J. Phys. Chem. A **1998,** *102,* 5749−5753

ARTICLES

Reduction of Ru(bpy)$_2$(AB)$^{2+}$ (bpy = 2,2′-bipyridine, AB = 2,2′:3′,2″:6″,2‴-quaterpyridine) in Aqueous Solution. A Pulse Radiolysis Study

Fiorella Casalboni,[1a] Quinto G. Mulazzani,*,[1a] Rosemary L. Cleary,[1b] and Michael D. Ward[1b]

Istituto di Fotochimica e Radiazioni d'Alta Energia del CNR, Via P. Gobetti 101, 40129 Bologna, Italy, and School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Received: February 19, 1998; In Final Form: May 1, 1998

The one-electron reduction of Ru(bpy)$_2$(AB)$^{2+}$, hereafter RuAB^{2+}, where bpy = 2,2′-bipyridine and AB = 2,2′:3′,2″:6″,2‴-quaterpyridine, in aqueous solution has been studied using pulse radiolysis. RuAB^{2+} is reduced by e_{aq}^- ($k = 6.2 \times 10^{10}$ M^{-1} s^{-1} at ambient ionic strength (I) and $k = 4.6 \times 10^{10}$ M^{-1} s^{-1} at $I = 0.1$ M) and by $CO_2^{\bullet -}$ radical ($k = 1 \times 10^8$ M^{-1} s^{-1} at $I = 0.1$ M), generating RuAB$^{\bullet +}$. The spectra of RuAB$^{\bullet +}$ and its conjugated acid (RuABH$^{\bullet 2+}$) were obtained; the pK_a of RuABH$^{\bullet 2+}$ (8.0) has been determined. The rate constants for the protonation of RuAB$^{\bullet +}$ ($k_H = 7.9 \times 10^9$ M^{-1} s^{-1}) and the deprotonation of RuABH$^{\bullet 2+}$ ($k_{-H} = 79$ s^{-1}) have been evaluated as have the rate constants for proton exchange ($k_f = 3.4 \times 10^7$ M^{-1} s^{-1} and $k_r = 5.5 \times 10^6$ M^{-1} s^{-1}) between the RuAB$^{\bullet +}$/RuABH$^{\bullet 2+}$ and $H_2PO_4^-$/HPO_4^{2-} couples. The results from this work are compared with those obtained previously for 13 Ru(II) complexes that contain bpy, bpm (2,2′-bipyrimidine), bpz (2,2′-bipyrazine), and pypm (2-(2′-pyridyl)pyrimidine) ligands. In addition, since RuAB^{2+} can be viewed as a substituted Ru(bpy)$_3^{2+}$ complex that contains a bpy residue, a comparison is also made of the reductions of RuAB^{2+} and bpy.

Introduction

The reduced forms (RuL$^{\bullet +}$) of 13 Ru(II)−diimine complexes (RuL^{2+}) that contain the symmetric 2,2′-bipyridine (bpy), 2,2′-bipyrimidine (bpm), and 2,2′-bipyrazine (bpz) ligands and the asymmetric 2-(2′-pyridyl)pyrimidine (pypm) ligand in aqueous solution have been recently characterized;[2] the complexes are of the form Ru(bpy)$_y$(bpm)$_m$(bpz)$_z^{2+}$ and Ru(bpy)$_{3-p}$(pypm)$_p^{2+}$, where $y + m + z = 3$, y, m, and $z = 0, 1, 2, 3$, and $p = 1, 2, 3$. It was found that the species RuL$^{\bullet +}$ can undergo protonation to give RuLH$^{\bullet 2+}$; of course, Ru(bpy)$_3^{\bullet +}$, because it lacks nitrogen atoms on the periphery of the ligands, cannot be involved in acid−base equilibria.

The recently synthesized and characterized Ru(bpy)$_2$(AB)$^{2+}$ complex,[3−5] hereafter called RuAB^{2+}, is schematically represented in Figure 1; it is a derivative of Ru(bpy)$_3^{2+}$ in which the 3′-H atom of one bpy ligand is replaced by a bpy residue. The resulting species possesses an unaltered Ru(bpy)$_3^{2+}$ structure and, due to the presence of the bpy residue, contains two protonable nitrogen atoms. Indeed, in the ground state, RuAB^{2+} undergoes protonation giving RuABH^{3+} for which a pK_a value of 1.9 has been reported in 1:1 acetonitrile−water in the presence of ~1 M KNO$_3$.[5]

As an extension of our previous work on Ru(II)−diimine complexes,[2,6] we have examined in detail the one-electron reduction of RuAB^{2+} in aqueous solution, using the pulse radiolysis technique.

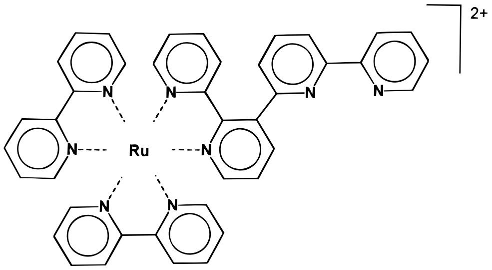

Figure 1. Schematic representation of the complex Ru(bpy)$_2$(AB)$^{2+}$ (= RuAB^{2+}).

Experimental Section

Materials. Ru(bpy)$_2$(AB)$^{2+}$, as its PF_6^- salt, was prepared as has been reported.[3,4] The absorption spectrum of this compound in water (λ_{max} 454 nm, ϵ_{max} 1.35×10^4 M^{-1} cm^{-1}) was found to be independent of pH in the range utilized in this work (4−13) and did not show any appreciable change within the time required to perform the experiments. Solutions were freshly prepared using Millipore (Milli-Q) water and were purged with Ar, saturated with N_2O, or degassed by standard vacuum line techniques. The pH of the solutions was adjusted with $HClO_4$, NaOH (Merck, Suprapur), or phosphate buffers. Sodium formate (Merck) and *tert*-butyl alcohol (Fluka) were used as received.

Pulse Radiolysis. Pulse radiolysis with optical absorption detection was performed using the 12 MeV linear accelerator at the FRAE-CNR Institute, Bologna.[7] The pulse experiments were performed at ambient temperature (22 ± 2 °C) on samples contained in Spectrosil cells of 1 or 2 cm optical path length.

---

* To whom correspondence should be addressed. Phone +39-051-6399822; Fax +39-051-6399844; E-mail qgm@bofra3.frae.bo.cnr.it.

S1089-5639(98)01220-1 CCC: $15.00

The solutions were protected from the analyzing light by means of a shutter and appropriate cutoff filters. The radiation dose per pulse was monitored by means of a charge collector placed behind the irradiation cell and calibrated with a N_2O-saturated solution containing 0.1 M HCO_2^- and 0.5 mM methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dication) by taking $G\epsilon = 9.32 \times 10^4$ at 602 nm.[8] Pulses of 20−100 ns duration were generally used which delivered doses of approximately 10−30 Gy per pulse; under the conditions utilized, 3−10 μM transient species were generally produced.

Generation of Reducing Radicals. The radiolysis of aqueous solutions produces e_{aq}^-, $^{\bullet}OH$, and $H^{\bullet}$ with G values (G = number of species formed per 100 eV of energy absorbed by the solution) of 2.6, 2.7, and 0.6, respectively.[9] Reducing conditions can be obtained in degassed or Ar-purged solutions by the scavenging of the hydroxyl radical with *tert*-butyl alcohol ($k_a = 6.0 \times 10^8$ M^{-1} s^{-1})[9] or HCO_2^- ($k_b = 3.2 \times 10^9$ M^{-1} s^{-1}).[9]

$$^{\bullet}OH + (CH_3)_3COH \rightarrow {}^{\bullet}CH_2C(CH_3)_2OH\ (95.7\%) + (CH_3)_3CO^{\bullet}\ (4.3\%) + H_2O \quad \text{(a)}$$

$$^{\bullet}OH + HCO_2^- \rightarrow CO_2^{\bullet -} + H_2O \quad \text{(b)}$$

Under acidic conditions, e_{aq}^- is scavenged by H^+ to yield $H^{\bullet}$ ($k_c = 2.3 \times 10^{10}$ M^{-1} s^{-1})[9] whereas the conversion of $H^{\bullet}$ into e_{aq}^- takes place in alkaline solution ($k_d = 2.2 \times 10^7$ M^{-1} s^{-1}).[9] In the current work, the dosimetry and a limited number of experiments were performed in N_2O-saturated solution ($[N_2O]$ = 25 mM); N_2O converts e_{aq}^- into $^{\bullet}OH$ radicals ($k_e = 9.1 \times 10^9$ M^{-1} s^{-1}).[9]

$$e_{aq}^- + H^+ \rightarrow H^{\bullet} \quad \text{(c)}$$

$$H^{\bullet} + OH^- \rightarrow H_2O + e_{aq}^- \quad \text{(d)}$$

$$e_{aq}^- + N_2O\ (+H_2O) \rightarrow N_2 + {}^{\bullet}OH + OH^- \quad \text{(e)}$$

Both e_{aq}^- and $CO_2^{\bullet -}$ are strong reducing agents ($E° = -2.87$ and -1.90 V, respectively);[10,11] $H^{\bullet}$ is also a strong reducing agent ($E° = -2.30$ V)[9] but also adds to coordinated bpy and bpz moieties.[12] On the other hand, $^{\bullet}CH_2C(CH_3)_2OH$ is a weak reducing agent ($E° = -0.1$ V).[13] The e_{aq}^-, $H^{\bullet}$, $CO_2^{\bullet -}$, and $^{\bullet}CH_2C(CH_3)_2OH$ species all decay via bimolecular processes with values of $2k = 1.1 \times 10^{10,9}$, $1.55 \times 10^{10,9}$, 1.3×10^9 (I = 0.1 M),[8] and 1.4×10^9 M^{-1} s^{-1},[14] respectively; their reactivities toward a variety of substrates is well documented.[15]

Results

The pulse irradiation of Ar-purged solutions containing *tert*-BuOH or formate resulted in the formation of the well-known spectrum of e_{aq}^- (λ_{max} 720 nm, ϵ_{max} 1.9×10^4 M^{-1} cm^{-1}),[9] which disappeared in several microseconds. In the presence of $RuAB^{2+}$ (15−80 μM), the decay of e_{aq}^- was more rapid and followed first-order kinetics with k_{obsd} increasing linearly with $[RuAB^{2+}]$. From the plot of k_{obsd} vs $[RuAB^{2+}]$ (see Supplementary Information), the bimolecular rate constant for reaction 1 was calculated to be $k_1 = 6.2 \times 10^{10}$ M^{-1} s^{-1} at ambient pH and I in the presence of 0.5 M *tert*-BuOH and 4.6×10^{10} M^{-1} s^{-1} at ambient pH and I = 0.1 M in the presence of 0.1 M HCO_2^-.

$$RuAB^{2+} + e_{aq}^- \rightarrow RuAB^{\bullet +} \quad (1)$$

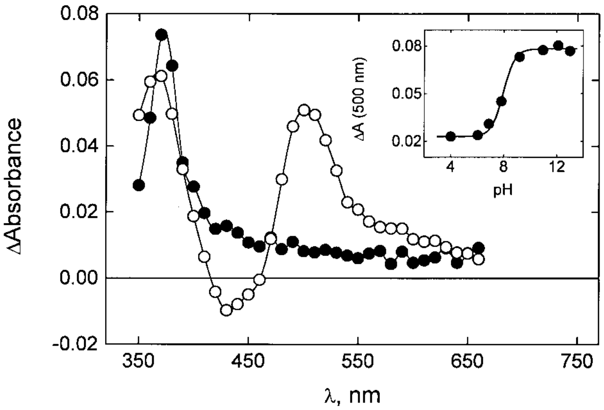

Figure 2. Observed spectra from the pulse radiolysis of Ar-purged solutions containing 50 μM $RuAB^{2+}$ and 0.1 M HCO_2^- at pH 12 (○) and pH 5.2 (●); dose per pulse = 9.7 Gy, optical path = 2 cm. Inset: effect of pH on ΔOD at 500 nm for solutions containing 0.1 mM $RuAB^{2+}$ and 0.5 M *tert*-BuOH; optical path = 1 cm, dose per pulse = 26 Gy.

After the spectrum of e_{aq}^- had completely disappeared, the residual absorption in the 350−650 nm region had a shape and size that depended on pH (Figure 2). From the changes in absorbance at 500 nm, which is the wavelength of the maximum difference between the two spectra shown in Figure 2, as a function of pH, the inset to Figure 2 was obtained; an analysis of this curve, which incorporated the appropriate corrections for the differences in G values in acidic and highly alkaline solution, gave an inflection point at pH = 8.0 ± 0.1.

In the presence of *tert*-BuOH, the spectrum originating from reaction 1 decayed via a process which was close to second order; the decay rate was relatively constant at pH ≥ 11 although at pH 9.2 it was about 10 times faster than that in more alkaline solution.

In the presence of HCO_2^- as a scavenger for $^{\bullet}OH$ radicals, the formation of the spectrum from reaction 1 was followed by a slower process which produced an increase of the absorbance. Saturation of the solution with N_2O so that $CO_2^{\bullet -}$ was the only species present in the system caused the disappearance of the fast formation of the transient absorption but did not affect the slower process. From the analysis of the formation of the transient spectrum as a function of $[RuAB^{2+}]$ under these conditions, the rate constant of reaction 2 (k_2) was determined to be 1×10^8 M^{-1} s^{-1}.

$$RuAB^{2+} + CO_2^{\bullet -} \rightarrow RuAB^{\bullet +} + CO_2 \quad (2)$$

When $RuAB^{2+}$ was reduced by e_{aq}^- at pH < 6, the spectrum initially observed was the same as that observed in alkaline solution; however, it evolved into that observed in acidic solution via a process that depended on $[H^+]$. From the data shown in Figure 3, the rate constant for the protonation of $RuAB^{\bullet +}$ in reaction 3 (k_H) was obtained (7.9×10^9 M^{-1} s^{-1}).

$$RuAB^{\bullet +} + H^+ \rightleftharpoons RuABH^{\bullet 2+} \quad (3)$$

The effect of the presence of phosphate ions (1.0−9.0 mM) on the decay of $RuAB^{\bullet +}$ was also investigated. It was found that the value of k_{obsd} for the conversion of $RuAB^{\bullet +}$ into $RuABH^{\bullet 2+}$ increased linearly with $[H_2PO_4^-]$, resulting in a value of $k_4 = 3.4 \times 10^7$ M^{-1} s^{-1}.

$$RuAB^{\bullet +} + H_2PO_4^- \rightleftharpoons RuABH^{\bullet 2+} + HPO_4^{2-} \quad (4)$$

Discussion

The reduction of $RuAB^{2+}$ by e_{aq}^- and by $CO_2^{\bullet -}$ radicals generates $RuAB^{\bullet +}$, which can be viewed as an $AB^{\bullet -}$ radical

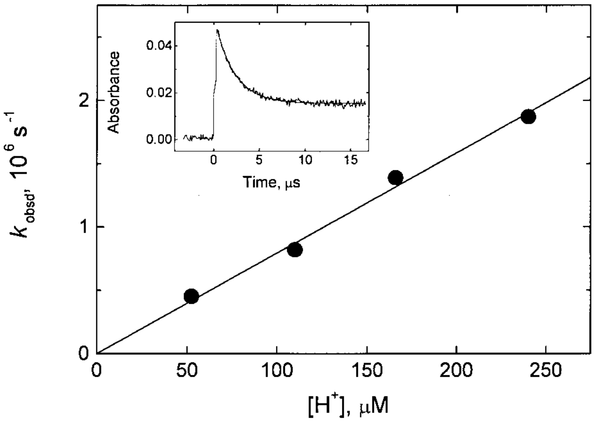

Figure 3. Effect of $[H^+]$ on the rate constant for protonation of $RuAB^{\bullet+}$ in degassed solutions containing 106 μM $RuAB^{2+}$, 0.5 M *tert*-BuOH, and varied $[HClO_4]$; λ_{mon} = 500 nm, optical path = 1 cm, dose per pulse = 21.5 Gy. Inset: decay observed in the presence of 52.5 μM $HClO_4$. The solid line represents a first-order fit to the data.

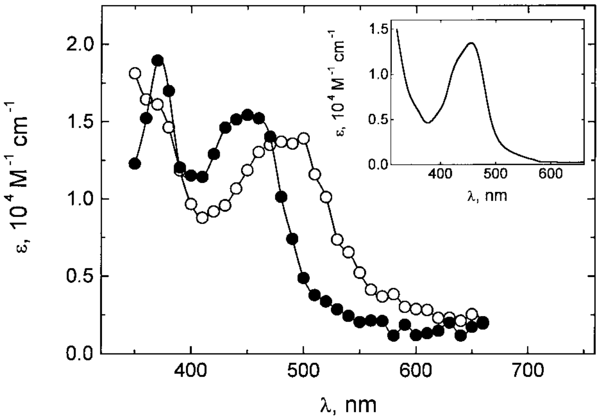

Figure 4. Absorption spectra of $RuAB^{\bullet+}$ (○) and $RuABH^{\bullet 2+}$ (●) obtained by correcting the spectra shown in Figure 2, assuming G = 2.6. Inset: spectrum of $RuAB^{2+}$.

coordinated to the Ru(II)$(bpy)_2$ moiety. The rate constants for the reduction of $RuAB^{2+}$ by e_{aq}^- are comparable to the rate constants reported for the reaction of $Ru(bpy)_3^{2+}$ with e_{aq}^- (k = 8.2 × 10^{10} and 5.6 × 10^{10} M^{-1} s^{-1} at low ionic strength and k = 3.1 × 10^{10} M^{-1} s^{-1} at I = 0.1 M);[15] k for the reduction of bpy by e_{aq}^- was reported to be (1.9−2.5) × 10^{10} M^{-1} s^{-1}.[15] The rate constant for the reduction of $RuAB^{2+}$ by $CO_2^{\bullet-}$ radical will be discussed below.

The observed spectrum of $RuAB^{\bullet+}$ (Figure 2), which shows two apparent bands at ca. 370 and 500 nm and a minimum at ca. 430 nm, is very similar to the observed spectrum of $Ru(bpy)_3^{\bullet+}$.[16] The pH dependence of the spectrum, which is not observed in the case of $Ru(bpy)_3^{\bullet+}$, is similar to that observed for the reduced complexes that contain at least one bpz, bpm, or pypm ligand. This effect is caused by the protonation of a heterocyclic N atom in the coordinated $AB^{\bullet-}$ radical to form $RuABH^{\bullet 2+}$ via reaction 3; the pK_a value of 8.0 ± 0.1 derived from the inset to Figure 2 is that of $RuABH^{\bullet 2+}$. The pK_a values of the 12 complexes previously investigated range between 6.3 and 9.2.[2] From the observed spectra and a knowledge of the radiation dose and the spectrum of the parent compound, the corrected spectra of $RuAB^{\bullet+}$ and $RuABH^{\bullet 2+}$, which are shown in Figure 4, were calculated assuming $G(-RuAB^{2+}) = G(e_{aq}^-)$ = 2.6. The spectra show an absorption band with λ_{max} 500 nm (ϵ_{max} 13 900 M^{-1} cm^{-1}) and a shoulder at 370 nm (ϵ 16 100 M^{-1} cm^{-1}) for $RuAB^{\bullet+}$ and λ_{max} 370 nm (ϵ_{max} 19 000 M^{-1} cm^{-1}) and 450 nm (ϵ_{max} 15 400 M^{-1} cm^{-1}) for $RuABH^{\bullet 2+}$. By analogy with the attribution made for the $RuL^{\bullet+}$ species previously investigated, the spectra of $RuAB^{\bullet+}$ and $RuABH^{\bullet 2+}$ are assigned as overlapping ligand-localized transitions within the reduced ligand and MLCT transitions between the metal center and the nonreduced ligands.[2,6b]

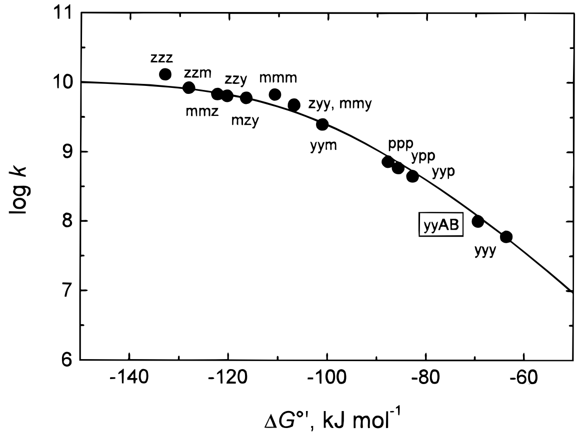

Figure 5. Plot of log k *vs* $\Delta G^{\circ\prime}$ for the reaction of $CO_2^{\bullet-}$ radical with 14 Ru(II) complexes containing bpy, bpm, bpz, pypm, and AB ligands. The solid line represents the best fit to the data. Abbreviations: y = bpy, m = bpm, z = bpz, p = pypm.

Rate Constant for the Reduction of $RuAB^{2+}$ by $CO_2^{\bullet-}$. The rate constant for the reduction of $RuAB^{2+}$ by $CO_2^{\bullet-}$ (k_2 = 1 × 10^8 M^{-1} s^{-1}) can be incorporated into the values obtained for the reduction by $CO_2^{\bullet-}$ of the 13 RuL^{2+} complexes previously investigated which have been discussed in terms of the driving force of the reaction.[2,6b,6c] Unfortunately, $E^\circ(RuAB^{2+/+})$ in water is not known although it has been reported[4] that in acetonitrile $RuAB^{2+}$ is reduced at a potential 60 mV less negative than is $Ru(bpy)_3^{2+}$. On the assumption that this difference is unaffected by the nature of the solvent and from the knowledge of E° = −1.22 V for the $Ru(bpy)_3^{2+/+}$ couple in water,[6b,c] a value of $E^\circ(RuAB^{2+/+})$ = −1.16 V in water can be derived. By using this value and $E^\circ(CO_2/CO_2^{\bullet-})$ = −1.9 V,[11] the value of $\Delta G^{\circ\prime}$ associated with reaction 2 can be calculated by means of eq 5, where w_p and w_r are the electrostatic work terms. In this case, w_p = 0 because one of the products is uncharged, whereas w_r is

$$\Delta G^{\circ\prime} = E^\circ(CO_2/CO_2^{\bullet-}) - E^\circ(RuAB^{2+/+}) + w_p - w_r \quad (5)$$

approximately −2.1 kJ mol^{-1}. As is shown in Figure 5, the value of k_2 fits very satisfactorily on the plot of log k vs $\Delta G^{\circ\prime}$ previously obtained for the other 13 complexes;[2,6b,c] the quality of the fit on the curve indicates that the intrinsic barrier ($\Delta G^{\ddagger}$(0)) of reaction 2 must be the same as that obtained for the other complexes (57 kJ mol^{-1}). This high value is a consequence of the unfavorable intrinsic kinetic parameters of the $CO_2^{\bullet-}$ radical ($\Delta G^{\ddagger}(0)$ = 97.0 kJ mol^{-1} and k_{se} = 1.4 × 10^{-3} M^{-1} s^{-1}, where k_{se} represents the self-exchange rate constant for the $CO_2/CO_2^{\bullet-}$ couple).[6c]

By using $E^\circ(RuAB^{2+/+})$ = −1.16 V and the procedure employed before,[2,6a] the value of $E^\circ_3(RuAB^{2+},H^+/RuABH^{\bullet 2+})$ = −0.86 V at pH 3 was calculated; this value is to be compared with the values determined for the other $RuLH^{\bullet 2+}$ species which range between −0.26 and −0.71 V.[2,6b] Thus, among the protonated one-electron reduced species examined, $RuABH^{\bullet 2+}$ is the strongest reducing agent.

Rate Constants for Protonation, Deprotonation, and Proton Exchange. The rate constant for the protonation of $RuAB^{\bullet+}$ (k_H = 7.9 × 10^9 M^{-1} s^{-1}) is ca. 40% smaller than that determined for the protonation of the $RuL^{\bullet+}$ species previously examined ($k_H = 1.3 \times 10^{10}$ M^{-1} s^{-1}).[2] This difference, although not dramatically large, is, however, outside the range of the experimental error and may indicate that the electron density on the basic nitrogen atoms in the coordinated $AB^{\bullet-}$ radical is lower than that on the coordinated $bpz^{\bullet-}$, $bpm^{\bullet-}$, and $pypm^{\bullet-}$ radicals in the $RuL^{\bullet+}$ complexes.

From the knowledge of the pK_a of $RuABH^{\bullet 2+}$, and hence the equilibrium constant for reaction 3, $k_{-H} = 79$ s^{-1} was calculated for the deprotonation of $RuABH^{\bullet 2+}$. This value is to be compared with values of 8.2−6500 s^{-1} for the RuL^{2+} complexes examined previously.[2] A plot of log k_{-H} for $RuLH^{\bullet 2+}$ and $RuABH^{\bullet 2+}$ as a function of $E°(Ru^{2+/+})$ is given in the Supporting Information. It should be noted here that the acidity of the protonated reduced species is controlled essentially by the value of k_{-H} inasmuch as k_H, with the exception of that of $RuAB^{\bullet+}$ as discussed above, has a constant value, indicating that the reaction is diffusion controlled.

From the knowledge of the pK_a values of $RuABH^{\bullet 2+}$ (8.0) and $H_2PO_4^-$ (7.21),[17] the equilibrium constant for reaction 4 could be calculated (6.2). From K_4 and k_4, $k_{-4} = 5.5 \times 10^6$ M^{-1} s^{-1} was calculated.

Decay of $RuAB^{\bullet+}$/$RuABH^{\bullet 2+}$. The approximate second-order decay of $RuAB^{\bullet+}$/$RuABH^{\bullet 2+}$ likely represents the disproportionation of these species. It was shown previously[2] that the decay of the three complexes containing bpy and pypm ligands occurs via pH-dependent second-order kinetics. In the case of $RuAB^{\bullet+}$/$RuABH^{\bullet 2+}$, however, the possibility cannot be ruled out that in the presence of *tert*-BuOH the decay of $RuAB^{\bullet+}$/$RuABH^{\bullet 2+}$ also contains a contribution from a reaction between the reduced species and the $^\bullet CH_2C(CH_3)_2OH$ radical similar to that which was shown to take place between that radical and $Ru(bpy)_3^{\bullet+}$.[16]

Protonation of the Excited State. The relationship pK_a − pK_a* = 4.8, where pK_a and pK_a* are derived from the acid equilibrium constants of the protonated one-electron reduced form $RuLH^{\bullet 2+}$ and the protonated excited-state $RuLH^{3+}$*, respectively, has been shown to be applicable for complexes that contain bpy, bpz, bpm, and pypm ligands with at least one protonable nitrogen atom.[2,6a,18,19] For these species, pK_a* values ranging between 1.5 and 4.4 were evaluated.[2] Applying this relationship to $RuAB^{2+}$ leads to a value of the pK_a* of $RuABH^{3+}$* in aqueous solution (3.2). This calculated value of pK_a* is to be compared with the value (2.28) measured in 1:1 acetonitrile−water in the presence of ∼ 1 M KNO_3.[5] Considering the large difference in media conditions, the calculated and the measured values appear to be in acceptable agreement.

Comparison between $RuABH^{\bullet 2+}$ and $bpyH^\bullet$. The protonated reduced species ($RuABH^{\bullet 2+}$) can be viewed as being composed of $Ru(bpy)_3^{2+}$ and $bpyH^\bullet$ residues. The reduction of free bpy in aqueous solution generates $bpyH^\bullet$ for which pK_a values of >14[21] and ∼ 24[22] have been estimated; $bpyH^\bullet$ undergoes further protonation to give $bpyH_2^{\bullet+}$ for which pK_a = 8.0 was determined.[22] The rate constant for the protonation of $bpy^{\bullet-}$ by H_3O^+ is believed to be on the order of 10^{11} M^{-1} s^{-1}; there is little chance to observe the species $bpy^{\bullet-}$ in acidic aqueous solution. The rate constant for proton transfer from water to $bpy^{\bullet-}$ is expected to be several orders of magnitude lower than that for proton transfer from H_3O^+. However, we have failed to observe the protonation of $bpy^{\bullet-}$ in aqueous alkaline (pH 12) solution under such conditions that the reaction between bpy and e_{aq}^- was complete in approximately 200 ns. In fact, the disappearance of the absorption band of e_{aq}^- (λ_{max} 720 nm) and the appearance of the absorption band of $bpyH^\bullet$ (λ_{max} 365)[21] occurred with the same kinetics, i.e., the appearance of the spectrum of $bpyH^\bullet$ was not delayed in comparison to the disappearance of the spectrum of e_{aq}^-. In addition, the spectrum of $bpyH^\bullet$, during its development, did not show any appreciable spectral shift. Under the assumption that a detectable difference between the spectra of $bpy^{\bullet-}$ and $bpyH^\bullet$ really exists, these observations suggest that the protonation of $bpy^{\bullet-}$ by water must occur with $k \geq 10^6$ M^{-1} s^{-1}.

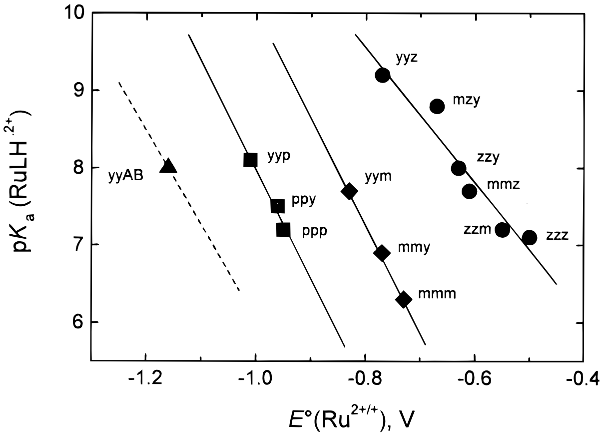

Figure 6. Plot of pK_a values for $RuLH^{\bullet 2+}$ and $RuABH^{\bullet 2+}$ as a function of $E°(Ru^{2+/+})$. Abbreviations: y = bpy, z = bpz, m = bpm, p = pypm. The slope of the dashed line passing through the point representing the $RuAB^{2+}$ complex is the average of the slopes of the three solid lines (see text).

The comparison between equilibrium 4 and equilibrium 6, for which values of $K = 4$, $k_6 = 3.2 \times 10^8$ M^{-1} s^{-1}, and $k_{-6} = 8 \times 10^7$ $M^{-1}s^{-1}$ were reported,[22] shows that the rate constants obtained for the $RuAB^{\bullet+}$/$RuABH^{\bullet 2+}$ couple are approximately 1 order of magnitude smaller than those obtained for the $bpyH^\bullet$/$bpyH_2^{\bullet+}$ couple, a fact that reflects the large difference in size between $RuAB^{2+}$ and bpy species.

$$bpyH^\bullet + H_2PO_4^- \rightleftharpoons bpyH_2^{\bullet+} + HPO_4^{2-} \qquad (6)$$

***pK*$_a$ of $RuABH^{\bullet 2+}$.** It was shown earlier[2] that a plot of the pK_a values of the $RuLH^{\bullet 2+}$ species vs the corresponding $E°(Ru^{2+/+})$ values generated three lines, each representing the group of complexes that had in common the same electron-accepting ligand. The value of the pK_a for $RuABH^{\bullet 2+}$ obtained here, when plotted against the estimated $E°(RuAB^{2+/+})$ value, does not fall on any of those three lines (Figure 6). However, it is possible to make a rough estimate from the plot of the redox and acid−base properties of the two other complexes, $Ru(bpy)(AB)_2^{2+}$ and $Ru(AB)_3^{2+}$, which together with the complex $Ru(bpy)_2(AB)^{2+}$ from the present study are part of another distinct family of Ru(II)−diimine complexes. If this family of complexes behaves in the same way as the others, and there is no reason to believe that this is not so, it is possible to identify the region where the points representing the pK_a and $E°(Ru^{2+/+})$ values of the three complexes would lie by drawing a line through the point representing $RuAB^{2+}$ and using as a slope the average of the slopes of the other three lines. This exercise permits us to conclude that it is most likely that the redox potential of these species will become less negative and the pK_a of the protonated reduced species less positive as the number of AB ligands in the complex is increased.[23]

Acknowledgment. This research has received financial support from Consiglio Nazionale delle Ricerche of Italy (Progetto Finalizzato Chimica Fine II e Progetto Strategico

Tecnologie Chimiche Innovative). A fellowship to F.C. from the Fondo Strutturale Europeo (FSE) of the European Communities is gratefully acknowledged. The authors thank Professor M. Z. Hoffman for many helpful discussions, A. Monti and Dr. A. Martelli for assistance with the pulse radiolysis experiments, and R. Cortesi for assistance with the use of computers.

Supporting Information Available: Plot of k_{obsd} for the decay of e_{aq}^- as a function of $[RuAB^{2+}]$ and plot of log k_{-H} vs $E°(Ru^{2+/+})$ (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Istituto FRAE−CNR. (b) University of Bristol.

(2) Casalboni, F.; Mulazzani, Q. G.; Clark, C. D.; Hoffman, M. Z.; Orizondo, P. L.; Perkovic, M. W.; Rillema, D. P. *Inorg. Chem.* **1997**, *36*, 2252−2257 and references therein.

(3) Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1993**, 1321−1325.

(4) Balzani, V.; Bardwell, D. A.; Barigelletti, F.; Cleary, R. L.; Guardigli, M.; Jeffery, J. C.; Sovrani, T.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 3601−3608.

(5) Guardigli, M.; Flamigni, L.; Barigelletti, F.; Richards, C. S. W.; Ward, M. D. *J. Phys. Chem.* **1996**, *100*, 10620−10628.

(6) (a) Sun, H.; Hoffman, M. Z.; Mulazzani, Q. G. *Res. Chem. Intermed.* **1994**, *7*, 735−754. (b) D'Angelantonio, M.; Mulazzani, Q. G.; Venturi, M.; Ciano, M.; Hoffman, M. Z. *J. Phys. Chem.* **1991**, *95*, 5121−5129. (c) Venturi, M.; Mulazzani, Q. G.; D'Angelantonio, M.; Ciano, M.; Hoffman, M. Z. *Radiat. Phys. Chem.* **1991**, *37*, 449−456. (d) Neshvad, G.; Hoffman, M. Z.; Mulazzani, Q. G.; Venturi, M.; Ciano, M.; D'Angelantonio, M. *J. Phys. Chem.* **1989**, *93*, 6080−6088. (e) Mulazzani, Q. G.; D′Angelantonio, M.; Venturi, M.; Boillot, M.-L.; Chambron, J.-C.; Amouyal, E. *New J. Chem.* **1989**, *13*, 441−447. (f) Venturi, M.; Mulazzani, Q. G.; Ciano, M.; Hoffman, M. Z. *Inorg. Chem.* **1986**, *25*, 4493−4498. (g) Mulazzani, Q. G.; Emmi, S.; Fuochi, P. G.; Hoffman, M. Z.; Venturi, M. *J. Am. Chem. Soc.* **1978**, *100*, 981−983.

(7) Hutton, A.; Roffi, G.; Martelli, A. *Quad. Area Ric. Emilia-Romagna* **1974**, *5*, 67−74.

(8) Mulazzani, Q. G.; D'Angelantonio, M.; Venturi, M.; Hoffman, M. Z.; Rodgers, M. A. J. *J. Phys. Chem.* **1986**, *90*, 5347−5352.

(9) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513−886.

(10) Schwarz, H. A. *J. Chem. Educ.* **1981**, *58*, 101−105.

(11) (a) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409−414. (b) Surdhar, P. S.; Mezyk, S. P.; Armstrong, D. A. *J. Phys. Chem.* **1989**, *93*, 3360−3363.

(12) (a) Baxendale, J. H.; Fiti, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1995−1998. (b) Mulazzani, Q. G.; Emmi, S.; Hoffman, M. Z.; Venturi, M. *J. Am. Chem. Soc.* **1981**, *103*, 3362−3370. (c) Mulazzani, Q. G.; Venturi, M.; Hoffman, M. Z. *Radiat. Phys. Chem.* **1988**, *32*, 71−78.

(13) Endicott, J. P. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleishauer, P. D., Eds., Wiley: New York, 1975; p 88.

(14) Simic, M.; Neta, P.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 3794−3800.

(15) Ross, A. B.; Mallard, W. G.; Helman, W. P.; Buxton, G. V.; Huie, R. E.; Neta, P. *NDRL-NIST Solution Kinetics Database, Ver. 2*; NIST Standard Reference Data, Gaithersburg, MD 1994.

(16) Mulazzani, Q. G.; D'Angelantonio, M.; Camaioni, N.; Venturi, M. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2179−2185.

(17) *Handbook of Chemistry and Physics*, 77th ed.; CRC Press: Boca Raton, FL, p 8-44.

(18) Sun, H.; Hoffman, M. Z. *J. Phys. Chem.* **1993**, *97*, 5014−5018.

(19) It is worth noting that the use of this relationship, together with pulse radiolysis data from ref 6e, has recently significantly contributed to clarifying the nature of the so-called "light-switch" mechanism of the $Ru(phen)_2(dppz)^{2+}$ complex.[20]

(20) Olson, E. J. C.; Hu, D.; Hörmann, A.; Jonkman, A. M.; Arkin, M. R.; Stemp, E. D. A.; Barton, J. K.; Barbara, P. F. *J. Am. Chem. Soc.* **1997**, *119*, 11458−11467.

(21) Mulazzani, Q. G.; Emmi, S.; Fuochi, P. G.; Venturi, M.; Hoffman, M. Z.; Simic, M. G. *J. Phys. Chem.* **1979**, *83*, 1582−1590.

(22) Krishnan, C. V.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1983**, *105*, 5617−5623.

(23) The recent observation[24] that the complexes $Ru(bpy)(AB)_2^{2+}$ and $Ru(AB)_3^{2+}$ in acetonitrile are reduced at a potential 30 mV less negative than is $Ru(bpy)_2(AB)^{2+}$ supports this conclusion.

(24) Cleary, R. L.; Byrom, K. J.; Bardwell, D. A.; Jeffery, J. C.; Ward, M. D.; Calogero, G.; Armaroli, N.; Flamigni, L.; Barigelletti, F. *Inorg. Chem.* **1997**, *36*, 2601−2609.