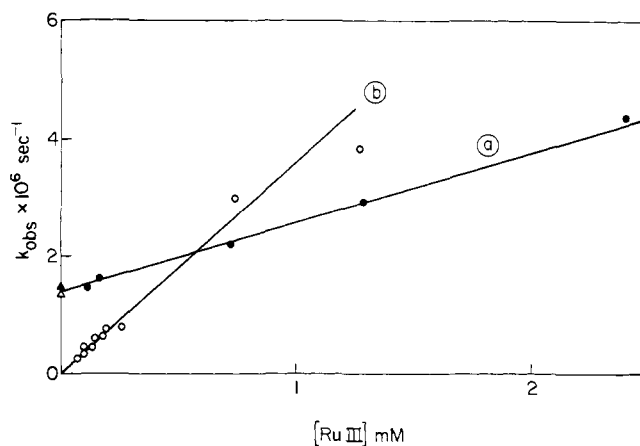

Figure 3. The dependence of the observed pseudo-first-order rate constant for the decay of the emission (a) and formation of the absorption (b) on $[Ru(bpy)_3^{3+}]$: ($\bullet$) decay of the chemiluminescence at 600 nm. (O) Formation of absorption at 455 nm. Rate constants taken from numerical integration (see text) conditions as in Figure 1, except for variable $[Ru(bpy)_3^{3+}]$ and $[Ru(bpy)_3^{3+}]/[acetate] = 0.1$. ($\blacktriangle$) First-order rate constant for decay of emission of Čerenkov excited $Ru(bpy)_3^{2+}$ (λ 600 nm). ($\triangle$) First-order rate constant for re-formation of bleached $Ru(bpy)_3^{2+}$ after Čerenkov excitation (λ 455 nm). Conditions for these are as in Figure 4.

$Ru(bpy)_3^{3+}$ is $(CT)Ru(bpy)_3^{2+*}$. We verified this identity by comparing the emission spectrum obtained from the reaction of e_{aq}^- with $Ru(bpy)_3^{3+}$ with the one obtained from Čerenkov excitation of $Ru(bpy)_3^{2+}$. The solution contained 10^{-4} M of either $Ru(bpy)_3^{3+}$ or $Ru(bpy)_3^{2+}$ and 0.5 M t-BuOH, 2 mM acetate buffer at $\mu = 1.5$ M and was saturated with either Ar or N_2O correspondingly. Under the latter conditions only small amounts of the $Ru(bpy)_3^{2+}$ in the Čerenkov excitation experiments are expected to be destroyed by reactions with the radiolytically produced radicals and none of the products absorbs light in the red range of the spectrum. The emission spectra thus obtained are compared in Figure 2b. The close correspondence between the two spectra leaves little doubt that both should be attributed to the same emitting state and the well-known spectroscopy of $Ru(bpy)_3^{2+}$ leads to the conclusion that this is most probably the $(CT)Ru(bpy)_3^{2+*}$ state.[6,9] The lifetime of the emitting state and the rate of its quenching by $Ru(bpy)_3^{3+}$ all accord with this identification (see below).

Decay Rate of the Emitting State. The decay rate of the chemically produced emission was found to depend on $[Ru(bpy)_3^{3+}]$. The linear dependence of the observed pseudo-first-order rate constant on $[Ru(bpy)_3^{3+}]$ (obtained from kinetic analysis of the emission signals such as in Figure 1b) is shown in Figure 3a. From the slope of the line in Figure 3a we obtain $k_7 = (1.8 \pm 0.2) \times 10^9$ M^{-1} s^{-1} and from the intercept $k_5 = (1.4 \pm 0.2) \times 10^6$ s^{-1}. The commonly observed value for the natural lifetime of $(CT)Ru(bpy)_3^{2+*}$ produced by light excitation corresponds to $k_5 = (1.6 \pm 0.2) \times 10^6$ s^{-1}.[14-17] The rate constant of reaction 7 has recently been reported[18] to be 1.6×10^9 M^{-1} s^{-1}. Note the substantial agreement between the values of the rate parameters obtained by the different methods.

Yield of the Chemically Produced $(CT)Ru(bpy)_3^{2+*}$. We can determine the fraction of e_{aq}^- reacting with $Ru(bpy)_3^{3+}$ that produces $(CT)Ru(bpy)_3^{2+*}$ if we proceed as follows. In one set of experiments we irradiate $Ru(bpy)_3^{2+}$ with Čerenkov light and measure the yield of light emission corresponding to a given amount of bleaching of $Ru(bpy)_3^{2+}$ absorption. In another set of experiments we measure the yield of light emission corresponding to a given amount of e_{aq}^- reacting with $Ru(bpy)_3^{3+}$. Comparison of (light emission)/($Ru(bpy)_3^{2+}$ bleached) from the first set of experiments with (light emis-
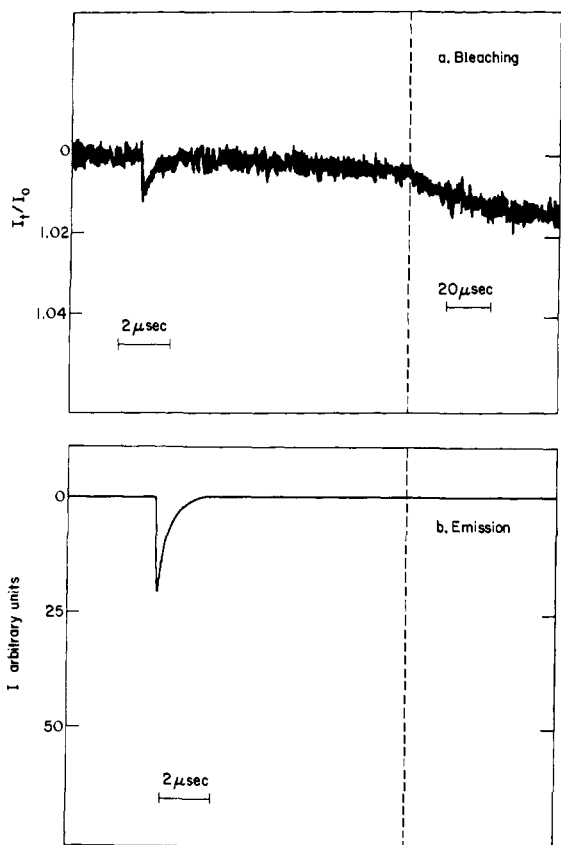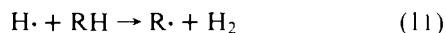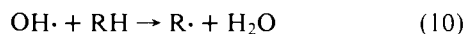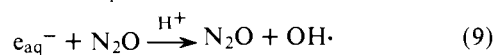
Figure 4. Calibration of emission intensity by bleaching of $Ru(bpy)_3^{2+}$ using Čerenkov excitation. (a) Bleaching at 455 nm. Note early re-formation of $Ru(bpy)_3^{2+}$ and later slow bleaching by 2-propanol radicals. (b) Emission at 600 nm. Conditions: 20-ns pulse width on 10^{-4} M $Ru(bpy)_3^{2+}$, 1 M 2-propanol, 1 N H_2SO_4, N_2O saturated at $\mu = 1.5$ M.

sion)/(e_{aq}^- reacting with $Ru(bpy)_3^{3+}$) from the second set gives the fraction of $e_{aq}^- + Ru(bpy)_3^{3+}$ proceeding by eq 3. If the conditions of measurement in the two sets of experiment are identical, an unknown but identical fraction of the total light emission will be measured for both sets. Since the optical geometry was the same in the Čerenkov excitation and $e_{aq}^- + Ru(bpy)_3^{3+}$ experiments and, since the spatial distribution of Čerenkov light is very similar to the distribution of e_{aq}^- in the irradiation cells, our calibration method is justifiable. For the Čerenkov excitation experiments 10^{-4} M $Ru(bpy)_3^{2+}$ in 1 M 2-propanol N_2O-saturated solutions at 1 N H_2SO_4 were irradiated with an electron pulse of 20-ns width. Both the intensity of the emission signal at 600 nm and the amount of $Ru(bpy)_3^{2+}$ bleached at 455 nm were monitored. In these solutions practically all e_{aq}^- are converted mainly to H atom and to a lesser extent to OH radicals on reacting with H^+ or N_2O. These radicals in turn react with 2-propanol to produce $(CH_3)_2\dot{C}OH$ radicals (reactions 8–11).

$$e_{aq}^- + H^+ \rightarrow H\cdot \qquad (8)$$

$$e_{aq}^- + N_2O \xrightarrow{H^+} N_2O + OH\cdot \qquad (9)$$

$$OH\cdot + RH \rightarrow R\cdot + H_2O \qquad (10)$$

$$H\cdot + RH \rightarrow R\cdot + H_2 \qquad (11)$$

All the primary radicals produced on water irradiation will therefore produce the alcoholic radicals which will then react with $Ru(bpy)_3^{2+}$.
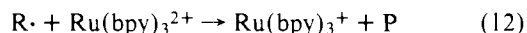
$$R\cdot + Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^+ + P \qquad (12)$$

Table I. Yield of Emission from $(CT)Ru(bpy)_3^{2+}$* Under Various Experimental Conditions

Reducing radical	[Ru-(bpy)$_3^{3+}$], M	Other additives,[a] M	I_{obsd}[b]	I_{cor}[e]
e_{aq}^-	1.0×10^{-4}	pH 4.5, 2 mM acetate	170	205
e_{aq}^-	1.1×10^{-4}	pH 4.6, 20 mM acetate	120[c]	223
e_{aq}^-	2.1×10^{-4}	pH 4.6, 2 mM acetate	168	196
e_{aq}^-	4.3×10^{-4}	pH 4.6, 2 mM acetate	167	208
e_{aq}^-	7.5×10^{-4}	pH 4.6, 2 mM acetate	151	220
e_{aq}^-	1.4×10^{-3}	pH 4.6, 2 mM acetate	131	260
e_{aq}^-	2.3×10^{-3}	pH 4.6, 2 mM acetate	109	302
H·	$(1-10) \times 10^{-3}$	1 N H_2SO_4	1.6	
Cd^+	$(1-8) \times 10^{-3}$	0.5 M $CdSO_4$, pH 4.6	1.1	
$h\nu$	$(1-8) \times 10^{-3}$			
Čerenkov excitation		10^{-4} M $Ru(bpy)_3^{2+}$ [d]	3.8	
$Ru(bpy)_3^+$	1×10^{-4}	2×10^{-3} M Ru-$(bpy)_3^{2+}$, pH 4.6	1.9	

[a] Unless otherwise stated all are Ar saturated containing 0.5 M *tert*-butyl alcohol at $\mu = 1.5$ M and irradiated with 2-ns pulse. [b] Emission intensity in arbitrary units, at 600 nm, relative to the first solution. [c] This yield is reduced by reaction of the e_{aq}^- with the larger concentration of acetic acid and corresponds to the same experimental conditions as in Figure 5 and Table II. [d] Containing 1 N H_2SO_4, 1 M 2-propanol, N_2O saturated at $\mu = 1.5$, 20-ns pulse. Yield normalized to 2-ns pulse. [e] Intensity corrected for inner filter effect assuming uniform concentrations throughout the cell and for competition for e_{aq}^- taking the same rate constants as in Table II. Correction for spur scavenging was also applied using $e_{aq}^-(t) = 2.7 + 1.4 \exp(-10^8 t)$.[33]

Reaction 12, however, is slow enough to permit us to measure the yield of bleaching of $Ru(bpy)_3^{2+}$ excited by the Čerenkov light (reaction 13, where $h\nu$ is the Čerenkov light).

$$Ru(bpy)_3^{2+} + h\nu \rightarrow (CT)Ru(bpy)_3^{2+}* \qquad (13)$$
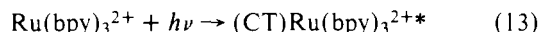
In Figure 4 we show the computer output of such a calibration experiment in the bleaching mode and the emission mode. As discussed above such experiments relate emission intensities to concentrations of excited states. Furthermore, the recovery of the bleached $Ru(bpy)_3^{2+}$ could be followed (corresponding to reaction 5 in absorption mode) before the much greater bleaching by reaction 12 became dominant (Figure 4a). We can thus compare the rate of decay of the emission with the rate of recovery of $Ru(bpy)_3^{2+}$ excited by Čerenkov light. Since both rate constants thus obtained were identical to within 10% (see the two points at the left margin in Figure 3, line a) we conclude that $(CT)Ru(bpy)_3^{2+}$* decays directly to the ground state.

The yields of the chemiluminescence under various conditions are summarized in Table I. All the experiments for these measurements were done under identical conditions except for the following differences: (a) The dose used was 10 times smaller (2-ns pulses) than that for the Čerenkov excitation experiments. Dosimetry was applied for both doses but it should be reemphasized here that our method for calibrating the amount of $(CT)Ru(bpy)_3^{2+}$* is independent of the dosimetry. (b) For the chemiluminescence experiments the solutions were Ar saturated (obviously to ensure reaction of e_{aq}^- with $Ru(bpy)_3^{3+}$) rather than N_2O saturated. Also in the chemiluminescence experiments $Ru(bpy)_3^{3+}$ and *t*-BuOH replaced the $Ru(bpy)_3^{2+}$ and 2-propanol of the Čerenkov experiments. (We find that the high concentration (we tried ~0.5 M) of 2-propanol needed to scavenge OH· and H· radicals reduced $Ru(bpy)_3^{3+}$ very fast. The same is true for methanol,

ethanol, or formate.) Once the amount of $(CT)Ru(bpy)_3^{2+*}$ produced by the reaction of e_{aq}^- with $Ru(bpy)_3^{3+}$ is determined, and once dosimetry is done, we can determine $f_{CT} = G(CT)Ru(bpy)_3^{2+*}/G_{e_{aq}^-}$, the fraction of the total yield of e_{aq}^- that produces $(CT)Ru(bpy)_3^{2+*}$. The yields reported in Table I were all extrapolated to the middle of the pulse and therefore represent the amount of $(CT)Ru(bpy)_3^{2+*}$ produced before an appreciable amount of it had decayed by reactions 5 and 7. However, the observed yields are seen in Table I to fall somewhat at $[Ru(bpy)_3^{3+}] \geq 1$ mM. This is attributed mainly to an inner filter effect (absorption into the LMCT bands of $Ru(bpy)_3^{3+}$ in this region of the spectrum) and to some extent to inaccuracy in the extrapolation technique. In the last column in Table I corrections for the inner filter effect and for the other reactions competing for e_{aq}^- were included. From the yield in Table 1 at $[Ru(bpy)_3^{3+}] \leq 1$ mM, where the corrections are relatively small, we calculate $f_{CT} = 0.38 + 0.05$. In calculating this value from the bleaching calibration experiments we assumed that $Ru(bpy)_3^{2+*}$ does not absorb light at 455 nm. However, as we show later, the maximum ϵ_{455} for this state that would concur with our later absorption experiments is 2300 M^{-1} cm^{-1}. This latter ϵ_{455} for $Ru(bpy)_3^{2+*}$ would raise f_{CT} to 45%.

This is a significant result since it indicates that only about 40% of the electrons transferred from e_{aq}^- end up in the $(CT)Ru(bpy)_3^{2+*}$ state. Since, as is discussed below, 100% of e_{aq}^- yields $Ru(bpy)_3^{2+}$, the rest of the 60% must arrive at the ground state via routes other than reactions 3, 5, and 7. It should be pointed out that this result is in surprisingly good agreement with the results of Martin et al.[7] These authors find that the absolute yield of chemiluminescence $\phi_{chem} = 0.015 \pm 0.004$. Since the quantum yield of photoluminescence by light excitation is 0.042 ± 0.002[17] it follows that f_{CT} obtained by Martin et al. is 36%, and considering the different and rather elaborate methods of calibration the agreement is much better than expected.

Formation of $Ru(bpy)_3^{2+}$. The yield and formation rate of ground state $Ru(bpy)_3^{2+}$ could be followed at the absorption maximum of its MLCT band at 455 nm. A typical result obtained in the absorption mode is shown in Figure 1a.

The absorption obtained immediately after the pulse is attributed to e_{aq}^-, which then decays very rapidly by reaction 1. After an observable time lag (corresponding to a time lapse during which $Ru(bpy)_3^{2\pm}$ and $(CT)Ru(bpy)_3^{2+*}$ do not decay to an appreciable extent) the buildup of $Ru(bpy)_3^{2+}$ can be seen to occur over a few microseconds. After the absorption from this stage levels off, further increase in absorption occurs over the tens of microseconds time range. This latter process is attributed to reduction of $Ru(bpy)_3^{3+}$ by $(CH_3)_2C(OH)$-$\dot{C}H_2$ radicals obtained from *tert*-butyl alcohol and will be discussed later.

The identity of the product obtained 7 μs after the onset of the electron pulse was determined unequivocally to be ground state $Ru(bpy)_3^{2+}$ by comparing its spectrum with that of the well-known spectrum of $Ru(bpy)_3^{2+}$ (Figure 2a). The spectrum of the radiolytically produced $Ru(bpy)_3^{2+}$ was corrected for destruction of $Ru(bpy)_3^{3+}$. If both e_{aq}^- and H atoms (see below) ultimately produce $Ru(bpy)_3^{2+}$ the assumption that $G(Ru(bpy)_3^{2+}) = G_{e_{aq}^-} + G_H = 3.3$ molecules/100 eV yields ϵ_{455} $(1.5 \pm 0.1) \times 10^4$ M^{-1} cm^{-1}. This value for ϵ_{455}, which is nearly identical with the one commonly accepted for $Ru(bpy)_3^{2+}$, substantiates these assumptions and indicates that close to 100% of e_{aq}^- do indeed produce $Ru(bpy)_3^{2+}$.

The rate of formation of $Ru(bpy)_3^{2+}$ can be seen in Figure 1 to proceed more slowly than the rate of decay of the emission from $(CT)Ru(bpy)_3^{2+*}$. Furthermore, this formation rate is more strongly dependent on $[Ru(bpy)_3^{3+}]$ than the rate of the decay of the emission. Two artifacts were suspected to cause this effect and were rejected after careful examination. One
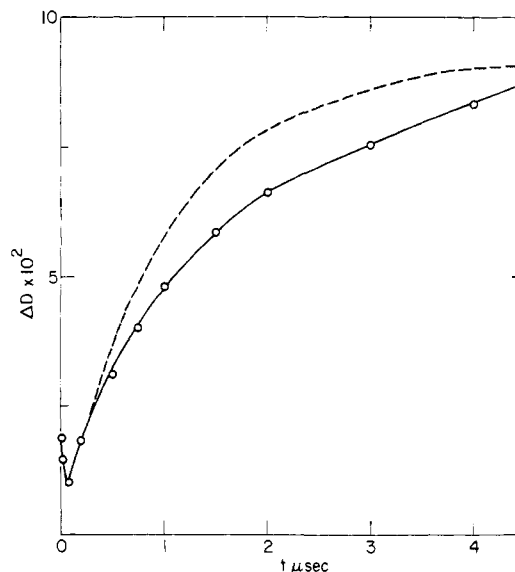

Figure 5. Numerical integration for the formation of $Ru(bpy)_3^{2+}$ using the set of reactions in Table II. (O), experimental points; dashed curve, calculated result neglecting any $Ru(bpy)_3^{2+\mp}$ and assuming $k_1 = k_2 + k_3$; solid curve, including all reactions of Table II. Conditions as in Figure 1 but 20 mM acetate buffer.

is the remote possibility that our flash boosted analyzing lamp might excite the $Ru(bpy)_3^{2+}$ back to $(CT)Ru(bpy)_3^{2+*}$ through some kind of complicated mechanism.[19] This possibility was rejected since insertion of an interference filter (433 $\pm$ 27 nm, 9% peak transmission) in the path of the analytical light and avoiding flashing the lamp (a combined effect of $\sim 10^4$ reduction in possible photolyzing light intensity) had a negligible effect on the rate of $Ru(bpy)_3^{2+}$ formation. Another artifact that would slow down the observed rate of formation is the occurrence of the reaction of H$\cdot$ atoms with $Ru(bpy)_3^{3+}$.

$$H\cdot + Ru(bpy)_3^{3+} \rightarrow H^+ + Ru(bpy)_3^{2+} \qquad (14)$$
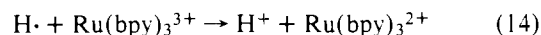
Apart from the initial yield, some H$\cdot$ atoms are produced from the reaction of e_{aq}^- with acetic acid present in the buffered solutions ($k_{15} = 1.8 \times 10^8$ M^{-1} s^{-1}).[21]

$$e_{aq}^- + CH_3CO_2H \rightarrow CH_3CO_2^- + H\cdot \qquad (15)$$

The contribution of H$\cdot$ atoms was evaluated by numerical integration of the whole series of reactions expected in this system which are summarized in Table II. The integration was performed using the program of Schmidt[22] designed for standard pulse radiolysis experiments. Summarized in Table II are also the various rate constants employed, taken either from well-documented sources or from this work. The only free parameter was the sum of the rate constants $k_6 + k_{16}[Ru(bpy)_3^{3+}]$.

$$Ru(bpy)_3^{2+\mp} + Ru(bpy)_3^{3+} \rightarrow Ru(bpy)_3^{2+}$$
$$+ Ru(bpy)_3^{3+} \qquad (16)$$
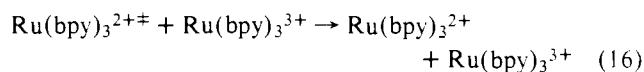
From Figure 5 it is clear that inclusion of eq 14 is not sufficient and that unless reactions 4, 6, and 16 are included a fit between the experimental and calculated results cannot be obtained. A satisfactory fit is obtained when $f_\pm = G(Ru(bpy)_3^{2+\mp})/G_{e_{aq}^-} = 0.55$ and k_6 and k_{16} are included. A typical fit is shown in Figure 5 where an experiment with the highest contribution from reaction 15 was chosen for display. The determination of the individual rate constants for the different modes of decay of $Ru(bpy)_3^{2\pm}$, k_6 and k_{16}, was obtained by repeating this fitting technique over $[Ru(bpy)_3^{3+}] = (0.1-1.4) \times 10^{-3}$ M.

Table II. Kinetics and Yields in the Reduction of $Ru(bpy)_3^{3+}$ by e_{aq}^- [a]

Reaction no.	Reaction	k, M^{-1} s^{-1} or s^{-1}	Method for k measurement	f_i[b]	Method for f_i measurement
3	$e_{aq}^- + Ru(III) \rightarrow Ru(II)^*$	2.0×10^{10}	Decay of e_{aq}^-, formation of $Ru(II)^*$ in emission and absorption modes	(0.38) 0.21	Yield of emission calibrated against Čerenkov excitation
4	$e_{aq}^- + Ru(III) \rightarrow Ru(II)^{\ddagger}$	3.1×10^{10}	Decay of e_{aq}^- and yields of emission	(0.55) 0.32	Yield of emission and material balance
2	$e_{aq}^- + Ru(III) \rightarrow Ru(II)$	3.4×10^{9} [c]	As above	(0.07) 0.03[c]	Initial yield of absorption
15	$e_{aq}^- + HA^d \rightarrow H + A^-$	1.8×10^{8}	Reference 21	0.37	Ratio of rates
8	$e_{aq}^- + H^+ \rightarrow H$	2.2×10^{10}	Reference 21	0.06	As above
5	$Ru(II)^* \rightarrow Ru(II)$	1.9×10^{6}	Decay of emission	0.89	As above
7	$Ru(II)^* + Ru(III) \rightarrow Ru(II) + Ru(III)$	1.8×10^{9}	Decay of emission	0.11	As above
16	$Ru(II)^{\ddagger} + Ru(III) \rightarrow Ru(II) + Ru(III)$	3.6×10^{9}	Numerical integration (cf. Figure 5)	0.9	Numerical integration
6	$Ru(II)^{\ddagger} \rightarrow Ru(II)$	4×10^{4} [c]	As above	0.1[c]	As above
14	$H + Ru(III) \rightarrow Ru(II) + H^+$	4.5×10^{9}	Formation of Ru(II) in acid	1.0	
10	$OH + (CH_3)_3COH \rightarrow H_2O + (CH_3)_2C(OH)\dot{C}H_2$	5.0×10^{8}	Reference 31	1.0	
20	$(CH_3)_2C(OH)CH_2 + Ru(III) \rightarrow Ru(II) + P$	1.9×10^{8}	Slow formation of Ru(II)		
21	$2(CH_3)_2C(OH)CH_2 \rightarrow P$	6.5×10^{8}	Reference 32		

[a] Included are reactions which are "irrelevant" to the reduction of $Ru(bpy)_3^{3+}$ by e_{aq}^- but which occurred under the conditions of Figure 5. [b] This is the fraction of the indicated radical which reacts to give the product i under the conditions of Figure 5. In parentheses is shown the experimental fraction of the reaction of $e_{aq}^- + Ru(bpy)_3^{3+}$ which yields the indicated Ru(II) species. [c] Upper limit. [d] HA = acetic acid.

The dependence of the pseudo-first-order, $k_6 + k_{16}$ $[Ru(bpy)_3^{3+}]$, thus obtained is shown in Figure 3b, and yields $k_{16} = (3.6 \pm 0.4) \times 10^9$ M^{-1} s^{-1} and $k_6 \leq 4 \times 10^4$ s^{-1}. Direct separation of the rate of formation on the raw data (such as Figure 1a) into three parallel exponential formations (corresponding to reactions 5 and 7, reactions 6 and 16, and reaction 14) is considered impractical.

Of major importance in this context is the yield of reaction 2, namely, direct electron transfer to the ground state of $Ru(bpy)_3^{2+}$. Determination of this yield was attempted by extrapolation of the kinetic curves (such as Figure 1a) to the middle of the electron pulse. A short glance at Figure 1a makes it clear that this yield is very small ($\leq 15\%$ of $G_{e_{aq}^-}$). However, using the extrapolation technique we obtained a yield of 7% of $G_{e_{aq}^-}$, which is close to the limit of accuracy of our technique. Part of the extrapolated absorption can be due to the products $Ru(bpy)_3^{2+\ddagger}$ and $(CT)Ru(bpy)_3^{2+*}$. Obviously very little, if any, of the e_{aq}^- enters directly into the ground state. Furthermore, this result also implies that the excited states produced, namely, $Ru(bpy)_3^{2+\ddagger}$ and $(CT)Ru(bpy)_3^{2+*}$, have a relatively small extinction coefficient at 455 nm (an average $\epsilon_{455} \leq 10^3$ M^{-1} cm^{-1}; if all of this absorption is attributed to $Ru(bpy)_3^{2+*}$ one gets $\epsilon_{455}^* \leq 2300$ M^{-1} cm^{-1}). From the different yields of $Ru(bpy)_3^{2+\ddagger}$, $(CT)Ru(bpy)_3^{2+*}$, and $Ru(bpy)_3^{2+}$ we can now conclude that $k_3 = k_1 f_{CT} = (2.0 \pm 0.4) \times 10^{10}$ M^{-1} s^{-1}, $k_4 = k_1 f_{\ddagger} = (3.1 \pm 0.6) \times 10^{10}$ M^{-1} s^{-1}, and $k_2 \leq 3.4 \times 10^9$ M^{-1} s^{-1}.

Absorption by the Excited States. As mentioned above, the formation of the excited states could be followed in the near UV region in the absorption mode. Since it is already clear at this stage that more than one product results from the reaction of e_{aq}^- with $Ru(bpy)_3^{3+}$ a detailed spectral analysis is somewhat more complicated. To unravel the contribution from $(CT)Ru(bpy)_3^{2+*}$ to the absorption in the near UV region the rate of the decay in this region was followed. The rate constants obtained from the decay of the emissions ($k_5 + k_7$ [Ru-$(bpy)_3^{3+}$]) were adapted and used to fit the first half-life of the decay of the absorption in this region. The only free parameter in this fit was therefore ΔD^∞, the residual absorption after

reactions 5 and 7 were complete. This residual absorption at λ 365 nm amounted to ~25% of ΔD°, the absorption at the end of reactions 2, 3, and 4. The contribution of the decay of $Ru(bpy)_3^{2+\ddagger}$ to the total decay at this wavelength region at 10^{-4} M $Ru(bpy)_3^{3+}$ is rather small in that time range. From these two values of ΔD and taking the yields of (CT)-$Ru(bpy)_3^{2+*}$ to be 38% of the total e_{aq}^- as determined above we can calculate the extinction coefficient at the desired wavelengths using $\epsilon_{CT} = (\Delta D^\circ - \Delta D^\infty)/[(CT)Ru(bpy)_3^{2+*}] + \epsilon_{Ru(II)}$. Note that a correction corresponding to the $Ru(bpy)_3^{2+}$ produced at the end of that period of time (equal to $\epsilon_{Ru(II)}$ at that wavelength) is needed rather than a correction for the destruction of $Ru(bpy)_3^{3+}$. Using this method we obtained λ_{max} 365 nm with ϵ_{365} $(2.3 \pm 0.3) \times 10^4$ M^{-1} cm^{-1} for the absorption by $(CT)Ru(bpy)_3^{2+*}$. (If $f_{CT} = 0.45$ then we calculate ϵ_{365} 2.0×10^4 M^{-1} cm^{-1}.) This is to be compared with λ_{max} 360 nm and ϵ_{360} 1.3×10^4 M^{-1} cm^{-1} obtained by Sutin and Creutz by laser flash photolysis of $Ru(bpy)_3^{2+}$. Calculating the extinction coefficients for $Ru(bpy)_3^{2+\ddagger}$ is even less accurate since the absorption is smaller and since corrections for both $Ru(bpy)^{2+}$ formed and $Ru(bpy)_3^{3+}$ destroyed are required. A crude estimate yields an ϵ_{355} 5900 $\pm$ 2000.

Reaction of $Ru(bpy)_3^{3+}$ with Other Radicals. The reaction of H· atoms with $Ru(bpy)_3^{3+}$ was measured in Ar-saturated 1 N H_2SO_4 solutions containing 0.5 M *tert*-butyl alcohol. In these solutions most e_{aq}^- would be converted to H· atom by reaction with H^+. The absorption spectrum obtained after reaction 14 is complete was very similar to that of $Ru(bpy)_3^{2+}$. The rate of formation of $Ru(bpy)_3^{2+}$ at 455 nm followed a pseudo-first-order rate law and the observed rate constant was linearly dependent on $[Ru(bpy)_3^{3+}]$ as can be seen in Figure 6a. The second-order rate constant thus obtained is $(4.5 \pm 0.1) \times 10^9$ M^{-1} s^{-1}. We do observe an emission spectrum similar to that shown in Figure 2b on pulse irradiating these solutions but we do not believe that this emission should be attributed to the reaction of H· atoms to yield $(CT)Ru(bpy)_3^{2+*}$. This conclusion is based on two facts: (a) The intensity of emission is much smaller than that obtained from the reaction of e_{aq}^- with $Ru(bpy)_3^{3+}$. (b) More convincingly, the formation of the

emission was faster than our time resolution even at the lowest [Ru(bpy)$_3$$^{3+}$] and was independent of this concentration. For these reasons we believe that the emission observed by us (and by Martin et al.[7]) under these conditions results from Čerenkov excitation of thermally produced or residual unoxidized Ru(bpy)$_3$$^{2+}$ and probably from the small amount of e_{aq}^- reacting directly with Ru(bpy)$_3$$^{3+}$ (<1%). Emission with similar characteristics was observed with all the reductants to be described below and in all cases we attribute this emission to similar artifacts.

The reaction of $(CH_3)_2C(OH)\dot{C}H_2$, produced by $\dot{O}H$ abstraction of H· atoms from *tert*-butyl alcohol radicals, with Ru(bpy)$_3$$^{3+}$ was observed under all conditions when *tert*-butyl alcohol was present (see, for example, the slow process in Figure 1a). The spectrum of the product was identical with that of Ru(bpy)$_3$$^{2+}$ and its yield was the same regardless of the acidity. At pH 4.6 in N$_2$O-saturated solutions, where the fast step for the formation of Ru(bpy)$_3$$^{2+}$ is eliminated by reaction 9, the yield after ~50 μs was the same as in Ar-saturated solutions. The ratio of the yield of Ru(bpy)$_3$$^{2+}$ in Ar-saturated solutions at the end of the slow process to the yield at the end of the fast one is 1.7 ± 0.2, which corresponds to the expected ratio of $(G_{e_{aq}^-} + G_{OH} + G_H)/(G_{e_{aq}^-} + G_H) = 1.8$. Although the *tert*-butyl alcohol is usually considered to be an inert radical, the features mentioned above clearly indicate that this radical reduces Ru(bpy)$_3$$^{3+}$ rather efficiently. The second-order rate constant obtained from the linear dependence of the observed pseudo-first-order rate constant on [Ru(bpy)$_3$$^{3+}$] (see Figure 6b) is $(1.9 \pm 0.2) \times 10^8$ M^{-1} s^{-1}. Because of this relatively low value, there is little chance of observing any emission from this reaction, if it goes via (CT)Ru(bpy)$_3$$^{2+*}$, even at the highest concentration of Ru(bpy)$_3$$^{3+}$ used.

In Ar-saturated solutions containing $(2-8) \times 10^{-4}$ M Ru(bpy)$_3$$^{3+}$, 0.5 M *tert*-butyl alcohol at pH 4.6 and 0.5 M CdSO$_4$ most of e_{aq}^- reacts with Cd^{2+} by the reaction

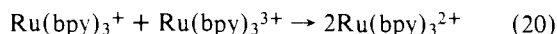$$e_{aq}^- + Cd^{2+} \rightarrow Cd^+ \tag{17}$$
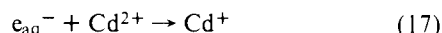
Cd$^+$ then reacts with Ru(bpy)$_3$$^{3+}$ to give Ru(bpy)$_3$$^{2+}$. Using the same procedure described above for the reaction of H· atoms, the second-order rate constant obtained is $k_{18} = (2.8 \pm 0.4) \times 10^9$ M^{-1} s^{-1}.

$$Cd^+ + Ru(bpy)_3^{3+} \rightarrow Cd^{2+} + Ru(bpy)_3^{2+} \tag{18}$$
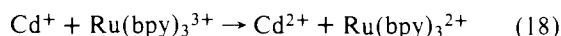
Similarly, when a solution containing 2×10^{-3} M Ru(bpy)$_3$$^{2+}$, and 10^{-4} M Ru(bpy)$_3$$^{3+}$ and 0.5 M *tert*-butyl alcohol at pH 4.6 is irradiated about 95% of e_{aq}^- reacts with Ru(bpy)$_3$$^{2+}$ (reaction 18, $k_{19} = 5.8 \times 10^{10}$ [20]).

$$e_{aq}^- + Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^+ \tag{19}$$

Ru(bpy)$_3$$^+$ could be followed at 510 nm[20,24] and was found to react with Ru(bpy)$_3$$^{3+}$ with a second-order rate constant of $(3.4 \times 0.3) \times 10^9$ M^{-1} s^{-1}.

$$Ru(bpy)_3^+ + Ru(bpy)_3^{3+} \rightarrow 2Ru(bpy)_3^{2+} \tag{20}$$

If reaction 20 produces (CT)Ru(bpy)$_3$$^{2+*}$ as an intermediate, then at the concentration of Ru(bpy)$_3$$^{3+}$ used the rate of formation of the emitting state would be five times slower than the natural rate of decay of (CT)Ru(bpy)$_3$$^{2+*}$. Consequently, the apparent lifetime of the excited state is ~five times the intrinsic lifetime and the maximum emission intensity attained will be ~1/5 that which would be observed if the total (CT)-Ru(bpy)$_3$$^{2+*}$ from 20 were produced instantaneously. If reaction 20 yielded one (CT)Ru(bpy)$_3$$^{2+*}$ for each Ru(bpy)$_3$$^+$ as compared to 0.4 in $e_{aq}^- + Ru(bpy)_3^{3+}$, then the expected emission intensity would be one-half that in the first line of Table I. Relative to the possible luminescence yield of 85 the observed yield in Table I corresponds to less than 3% (CT)-Ru(bpy)$_3$$^{2+*}$ in the product of eq 20. This conclusion is in
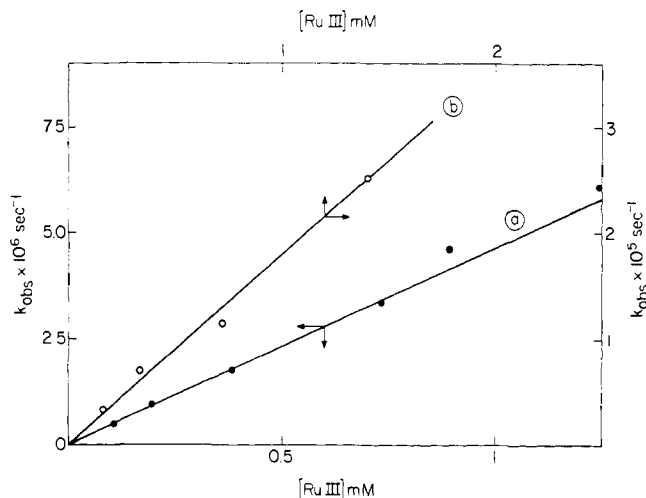

Figure 6. The dependence of the observed first-order rate constant on [Ru(bpy)$_3$$^{3+}$] for the reduction by (a) H· atoms; (b) $(CH_3)_2C(OH)CH_2$ radicals.

disagreement with the one obtained in ref 5 where reaction 20 in acetonitrile was observed to result in high yields of luminescence. We, however, can say nothing about the possibility that Ru(bpy)$_3$$^{2+\mp}$ is formed in this reaction.

Throughout this study we ignore the effect of the reaction of Ru(bpy)$_3$$^{3+}$ with hydrogen peroxide produced by the electrons pulse ($G_{H_2O_2} \leq 0.7$ molecules/100 eV). Although this reaction is known to reduce Ru(bpy)$_3$$^{3+}$, its rate is much too slow[12] to affect any of the above discussed results.

On the Production of Excited States by the Reaction with e_{aq}^-. A large part of this study was devoted to the determination of the yields of the various possible pathways of the reaction of e_{aq}^- with Ru(bpy)$_3$$^{3+}$. An important conclusion of this effort is that a very small fraction of e_{aq}^-, if any, results directly in ground state Ru(bpy)$_3$$^{2+}$ while the large majority yields the excited state (CT)Ru(bpy)$_3$$^{2+*}$ and another product, Ru(bpy)$_3$$^{2+\mp}$. The reduction of several transition-metal complexes by e_{aq}^- was previously postulated to yield excited states of the reduced complex,[25] yet this assumption was rarely verified. The proposition that Co(bpy)$_3$$^{3+}$ and similar chelates[24] yield on reduction by e_{aq}^- excited states or coordinated radical complexes was later challenged.[26] On the other hand, nitrobenzoato pentaammine Co(III) complexes were shown to yield on similar reduction coordinated radical complexes and probably excited states.[27] The standard free energy for the reduction of Ru(bpy)$_3$$^{3+}$ by e_{aq}^- to Ru(bpy)$_3$$^{2+}$ is -4.04 eV ($E^\circ_{aq}/e_{aq}^- = -2.77$ V;[25] $E^\circ_{Ru(III)/Ru(II)} = 1.27$ V[4]) while its ΔG° for the reduction to (CT)Ru(bpy)$_3$$^{2+*}$ is -1.93 eV ($E^\circ_{Ru(III)/CT} = -0.84$ V).[28] In spite of the 2-eV excess free energy for the reaction to the ground state over the reaction to the charge transfer state the latter proceeds with a near diffusion-controlled rate while the former is at least an order of magnitude slower. This behavior for solvated electron reactions has been rationalized by Marcus[10] in that the large ΔG° for the reduction into the ground state brings the reaction to the "inverted" region of his theory.[10] Similar "inverted" region behavior for electron transfer from various trivalent polypyridines complexes to (CT)Ru(bpy)$_3$$^{2+*}$ was recently observed.[18]

The Marcus equation for outer-sphere electron transfer reactions gives for transfer from A to B

$$k_{AB} = (k_{AA}k_{BB}K_{AB}f_{AB})^{1/2} \tag{21}$$

where $\log f_{AB} = (\log K_{AB})^2/(4 \log (k_{AA}k_{BB})/Z^2)$, k_{AA} and k_{BB} are the self-exchange rates for the oxidizing and reducing pairs, respectively, K_{AB} is the equilibrium constant for the transfer from B to A, and Z is a collision number. This equa-

tion can be used to compare the rates of reaction of e_{aq}^- with $Ru(bpy)_3^{3+}$ to produce $(CT)Ru(bpy)_3^{2+*}$ or to produce $Ru(bpy)_3^{2+}$. Since it can be expected that k_{AA} for the self-exchange of $Ru(III)/(CT)Ru(II)*$ is very similar to k_{AA} for $Ru(III)/Ru(II)$,[18] and k_{BB} for e_{aq}^- exchange (between traps) is the same in both reactions, it seems that the factor slowing the rate to the ground state must be the excess free energy expressed in the value of K_{AB}. (We should note here that the $(CT)Ru(bpy)_3^{2+*}$ states may derive wholly or in part from an antecedent state produced by the initial reaction of e_{aq}^-, and that the reaction to produce this initial state would be still less exothermic than the direct reaction to produce (CT)-$Ru(bpy)_3^{2+*}$. $Ru(bpy)_3^{2+\pm}$ may also have an antecedent.) Indeed with remarkable prescience Marcus[10c] has discussed an example which fits very closely to the case of $Ru(bpy)_3^{3+}$. To quote: ". . . a reaction for which ΔF_{int}° is as negative as -4 eV (in our case -4.17 eV) and in which the fluorescence occurs at say 6000 Å ($\sim$6100 Å for $(CT)Ru(bpy)_3^{2+*}$) . . . and $\lambda/4$ for reactions is about 0.4 eV . . . then $\Delta F*$ for the reaction leading to the ground state and excited state of the product is 0.9 and 0.025 eV, respectively".[10c] He has also suggested[10b] that ligands such as bipyridyl or *o*-phenanthroline could favor the formation of excited states over the ground state.

The rates of reduction of $Ru(bpy)_3^{3+}$ by the other reductants studied here are in accordance with this discussion. On one hand the rates of H·, Cd⁺, and $Ru(bpy)_3^+$ to give ground state $Ru(bpy)_3^{2+}$ are faster than that of e_{aq}^- and they all approach the diffusion-controlled limit despite the smaller ΔG° for their reactions. On the other hand, none seems to yield sizable amounts of $(CT)Ru(bpy)_3^{2+*}$. The much greater reorganization of solvent molecules around the H⁺ produced on electron transfer from H· atoms should make this reaction to the ground state even slower (as well as the transfer to CT state), compared to that of e_{aq}^-.[29] The possibility, however, that H· atoms react through an H· atom adduct intermediate whose lifetime is <10 ns cannot be rejected. Such addition is less probable in the other cases.

Another fact that was revealed in this study is that a large portion of e_{aq}^- yield another intermediate $Ru(bpy)_3^{2+\pm}$ which differs from $(CT)Ru(bpy)_3^{2+*}$ and which is longer lived than the latter. This other intermediate might be either another excited state or a coordinated radical. An assignment of the excited state is difficult since if this really is an excited state is is evidently not accessible by light excitation. The identification of a coordinated radical, on the other hand, is premature with the amount of data available. At any rate, this species must lie at an energy level higher than that of the ground state and therefore exhibits the same "inverted" region behavior as discussed for the formation of $Ru(bpy)_3^{2+*}$.

References and Notes

(1) Work performed under the auspices of the Division of Physical Research of the U.S. Energy Research and Development Administration.
(2) Although the (CT)Ru(bpy)₃²⁺* consists of at least three different states, all in thermal equilibrium (see ref 9), we shall refer to them as a single entity for the sake of brevity.
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