3362 *J. Am. Chem. Soc.* **1981**, *103*, 3362–3370

sidered physiologically acceptable is closer to T_d symmetry than the FeS_4 unit in I.

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Supplementary Material Available: Listings of observed and calculated structure factors for compounds I and II (39 pages). Ordering information is given on any current masthead page.

Generation of Rhodium(II) and Rhodium(I) from the One-Electron Reduction of Tris(2,2′-bipyridine)rhodium(III) Ion in Aqueous Solution[1]

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Abstract: The reaction of $Rh(bpy)_3^{3+}$ with radiation-generated reducing radicals (e_{aq}^-, $\cdot CO_2^-$, and $(CH_3)_2\dot{C}OH$) in aqueous solution quantitatively and rapidly ($k = 10^9–10^{10}\ M^{-1}\ s^{-1}$) yields $Rh(bpy)_3^{2+}$ (λ_{max} 485 nm, ϵ_{max} $1.0 \times 10^3\ M^{-1}\ cm^{-1}$) which undergoes slow ($k = 0.45 \pm 0.05\ s^{-1}$ at pH 3–10) loss of bpy at room temperature. $Rh(bpy)_3^{2+}$ reacts with O_2 ($k = 4.9 \times 10^8\ M^{-1}\ s^{-1}$) via electron transfer. In alkaline solution, $Rh(bpy)_3^{2+}$ undergoes disproportionation with ligand-labilized Rh(II) to form $Rh(bpy)_3^{3+}$ and red-violet $Rh(bpy)_2^+$. At pH >10, ligand-labilized Rh(II) reduces $Rh(bpy)_3^{3+}$ resulting in a redox-catalyzed ligand-labilization chain reaction; at pH 14, $G(bpy) \simeq G(-Rh(bpy)_3^{3+}) > 300$. The nature of O_2-sensitive $Rh(bpy)_2^+$, its spectrum, and state of aggregation is highly dependent upon the pH of the solution, [Rh(I)], and the nature and concentration of the counteranion. At least four forms of $Rh(bpy)_2^+$ are clearly identified: (a) a red-violet soluble form (λ_{max} 518 nm, ϵ_{max} 9500 $M^{-1}\ cm^{-1}$) which is formulated as $Rh(bpy)_2(OH)_n^{(1-n)}$ and may be dimeric via hydroxide bridging (in neutral solution, very small changes in pH have a large effect on the spectrum which shows a main band at ~415 nm and a well-defined shoulder in the 470-nm region); (b) a violet insoluble form represented as $Rh(bpy)_2X$ where $X = Cl^-$, ClO_4^-, etc.; (c) a transient green form observed when the red-violet form is acidified which is formulated as $Rh(bpy)_2(OH_2)_n^+$; (d) a colorless form in acidic solution which is assigned as a hydride in which the metal center is formally Rh(III), e.g., $RhH(bpy)_2^{2+}$. At "natural" pH, H_2 is produced with an efficiency of ~25% in the absence of any catalyst. The relevance of these results to solar energy conversion schemes is examined.

Introduction

Recent studies[3,4] of the excited-state electron-transfer reaction of $*Ru(bpy)_3^{2+}$ with $Rh^{III}(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) have shown that H_2 is generated from the reduction of H_2O through the intermediacy of $Rh^{II}(bpy)_3^{2+}$ and $Rh^{I}(bpy)_2^+$. From the point of view of photochemical conversion of solar energy, this result is very exciting; at the same time, only few detailed kinetic and mechanistic studies have been carried out.[5] Although $Rh(bpy)_2^+$ can be generated[6,7] by the direct action of aqueous BH_4^- on $Rh(bpy)_3^{3+}$, it is clear that only fast kinetics techniques can be utilized to characterize $Rh(bpy)_3^{2+}$ and the resulting Rh(II) and Rh(I) species.

Recently, in our examination[8] of the one-electron reduction of $Co^{III}(bpy)_3^{3+}$ using the radiation chemical techniques of fast kinetics pulse radiolysis and steady-state continuous radiolysis, we found that $Co^{II}(bpy)_3^{2+}$ undergoes slow ($k = 3.4\ s^{-1}$ at pH 0.5–10.5) ligand labilization in aqueous solution; by way of comparison, the electrochemical reduction of $Rh(bpy)_3^{3+}$ in CH_3CN solution[9] also results in ligand labilization. Because of the periodic relationship of Co and Rh, the growing interest in redox reactions arising from the excited-state reactions of Rh complexes,[10,11] and our continuing investigation of the interaction of radiation-generated free radicals with polypyridines[12] and their coordination complexes,[8,13,14] we have examined in detail the one-electron reduction of $Rh(bpy)_3^{3+}$ in aqueous solution. We report here on the behavior of $Rh(bpy)_3^{2+}$, the nature of the Rh(I) species, and the implications of these results to photochemical conversion and storage of solar energy.

Experimental Section

Materials. $Rh(bpy)_3Cl_3 \cdot 5H_2O$ was prepared and purified according to literature procedures.[15] A sample of the complex, prepared according to the procedures of Crosby and Elfring,[16] was kindly provided by Dr. F. Bolletta and showed identical behavior. The ClO_4^- salt was also used in some experiments. Aqueous solutions of $Rh(bpy)_3^{3+}$ are stable in acidic, neutral, and alkaline media; no changes in the absorption spectrum

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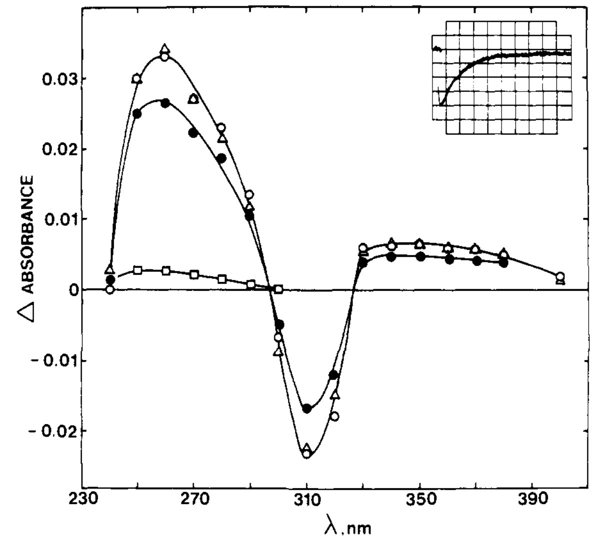

Figure 1. Spectral changes in the pulse radiolysis of 1.2×10^{-5} M $Rh(bpy)_3^{3+}$ solution containing 0.1 M HCO_2^- at pH 7.3; optical path length = 2 cm, dose/pulse = 120 rd. (○) Ar-purged, (△) N_2O-saturated, ΔAbs measured 70 μs after the pulse. (●) ΔAbs measured at maximum change immediately after the pulse; (□) ΔAbs measured ~1.5 ms after the pulse; solution saturated with N_2O containing ~2% air. Inset: CRO trace monitored at 250 nm for solution saturated with N_2O containing ~2% air. Abscissa = 200 μs/div; ordinate = 1.79% abs/div.

are detectable as a function of pH. The purification of $(CH_3)_2CHOH$, $(CH_3)_2CO$, $NaHCO_2$, N_2O, and H_2O has been described.[8,12-14] The pH of the solutions was adjusted with NaOH, H_2SO_4, or $HClO_4$. Commercial buffers (Merck, Titrisol) up to 10% by volume were also used for buffering in the range pH 4-10.

Procedures. Continuous radiolyses were carried out at room temperature on 10-25-mL samples of solution contained in silica vessels fitted with silica spectrophotometer cells on a side arm. The irradiation vessels were also fitted with a separate compartment through which it was possible to add a given reactant to the irradiated solutions under oxygen-free conditions. Spectra were recorded with a Perkin-Elmer Model 555 spectrophotometer. The samples were deaerated by purging with Ar, saturating with N_2O (2.5×10^{-2} M), or using freeze-thaw procedures on a vacuum line. The absorbed radiation dose from the ^{60}Co γ source was determined by Fricke dosimetry and had a value of 1.5×10^{17} eV g^{-1} min^{-1}.

Pulse radiolysis with optical absorption detection was performed at the C.N.R. Laboratory (Bologna) using facilities and dosimetry procedures that have already been described.[17] In order to avoid or minimize photolytic effects induced by the analyzing light, the solutions were exposed to the minimum amount of UV light through the use of a shutter and cutoff filters. In all experiments, the sample was irradiated with a single pulse. Where the spectra of long-lived species were obtained, the sample was contained in a modified spectrophotometer cell and spectra were recorded in less than 2 min on a Beckman ACTA CIII spectrophotometer.

Analyses. Gas analyses were performed on 25-mL samples which had been degassed or saturated with N_2O prior to irradiation. The gaseous products were removed from the irradiated samples by an automatic Toepler pump; their total volume was measured in a gas buret. The gas was then analyzed by vapor phase chromatography. Free bpy was extracted with *n*-heptane from solutions made alkaline; the spectrum of the organic phase was compared with that from a standard aqueous bpy solution. From a knowledge of the radiation dose delivered to the solutions and the rate of formation of product, the *G* values (number of molecules formed per 100 eV of energy absorbed by the solution) of the reaction were calculated.

Generation of Reducing Radicals. The generation of e_{aq}^-, $\cdot CO_2^-$, and $(CH_3)_2\dot{C}OH$ as the principal reductant by the use of selective scavengers in the radiolysis of aqueous solutions has been described in detail many times before.[8,12-14]

Results

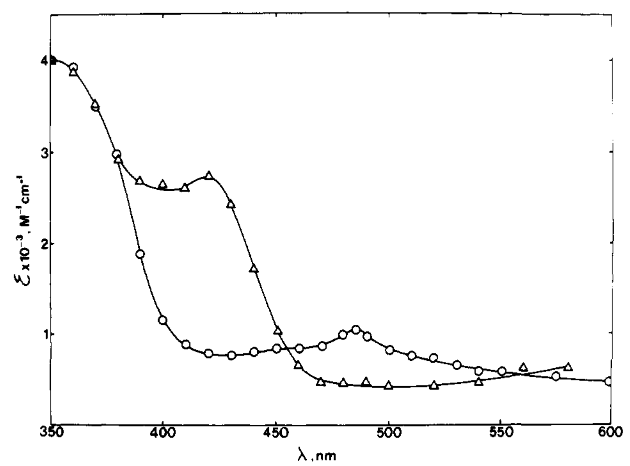

Figure 2. Spectra of pulse radiolysis transients. (○) Visible spectrum of $Rh(bpy)_3^{2+}$ measured ~80 μs after the pulse; optical path length = 2 cm, dose/pulse = 1.5 krd. The following conditions were used: (a) 50 μM $Rh(bpy)_3^{3+}$, 0.5 M 2-propanol, Ar-purged solution, natural pH; (b) same but at pH 3; (c) same but at pH 10; (d) 50 μM $Rh(bpy)_3^{3+}$, 0.5 M 2-propanol, 0.1 M acetone, Ar-purged solution, natural pH. In evaluating ε, $G(Rh(bpy)_3^{2+}) = 6.0$ was assumed. (△) Visible spectrum of product of reaction of H atoms and $Rh(bpy)_3^{3+}$ at pH 1 in the presence of 0.5 M *tert*-butyl alcohol measured ~80 μs after the pulse; optical path length = 2 cm, dose/pulse = 1.5 krd; Ar-purged solutions. The observed spectrum was corrected for incomplete scavenging of H and for the decay of the transient. In evaluating ε, *G*(transient) = 3.3 was assumed.

Table I. Rate Constants for the Reaction of $Rh(bpy)_3^{3+}$ with Radiation-Generated Radicals in Aqueous Solution

radical	*k*, M^{-1} s^{-1}
e_{aq}^-	$(8.1 \pm 0.5) \times 10^{10}$ [a]
$\cdot CO_2^-$	$(6.2 \pm 0.6) \times 10^9$ [b]
$(CH_3)_2\dot{C}OH$	$(1.8 \pm 0.2) \times 10^9$ [c]
H	$(1.9 \pm 0.2) \times 10^9$ [d]

[a] $1-2 \times 10^{-5}$ M $Rh(bpy)^{3+}$, 0.5 M CH_3OH, neutral pH, Ar-purged solution. Observations at 270 nm (transient formation), 320 nm (substrate bleaching), and 578 nm (e_{aq}^- decay); dose/pulse = 150-250 rd. [b] $1-5 \times 10^{-5}$ M $Rh(bpy)_3^{3+}$, 0.1 M HCO_2^-, neutral pH, N_2O-saturated solution. Observations at 270, 320, and 350 nm; dose/pulse = 0.1-1.2 krd. [c] $0.25-5 \times 10^{-4}$ M $Rh(bpy)_3^{3+}$, 0.1 M $(CH_3)_2CHOH$, pH 1-10, Ar-purged or N_2O-saturated solution. Observations at 270, 320, 350, and 485 nm; dose/pulse = 0.12-1.5 krd. [d] 1×10^{-4} M $Rh(bpy)_3^{3+}$, 0.5 M *tert*-butyl alcohol, pH 1, Ar-purged solution. Observations at 350 nm; dose/pulse = 1.2 krd.

Pulse Radiolysis. The reaction of $Rh(bpy)_3^{3+}$ with reducing radicals yields the absorbance changes recorded in Figure 1. In the presence of O_2, the extent of the absorbance changes is slightly reduced because the decay of the initial transient is enhanced. The residual absorption is similar to the absorption of $O_2^-\cdot$ radical anion.[18] From the pseudo-first-order decay of the initial transient in the presence of O_2, a second-order rate constant of $(4.9 \pm 0.4) \times 10^8$ M^{-1} s^{-1} is calculated. By knowing the radiation dose delivered to the solution, the *G* value of the reducing radical, and the absorbance change that is observed, the absorption spectrum of the initial transient in the absence of O_2 can be evaluated. This spectrum, shown in Figure 2, for the visible and near-UV region where no correction for the depletion of the substrate is required, is independent of pH (2-10) and the nature of the reducing radical. The spectrum shown in Figure 2 is the average of spectra obtained at pH 2, 7.3 (5% buffer), and 10. At pH 7.3 the same spectrum was obtained in the presence of 0.5 M 2-propanol (Ar-purged solution) and in the presence of both 2-propanol (0.5 M) and acetone (0.1 M). The spectrum was also not affected by changing $[Rh(bpy)_3^{3+}]$ (25-500 μM). In comparison, the spectrum of the product from the reaction of H atoms with $Rh(bpy)_3^{3+}$ at pH 1 in the presence of 0.1 M *tert*-butyl alcohol is decidedly different (Figure 2).

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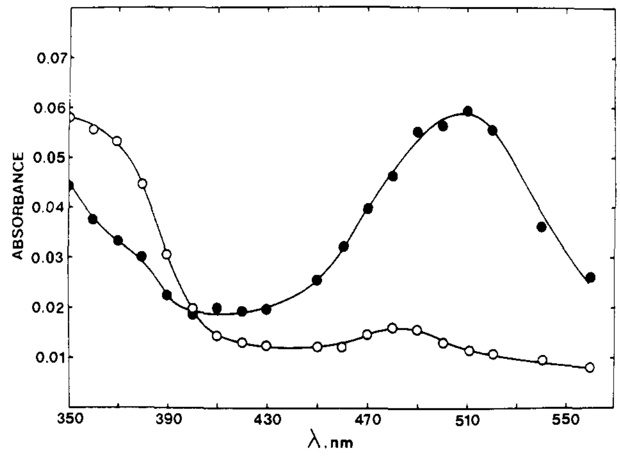

Figure 3. Spectral changes observed in the pulse radiolysis of 5×10^{-5} M $Rh(bpy)_3^{3+}$ Ar-purged solution containing 0.1 M 2-propanol at pH 10; optical path length = 2 cm; dose/pulse = 1 krd. ○, zero time on 0.5 s/div sweep; ●, $t \simeq 5$ s. Assuming $G = 3.0$, $\epsilon_{510} \simeq 1 \times 10^4$ M^{-1} cm^{-1} for the secondary absorption.

By monitoring the decay of e_{aq}^- or the formation of the initial transient absorption, the rate constants of the initial reactions are established (Table I).

At pH 10, the initial transient undergoes transformation cleanly and slowly forming a secondary absorption with λ_{max} ~510 nm (Figure 3). The conversion follows strict first-order kinetics with $k_{obsd} = 0.90 \pm 0.05$ (std dev) s^{-1} independent of $[Rh(bpy)_3^{3+}]$ (25–500 μM), radiation dose (1–5 krd), and the nature of the reducing radical. A similar value of k_{obsd} was obtained in the presence of 0.1 M HCO_2^- at pH 10. However, the value of k_{obsd} is highly affected by the presence of adventitious impurities, presumably O_2. Higher values of k_{obsd} are paralleled by the formation of less secondary absorption in the visible. The decay kinetics remain the same at pH 7.3–11; however, at pH 7.3, the species absorbing at ~500 nm is less intense by a factor of ~2 than in more alkaline solution.

At pH <7, the disappearance of the primary transient monitored at 340 nm occurs in the time frame of seconds, continuing for at least 50 s with poorly defined kinetics. The absorbance of secondary species absorbing at ~500 nm is less intense by a factor of >10 than at pH 10–11; in fact, as the pH is decreased, the absorbance at 500 nm is diminished to the point of disappearance. At pH 0–4 (controlled by $HClO_4$) in 0.1 M 2-propanol, the primary transient is seen as before, but no formation of any secondary absorption is visible. The primary transient disappears almost completely via $[ClO_4^-]$-dependent pseudo-first-order kinetics, leaving only a slight variation of the original substrate spectrum.

The species formed from the reaction of H atoms with $Rh(bpy)_3^{3+}$ in acidic *tert*-butyl alcohol solution shown in Figure 2 decays via second-order kinetics in the 2-ms time frame representing bimolecular reaction with itself or $\cdot CH_2C(CH_3)_2OH$.

Single Pulse Spectroscopy. Upon the free-radical reduction of low concentrations ($\leq 2 \times 10^{-4}$ M) of $Rh(bpy)_3(ClO_4)_3$ with low radiation doses (2–3 krd) at pH 10, the final spectrum is that of the species with λ_{max} 512 nm (Figure 4). An increase in the concentration of $Rh(bpy)_3(ClO_4)_3$ and/or the radiation dose yields the final spectrum of the species absorbing at ~565 nm. Nevertheless, the visible spectral region shows significant variations as a function of time after the reduction of $Rh(bpy)_3(ClO_4)_3$ (Figure 4). After 20 min, the solution remains clear but within 1 h, formation of a violet precipitate is seen. When the solution and precipitate are exposed to air, the precipitate dissolves and the color of the solution bleaches. The spectrum of the residual solution is consistent with the formation of $Rh(bpy)_2(OH)_2^+$ and free bpy; the latter is extracted from the aerated solution yielding $G \simeq 3$. It should be noted that the spectrum of the solution taken at 2 min in the single pulse spectroscopy experiment is exactly the same as that taken at 5 s in the pulse radiolysis experiment (λ_{max} ~510 nm). In contrast, at 20 min in the single pulse spectroscopy experiment, λ_{max} = 390 and 565 nm (Figure 4).

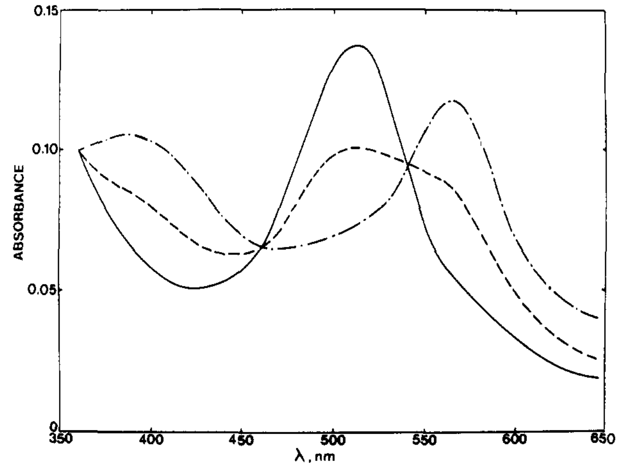

Figure 4. Visible spectra from the single pulse experiment: $[Rh(bpy)_3(ClO_4)_3]$ = 230 μM, 0.1 M 2-propanol, Ar-purged solution, pH 10, optical path length = 1 cm, dose/pulse = 6.5 krd. Spectra determined at 2 min (—), 5 min (- - -), and 20 min (-·-·-) after the pulse. Upon standing beyond 20 min, the clear solution became turbid and a precipitate formed. Assuming ϵ_{510} = 9500 M^{-1} cm^{-1} for the initially absorbing species, $\epsilon_{565} \geq 8400$ M^{-1} cm^{-1} for the violet species.

At pH 7.3, the spectrum taken at 2 min after the single pulse shows λ_{max} ~500 nm with an absorbance one-half that seen at pH 10 under identical conditions. When the solution is opened to air, the color is lost and free bpy is extracted.

Continuous Radiolysis. At pH 10, continuous radiolytic reduction of 5×10^{-4} M $Rh(bpy)_3(ClO_4)_3$ produces a turbid violet solution with the presence of a violet precipitate. The spectrum of this mixture shows a visible absorption very similar to that observed in the single pulse experiments after the appearance of turbidity (a band at 565 nm superimposed on the scattered light). Under an atmosphere of Ar, the solution at pH 10 and the precipitate are stable for at least 3 months; no H_2 is generated during that period. When saturated with N_2O, the solution and precipitate disappear within 5 days. Upon addition of air, the precipitate disappears and the solution bleaches very rapidly.

By using $Rh(bpy)_3Cl_3$ (up to 5×10^{-4} M), the irradiated solutions remain clear at every pH. The formation of the violet precipitate is observed, however, if the solution at pH 10 is mixed with excess Cl^- or ClO_4^- prior to or subsequent to irradiation.

The results of a typical experiment at pH in 5% buffer solution are shown in Figures 5 and 6. The UV spectral changes show the progressive disappearance of the absorption of $Rh(bpy)_3^{3+}$ with clean isosbestic points at 248, 296, and 325 nm and the appearance of two main bands at 240 and 280 nm. From the change in the absorbance at 318 nm, a G value for the disappearance of $Rh(bpy)_3^{3+}$ of 2.6 ± 0.1 is evaluated. In the visible spectral region, the irradiation causes the appearance of an absorption in the 515–520-nm region with a well-defined shoulder at 350 nm. A slight red shift of the main visible band takes place as the concentration of the absorbing species is increased upon successive irradiation. The spectrum obtained after exhaustive radiolysis of $Rh(bpy)_3^{3+}$ (150 μM) shows λ_{max} 518 nm that remains stable in deaerated solution. This latter spectrum, attributed to $Rh(bpy)_2^+$, is exactly the same as that obtained when $Rh(bpy)_3Cl_3$ is quantitatively reduced with $NaBH_4$ in alkaline solution[7] which results in the evaluation of the ϵ value for the red-violet species as 9500 M^{-1} cm^{-1} at 518 nm at pH 11. Using this latter value for the irradiation at pH 10, a G value of ~2 for the linear increase in the visible absorption is evaluated. Exposure to O_2 of the red-violet solution causes the complete disappearance of any absorption at λ >400 nm. At the same time, absorption in the UV shows the characteristic bands[4] of $Rh(bpy)_2(OH)_2^+$ and $Rh(bpy)_3^{3+}$.

Irradiation at pH ≥11 results in a more rapid disappearance of the $Rh(bpy)_3^{3+}$ absorption with $Rh(bpy)_2(OH)_2^+$ and bpy

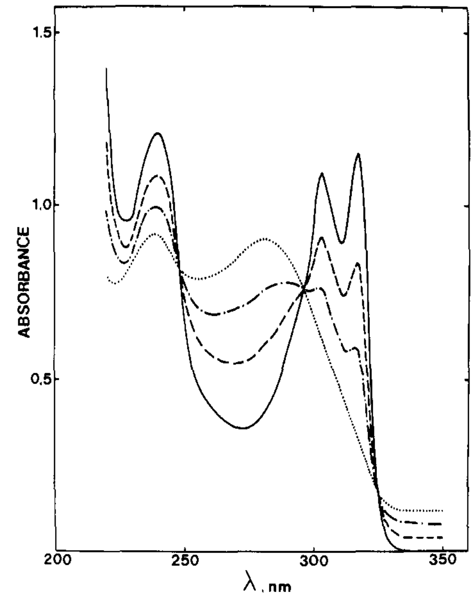

Figure 5. UV spectral changes observed from the continuous radiolysis of deaerated $Rh(bpy)_3Cl_3$ (150 μM) solution containing 0.25 M 2-propanol, 0.05 M acetone, and 5% buffer solution at pH 10. Optical path length = 2 mm; dose = 1.04 × 10^{20} eV L^{-1} min^{-1} (1.67 krd min^{-1}). Irradiation time: zero time (—), 10 min (– –), 20 min (–•–), 30 min (•••). No postirradiation effects were observed. Isosbestic points were observed at 248, 296, and 325 nm. The spectra contain a small contribution from acetone (λ_{max} 270 nm).

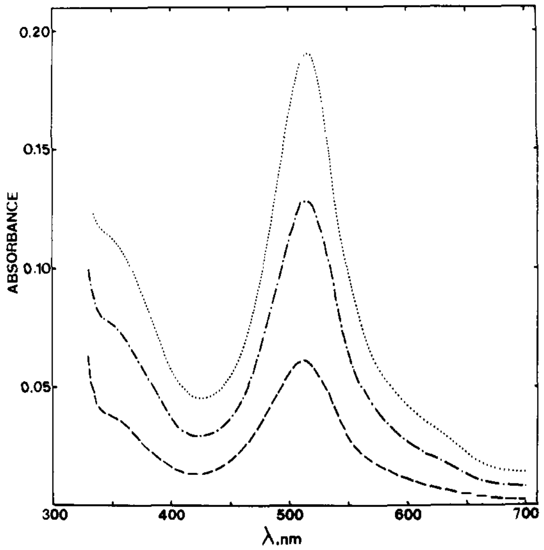

Figure 6. Visible spectral changes observed from the continuous radiolysis of $Rh(bpy)_3Cl_3$ solution. Conditions and symbols the same as for Figure 5. The zero-time spectrum is not shown inasmuch as Rh(bpy)$_3^{3+}$ does not absorb at λ >350 nm. The conversion to products is linear up to ~70%.

formed as the major products (Figure 7). Further irradiation of this mixture results in the reduction of $Rh(bpy)_2(OH)_2^+$ to the red-violet species. Although bpy can be extracted quantitatively from these irradiated basic solutions, Rh(bpy)$_3^{3+}$ is not re-formed upon exposure to O_2.

Between pH 6.5 and 10, the formation of species absorbing in the visible is still observed as a result of irradiation. The intensity of the visible absorption decreases with decreasing pH (Figure 8). Furthermore, as the pH is decreased, the shape of the visible absorption progressively changes. As shown in Figure 9, a new band with λ_{max} 415 nm, in addition to the band at ~500 nm, is present at pH 7.2 (10% buffer solution). The solution, when kept under vacuum, shows very minor changes in the course of 3 days. Addition of NaOH to pH $\simeq$11 results in the same spectrum as obtained from the irradiation of alkaline solutions. Addition of O_2 to the solution irradiated at pH 7.2 results in the formation of Rh(bpy)$_3^{3+}$ in a high yield that is increased with increasing radiation dose.

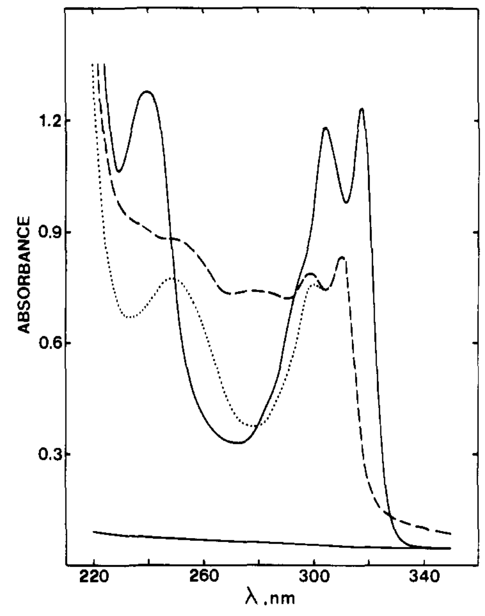

Figure 7. UV spectral changes (vs. air) observed from the continuous radiolysis of deaerated $Rh(bpy)_3Cl_3$ (150 μM) solution containing 0.1 M 2-propanol at pH 14. Optical path length = 2 mm. Unirradiated solution (—); immediately after irradiation with 2.87 × 10^{19} eV L^{-1} (0.465 krd) (– – –); irradiated solution opened to air and extracted twice with *n*-heptane removing 150 μM of free bpy (•••). Lower solid line is the spectrum of the cell containing H_2O vs. air.

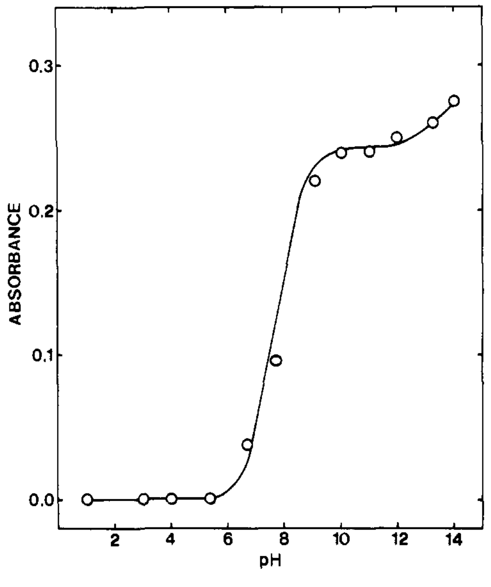

Figure 8. Dependence of absorbance of Rh(I) at 515 nm as a function of pH. [$Rh(bpy)_3Cl_3$] = 150 μM, [2-propanol] = 0.1 M, 2-cm optical path length; irradiation dose = 3.37 × 10^{20} eV L^{-1} (5.40 krd). pH control: 1–4, H_2SO_4; 5.4, 5% buffer; 6.7 and 7.6, $H_2PO_4^-/HPO_4^{2-}$; 9.1 and 10, 5% buffer; 11–14, NaOH.

In the irradiation of acidic solutions (pH 1–5.4), no detectable absorbance in the visible is generated; only minor changes in the UV is seen. Addition of O_2 to the solution after irradiation has only a modest effect on the spectrum. Upon addition of NaOH, bpy is extracted from the resulting alkaline solutions. *G*(bpy) decreases upon increasing dose and is considerably reduced by the use of $HClO_4$ instead of H_2SO_4. However, addition of NaOH to pH $\simeq$ 11 under O_2-free conditions causes the immediate formation of the same spectrum of the red-violet species as observed from the irradiation of alkaline solutions. Depending upon the acid used in preparing the acidic solutions to be irradiated,

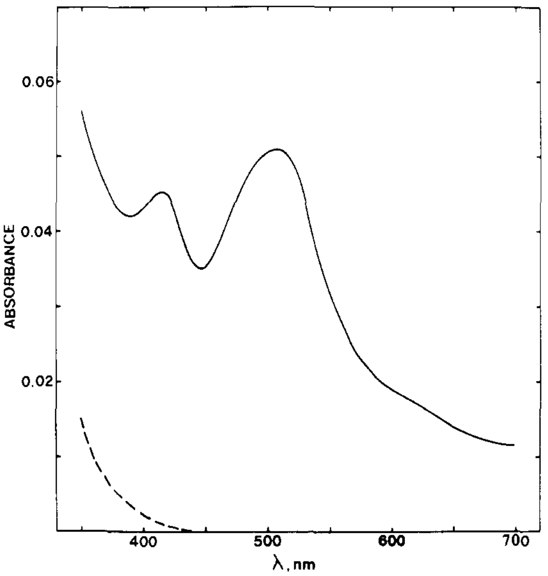

Figure 9. Visible spectral changes observed from the continuous radiolysis of deaerated $Rh(bpy)_3Cl_3$ (150 μM) solution containing 0.1 M 2-propanol and 10% buffer solution at an initial pH of 7.2. Optical path length = 2 mm; dose = 2.78×10^{21} eV L^{-1} (44.5 krd). After radiolysis, —; after addition of O_2, – – –.

the addition of NaOH to the irradiated solution produces the violet precipitate ($HClO_4$) or the red-violet solution (H_2SO_4). By using H_2SO_4 to prepare the acidic solution, the *G* value of the red-violet species has been deduced for the irradiated solution made alkaline. This *G* value is lower for solutions originally acidic than for those originally alkaline and, as observed for *G*(bpy) from acidic solution, decreases upon increasing radiation dose.

Data concerning *G*(bpy), *G*(Rh(I)), and $G(-Rh(bpy)_3^{3+})$ are shown in Figure 10 as a function of pH. Values of *G*(Rh(I)) were obtained at pH <10 from the alkalinization to pH ≥11 (with NaOH under an atmosphere of He) of irradiated solutions using ϵ_{max} 9500 M^{-1} cm^{-1} for $Rh(bpy)_2^+$ at its visible absorption maximum. At pH >10, the absorbance of $Rh(bpy)_2^+$ was measured directly. Values of *G*(bpy) were obtained from irradiated solutions mixed immediately with air, made alkaline, and extracted with *n*-heptane. As noted above, $G(-Rh(bpy)_3^{3+}) = 2.6$ at pH 10. However, at pH 11, as Figure 10 shows, the *G* value for the loss of substrate, as determined spectrophotometrically immediately (within ~1 min) after radiolysis, is ~10. Increasing the pH of the radiolyzed solution causes $G(-Rh(bpy)_3^{3+})$ to rise precipitously; at pH 14, $G > 300$. Although Figure 10 does not show *G*(bpy) at pH > 10, under these conditions, $G(bpy) \simeq G(-Rh(bpy)_3^{3+})$. At pH ≥11, we have observed a postirradiation reaction leading to the complete conversion of the substrate to $Rh(bpy)_2(OH)_2^+$. The rate of this reaction is enhanced by an increase in radiation dose and pH.

Yields of H_2 were measured as a function of pH from the irradiation of degassed solutions containing 0.1 M 2-propanol and 5×10^{-4} M $Rh(bpy)_3^{3+}$. The values of $G(H_2)$ at pH 2.0, 4.3, 6.2, 8.3, and 10.0 are 3.6, 1.8, 1.5, 1.0, and 1.1, respectively, for an absorbed dose of 50 krd. Experiments have indicated that $G(H_2)$ increases with increasing radiation dose, an effect that is more pronounced at pH 5 than at pH 2 or 8. In comparison, at pH 10 in N_2O-saturated 2-propanol solutions containing $Rh(bpy)_3^{3+}$, $G(H_2) = 1.0$, $G(N_2) = 5.1$, and $G(bpy) = 0.2$.

Discussion

Reduction of $Rh(bpy)_3^{3+}$. The radiolysis of aqueous solutions generates the primary radicals and molecular products according to reaction 1 where the numbers in parentheses represent the *G* values of the species.

$$H_2O \rightsquigarrow e_{aq}^- \ (2.8),\ OH\ (2.8),\ H\ (0.6),\ H_2\ (0.45),\ H_2O_2\ (0.8) \quad (1)$$

In N_2O-saturated solution, e_{aq}^- is rapidly converted to OH; in acidic solution (pH <3), e_{aq}^- is converted to H. Both H and OH can be scavenged by HCO_2^- and $(CH_3)_2CHOH$ to generate $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$ radicals, respectively. The reaction of e_{aq}^- with $(CH_3)_2CO$ also yields $(CH_3)_2\dot{C}OH$ radicals. Both H and e_{aq}^- are scavenged by O_2 to give the HO_2/O_2^- conjugate pair. In the presence of *tert*-butyl alcohol, OH radicals are scavenged resulting in the generally unreactive $\cdot CH_2(CH_3)_2COH$ radical. In this work, CH_3OH was used only in some preliminary experiments for the determination of the rate constant for the reaction of $Rh(bpy)_3^{3+}$ with e_{aq}^-. The resulting $\cdot CH_2OH$ radical from the scavenging of OH reacts relatively slowly with $Rh(bpy)_3^{3+}$ ($k \simeq 2 \times 10^8$ M^{-1} s^{-1}), and, as observed[14] with $Co(bpy)_3^{3+}$, the reaction proceeds, at least in part, via addition of the radical to the ligand.

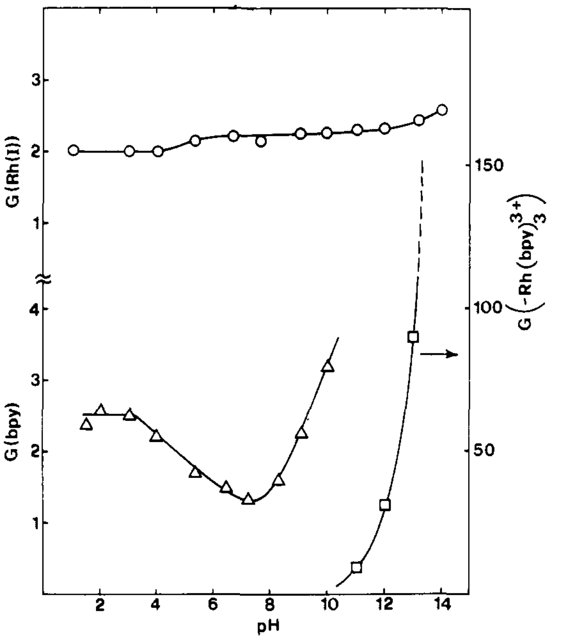

Figure 10. *G*(bpy), *G*(Rh(I)), and $G(-Rh(bpy)_3^{3+})$ as a function of pH from the continuous radiolysis of deaerated $Rh(bpy)_3Cl_3$ (150 μM) solution containing 0.1 M 2-propanol. Conditions are the same as for Figure 8 except for the determination of $G(-Rh(bpy)_3^{3+})$ where the radiation dose was 6.10×10^{19} eV L^{-1} (0.98 krd) and the optical path was 2 mm.

The reaction of reducing radicals (e_{aq}^-, $\cdot CO_2^-$, $(CH_3)_2\dot{C}OH$) with $Rh(bpy)_3^{3+}$ gives, in the first instance, $Rh(bpy)_3^{2+}$ (reaction 2), the pH-independent spectrum of which is shown in Figure 2.

$$Rh(bpy)_3^{3+} + e^- \rightarrow Rh(bpy)_3^{2+} \quad (2)$$

The rate constants for reaction 2, given in Table I, are very similar to those obtained[8] for the corresponding reactions of $Co(bpy)_3^{3+}$. In contrast, although $Ru(bpy)_3^{2+}$ is reduced rapidly ($k = 8.2 \times 10^{10}$ M^{-1} s^{-1})[13] by e_{aq}^-, one-electron reduction by $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$, which are weaker reductants than e_{aq}^-, is not observed ($k < 10^6$ M^{-1} s^{-1}). In fact, the reaction observed when $(CH_3)_2\dot{C}OH$ reacts with $Ru(bpy)_3^{2+}$ is addition to the ligand ($k \simeq 1.5 \times 10^8$ M^{-1} s^{-1}).[14] $Ru(bpy)_3^+$ has been assigned[19] as a species containing a reduced-bpy ligand–radical coordinated to a Ru(II) center rather than as a Ru(I) species; the intense sharp absorption band at 360 nm exhibited by $Ru(bpy)_3^+$ [13] is seen also in reduced free bpy.[20] In comparison, neither $Co(bpy)_3^{2+}$ [8] nor $Rh(bpy)_3^{2+}$ shows that sharp band. We conclude that $Rh(bpy)_3^{2+}$ can be described as a complex of Rh(II).

Behavior of $Rh(bpy)_3^{2+}$. The reaction of $Rh(bpy)_3^{2+}$ with O_2 is clearly electron transfer in nature and can be described by reaction 3. The value of k_3 (4.9×10^8 M^{-1} s^{-1}) is very similar

$$Rh(bpy)_3^{2+} + O_2 \rightarrow Rh(bpy)_3^{3+} + O_2^- \quad (3)$$

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(19) Tokel-Tokvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582. Baxendale, J. H.; Fiti, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1995.

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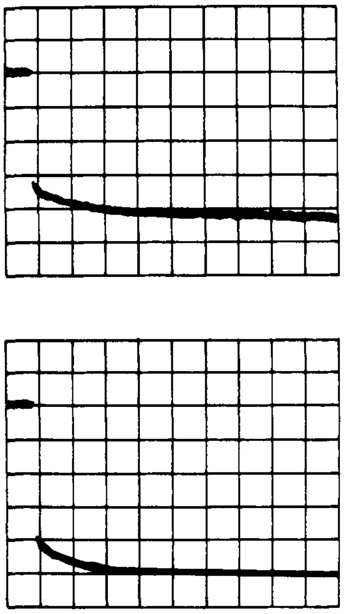

Figure 11. CRO traces relating to the ring-opening equilibrium of $Rh(bpy)_3^{2+}$. Solutions contain 540 μM $Rh(bpy)_3^{3+}$, 0.5 M 2-propanol, 0.1 M acetone at pH 10. Optical path length = 2 cm; wavelength of observation = 485 nm. Upper trace: abscissa = 200 μs/div, ordinate = 1.03% abs/div, dose/pulse = 1.4 krd. Lower trace: abscissa = 100 μs/div, ordinate = 2.60% abs/div, dose/pulse = 4.2 krd.

to that of the reaction between O_2 and Rh(II)–ammine complexes in which O_2 addition has been proposed.[21]

The decay of $Rh(bpy)_3^{2+}$ in deaerated neutral and alkaline solution is accompanied by the formation of the species absorbing in the 500-nm region which can be assigned, without hesitation, to $Rh(bpy)_2^+$. The transformation of $Rh(bpy)_3^{2+}$ to $Rh(bpy)_2^+$ requires the occurrence of ligand labilization and further reduction of the metal center. Because the rather slow formation of $Rh(bpy)_2^+$ occurs via unequivocably first-order, but not pseudo-first-order, kinetics, we agree with Brown et al.[5] that the rate-determining step is intramolecular ligand labilization followed by rapid reduction of the resulting Rh(II)–bis(bpy) species. In the absence of any reducing species,[22] $Rh(bpy)_2^+$ can be formed only via an electron-transfer disproportionation reaction involving Rh(II) species.

Therefore, we suggest that the rate constant of the observed decay of $Rh(bpy)_3^{2+}$ and formation of $Rh(bpy)_2^+$ ($k_{obsd} = 0.90 \pm 0.05\ s^{-1}$) is related to reaction 4. Here, the species designated

$$Rh(bpy)_3^{2+} \rightleftarrows Rh(bpy)_2^{2+} + bpy \qquad (4)$$

as "$Rh(bpy)_2^{2+}$" could be four-coordinate $Rh(bpy)_2^{2+}$, five-coordinate $Rh(bpy)_2OH_2^{2+}$, or six-coordinate $Rh(bpy)_2(OH_2)_2^{2+}$.[5] Any Rh(II)–aquo species would exhibit acid–base behavior with deprotonation reactions probably occurring in the alkaline pH range. For $Rh(bpy)_2(OH_2)_2^{3+}$, the pK_a values are 4.4 and 6.4.[4] As in the case of $Co(bpy)_3^{2+}$, reaction 4 would be a composite of ring-opening and ligand-labilization equilibria (reactions 5 and

$$Rh(bpy)_3^{2+} \rightleftarrows Rh(bpy)_2(bpy\text{-})^{2+} \qquad (5)$$

6) with acid- and base-catalyzed components. Brown et al.[5]

$$Rh(bpy)_2(bpy\text{-})^{2+} \rightleftarrows Rh(bpy)_2^{2+} + bpy \qquad (6)$$

estimated $k_5 \sim 10^5\ s^{-1}$. From this rate constant, $t_{1/2}$ for reaction 5 would be ~7 μs which should enable reaction 5 to be observed if the spectra of the two species were significantly different from each other. We have not observed spectral changes on that time frame but have done so on a time frame ~10× slower (Figure 11). The rates of these small spectral changes are independent of [$Rh(bpy)_3^{3+}$] (50–500 μM). From these observations we conclude that k_5 cannot be $<10^4\ s^{-1}$. With the reverse of reaction 5 probably equally rapid, the rate-determining step of reaction 4 would be reaction 6.

It is clear that $Rh(bpy)_3^{2+}$ is not the only direct precursor to the red Rh(I) species inasmuch as the formation of $Rh(bpy)_2^+$ is not second order in $Rh(bpy)_3^{2+}$. Therefore, any electron-transfer disproportionation reactions must be more rapid than the rate-determining ligand-labilization step. Consideration of the observed rate of formation of $Rh(bpy)_2^+$ and the concentrations of the species involved leads to the conclusion that any disproportionation step must have $k > 10^6\ M^{-1}\ s^{-1}$. This estimated lower limit is not unreasonable for dipositive species ($Rh(bpy)_2^{2+}$, $Rh(bpy)_3^{2+}$, or $Rh(bpy)_2(bpy\text{-})^{2+}$) reacting at or near the diffusion-controlled limit. In fact, the disproportionation of $Rh(NH_3)_4^{2+}$ occurs[21] with $k = 1.4 \times 10^7\ M^{-1}\ s^{-1}$. Deprotonation of Rh(II)–aquo complexes in neutral and alkaline solution would yield species with lower positive charges and even faster diffusion-controlled collision rates.

The observation that one of the final products of the overall reaction is the re-formation of $Rh(bpy)_3^{3+}$ suggests the involvement of $Rh(bpy)_3^{2+}$ in the electron-transfer disproportionation process (reaction 7); Brown et al.[5] estimate k_7 to be $\sim 10^8\ M^{-1}\ s^{-1}$.

$$Rh(bpy)_3^{2+} + Rh(bpy)_2^{2+} \rightarrow Rh(bpy)_3^{3+} + Rh(bpy)_2^{+} \qquad (7)$$

Application of the steady-state approximation for $Rh(bpy)_2^{2+}$ to slow reaction 4 and fast reaction 7 results in $k_{obsd} = 2k_4$ so that $k_4 = 0.45 \pm 0.05\ s^{-1}$. As noted above, the value of k_{obsd} is highly affected by the level of impurities, presumably O_2, in the solution. The value of k_4 appears to be constant in the range pH 3–10.

The yields of free bpy and the loss of the substrate in the continuous radiolysis experiments provide some insights into the mechanism of the reaction. In the first place, reduction of $Rh(bpy)_3^{3+}$ by $NaBH_4$ in alkaline solution produces $Rh(bpy)_2^+$ quantitatively.[7] Exposure of the red-violet Rh(I) species to O_2 at pH ≥11 yields $Rh(bpy)_2(OH)_2^+$ and free bpy in 1:1 stoichiometry. Thus, oxidation of $Rh(bpy)_2^+$ by O_2 in the presence of a stoichiometric amount of free bpy does not result in the reincorporation of bpy when pH ≥11. However, at pH 10 the oxidation generates a mixture of $Rh(bpy)_3^{3+}$ and $Rh(bpy)_2(OH)_2^+$, the ratio of which increases with increasing concentration of $Rh(bpy)_2^+$ and bpy. This ratio also increases with decreasing pH reaching a maximum in the neutral region. In strongly acidic solutions, where $Rh(bpy)_2^+$ is present in a colorless form, the regeneration of $Rh(bpy)_3^{3+}$ upon exposure to O_2 is not observed.

Because of the bpy-reincorporation process and the occurrence of a chain reaction in strongly alkaline solutions, the values of G(bpy) shown in Figure 10 do not give a direct indication of the yield of bpy from reactions 4–7. However, these data and those for the formation and disappearance of other species must be consistent with the mechanism proposed which predicts, at pH ≤10, $G(-Rh(bpy)_3^{3+}) = G(Rh(bpy)_2^+) = G(bpy) \sim 3$. A value of $G(-Rh(bpy)_3^{3+}) = 2.6 \pm 0.1$ has been evaluated with great care at pH 10 where we also obtain $G(bpy) = 3.2$ at a low radiation dose (~5 krd) where the regeneration of $Rh(bpy)_3^{3+}$ is almost undetectable. At pH ≤4, G(bpy) is dose dependent but appears to be ~3 from a zero-dose extrapolation in solutions containing H_2SO_4. Despite the form of $Rh(bpy)_2^+$ that exists in the different pH regions and the effect of dose on G in acidic solutions, it is clear that $G(Rh(bpy)_2^+)$ has a virtually constant value of ~2 across the entire pH range (Figure 10).

The value of $G(Rh(bpy)_2^+)$ does not depend on the nature of the reducing species involved. At pH 10, we have detected the same amount of $Rh(bpy)_2^+$ upon continuous irradiation of the following solutions with constant dose: (1) deaerated 0.1 M 2-propanol, (2) deaerated solution containing 0.25 M 2-propanol and 0.05 M acetone, (3) N_2O-saturated 0.1 M HCO_2^-. In the latter case, since $G(N_2) = 3.1$ from the scavenging of e_{aq}^- by N_2O, $\Delta G(N_2) = 2$ corresponding to the oxidation of $Rh(bpy)_2^+$ by N_2O from which $G(Rh(bpy)_2^+)$ is evaluated.

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[21] Lilie, J.; Simic, M. G.; Endicott, J. F. *Inorg. Chem.* **1975**, *14*, 2129.

[22] In the pulse experiments, the reducing radicals have long disappeared by the time the formation of $Rh(bpy)_2^+$ occurs. In the continuous radiolysis experiments, although the reducing radicals establish a low steady-state concentration, their disappearance is exclusively via reaction with $Rh(bpy)_3^{3+}$ which is always present in enormous kinetic excess.

In order to explain the less-than-stoichiometric yield of $Rh(bpy)_2^+$, we must take into account reactions of H_2O_2 which is formed as a primary product in reaction 1 with $G = 0.8$. In the first place, no reaction between $Rh(bpy)_3^{2+}$ and radiolytically produced H_2O_2 is detected. However, we do know that a red-violet solution of $Rh(bpy)_2^+$ is immediately decolorized upon the addition of H_2O_2, a reaction which, in highly alkaline solutions, is likely to proceed via the formation of a HO_2^- adduct; hydroperoxide complexes of Rh and Co have been reported.[23] It is reasonable that if such a species is formed, it would be unstable and yield $Rh(bpy)_2(OH)_2^+$. We assume, therefore, that $Rh(bpy)_2^+$ is oxidized according to the stoichiometry of reaction 8. In acidic

$$Rh(bpy)_2^+ + H_2O_2 \xrightarrow{2H^+} Rh(bpy)_2(OH_2)_2^{3+}/Rh(bpy)_2(OH)_2^+ \quad (8)$$

solutions, the equation for material balance should include the reduction of $bpyH^+$ ($pK_a = 4.33$)[24] by $(CH_3)_2\dot{C}OH$ or some reduced intermediate. The occurrence of this reaction would reduce both $G(Rh(bpy)_2^+)$ and $G(bpy)$ and its effect should increase with increasing dose. The experimental results from this work are in general agreement with these expectations. It should be noted that the involvement of H_2O_2 in back-reactions of radiolytically generated $Ni_2(CN)_6^{4-}$ has been identified in previous work.[25]

It is interesting to note that at pH 11 in the presence of 0.1 M 2-propanol, up to ~70% conversion of $Rh(bpy)_3^{3+}$ and/or $Rh(bpy)_2(OH)_2^+$ to $Rh(bpy)_2^+$ is achieved with stoichiometric bpy production; 1 equiv of free bpy is extracted per equivalent of $Rh(bpy)_3^{3+}$ initially present. This fact strongly suggests that $bpyH\cdot$ radicals, generated by the action of e_{aq}^- on bpy,[12] are converted back to bpy by a reaction with $Rh(bpy)_3^{3+}$ and/or $Rh(bpy)_2(OH)_2^+$.

The precipitous rise in $G(bpy)$ and $G(-Rh(bpy)_3^{3+})$ at pH >10 requires the introduction of another mechanistic step: a ligand-labilization chain reaction involving the $Rh(bpy)_3^{3+}$ substrate. A similar redox-catalyzed ligand-labilization reaction has been seen[26-28] for $Cr(bpy)_3^{3+}$ in which the conversion of the reduced $Cr(bpy)_3^{2+}$ species to $Cr(bpy)_2(OH_2)_2^{2+}$ leads to the reduction of the substrate; the $Cr(bpy)_3^{3+/2+}$ couple has a more positive potential than the $Cr(bpy)_2(OH_2)_2^{2+/+}$ couple. The observations reported here for the reduction of $Rh(bpy)_3^{3+}$ suggest that reaction

$$Rh(bpy)_2(OH)_2^0 + Rh(bpy)_3^{3+} \rightarrow Rh(bpy)_3^{2+} + Rh(bpy)_2(OH)_2^+ \quad (9)$$

9 is an important pathway in highly alkaline solution in competition with other modes of decay of $Rh(bpy)_2(OH)_2^0$ such as reactions 10 and 11; reaction 11 would be followed by rapid

$$2Rh(bpy)_2(OH)_2^0 \rightarrow Rh(bpy)_2(OH)_2^+ + Rh(bpy)_2^+ (+\ 2OH^-) \quad (10)$$

$$Rh(bpy)_2(OH)_2^0 + Rh(bpy)_3^{2+} \rightarrow Rh(bpy)_2(OH)_2^+ + Rh(bpy)_3^+ \quad (11)$$

elimination of bpy from $Rh(bpy)_3^+$. Inasmuch as $Rh(bpy)_3^{2+}$ in highly alkaline medium should be viewed as an equilibrium mixture of that species and $Rh(bpy)_2(bpy-)(OH)^+$, the lengthening of the chain reaction and the increase in G with increasing pH can be attributed to the displacement of monodentate bpy by OH^-. From our observations we conclude that the potential for the $Rh(bpy)_2(OH_2)_2^{2+/+}$ couple becomes more negative as a result of deprotonation and that the $Rh(bpy)_3^{3+/2+}$ couple has a more negative potential than does the $Rh(bpy)_2(OH_2)_2^{2+}/Rh(bpy)_2^+$ couple but a less negative potential than $Rh(bpy)_2(OH)_2^{+/0}$. Because of the high concentration of $Rh(bpy)_3^{3+}$ in reaction 9 relative to that of the reduced intermediates, the value of k_9 can easily be in the $10^6 - 10^7$ M^{-1} s^{-1} range representing a difference between the potentials of the $Rh(bpy)_3^{3+/2+}$ and $Rh(bpy)_2(OH)_2^{+/0}$ couples of 0.1–0.2 V.

With regard to the postirradiation conversion of $Rh(bpy)_3^{3+}$ to $Rh(bpy)_2(OH)_2^+$ at pH ≥11, the effect is consistent with an electron-transfer reaction between $Rh(bpy)_3^{3+}$ and $Rh(bpy)_2^+$ (reaction 12) resulting in the formation of $Rh(bpy)_2^{2+}$ which is

$$Rh(bpy)_3^{3+} + Rh(bpy)_2^+ \rightleftarrows Rh(bpy)_3^{2+} + Rh(bpy)_2^{2+} \quad (12)$$

susceptible to coordination by OH^- (reaction 13). An increase

$$Rh(bpy)_2^{2+} + 2OH^- \rightleftarrows Rh(bpy)_2(OH)_2^0 \quad (13)$$

in radiation dose increases $[Rh(bpy)_2^+]$ and shifts the position of equilibrium of reaction 12 to the right; an increase in pH does the same for reaction 13. The resulting $Rh(bpy)_2(OH)_2^0$ will then react via reaction 9.

In highly acidic solution $Rh(bpy)_3^{2+}$ is formed and shows the same spectrum as at higher pH values. However, no red Rh(I) species are formed from the complete disappearance of $Rh(bpy)_3^{2+}$ and the final products in the solution have UV spectra very similar to those of the original substrate. Unfortunately, the mechanism by which $Rh(bpy)_2^+$ in its colorless form is generated in highly acidic solutions is not very clear. In the presence of H_2SO_4 at pH 1 and 2, we have observed a moderately fast (millisecond time frame) pH-independent component that is essentially first order at low doses (~1 krd). At pH 3, this component is not observed any further and the absorption of $Rh(bpy)_3^{2+}$ is seen to decay via a first-order process for which $k_{obsd} \sim 1$ s^{-1}. At pH 1 and 2, after the fast component, the absorption disappears almost completely via first-order processes for which $k = 10$ and 3 s^{-1} at pH 1 and 2, respectively. It appears that the first-order component observed at pH ≤2 represents the rate-determining step, presumably ring opening, in the protonation of $Rh(bpy)_3^{2+}$ to $Rh(bpy)_2(-bpyH)^{3+}$. This latter species would appear to show a pK_a of 2–3, a value that is not unreasonable for monodentate $bpyH^+$ coordinated to a +2 metal center; the pK_a for free $bpyH_2^{2+}$ is –0.2.[24] The other component of the decay should represent the rate-determining step for a disproportionation reaction involving $Rh(bpy)_2(-bpyH)^{3+}$ and $Rh(bpy)_2^{2+}$, the latter presumably as $Rh(bpy)_2(OH_2)_2^{2+}$, acting as an oxidant similar to its behavior at pH ~10. The reason for the moderate pH effect on the rate constant related to the rate-determining step, which, according to our mechanism, would be the release of $bpyH^+$, probably residues in the differences in the ionic strengths of the solutions. In the pH range where the formation of $Rh(bpy)_2(-bpyH)^{3+}$ is not detected (pH ≥3), the disproportionation step should be described by reaction 7 and should be followed by the conversion (which appears to be moderately slow) of $Rh(bpy)_2^+$ to a colorless form.

Finally, the clear involvement of ClO_4^- in the decay of $Rh(bpy)_3^{2+}$ in acidic solutions must be mentioned briefly. This reaction shows second-order rate constants of 420, 1100, and 1500 M^{-1} s^{-1} at pH 0, 1, and 2, respectively, and cannot be electron transfer in nature. It is reasonable to assume that ClO_4^- engages in an inner-sphere path with $Rh(bpy)_2(-bpyH)^{3+}$ after the ring-opening process has occurred. A comparable mechanism has been recently proposed[29] in which Ru(II)–bpy complexes reduce ClO_4^- via formation of Ru(IV)–oxo intermediates.

Nature of $Rh(bpy)_2^+$. From the variation of λ_{max} and ϵ_{max} and the fact that a violet Rh(I) species precipitates out of aqueous solution, it is quite clear that the nature of the species designated as "$Rh(bpy)_2^+$" depends upon the pH of the solution, the concentration of Rh(I), and the nature and concentration of the counterion. It is entirely likely that $Rh(bpy)_2^+$ can exist as monomeric, polymeric, and aggregated material. Although further

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work on the system will clarify the issue, it should be recognized that we have clearly identified at least four forms of $Rh(bpy)_2^+$.

(a) **Red-Violet Soluble Form.** This species at a concentration of $\sim 10^{-4}$ M exhibits λ_{max} 518 nm and ϵ_{max} 9500 M^{-1} cm^{-1} and is stable in alkaline solution in the absence of air. The same species can be obtained by the electrolytic reduction of $Rh(bpy)_3^{3+}$ (although ϵ_{max} appears to have been underestimated)[4] or by the reduction of $Rh(bpy)_2(OH)_2^+$ by amalgamated Zn followed by OH^- addition.[5] We have demonstrated[7] that this form of $Rh(bpy)_2^+$ contains at least one OH^-. We have observed, in fact, that the irradiation ($\sim$34 krd) of a deaerated solution of $Rh(bpy)_3^{3+}$ (150 μM) containing 0.1 M 2-propanol at pH 10.5 results in a depletion of OH^- to an extent much greater than expected. The same phenomenon has been observed[7] in the course of the reduction of $Rh(bpy)_3^{3+}$ by BH_4^-. This species is formulated as $Rh(bpy)_2(OH)_n^{1-n}$ and may be dimeric via hydroxide bridging. At pH 7.0, the spectrum we obtain for $Rh(bpy)_2^+$ in phosphate buffer is the same as that given by Brown et al.[5] with a main band at $\sim$415 nm and a well-defined shoulder in the 470 nm region. As seen in Figure 9, a very small change in pH to 7.2 has a large effect on this spectrum, indicating that it is related to an equilibrium mixture of various forms of $Rh(bpy)_2^+$. From Figure 8, an apparent pK_a of 7.7 ± 0.3 for a $Rh(bpy)_2^+$ species is seen. The slight increase in absorbance at λ_{max} observed at pH >12 (Figure 8) is not attributed to another acid–base conversion inasmuch as solutions at pH 10 made alkaline to pH 14 do not show such a change. The effect appears to be due to an increase in G(Rh(I)), possibly resulting from the scavenging of HO_2^- by $Rh(bpy)_2(OH)^0$ to generate OH radicals.

(b) **Violet Insoluble Form.** This form can be represented simply as $Rh(bpy)_2X$, where X can be Cl^-, ClO_4^-, BH_4^-, NO_3^-, etc. The large red shift that is observed during the process of separation of $Rh(bpy)_2X$ is probably due to an oligomerization process.[30] This phenomenon is nicely depicted in Figure 4. The brown precipitate reported by Kirch et al.[4] to be the precursor of H_2 formation at pH 7 can be viewed as $Rh(bpy)_2X$ in a state of protonation appropriate to that pH. Under the conditions in which we have been working, this brown precipitate has never been observed, presumably because the concentrations of our species have been lower. For reference, we estimate K_{sp} for $Rh(bpy)_2ClO_4$ to be $\sim 10^{-8}$ at pH 10.

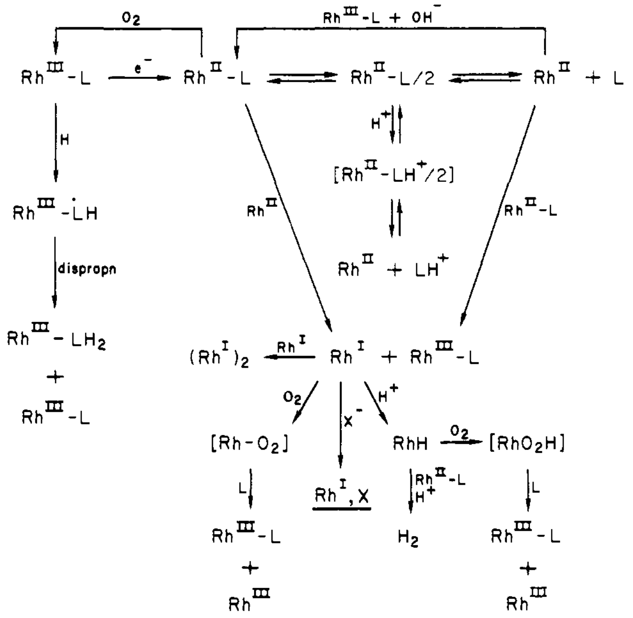
(c) **Green Form.** A transient green color is observed when red-violet solutions of $Rh(bpy)_2^+$ are mixed with HCl or H_2SO_4. The spectrum of this green species shows the same band at $\sim$415 nm that is observed at pH 7. From an extrapolation of the absorbance to zero time, we estimate ϵ_{415} 5400 ± 300 M^{-1} cm^{-1}. In our opinion the green form of $Rh(bpy)_2^+$ can be viewed as $Rh(bpy)_2(OH_2)_n^+$ which, at pH ≥7, is in equilibrium with the form (or forms) of $Rh(bpy)_2^+$ containing OH^-.

(d) **Colorless Form.** At pH ≤6, $Rh(bpy)_2(OH_2)_n^+$ is unstable with respect to the colorless form of $Rh(bpy)_2^+$. This colorless form shows two main absorption bands in the 240- and 300-nm regions characteristic of protonated free bpy, and bpy complexes in general. In view of the similarities among the spectra of this form of $Rh(bpy)_2^+$, $Rh(bpy)_3^{3+}$, and $bpyH^+$, the changes in absorption induced by the continuous irradiation of acidic solutions are rather small and difficult to interpret. The absence of visible absorption bands of $Rh(bpy)_2^+$ in acidic solution is consistent with its assignment as an hydride in which the metal center is formally Rh(III) (reaction 14). Represented as $RhH(bpy)_2^{2+}$, its quantitative conversion to $Rh(bpy)_2(OH_2)_2^{3+}$ by O_2 is expected to proceed via formation of an hydroperoxide complex.[23]

$$Rh(bpy)_2^+ + H^+ \rightarrow RhH(bpy)_2^{2+} \qquad (14)$$

Irrespective of the exact nature of the $Rh(bpy)_2^+$ species, they are sensitive to O_2 in solution or in the solid state. From our evidence, the products in all cases have the spectra of $Rh(bpy)_3^{3+}$, $Rh(bpy)_2(OH_2)_2^{3+}$, or its conjugate bases. Although the direct two-electron oxidation of $Rh(bpy)_2^+$ by O_2 is thermodynamically allowed, the potential of the $Rh(bpy)_2(OH)_2^+/Rh(bpy)_2^+$ couple having been reported[5] to be $\sim$–0.25 V at pH 8 with E^0 for the O_2/H_2O_2 couple being +0.68 V at pH 0 and –0.08 V at pH 14,[31] the reincorporation of bpy argues against such a step. We are inclined to believe that the process proceeds, in general, via formation of an O_2 adduct which, depending on the pH of the solution, could yield or equilibrate with the hydroperoxide form. In strongly alkaline solutions, the reincorporation of bpy is not observed, presumably because bpy would have to displace OH^- instead of H_2O from the sixth ligand position to form the monodentate intermediate. In acidic solutions (pH ≤4), bpy will be present as $bpyH^+$ which, as a poor ligand, has lessened propensity for reincorporation; the process, in fact, is not observed.

Scheme I



Relevance to Solar Energy Conversion Schemes. Kirch et al.[4] have claimed that $Rh(bpy)_2^+$ is the precursor to the formation of H_2, possibly via hydride formation (reaction 14), in the photochemical system containing $Ru(bpy)_3^{2+}$, $Rh(bpy)_3^{3+}$, triethanolamine, and Pt catalyst. They have reported that the formation of H_2 is pH dependent with a maximum rate at pH 7.5 ± 0.5 although they do not report any quantum yields. Brown et al.[5] have determined Φ_{H_2} to be 0.11 ± 0.01 at pH 8.1 in a similar system. In our experiments with deaerated solutions of $Rh(bpy)_3^{3+}$, the "background" level of H_2, arising from the primary radiolytic acid (reaction 1), the scavenging of e_{aq}^- by H^+, and the abstraction reaction of H and 2-propanol, corresponds to $G(H_2)$ = 3.3 in acidic solution and 1.1 in neutral and alkaline solution. At "natural" pH,[32] the yield of H_2 above background corresponds to G = 0.4 at 30 krd and 0.8 at 150 krd. Inasmuch as $G(Rh(bpy)_3^{2+})$ = 6.0 under these conditions and the formation of H_2 is a two-equivalent process, the maximum efficiency in the uncatalyzed system is $\sim$25%. It is to be noted that Kirch et al.[4] have observed the uncatalyzed photochemical formation of H_2 in the $Ru(bpy)_3^{2+}/Rh(bpy)_3^{3+}$/EDTA system at pH 5.2.

We can now speculate on the nature of the species that gives rise to H_2 in the uncatalyzed systems. $Rh(bpy)_2^+$ is perfectly stable in O_2-free acidic and alkaline solutions; $Rh(bpy)_2ClO_4$, dispersed as a solid in a solution at pH 10, has been kept for at least 3 months without the generation of H_2. Rh(II) species are one-electron transport agents and are only present at very low steady-state concentrations under continuous irradiation conditions. We, therefore, conclude that neither $Rh(bpy)_2^+$ (its various aquated, hydroxylated, and/or dimeric forms) nor $RhH(bpy)_2^{2+}$,

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[30] Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G., II *Inorg. Chem.* **1978**, *17*, 828.

[31] "Handbook of Chemistry and Physics", 59th ed.; Chemical Rubber Co.; Cleveland, Ohio, 1978–79.

[32] Prior to irradiation, the pH of Ar-purged solutions is $\sim$7. Upon irradiation in the absence of buffer, the final pH is $\sim$5.

nor Rh(II), is capable of generating H_2 *by itself* at appreciable rates in the uncatalyzed systems. Nevertheless, of all these intermediates, the most logical candidate[4] for uncatalyzed H_2 formation is $RhH(bpy)_2^{2+}$. Now, during the continuous radiolysis and photolysis experiments in the natural pH region, $Rh(bpy)_3^{2+}$, which is a good reductant, could be capable of reducing $RhH(bpy)_2^{2+}$ (reaction 15). Kirch et al.[4] report that the third step

$$Rh(bpy)_3^{2+} + RhH(bpy)_2^{2+} \rightarrow Rh(bpy)_3^{3+} + RhH(bpy)_2^{+} \quad (15)$$

in the reduction of $Rh(bpy)_3^{3+}$ occurs at −1.15 V at pH 10.7 and −0.90 V at pH 7.0. From what we now know about the various forms of $Rh(bpy)_2^{+}$, it follows that $RhH(bpy)_2^{2+}$ is a stronger oxidant than is $Rh(bpy)_2(OH)_n^{1-n}$. Interaction of $RhH(bpy)_2^{+}$ with H^+ could lead to H_2 according to reaction 16. Another

$$RhH(bpy)_2^{+} + H^+ \rightarrow Rh(bpy)_2^{2+} + H_2 \quad (16)$$

possible pathway, represented by reaction 17, is similar to the

$$2RhH(bpy)_2^{+} \rightarrow H_2 + 2Rh(bpy)_2^{+} \quad (17)$$

binuclear homolytic mechanism for the generation of H_2 from hydridocobaloxime.[33] According to this kinetic scheme, the yield of H_2 should increase to a plateau as $RhH(bpy)_2^{2+}$ builds up in the system and reaches a steady-state concentration.[34] Our determination of the dependence of $G(H_2)$ as a function of irradiation time is in accord with this mechanism. Experiments designed to optimize the uncatalyzed yield of H_2 are currently in progress.

Conclusions

It is clear that the one-electron reduction of $Rh(bpy)_3^{3+}$ in aqueous solution yields a very rich chemistry that must be understood in detail if complex redox systems involving this substance are to be utilized. Both $Rh(bpy)_3^{2+}$ and $Rh(bpy)_2^{+}$ are involved in highly complex interlocking ligand-labilization, acid–base, redox, and aggregation reactions. Using the symbol Rh–L to represent tris(bpy)species, Rh–L/2 to represent a species with a monodentate ligand, and Rh to represent ligand-labilized species which may or may not contain coordinated H_2O or OH^-, we summarize our current findings in Scheme I.

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(33) Chao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129.

(34) As the concentration of $RhH(bpy)_2^{2+}$ builds up, direct reduction of that species to $RhH(bpy)_2^{+}$ by radiation-generated reducing radicals or, in the case of the photochemical system, $^*Ru(bpy)_3^{2+}$ can occur.

The Nonadiabaticity Problem of Outer-Sphere Electron-Transfer Reactions. Reduction and Oxidation of Europium Ions

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Abstract: A new type of approach to the nonadiabaticity problem of outer-sphere electron-transfer reactions is presented. The approach is based on the analysis of the change in the rate constants of the reactions of the species under consideration with a homogeneous family of redox partners having variable redox potential. In favorable cases such an analysis allows us to disentangle the effects of intrinsic barrier (nuclear term) and nonadiabaticity (electronic term) on the rate constant. The literature data for the reactions of $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_6^{3+}$, Fe^{2+}, Fe^{3+}, Eu^{2+}, and Eu^{3+} with a homogeneous family of partners have been collected and the log k_{12} vs. ΔG plots have been drawn and examined. For $Ru(NH_3)_6^{n+}$ and Fe^{n+} the plots indicate small ($Ru(NH_3)_6^{n+}$) and large (Fe^{n+}) intrinsic barriers and adiabatic or nearly adiabatic behavior (adiabaticity factor, $\kappa > 10^{-3}$) in the ΔG range 0 to −1.5 eV. For Eu^{n+}, different plots are obtained for Eu^{2+} oxidation or Eu^{3+} reduction. These plots suggest a strongly nonadiabatic behavior of europium ions ($\kappa \simeq 10^{-6}$) at moderately negative ΔG values. A theoretical estimate of the adiabaticity factor based on spectroscopic information yields $\kappa \leq 10^{-5}$ for electron-transfer reactions between ground-state Eu^{n+} ions and adiabatic-type partners. At large and negative ΔG values more efficient but different channels become available for Eu^{2+} oxidation or Eu^{3+} reduction. These channels are tentatively assigned to paths involving different charge-transfer intermediates. The role played by excited states in electron-transfer reactions is discussed.

The rate constants of outer-sphere electron-transfer reactions (eq 1) are usually discussed in the literature on the basis of the

$$A_1 + A_2 \xrightarrow{k_{12}} A_1^+ + A_2^- \quad (1)$$

Marcus equation (eq 2),[2] where Z is the collision frequency of

$$k_{12} = pZe^{-(\Delta G^* + w_r)/RT} \quad (2)$$

neutral molecules in solution, ΔG^* is the free activation energy, w_r is the work required to bring the reactants together, and p is the probability of electron transfer in the activated complex. According to Sutin,[3-5] eq 2 can be recast as in eq 3, where K_0 is

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(2) Marcus, R. A. *Faraday Discuss. Chem. Soc.* **1960**, *29*, 21; *Annu. Rev. Phys. Chem.* **1964**, *15*, 155; *J. Chem. Phys.* 1965, *43*, 679; *Electrochim. Acta* 1968, *13*, 995. In "Tunneling *in Biological Systems*"; Chance, B., De Vault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds.; Academic Press: New York, 1979; p 109.

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