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Radiolytic and Electrochemical Reduction of Ru(bpz)$_3^{2+}$ in Aqueous Solution. Stability, Redox, and Acid-Base Properties of Ru(bpz)$_3^{+}$ [1]

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The reduction of Ru(bpz)$_3^{2+}$ in aqueous solution has been investigated by using radiolytic and electrochemical techniques. The one-electron reduction of Ru(bpz)$_3^{2+}$ by e_{aq}^-, CO$_2^{\bullet-}$, and (CH$_3$)$_2$ĊOH radicals is rapid (k = (5-9) × 10^{10}, 1.3 × 10^{10}, and 3.5 × 10^9 M^{-1} s^{-1}, respectively) and quantitative; the products of these reactions are Ru(bpz)$_3^+$, which can be represented as Ru(bpz)$_2$(bpz$^{\bullet-}$)$^+$, in alkaline solution and its conjugate acid Ru(bpz)$_2$(bpzH$^\bullet$)$^{2+}$ (pK_a = 7.1 ± 0.3) in acidic solution. In the absence of oxygen, Ru(bpz)$_3^+$ is stable; in the presence of MV^{2+}, an equilibrium is established with k(Ru(bpz)$_3^+$ + MV^{2+}) = 1.3 × 10^8 M^{-1} s^{-1}, k(Ru(bpz)$_3^{2+}$ + MV$^{\bullet+}$) = 1.7 × 10^7 M^{-1} s^{-1}, and K_{eq} = 7.6. From these data and from cyclic voltammetric measurements a value of $E°$(Ru(bpz)$_3^{2+/+}$) = -0.50 V has been derived for alkaline aqueous solution. When the pH of the solution is changed from alkaline to acidic, E_{pc} shifts toward less negative potentials by about 170 mV. Accordingly, Ru(bpz)$_2$(bpzH$^\bullet$)$^{2+}$ is unable to reduce MV^{2+}; it is unstable ($t_{1/2}$ ~ 20 s), presumably toward a disproportionation reaction leading to the starting material and to the doubly reduced species Ru(bpz)$_2$(bpzH$_2$)$^{2+}$. The latter is also generated by controlled-potential electrolysis of Ru(bpz)$_3^{2+}$ in acidic solution; it can be electrochemically oxidized back to Ru(bpz)$_3^{2+}$, or it can generate Ru(bpz)$_2$(bpz$^{\bullet-}$)$^+$ slowly ($t_{1/2}$ ~ 1 h) upon reaction with OH$^-$ under oxygen-free conditions.

Introduction

A few years ago Crutchley and Lever[3] demonstrated that Ru(bpz)$_3^{2+}$ (bpz = 2,2′-bipyrazine) is superior to Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) as a photosensitizer in model systems for the reduction of water. Following that report, many investigations have been devoted to the characterization of the chemical, photophysical, photochemical, and electrochemical properties of Ru(bpz)$_3^{2+}$, and to the definition of its role and abilities in the model systems.[4-16] The luminescent excited state of the complex, *Ru(bpz)$_3^{2+}$, is reductively quenched by sacrificial electron donors such as EDTA (ethylenediaminetetraacetate) or TEOA (triethanolamine) according to reaction 1.

$$^*\text{Ru(bpz)}_3^{2+} + \text{EDTA/TEOA} \rightarrow \text{Ru(bpz)}_3^{+} + \text{EDTA}_{ox}/\text{TEOA}_{ox} \quad (1)$$

In the presence of methylviologen (1,1′-dimethyl-4,4′-bipyridinium ion, MV^{2+}) as an electron relay, Ru(bpz)$_3^+$ reduces MV^{2+} to MV$^{\bullet+}$ (reaction 2); in the presence of a suitable redox catalyst, MV$^{\bullet+}$ reduces H$_2$O to H$_2$ (reaction 3).

$$\text{Ru(bpz)}_3^{+} + \text{MV}^{2+} \rightarrow \text{Ru(bpz)}_3^{2+} + \text{MV}^{\bullet+} \quad (2)$$

$$\text{MV}^{\bullet+} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{MV}^{2+} + {}^1/_2\text{H}_2 + \text{OH}^- \quad (3)$$

Although the role of Ru(bpz)$_3^+$ in photochemical model systems is apparent, the characterization of this species in aqueous solution has received very little attention until recently. In a recent report[16] some information about Ru(bpz)$_3^+$ generated via the flash photolysis of aqueous solutions containing Ru(bpz)$_3^{2+}$ and EDTA was presented. We report here the results of the radiolytic and electrolytic reduction of Ru(bpz)$_3^{2+}$ in acidic and alkaline aqueous solutions.

Experimental Section

Materials. Ru(bpz)$_3^{2+}$, in the form of the PF$_6^-$ salt, was prepared according to the method of Rillema et al.[8] A sample of the compound was kindly provided by Professor A. B. P. Lever; both samples exhibited the same behavior. The compound was stable under all the concentration and pH conditions used in this study. Methylviologen dichloride (Aldrich), sodium formate (Merck), 2-propanol (Baker), and sodium sulfate (Merck, Suprapur) were used as received. Distilled water was further purified by distillation from acidic dichromate and alkaline permanganate and then was fractionated in an all-silica apparatus. Alternatively, the solutions were prepared by using water that had been purified by passage through a Millipore purification train. The solutions were saturated with purified N$_2$O, purged with Ar, or degassed by standard vacuum-line techniques. The pH of the solutions was adjusted with H$_2$SO$_4$ or NaOH (Merck, Suprapur) or with phosphate buffers.

Procedures. Continuous radiolyses were carried out at room temperature on 10-20-mL samples contained in silica or Pyrex vessels that were provided with silica optical cells on a side arm; some vessels were also fitted with a separate compartment through which it was possible to add the required amount of concentrated H$_2$SO$_4$ or NaOH to the irradiated solutions under oxygen-free conditions. Absorption spectra were recorded with Perkin-Elmer Model 555 or Lambda 5 spectrophotometers. The radiation source was a ^{60}Co-Gammacell (AEC, Ltd.) with a dose rate of ~7.5 Gy min^{-1}. The absorbed radiation dose was determined with the Fricke chemical dosimeter by taking G(Fe^{3+}) = 15.5, where G(X) = number of molecules of species X formed per 100 eV of energy absorbed by the solution.

Pulse radiolyses with optical absorption detection were performed by using the 12-MeV linear accelerator of the FRAE Institute of CNR, Bologna, Italy.[17] The pulse irradiations were performed at room temperature on samples contained in Spectrosil cells of 2-cm optical path length. The solutions were protected from the analyzing light by means of a shutter and appropriate cutoff filters. The radiation dose per pulse

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was monitored by means of a charge collector placed behind the irradiation cell and calibrated with a 0.1 M KSCN aqueous solution saturated with O_2 using $G\epsilon = 2.15 \times 10^4$ at 500 nm[18] or with a N_2O-saturated solution containing 0.1 M HCO_2^- and 0.5 mM MV^{2+} using $G\epsilon = 9.32 \times 10^4$ at 602 nm.[19]

Electrochemistry. Controlled-potential electrolyses were performed with Amel Model 563 Electrochemolab equipment. Cyclic voltammetry was performed on Ar-purged aqueous solutions containing 0.1 M Na_2SO_4 as a supporting electrolyte with an Amel 448 oscillographic polarograph with a platinum wire as the counter electrode and a standard calomel electrode (SCE) as the reference electrode. In alkaline solution (pH ~11), the working electrode was a platinum microsphere; in acidic solution (pH ~3.5) a glassy-carbon electrode (GCE) was used instead. The spectra of electrochemically reduced species were obtained at a gold grid used as an OTTLE (optical transparent thin layer electrode) placed between the windows of a 2-mm spectrophotometric cell directly mounted in a Cary 219 spectrophotometer. The counter electrode was a Pt wire separated from the cathodic compartment by a frit; an Ag wire acted as a quasi-reference electrode. In order to establish the correct working conditions, cyclic voltammetry was performed prior to the electrolysis.

Generation of Reducing Radicals. The radiolysis of an aqueous solution generates e_{aq}^-, OH radicals, H atoms, and molecular products (H_2 and H_2O_2) according to reaction 4 where the numbers in parentheses

$$H_2O \rightsquigarrow e_{aq}^-\ (2.8),\ OH\ (2.8),\ H\ (0.6),\ H_2\ (0.45),\ H_2O_2\ (0.8) \qquad (4)$$

represent the G values for the individual species. In N_2O-saturated (25 mM) solution, e_{aq}^- is converted to OH according to reaction 5; in acidic

$$e_{aq}^- + N_2O \xrightarrow{H_2O} N_2 + OH + OH^- \qquad (5)$$

$$k = 8.7 \times 10^9\ M^{-1}\ s^{-1} \quad \text{(ref 20)}$$

solution, e_{aq}^- is converted to H according to reaction 6. In the presence

$$e_{aq}^- + H^+ \rightarrow H \qquad (6)$$

$$k = 2.2 \times 10^{10}\ M^{-1}\ s^{-1} \quad \text{(ref 20)}$$

of HCO_2^- (0.1 M) or 2-propanol (1%, 0.13 M), reactions 7 and 8 take

$$H/OH + HCO_2^- \rightarrow H_2/H_2O + CO_2^{\bullet -} \qquad (7)$$

$$k = 3 \times 10^8/3 \times 10^9\ M^{-1}\ s^{-1} \quad \text{(ref 21, 22)}$$

$$H/OH + (CH_3)_2CHOH \rightarrow H_2/H_2O + (CH_3)_2\dot{C}OH \qquad (8)$$

$$k = 5 \times 10^7/1.3 \times 10^9\ M^{-1}\ s^{-1} \quad \text{(ref 21, 22)}$$

place, respectively. The reaction of OH with 2-propanol is known[23] to produce, in addition to $(CH_3)_2\dot{C}OH$, ~15% of the β-radical, $^{\bullet}CH_2CH(CH_3)OH$. Thus, in solutions containing HCO_2^- or 2-propanol the major reactive species are e_{aq}^- and $CO_2^{\bullet -}$ or $(CH_3)_2\dot{C}OH$ radicals; if the solution is also acidic and/or saturated with N_2O, the reactive species are $CO_2^{\bullet -}$ or $(CH_3)_2\dot{C}OH$ radicals only. These radicals are strong reducing agents ($E°(CO_2/CO_2^{\bullet -}) = -2.0$ V;[24] $E°((CH_3)_2CO + H^+/(CH_3)_2\dot{C}OH) = -1.2$ V).[25]

Results

Pulse Radiolysis. The pulse irradiation of Ar-purged solutions containing $Ru(bpz)_3^{2+}$ (25–50 μM) and 0.1 M HCO_2^- at natural pH produced initially the absorption of e_{aq}^- (λ_{max} = 720 nm, $\epsilon = 1.9 \times 10^4\ M^{-1}\ cm^{-1}$),[26] which disappeared via first-order process with k_{obsd} proportional to the concentration of $Ru(bpz)_3^{2+}$. Under these conditions (μ = 0.1) the bimolecular rate constant for the reduction of $Ru(bpz)_3^{2+}$ by e_{aq}^- (reaction 9) was $(4.7 \pm 0.1) \times 10^{10}\ M^{-1}\ s^{-1}$. At $\mu \sim 0$ in the presence of 0.13 M 2-propanol, $k_9 = (9.0 \pm 1.0) \times 10^{10}\ M^{-1}\ s^{-1}$.

$$Ru(bpz)_3^{2+} + e_{aq}^- \rightarrow Ru(bpz)_3^+ \qquad (9)$$

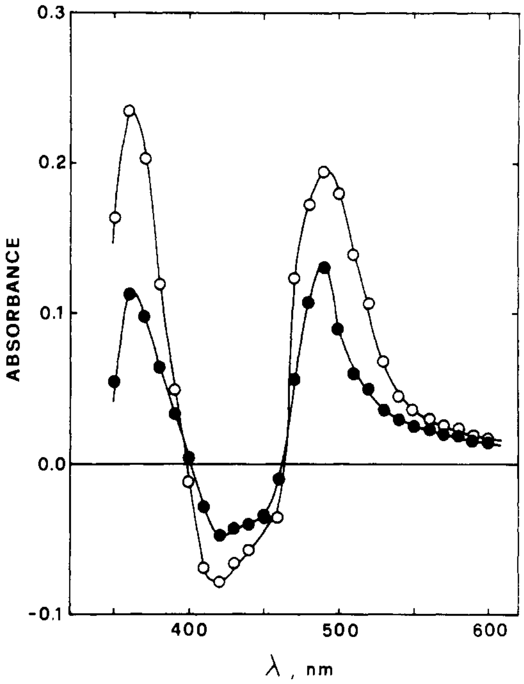

Figure 1. Observed spectra obtained from the pulse radiolysis of N_2O-saturated solutions containing 0.1 M HCO_2^- and ~50 μM $Ru(bpz)_3^{2+}$ at pH 11 (○) and 2.8 (●). Dose per pulse = 13 Gy; optical path length = 2 cm.

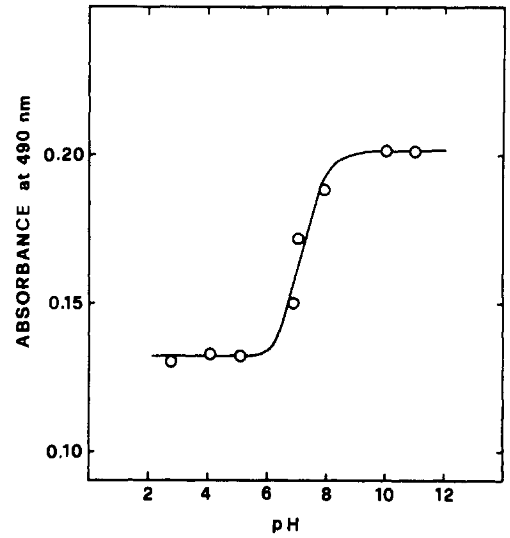

Figure 2. Effect of pH on the absorbance at 490 nm obtained from the pulse radiolysis of N_2O-saturated solutions containing 0.1 M HCO_2^- and ~50 μM $Ru(bpz)_3^{2+}$. Dose per pulse = 13 Gy; optical path length = 2 cm.

In the presence of HCO_2^- the disappearance of the absorption of e_{aq}^- was paralleled by the appearance of absorption bands at ~360 and ~490 nm and by an increase of transmission in the 400–460-nm region (Figure 1). The spectrum obtained after the disappearance of e_{aq}^- (not shown in Figure 1) was almost doubled by a process occurring in a longer time frame. In N_2O-saturated

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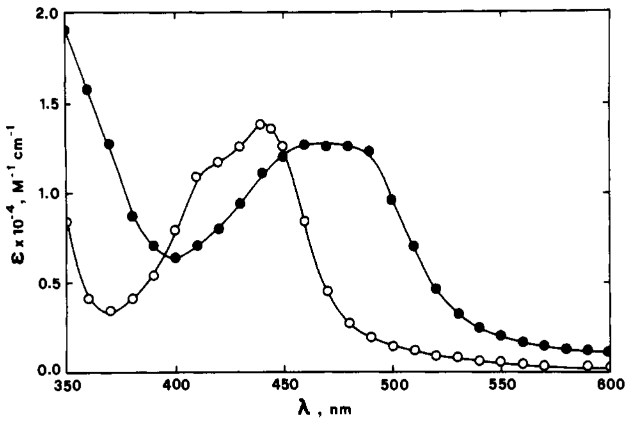

Figure 3. Visible spectra of $Ru(bpz)_3^{2+}$ (○) and $Ru(bpz)_3^{+}$ (●). The spectrum of $Ru(bpz)_3^{+}$ was obtained from the pulse irradiation (dose per pulse = 14 Gy) of Ar-purged or N_2O-saturated solutions containing 50 μM $Ru(bpz)_3^{2+}$ and 0.13 M 2-propanol at pH 11.1; the observed spectra were indistinguishable and were corrected for the bleaching of $Ru(bpz)_3^{2+}$ assuming $G = 6.2$.

solution, where the only species able to react with $Ru(bpz)_3^{2+}$ is the $CO_2^{\bullet -}$ radical (reaction 10), only one process was observed

$$Ru(bpz)_3^{2+} + CO_2^{\bullet -} \rightarrow Ru(bpz)_3^{+} + CO_2 \qquad (10)$$

that followed first-order kinetics with k_{obsd} proportional to the concentration of $Ru(bpz)_3^{2+}$; $k_{10} = (1.3 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1} and was independent of pH (2.8–11.3). The spectra obtained from the pulse irradiation of Ar-purged or N_2O-saturated solutions containing $Ru(bpz)_3^{2+}$ and HCO_2^- were indistinguishable. As shown in Figure 1, however, the spectrum was pH dependent. This dependence was investigated by monitoring the maximum absorbance at 490 nm obtained from the irradiation (13 Gy/pulse) of N_2O-saturated solutions containing 50 μM $Ru(bpz)_3^{2+}$ and 0.1 M HCO_2^-. The results, shown in Figure 2, indicate that the species produced by reaction 10 is involved in an acid–base equilibrium with $pK_a = 7.1 \pm 0.3$.

In the presence of 2-propanol, the results were very similar to those obtained in the presence of HCO_2^-. The bimolecular rate constant for the reduction of $Ru(bpz)_3^{2+}$ by $(CH_3)_2\dot{C}OH$ (reaction 11), was $(3.5 \pm 0.5) \times 10^9$ M^{-1} s^{-1} at natural pH and pH 11. The

$$Ru(bpz)_3^{2+} + (CH_3)_2\dot{C}OH \rightarrow Ru(bpz)_3^{+} + (CH_3)_2CO + H^+ \qquad (11)$$

spectra obtained from the pulse irradiation of Ar-purged or N_2O-saturated solutions containing $Ru(bpz)_3^{2+}$ and 2-propanol at pH 11.1 were indistinguishable. From these spectra, the spectrum of the reduced species at pH 11.1 was calculated by correcting for the bleaching of $Ru(bpz)_3^{2+}$ assuming $G = 6.2$ (Figure 3).

The species arising from the reactions of $Ru(bpz)_3^{2+}$ with e_{aq}^- and/or $CO_2^{\bullet -}$ in alkaline solution did not show any appreciable decay on the longest time frame available (5 s/div). At pH 2.8, a partial decay (~50%) of the absorption initially formed at 490 nm was observed in that time frame. Due to the instability of the analyzing light in this time frame, a meaningful characterization of the decay was not possible. The irradiation of the system, contained in a modified spectrophotometric cell, with a pulse of electrons, showed that the decay was completed in ~1–1.5 min.

The reactivity toward methylviologen of the product originating from the reduction of $Ru(bpz)_3^{2+}$ by $CO_2^{\bullet -}$ or $(CH_3)_2\dot{C}OH$ was investigated as a function of pH and $[MV^{2+}]$. In the first place, $Ru(bpz)_3^{+}$ is able to generate $MV^{\bullet +}$ ($\lambda_{max} = 602$ nm, $\epsilon = 1.37 \times 10^4$ M^{-1} cm^{-1})[27] in neutral or alkaline, but not acidic, solution. The irradiation (4.3 Gy/pulse) of N_2O-saturated solutions containing 53 μM $Ru(bpz)_3^{2+}$, 0.13 M 2-propanol, and increasing amounts of MV^{2+} (5–30 μM) at pH 11.1 showed that the disappearance of $Ru(bpz)_3^{+}$ (monitored at 490 nm) and the appearance of $MV^{\bullet +}$ (monitored at 600 nm) occurred according to identical first-order kinetics with k_{obsd} increasing with increasing concentration of MV^{2+} (Figure 4); reaction 12, at pH 11.1, is described by the equation $k_{obsd} = 9.0 \times 10^2 + (1.3 \times 10^8)[MV^{2+}]$ s^{-1}.

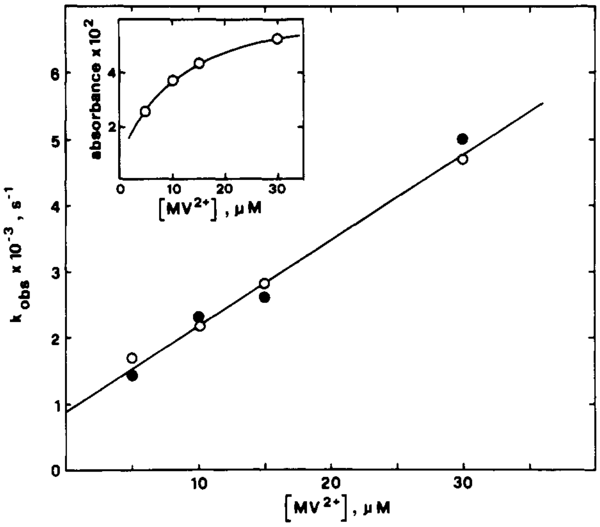

Figure 4. Observed rate constants as a function of $[MV^{2+}]$ obtained from the decrease of absorbance at 490 nm (○) and from the increase of absorbance at 600 nm (●) induced by the pulse irradiation of N_2O-saturated solutions containing 53 μM $Ru(bpz)_3^{2+}$ and 0.13 M 2-propanol at pH 11.1. Inset: maximum absorbance detected at 600 nm as a function of the initial concentration of MV^{2+}. Dose per pulse = 4.3 Gy; optical path length = 2 cm.

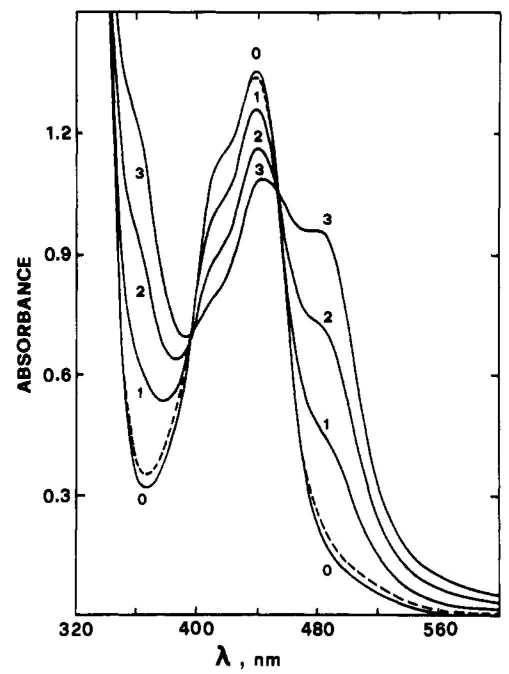

Figure 5. Spectral changes induced by the continuous irradiation of a degassed solution containing 97 μM $Ru(bpz)_3^{2+}$ and 0.1 M HCO_2^- at pH 11.3. Dose rate = 7.55 Gy min^{-1}; optical path length = 1 cm. Curve 0 is the spectrum of the unirradiated solution; curves 1–3 are the spectra obtained after 5.3, 10.6, and 15.9 min of irradiation, respectively. The broken line represents the spectrum of the irradiated solution after equilibration with air.

$$Ru(bpz)_3^{+} + MV^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ru(bpz)_3^{2+} + MV^{\bullet +} \qquad (12)$$

Continuous Radiolysis. The continuous irradiation of deaerated solutions containing 0.1 mM $Ru(bpz)_3^{2+}$ in the presence of 2-propanol or HCO_2^- produced spectral changes that were dependent on the pH of the solution; at a given pH, the nature of the radical scavenger had only a modest effect on the extent of these changes.

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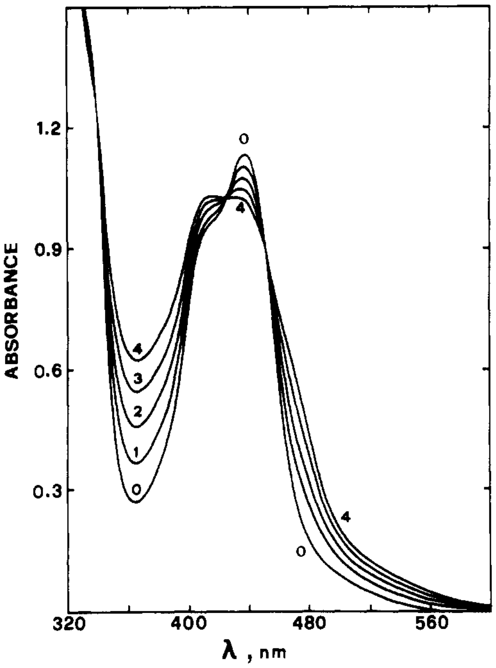

Figure 6. Spectral changes induced by the continuous irradiation of a degassed solution containing 82 μM $Ru(bpz)_3^{2+}$ and 0.1 M HCO_2^- at pH 2.9. Dose rate = 7.55 Gy min^{-1}; optical path length = 1 cm. Curve 0 is the spectrum of the unirradiated solution; curves 1–4 are the spectra obtained after 5.3, 10.6, 15.9, and 21.2 min of irradiation, respectively.

The spectral changes produced by the irradiation of a degassed solution containing 97 μM $Ru(bpz)_3^{2+}$ and 0.1 M HCO_2^- at pH 11.3 are shown in Figure 5. The band at 440 nm of $Ru(bpz)_3^{2+}$ decreased with increasing dose while new absorption bands formed at ~360 and ~480 nm. Two isosbestic points were observed at 396 and 452 nm, which were maintained up to a total dose of ~150 Gy. Further irradiation of the sample produced spectral changes similar to those initially observed, but the isosbestic points were lost. In the absence of air the spectrum of the irradiated solution showed only modest variations after many hours; a rapid reaction took place, however, when the solution was exposed to air causing the original absorption of $Ru(bpz)_3^{2+}$ to be recovered within a few percent. As is shown in Figure 5, however, some differences remained between the spectrum of the unirradiated solution and that of the solution irradiated and then exposed to air. In another experiment, 10 mL of the same degassed solution was irradiated with a dose of 100 Gy, which produced spectral changes consistent with those described in Figure 4. When the irradiated solution was mixed with 0.5 mL of deaerated 0.1 M MV^{2+} under a He atmosphere, the original yellow-orange color turned immediately to blue-green. The spectrum of the mixed solutions showed clearly the characteristic absorption bands of $MV^{\bullet+}$ at 395 and 602 nm onto which the original spectrum of $Ru(bpz)_3^{2+}$ was superimposed. $MV^{\bullet+}$, which was formed nearly quantitatively, was stable under these conditions but disappeared upon exposure to air. The spectrum of the aerated solution indicated a full recovery of the original $Ru(bpz)_3^{2+}$.

In Figure 6 are shown the spectral changes obtained from the continuous irradiation of a degassed solution containing 82 μM $Ru(bpz)_3^{2+}$ and 0.1 M HCO_2^- at pH 2.9; the absorption decreases in the 440-nm region while increasing in the 300–420- and 450–650-nm regions with increasing dose. Three clean isosbestic points were obtained at 300, 424, and 450 nm; no significant post-irradiation changes were observed when the solution was kept free of air. The exposure of the irradiated solution to air caused small spectral changes to occur on the time scale of ~50 h. When the solution was made alkaline, the original spectrum of $Ru(bpz)_3^{2+}$ was only partially recovered. However, if the pH of the irradiated solution was changed from acidic to alkaline under deaerated conditions, the spectrum of the solution was the same as that obtained upon irradiation of an originally alkaline solution (Figure 5). The complete conversion of the acidic to the alkaline form of the spectrum occurred in about 2 h; in contrast, the conversion of the alkaline to the acidic form of the spectrum was completed during the mixing time.

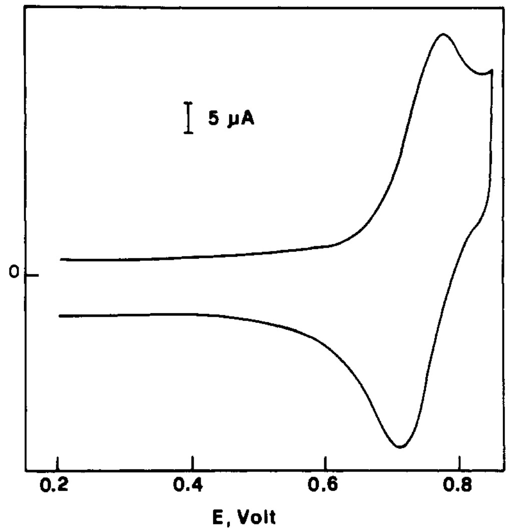

Figure 7. Cyclic voltammogram of an aqueous solution containing 0.12 mM $Ru(bpz)_3^{2+}$ and 0.1 M Na_2SO_4 (pH 11.4) at a Pt electrode. Scan rate = 100 mV/s; SCE reference electrode.

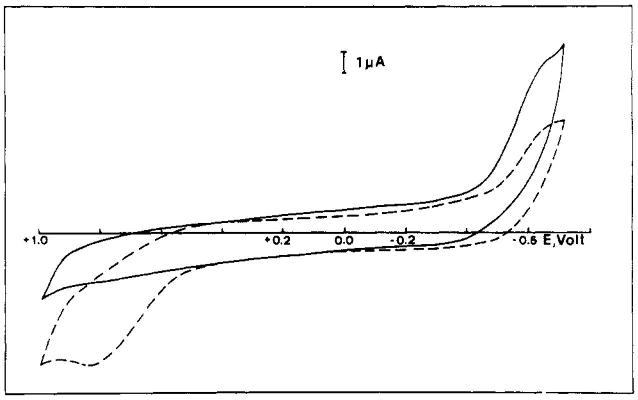

Figure 8. Cyclic voltammograms of an aqueous solution containing 0.12 mM $Ru(bpz)_3^{2+}$ and 0.1 M Na_2SO_4 (pH 3.5) at a GCE: solid line, before electrolysis; broken line, after partial electrolysis at –0.65 V vs. SCE. Scan rate = 100 mV/s; SCE reference electrode.

From the changes in absorbance at 480 nm shown in Figure 5, the *G* value of the conversion of $Ru(bpz)_3^{2+}$ into $Ru(bpz)_3^+$ was calculated assuming $\Delta\epsilon = 1 \times 10^4$ M^{-1} cm^{-1} (Figure 3). Regardless of the nature of the radical scavenger used, the *G* values decreased slightly with increasing dose. The zero-dose-extrapolated values were $G = 6.5$ and 6.0 at pH 11.3 in the presence of 0.1 M HCO_2^- and 0.13 M 2-propanol, respectively.

Electrochemistry. A preliminary voltammetric analysis of the system performed with different electrode materials showed that a number of electron-transfer processes occurred. However, in order to obtain data comparable with those obtained by pulse and continuous radiolysis, only the first uptake of electrons was investigated. The cyclic voltammograms for 0.12 mM $Ru(bpz)_3^{2+}$ in Ar-purged solutions containing 0.1 M Na_2SO_4 at pH 11.4 and pH 3.5 are shown in Figures 7 and 8. At pH 11.4, a reduction peak ($E_{pc} = -0.77$ V vs. SCE) and a reversal anodic peak ($E_{pa} = -0.71$ V vs. SCE) were observed (Figure 7); very similar behavior was observed with the GCE. ΔE_p was independent of the scan rate (0.04–1.0 V/s); i_{pa}/i_{pc} was ~1, independent of scan rate. At pH 3.5 with the GCE, a reduction peak at –0.60 V vs. SCE was observed at a scan rate of 100 mV/s. No reversal anodic peaks were observed up to +1.0 V (Figure 8). However, the cyclic voltammetry performed after electrolysis at –0.65 V showed an oxidation peak at +0.75 V (Figure 8). From the electrolysis a value of $n_{app} > 10$ was calculated, where n_{app} represents the number of faradays per mole.

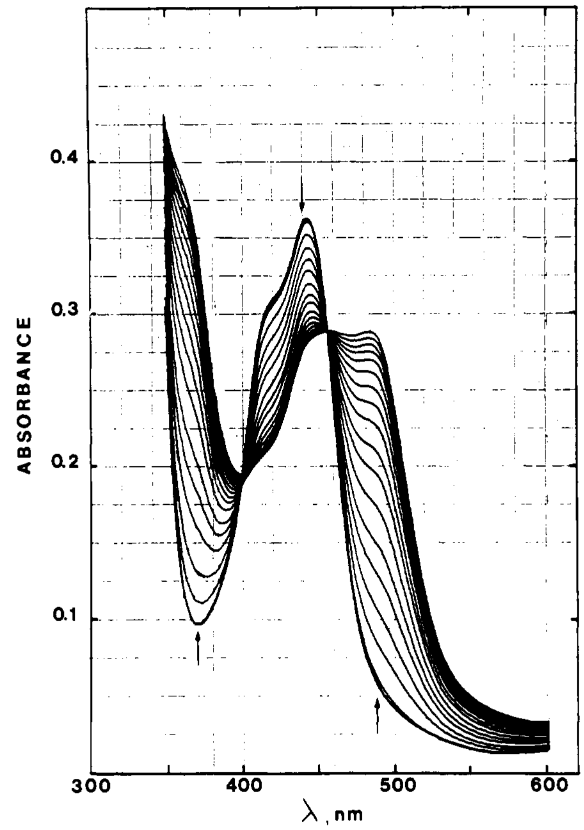

Figure 9. Spectral changes observed during the electrolysis ($E = -0.85$ V vs. AgRE) at a gold minigrid electrode of 0.12 mM $Ru(bpz)_3^{2+}$ in Ar-purged aqueous solution containing 0.1 M Na_2SO_4 at pH 11.4. Optical path length = 2 mm. The initial spectrum and the direction of the spectral changes are indicated by the arrows.

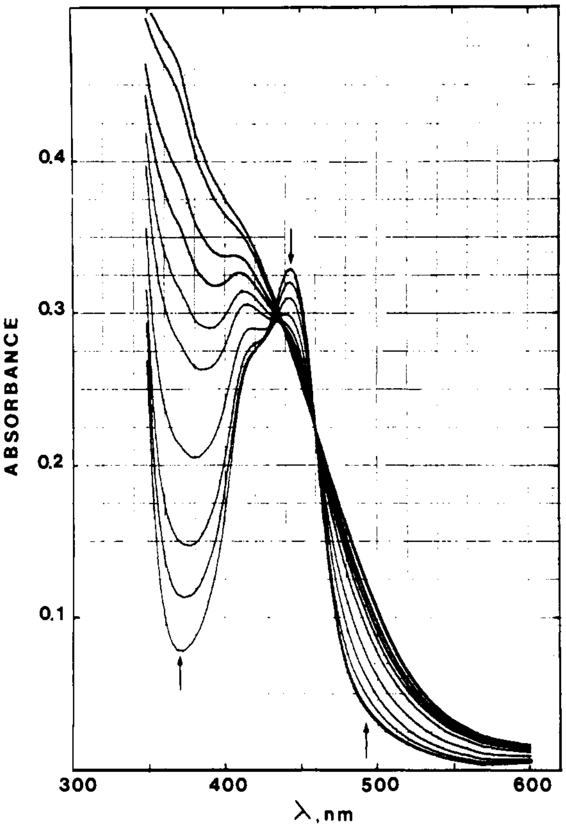

Figure 10. Spectral changes observed during the electrolysis ($E = -0.75$ V vs. AgRE) at a gold minigrid electrode of 0.12 mM $Ru(bpz)_3^{2+}$ in Ar-purged aqueous solution containing 0.1 M Na_2SO_4 at pH 3.5. Optical path length = 2 mm. The initial spectrum and the direction of the spectral changes are indicated by the arrows.

The controlled-potential electrolysis at −0.85 V vs. AgRE on the gold minigrid electrode of an Ar-purged solution containing 0.12 mM $Ru(bpz)_3^{2+}$ and 0.1 M Na_2SO_4 at pH 11.4 produced the spectral changes shown in Figure 9. As the electrolysis proceeded, the absorption band of $Ru(bpz)_3^{2+}$ at 440 nm decreased and new bands at ~360 and ~480 nm were formed. Well-defined isosbestic points were observed at 400 and 455 nm. The original spectrum of $Ru(bpz)_3^{2+}$ was obtained when the reduced solution was electrolyzed at −0.2 V vs. AgRE. The spectral changes observed upon electrolysis at −0.65 V vs. AgRE of the same solution at pH 3.4 are shown in Figure 10. Except for a decrease of the absorption in the 440-nm region, the electrolysis caused the absorption of the solution to increase over the spectral range investigated (350–600 nm). An isosbestic point was observed at 460 nm. The electrochemical oxidation of the reduced solution produced a spectrum similar to that observed prior to the electrolysis.

Discussion

The pulse and continuous radiolysis results show that the reactions between reducing radicals (e_{aq}^-, $CO_2^{\bullet-}$, and $(CH_3)_2\dot{C}OH$) and $Ru(bpz)_3^{2+}$ are electron transfer in nature, generating initially and quantitatively $Ru(bpz)_3^+$; no evidence is obtained for the formation of adducts upon the reaction of $CO_2^{\bullet-}$ and $(CH_3)_2\dot{C}OH$, in contrast with other metal complexes containing bpy and phen (1,10-phenanthroline) and their derivatives.[28,29]

The variations of the spectrum of $Ru(bpz)_3^+$ with the pH of the medium (Figures 1 and 2) indicate clearly that the reduced species is involved in an acid–base equilibrium (reaction 13) with

$$Ru(bpz)_2(bpz^{\bullet-})^+ + H^+ \rightarrow Ru(bpz)_2(bpzH^{\bullet})^{2+} \quad (13)$$

the acidic form showing $pK_a = 7.1 \pm 0.3$. By analogy with $Ru(bpy)_3^+$,[30] the product of the one-electron reduction of $Ru(bpy)_3^{2+}$, $Ru(bpz)_3^+$, is viewed[5,6,8] as a Ru(II) species containing a coordinated $bpz^{\bullet-}$ radical. The acidic form of the reduced species can be viewed as a Ru(II) species containing a coordinated $bpzH^{\bullet}$ radical. It should be noted that the pK_a of $Ru(bpz)_2(bpzH)^{3+}$, the protonated form of the complex, is −2.2;[7] the pK_a for $^*Ru(bpz)_2(bpzH)^{3+}$, the protonated form of the excited state of $Ru(bpz)_3^{2+}$, is 2.0 (3.8 calculated).[7] Inasmuch as the latter species can be represented as a Ru(III) species containing a $bpz^{\bullet-}$ radical, $Ru(bpz)_3^+$ is the analogue of $^*Ru(bpz)_3^{2+}$ insofar as the ligands are concerned. The difference in the pK_a values of their corresponding protonated forms reflects mainly the total charge on the species.

The spectrum we have obtained for $Ru(bpz)_3^+$ in alkaline solution (Figure 3) is similar to that obtained by Crutchley and Lever[3] by the photoinduced reduction of $Ru(bpz)_3^{2+}$ in ethanol. By analogy to the spectrum of $Ru(bpy)_3^+$,[31] the visible absorption band of $Ru(bpz)_3^+$ is probably a composite of contributions from $bpz^{\bullet-}$ and charge-transfer features.

In contrast to $Ru(bpy)_3^+$, which was unstable in aqueous solutions even at pH 13,[32] $Ru(bpz)_3^+$ is stable in the absence of air in aqueous alkaline (pH ≥10) solution. The instability of $Ru(bpz)_3^+$ in the presence of oxygen has been attributed to the occurrence of reaction 14, for which $k_{14} = 5.8 \times 10^8\ M^{-1}\ s^{-1}$.[16]

$$Ru(bpz)_3^+ + O_2 \rightarrow Ru(bpz)_3^{2+} + O_2^{\bullet-} \quad (14)$$

Reaction 14 is probably followed by the pH-dependent disproportionation of $O_2^{\bullet-}$, which leads to the formation of oxygen and hydrogen peroxide.[33] We note, however, that the oxidation of

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$Ru(bpz)_3^+$ by O_2 does not produce $Ru(bpz)_3^{2+}$ quantitatively (Figure 5), possibly due to reactions initated by the addition of $O_2^{\bullet -}$ to $Ru(bpz)_3^+$, similar to those occurring when $MV^{\bullet +}$ reacts with $O_2^{\bullet -}$ in DMF.[34]

The linear relationship describing equilibrium reaction 12 between $Ru(bpz)_3^+$ and MV^{2+} yields an intercept and a slope representing $k_r[Ru(bpz)_3^{2+}]$ and k_f, respectively. From the knowledge of k_r (1.7×10^7 M^{-1} s^{-1}) and k_f (1.3×10^8 M^{-1} s^{-1}), the value of K_{12} (7.6) can be calculated. The value of k_f obtained here compares well with the value obtained previously ($k = 4.5 \times 10^8$ M^{-1} s^{-1})[16] in the presence of 0.1 M EDTA at pH 8.7 and 11.0, when the large difference in ionic strength is taken into account.

K_{12} can also be derived from the knowledge of the concentrations of the species in the system at equilibrium which can be obtained from the absorbance at 600 nm (Figure 4, inset) and from the knowledge of ϵ_{600} for $MV^{\bullet +}$ and $Ru(bpz)_3^+$ and the radiation dose. The amount of $MV^{\bullet +}$ that was formed directly via reaction 15, which competes with reaction 11, was calculated

$$MV^{2+} + (CH_3)_2\dot{C}OH \rightarrow MV^{\bullet +} + (CH_3)_2CO + H^+ \qquad (15)$$

on the basis of $k_{11} = 3.5 \times 10^9$ M^{-1} s^{-1} and $k_{15} = 2.9 \times 10^9$ M^{-1} s^{-1}.[35] Finally a correction was introduced, taking into account the reaction between $MV^{\bullet +}$ and the β-radical.[19] The application of these calculations to each experiment shown in Figure 4 yielded $K_{12} = 7.1 \pm 0.5$, in very good agreement with the value obtained from the kinetic data. From the knowledge of K_{12} and $E°(MV^{2+/+})$ (−0.44 V),[36] a value of $E°(Ru(bpz)_3^{2+/+}) = -0.50$ V is calculated for alkaline aqueous solution.

The electrochemical data obtained by using aqueous alkaline solutions of $Ru(bpz)_3^{2+}$ are entirely consistent with the results obtained radiolytically under equivalent conditions. There is no question that the products obtained by the electrochemically or radiolytically induced reduction of $Ru(bpz)_3^{2+}$ in alkaline solutions are the same (compare Figures 5 and 9). The electrochemical measurements confirm the reversibility of the system and the value of the redox potential for the $Ru(bpz)_3^{2+/+}$ couple derived from the pulse radiolysis observations. The electrochemistry of $Ru(bpz)_3^{2+}$ in CH_3CN has been previously investigated;[3,5,6,8] while there is agreement concerning the number of reversible one-electron transfers, the reported values of $E_{1/2}$ for the $Ru(bpz)_3^{2+/+}$ couple range between −0.68 and −0.86 V vs. SCE.

In acidic solution, $Ru(bpz)_2(bpzH^\bullet)^{2+}$ does not reduce MV^{2+} because the protonation of the coordinated $bpz^{\bullet -}$ radical causes the redox potential of the $Ru(bpz)_3^{2+} + H^+/Ru(bpz)_2(bpzH^\bullet)^{2+}$ couple to be less negative than that of the $MV^{2+/+}$ couple; E_{pc} is seen to shift by about 170 mV toward less negative potentials when the pH of the solution is changed from pH 11.4 to 3.5. The inability of $Ru(bpz)_2(bpzH^\bullet)^{2+}$ to reduce MV^{2+} to $MV^{\bullet +}$ and the fact that the pK_a of the species is 7.1 are among the factors accounting for the decrease of $\Phi(MV^{\bullet +})$ with decreasing pH observed in the photolysis of the $Ru(bpz)_3^{2+}/MV^{2+}/EDTA$ system.[15]

Whereas $Ru(bpz)_2(bpz^{\bullet -})^+$ is the stable product of the reduction of $Ru(bpz)_3^{2+}$ in alkaline solution, $Ru(bpz)_2(bpzH^\bullet)^{2+}$ is unstable, converting slowly ($t_{1/2} \sim 20$ s) into a species that absorbs considerably less than $Ru(bpz)_2(bpz^{\bullet -})^+$ in the 490-nm region. The controlled-potential electrolysis and the continuous radiolysis of acidic solutions of $Ru(bpz)_3^{2+}$ produce the very same spectral changes (compare Figures 6 and 10). Furthermore, the acidification of $Ru(bpz)_2(bpz^{\bullet -})^+$ generates rapidly (within the time of mixing) the same spectrum as is obtained upon the reduction in acidic solution. However, when the reduced system (in acidic solution) is make alkaline, the spectrum of $Ru(bpz)_2(bpz^{\bullet -})^+$ is regenerated very slowly. These facts, together with the absence of a reversal oxidation peak in the cyclic voltammogram of $Ru(bpz)_3^{2+}$ in acidic solution, rule out the long-term existence of $Ru(bpz)_2(bpzH^\bullet)^{2+}$ in acidic solution. We suggest that $Ru(bpz)_2(bpzH^\bullet)^{2+}$ undergoes disproportionation reaction 16 leading

$$2\ Ru(bpz)_2(bpzH^\bullet)^{2+} \rightarrow Ru(bpz)_2(bpzH_2)^{2+} + Ru(bpz)_3^{2+} \qquad (16)$$

to the doubly reduced species $Ru(bpz)_2(bpzH_2)^{2+}$ and the starting compound. In order for reaction 16 to occur, the redox potential of the $(Ru(bpz)_2(bpzH^\bullet)^{2+} + H^+)/Ru(bpz)_2(bpzH_2)^{2+}$ couple must be more positive than that of the $(Ru(bpz)_3^{2+} + H^+)/Ru(bpz)_2(bpzH^\bullet)^{2+}$ couple (at the same pH). Under these conditions the electrochemical reduction of $Ru(bpz)_3^{2+}$ in acidic solution could give directly $Ru(bpz)_2(bpzH_2)^{2+}$. The high n_{app} number (>10) and the trend of the absorption in the 370-nm region (Figure 10) suggest that further reduction of $Ru(bpz)_2(bpzH_2)^{2+}$ to, presumably, $Ru(bpz)(bpzH_2)_2^{2+}$, $Ru(bpzH_2)_3^{2+}$, $Ru(bpzH_2)_2(bpzH_4)^{2+}$, etc. takes place. Surprisingly enough, the electrochemically induced conversion of these species back to $Ru(bpz)_3^{2+}$ is a rather efficient process. The OH^--induced conversion of $Ru(bpz)_2(bpzH_2)^{2+}$ to $Ru(bpz)_2(bpz^{\bullet -})^+$ may occur via a comproportionation reaction between $Ru(bpz)_3^{2+}$ and the product of the slow OH^- attack on the doubly reduced, doubly protonated species.

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Registry No. MV^{2+}, 4685-14-7; $Ru(bpz)_3^{2+}$, 75523-96-5; $Ru(bpz)_2(bpz^{\bullet -})^+$, 75523-97-6; CO_2^-, 14485-07-5; $(CH_3)_2\dot{C}OH$, 5131-95-3; $(CH_3)_2CHOH$, 67-63-0; HCO_2^-, 71-47-6.

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