(DPA)(MAL)$_2$, and 7.3 for Tb(DPA)$_2$(MAL). With the steric bulk of the DPA ligand being considerably larger than that of the MAL ligand, it would appear that it is more difficult for the MAL ligand to bind in a terdentate manner as the steric crowding of the achiral part of the complex becomes appreciable.

The study of optical activity in lanthanide complexes is complicated considerably by the high degree of lability in these complexes, and it is doubtful that the same degree of information can be obtained for these complexes relative to that which has been already collected for inert Co(III) and Cr(III) complexes. Consequently, in lanthanide chemistry one must speak primarily of dominant species in solution and recognize the possibility that other forms may coexist along with the major component. Nevertheless, with careful choice of complex systems (and avoidance of polynuclear complexes), a great deal of information may be obtained from chirooptical techniques and from CPL in particular.

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Registry No. Tb(DPA)$_3^{3-}$, 38682-37-0; Tb(DPA)$_2$(MAL)$^{3-}$, 73663-68-0; Tb(DPA)(MAL)$_2^{3-}$, 73663-69-1; Tb(MAL)$_2^-$, 73663-70-4.

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Ion-Multiplet Formation and the Photoanation of Tris(2,2′-bipyridine)ruthenium(II)

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[Ru(bpy)$_3$]Br$_2$ in dimethylformamide loses one bipyridine upon irradiation at 458 nm, with an overall quantum yield of 3×10^{-4} with 0.017 M Br$^-$ present. The quantum yields of the two photoproducts, [Ru(bpy)$_2$(DMF)Br]$^+$ and [Ru(bpy)$_2$Br$_2$], are linearly dependent on bromide concentration within the range $0.0016 < [\mathrm{Br}^-] < 0.017$ M. The results are consistent with a model based on ion pairs and ion triplets as the photoactive species.

Introduction

For some time [Ru(bpy)$_3$]$^{2+}$ has been used extensively as a triplet sensitizer, in both luminescence and photochemical applications.[2–4] More recently the redox properties of excited state [Ru(bpy)$_3$]$^{2+}$ have come under intense scrutiny,[5–9] in particular because of the suggestion that photocatalytic decomposition of water may be feasible with this or related complexes.[10–13]

Although once thought to be photochemically inert,[2,14] it is now recognized that a permanent substitutional photochemistry does exist for [Ru(bpy)$_3$]$^{2+}$. Demas and Adamson first reported a slight photosensitivity of the chloride salt in water and in 0.05 M H$_2$SO$_4$, detected by a diminished [Ru(bpy)$_3$]$^{2+}$ luminescence intensity.[15] Van Houten and Watts reported the apparent substitution of the chloride salt in 0.1 M HCl at 95 °C, monitoring both changes in the absorption spectrum and the decrease in luminescence intensity.[16] They also observed the release of bipyridine through the appearance of its characteristic fluorescence spectrum, and in addition they concluded that photochemistry and luminescence originate from different excited states.[16] No photoreactivity was observed under the same conditions at room temperature.

At about the same time we observed photosubstitutional behavior for several [Ru(bpy)$_3$]$^{2+}$ salts in some organic solvents at room temperature, with quantum yields on the order of 10^{-3} or less.[17,18] In general the quantum yields were found to increase with anion concentration (except for NO$_3^-$, SO$_4^{2-}$, and ClO$_4^-$, which slowed the reaction), suggesting the involvement of ion pairing in the process. In dimethylformamide (DMF) two, and sometimes more, photoproducts appeared, one of them the [Ru(bpy)$_2$X$_2$] complex, where X$^-$ was the original counterion.

More recently photosubstitutional behavior of the chloride salt in some chlorinated solvents has been noted, with [Ru(bpy)$_2$Cl$_2$] reported as the product.[19] The quantum yield was 0.02, much higher than in DMF or ethanol.[18]

In our earlier work the thiocyanate salt was investigated quantitatively in DMF.[18] Two products were formed, identified as [Ru(bpy)$_2$(DMF)(NCS)]$^+$ and [Ru(bpy)$_2$(NCS)$_2$]. In any single experiment these were formed in nearly constant ratio, as indicated by the presence of isosbestic points in sequential absorption spectra of the photolysate. However, the relative quantum yields of the two products varied with thiocyanate concentration, the dithiocyanato complex being more strongly dependent on [SCN$^-$].

Although it was clear that ion-pair formation was a necessary condition for photolysis to occur, the mechanism by which the products were formed could not be conclusively established. Two possible reaction schemes were proposed.[18] The first involved a classical secondary photolysis, in which one ligand (A$^-$) would coordinate to form the first product,

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$[Ru(bpy)_2(DMF)A]^+$, followed by a second photoreaction in which a DMF molecule would be replaced by another ligand to form $[Ru(bpy)_2A_2]$.

The alternative ion multiplet model suggested that the two products were formed from $[Ru(bpy)_3]^{2+}$ in different states of ion aggregation: $[Ru(bpy)_2(DMF)A]^+$ from the ion pair and $[Ru(bpy)_2A_2]$ from the ion triplet.

We felt previously that the latter model explained the observations somewhat more effectively, especially the isosbestic point behavior and the observed thiocyanate dependence of the quantum yield for disappearance of $[Ru(bpy)_3]^{2+}$. However, we also noted photoconversion between the bis complexes when examined separately, as well as an induction period in the formation of the dithiocyanato complex, a classical indication of secondary photolysis.

Experimental Section

$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ was obtained from G. F. Smith Co. and dimethylformamide (spectrograde, $H_2O < 0.05\%$) from Aldrich. Analyses were performed by Galbraith Microanalytical Laboratories.

A. Preparation of $[Ru(bpy)_3]Br_2 \cdot 6H_2O$. $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ was dissolved in C_2H_5OH/H_2O (1:1) and passed through a Dowex 1-X8 column in Br^- form, utilizing less than 5% of the resin capacity. Red crystals were obtained upon evaporation of the solution under a stream of nitrogen. Anal. Calcd for $[Ru(C_{10}H_8N_2)_3]Br_2 \cdot 6H_2O$: C, 43.02; H, 4.33; Br, 19.08. Found: C, 43.85; H, 4.42; Br, 18.57.

B. Preparation of $[Ru(bpy)_2Br_2] \cdot H_2O$. $[Ru(bpy)_3]Br_2 \cdot 6H_2O$ (0.2 g) was dissolved in ethanol (15 mL), placed in a cylindrical spectrophotometer cell (5-cm path length), deoxygenated by bubbling nitrogen gas through the cell, and irradiated for 3 days with an unfiltered 150-W xenon lamp. The black crystals which formed were filtered, washed with ethanol, and dried in vacuo. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2Br_2] \cdot H_2O$: C, 40.65; H, 3.07; Br, 27.04. Found: C, 40.90; H, 2.93; Br, 26.71.

C. Experimental Design. Solutions of $[Ru(bpy)_3]Br_2$ and Bu_4NBr (tetrabutylammonium bromide) in DMF were placed in a 1.0-cm cylindrical spectrophotometer cell and irradiated with the 457.9-nm line of a Spectra Physics 164-03 argon ion laser. The beam was dispersed with a double concave lens so as to illuminate the entire cell window. All solutions were deoxygenated by bubbling N_2 into the cell for 10 min. Photolysis was interrupted periodically, and visible absorption spectra were recorded. The spectrum of the photolysate remained constant for periods of several hours, so that dark reactions could be ignored.

The laser power settings varied from 100 to 250 mW, depending on the current state of adjustment of the laser. Ferrioxalate actinometry[20,21] was used to determine the incident light intensity, which was found to be 55% of the meter readings from the laser power supply. These corrected meter readings were then used for quantum yield determinations.

More concentrated solutions of $[Ru(bpy)_3]Br_2$ in DMF were photolyzed with a 140-W Cenco Hg lamp for several hours, and the products were separated chromatographically by using DMF-equilibrated Sephadex LH-20, eluting with DMF and gravity feed. The sample size was 3 mL and the column depth about 40 cm. The spectra of the product bands were recorded and used as reference spectra in the data treatment.

Results

Irradiation of a solution of $[Ru(bpy)_3]Br_2 \cdot 6H_2O$ (30 mg) and Bu_4NBr (0.1 g) in DMF (3 mL) produced a mixture of complexes which separated into three bands on Sephadex LH-20. The first band (purple) eluted was $[Ru(bpy)_2Br_2]$, as confirmed by its absorption spectrum. The second band (red) contained small amounts of material (5–10% of total Ru). The elution behavior was quite similar to that of $[Ru(bpy)_2(DMF)(NCS)]^+$ in the thiocyanate system,[18] so that an identification as $[Ru(bpy)_2(DMF)Br]^+$ is suggested. The absorption spectra of the monobromo and monothiocyanato complexes were also quite similar, and in each case the position of the first band was intermediate between that of $[Ru(bpy)_3]^{2+}$ and the $[Ru(bpy)_2A_2]$ complex (see Table I). Conductivity data support the conclusion that the second band material was a (+1, −1) salt. The molar conductivity in DMF (using extinction coefficients as determined later to determine concentration) was found to be 70 ± 15 Ω^{-1} M^{-1} cm^{-1} (the uncertainty is primarily in the extinction coefficient). In comparison, the molar conductivity for the (+2, −1) salt, $[Ru(bpy)_3]Br_2$, was 203 and for $NaClO_4$ was 60.1.

Table I. Spectral Data for Species Found after Irradiation of $[Ru(bpy)_3]Br_2$ in DMF

complex	order of elution on LH-20/DMF	λ_1^{max}, nm (ϵ)	λ_2^{max}, nm (ϵ)
$[Ru(bpy)_2Br_2]$	I	551 (1.22×10^4)	373 (1.33×10^4)
$[Ru(bpy)_2(DMF)Br]^+$	II	524 (0.82×10^4)	360 (0.77×10^4)
$[Ru(bpy)_3]Br_2$	III	454 (1.46×10^4)	

The final complex (orange) eluted was the starting material, $[Ru(bpy)_3]^{2+}$. Absorption spectral data for these complexes are given in Table I. The extinction coefficients for the two product species were determined as part of the data-handling procedure.

We experienced some difficulty in dissolving solid $[Ru(bpy)_2Br_2]$ in DMF, often finding that a thermal reaction had occurred in the process (as evidenced by the appearance of a peak at 600 nm), and extinction coefficients determined in this way were not reproducible. We note also a difference by a factor of 2 in literature values for the extinction coefficient of this complex in CH_2Cl_2.[22,23]

An additional photoproduct was occasionally observed as a green band on the Sephadex column (eluting in front of the tris complex), which disappeared before reaching the bottom of the column. The occurrence was not reproducible.

Lower concentrations (4.62×10^{-5} M) of $[Ru(bpy)_3]Br_2$ in DMF, generally with added bromide, were photolyzed in a 1.0-cm cell, and the spectra were recorded at intervals. Three isosbestic points were apparent in the sequential spectra, although the wavelengths varied with bromide concentration. This implies that the products were formed in constant ratio in a single experiment, but the ratio itself changed as a function of $[Br^-]$. A typical series of sequential spectra is illustrated in Figure 1.

The spectrum of the photolysate at a particular irradiation time was resolved as a sum of reference spectra for the two products and the starting material.

$$A(\lambda) = \alpha R(\lambda) + \beta P_1(\lambda) + \gamma P_2(\lambda) \qquad (1)$$

Here $A(\lambda)$ is the spectrum of the reaction mixture and $R(\lambda)$, $P_1(\lambda)$, and $P_2(\lambda)$ are the spectra of $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(DMF)Br]^+$, and $[Ru(bpy)_2Br_2]$, respectively. We could not detect significant spectral changes for any of the species over the range of bromide concentration used. The reference spectra of the products were obtained from fractions isolated by column chromatography. The extinction coefficient of the dibromo complex could have been estimated (although not very well) but the monobromo complex could not be isolated as a solid. In any case, the magnitudes of the coefficients α, β, and λ must be proportional to the concentration in the reaction mixture but inversely proportional to the concentrations in the solutions used to generate the reference spectra.

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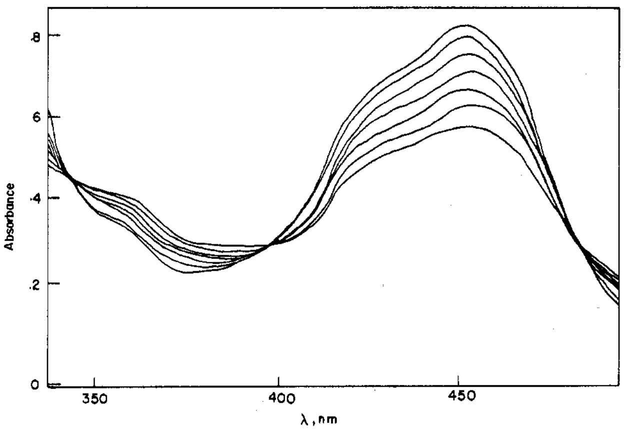

Figure 1. Sequential absorption spectra from the irradiation of an N_2-saturated solution of 4.62×10^{-5} M $[Ru(bpy)_3]Br_2$ and 1.58×10^{-3} M $(C_4H_9)_4Br$ in DMF. Excitation was with the 457.9-nm line of an argon laser (170 mW).

For each bromide concentration and irradiation time, then, values of α, β, and γ were determined. These were converted into mole fractions by first assuming that α, β, and γ were proportional to the concentrations, C_i, of the species with which they were associated.

$$C_R = \delta_R\alpha \qquad C_{P_1} = \delta_{P_1}\beta \qquad C_{P_2} = \delta_{P_2}\gamma$$

Since the $t = 0$ spectrum was used as the reference for $[Ru(bpy)_3]^{2+}$ at each bromide concentration, α_0 was by definition 1.00, and the proportionality constant, δ_R, was just C_0, the initial concentration of the tris species. If we assume that the total amount of ruthenium is conserved within these three complexes

$$C_0\alpha + \delta_{P_1}\beta + \delta_{P_2}\gamma = C_0$$

or

$$\frac{C_0(1-\alpha)}{\beta} = \delta_{P_2}\left(\frac{\gamma}{\beta}\right) + \delta_{P_1} \qquad (2)$$

then the proportionality constants, δ_{P_1} and δ_{P_2}, may be determined by subjecting all sets of α, β, and γ to a linear regression analysis. The plot is shown in Figure 2.

The proportionality constants, δ_{P_1} and δ_{P_2}, were also used to calculate the extinction coefficients in Table I, since each is equal to the concentration of the respective species represented in the reference spectra used.

Figure 3 shows a typical photolysis reaction profile, with mole fractions determined as above. The rates of appearance of each product and disappearance of the tris complex were constant, within experimental error, throughout the reaction, which in this case was carried to 40% completion. At other bromide concentrations the same pattern of constant rates was observed, even past 60% completion.

Quantum yields for formation of each product and for disappearance of $[Ru(bpy)_3]^{2+}$ were determined from the observed rates and were found to increase as the bromide ion concentration was increased. The same type of behavior was previously noted with thiocyanate as the anion.[18] The quantum yields are listed in Table II.

Discussion

In Figure 4 the quantum yields for the formation of $[Ru(bpy)_2Br_2]$ and for the disappearance of $[Ru(bpy)_3]^{2+}$ are plotted against bromide concentration. The dependence on bromide over the concentration range of this study is approximately linear in all cases, except when no bromide was added ($[Br^-] = 9.2 \times 10^{-5}$ M from the $[Ru(bpy)_3]Br_2$ used).

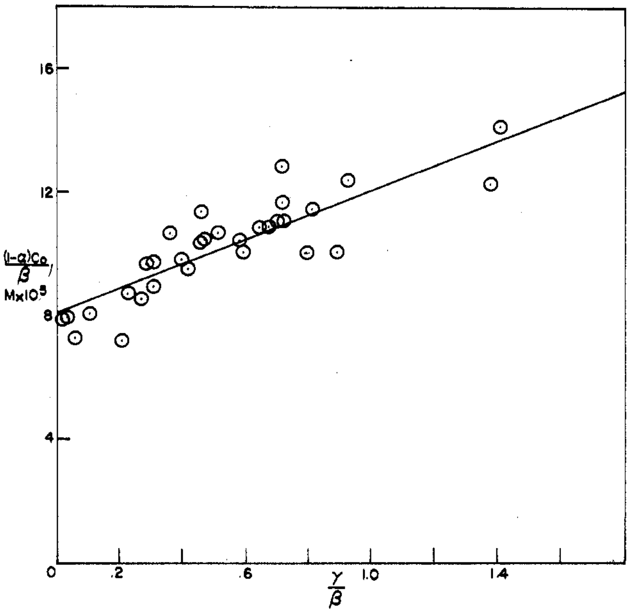

Figure 2. Plot from eq 2 to determine concentrations of $[Ru(bpy)_2(DMF)Br]^+$ and $[Ru(bpy)_2Br_2]$ used to obtain reference spectra; α, β, and γ are the coefficients by which the reference spectra had to be multiplied in order to sum up to the observed spectrum of the photolysate.

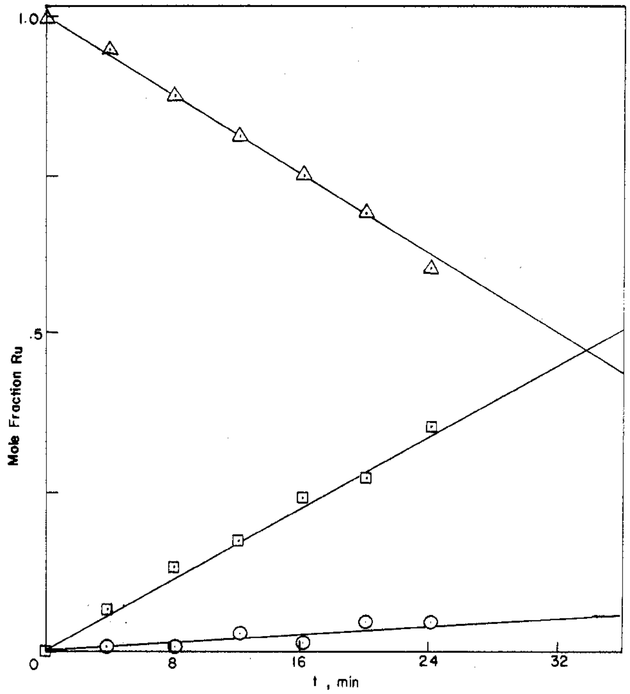

Figure 3. Typical reaction profile illustrating the formation of $[Ru(bpy)_2(DMF)Br]^+$ (□) and $[Ru(bpy)_2Br_2]$ (⊙) and the disappearance of $[Ru(bpy)_3]^{2+}$ (△). The values here resulted from an analysis of the data from Figure 1.

The excited-state lifetime of $[Ru(bpy)_3]^{2+}$ is 0.8 μs,[24] so that, at least in principle, a bimolecular process, involving collision of a bromide ion with an excited-state complex, could explain the quantum yield data. However, ion pair formation was implicated in the photolysis of the thiocyanate salt,[18] so it is reasonable to assume that here too the photoactive species are ion pairs (or triplets), even though no saturation of the

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Table II. Quantum Yields for Disappearance of $[Ru(bpy)_3]^{2+}$ (ϕ_R) and Appearance of $[Ru(bpy)_2(DMF)Br]^+$ (ϕ_{P_1}) and $[Ru(bpy)_2Br_2]$ (ϕ_{P_2}) at Various Bromide Concentrations

$[Br^-]$, M	ϕ_R	ϕ_{P_1}	ϕ_{P_2}
9.2×10^{-5} [a]	4.1×10^{-5}	4.4×10^{-5}	0
1.58×10^{-3}	1.0×10^{-4}	0.95×10^{-4}	1.2×10^{-5}
3.16×10^{-3}	1.6×10^{-4}	1.2×10^{-4}	2.4×10^{-5}
5.27×10^{-3}	2.1×10^{-4}	1.7×10^{-4}	2.5×10^{-5}
5.83×10^{-3}	1.3×10^{-4}	1.1×10^{-4}	2.3×10^{-5}
8.71×10^{-3}	1.5×10^{-4}	1.1×10^{-4}	3.6×10^{-5}
1.13×10^{-2}	2.1×10^{-4}	1.5×10^{-4}	4.8×10^{-5}
1.15×10^{-2}	2.0×10^{-4}	1.5×10^{-4}	4.0×10^{-5}
1.65×10^{-2}	2.8×10^{-4}	2.1×10^{-4}	6.8×10^{-5}

[a] No added Br^-.

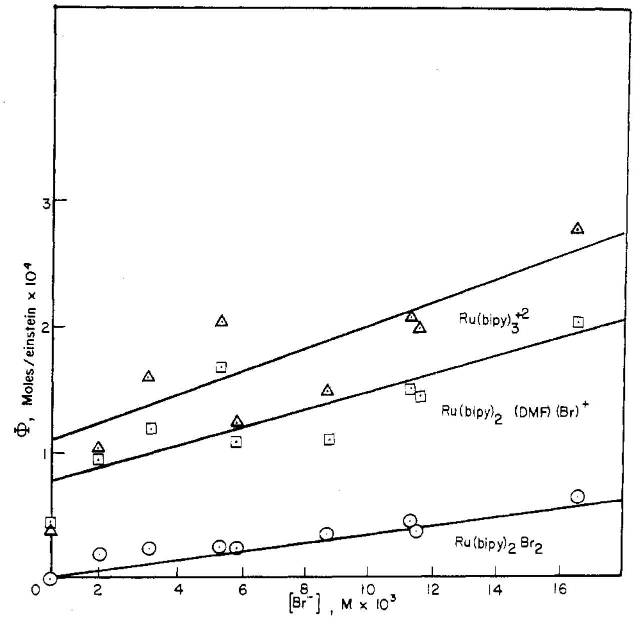

Figure 4. Dependence on bromide concentration of the quantum yields for formation of $[Ru(bpy)_2(DMF)Br]^+$ (□) and $[Ru(bpy)_2Br_2]$ (⊙) and the disappearance of $[Ru(bpy)_3]^{2+}$ (△). The straight lines were obtained from a linear regression, with correlation coefficients of 0.83 for $[Ru(bpy)_3]^{2+}$, 0.76 for $[Ru(bpy)_2(DMF)Br]^+$, and 0.97 for $[Ru(bpy)_2Br_2]$.

quantum yield is evident in Figure 4.

As in the thiocyanate system, the presence of isosbestic points in sequential spectra indicates formation of products in constant ratio. Unlike the thiocyanate system, no induction periods were observed, and we conclude that the products are formed independently. The two models considered for the thiocyanate system, secondary photolysis and the ion pair/ion triplet model, were not completely satisfactory in explaining the thiocyanate data, but the latter does appear more reasonable in the present study.

The ion multiplet model, as described in the Introduction, can be written as follows, with one modification allowing the formation of the monoanated complex from the ion triplet:

$$R \xrightarrow{h\nu} R^* \qquad (3)$$

$$R^* + Br^- \underset{}{\overset{K_1}{\rightleftharpoons}} R^*{\cdot}Br^- \qquad (4)$$

$$R^*{\cdot}Br^- + Br^- \overset{K_2}{\rightleftharpoons} R^*{\cdot}2Br^- \qquad (5)$$

$$R^*{\cdot}Br^- \xrightarrow{\phi_1} P_1 \qquad (6)$$

$$R^*{\cdot}2Br^- \xrightarrow{\phi_2} P_1 + Br^- \qquad (7)$$

$$R^*{\cdot}2Br^- \xrightarrow{\phi_3} P_2 \qquad (8)$$

Table III. Quantum Yields and Ion-Pair Formation Constants

ϕ_1	1.85×10^{-4}
$\phi_2 K_2$	1.25×10^{-2}
$\phi_3 K_2$	3.6×10^{-3}
K_1 (estd)	3300

K_1 and K_2 are the formation constants for the ion pair and ion triplet, respectively. We have assumed, because of the 0.8-μs lifetime, that the process can best be described in terms of ion-multiplet formation by the excited-state complex rather than excitation of a preexisting ion multiplet, but in any case the critical assumption is that only the ion multiplets will react to yield products. Thus the observed quantum yields are proportional to the fraction of excited-state molecules present as ion pairs or ion triplets. From eq 4 and 5

$$f_2 = \frac{K_1[Br^-]}{1 + K_1[Br^-] + K_1K_2[Br^-]^2} \qquad (9)$$

$$f_3 = \frac{K_1K_2[Br^-]^2}{1 + K_1[Br^-] + K_1K_2[Br^-]^2} \qquad (10)$$

where f_2 and f_3 are the fractions of $[Ru(bpy)_3{}^{2+}]^*$ present as ion pairs and ion triplets, respectively. The observed quantum yield for the formation of $[Ru(bpy)_2(DMF)Br]^+$ is then $\phi_{P_1} = f_2\phi_1 + f_3\phi_2$ or

$$\phi_{P_1} = \frac{\phi_1K_1[Br^-] + \phi_2K_1K_2[Br^-]^2}{1 + K_1[Br^-] + K_1K_2[Br^-]^2} \qquad (11)$$

Likewise the observed quantum yield for formation of $[Ru(bpy)_2Br_2]$ is

$$\phi_{P_2} = \frac{\phi_3K_1K_2[Br^-]^2}{1 + K_1[Br^-] + K_1K_2[Br^-]^2} \qquad (12)$$

What was observed (Figure 4) was a linear dependence of both ϕ_{P_1} and ϕ_{P_2} on $[Br^-]$, except at very low bromide concentrations, where ϕ_{P_1} was significantly lower than what would be extrapolated. These observations are consonant with eq 11 and 12 if it is assumed that the term $K_1[Br^-]$ predominates in the denominator except at very low bromide. In that case the approximate expressions are

$$\phi_{P_1} = \phi_1 + \phi_2K_2[Br^-] \qquad (13)$$

and

$$\phi_{P_2} = \phi_3K_2[Br^-] \qquad (14)$$

Equation 14 predicts a straight line passing through the origin, which from Figure 4 is seen to be very nearly true. A linear regression on the data in Table II yields an intercept of 4×10^{-6}, which is about one standard deviation from zero. Equations 13 and 14 were used to calculate values of ϕ_1, ϕ_2K_2, and ϕ_3K_2, which are listed in Table III (a plot of $[Br^-]/\phi$ vs. $[Br^-]$ was more convenient for this purpose than ϕ vs. $[Br^-]$).

At higher bromide concentrations a saturation effect should eventually take over, as the $K_1K_2[Br^-]^2$ term in the denominators of eq 11 and 12 becomes important. We were not able to reach concentrations high enough to see this, but saturation was observed in the thiocyanate system.[18] At very low bromide concentrations the quantum yields also decrease more rapidly as $K_1[Br^-]$ approaches and becomes smaller than unity. Only one photolysis experiment, the one with no added bromide, extended beyond the linear range. The quantum yield for $[Ru(bpy)_2Br_2]$ formation was already too small to be determined, while that for $[Ru(bpy)_2(DMF)Br]^+$ did indeed fall below the line in Figure 4.

The observed quantum yield for $[Ru(bpy)_2(DMF)Br]^+$ formation in this experiment ($[Br^-] = 9.2 \times 10^{-5}$ M) could be used to estimate K_1 from eq 11 at 3300 M^{-1}, although this value is, of course, subject to considerable uncertainty. An estimate for K_2 was not possible, since there was no indication of saturation at high $[Br^-]$.

Conductometric and spectrophotometric determinations of ion-pair formation constants in DMF of some Cr(III) and Co(III) complexes with Br^- show typical values near 800 for (1+, 1−) ion pairs[25-27] and 9200 for one example of a (2+, 1−) pair.[25] Our estimated value of 3300 for K_1 appears reasonable in this light. Data on ion triplet formation constants are sparse, but one determination for *cis*-$[Co(en)_2(DMF)Cl]^{2+}$ with Cl^- in DMF resulted in a K_2 of 80.[25] With bromide ion we might expect smaller values.

The data in Table III indicate that $\phi_2 > \phi_3$, that is, the ion triplet is about three times more likely to yield the monobromo than the dibromo complex. If K_2 were estimated at 20 M^{-1}, ϕ_1 and ϕ_3 would be quite comparable, and $[Ru(bpy)_2(DMF)Br]^+$ would form more readily from the ion triplet than from the ion pair by about a factor of 3.

Conclusion

In contrast with earlier studies using thiocyanate,[18] photoanation of $[Ru(bpy)_3]^{2+}$ by bromide ion in DMF can be fairly well accounted for by eq 11 and 12. These equations resulted from a model involving formation of both ion pairs and ion triplets as photoactive species. However, identical bromide dependences can be obtained from another model in which a monodentate bipyridine intermediate is formed from the ion pair as the single photochemical process, followed by thermal reactions (including further ion pairing of the intermediate) to form mono- and dianated species.[28]

We have interpreted our data in terms of the ion pair/ion triplet model because the derived formation constants appear reasonable and because no evidence for the monodentate intermediate has yet been found, even though a stable iridium(III) analogue has recently been reported.[29] It is in fact difficult to conceive of the dissociation of bipyridine proceeding other than through a monodentate intermediate (although not necessarily Ru(II)!), with which, however, both of the models presented here are consistent. It remains an interesting problem to differentiate between these closely related mechanisms.

A final point concerns the actual substitution mechanism. Although our treatment of the observable photoproducts (or even a model based on a monodentate–bipyridine intermediate) leads perhaps to the conclusion that classical ligand substitution is occurring, the rich redox chemistry of excited-state $[Ru(bpy)_3]^{2+}$ suggests also the possibility that the reaction proceeds through a Ru(III) or (in the presence of Br^-, for example) Ru(I) intermediate.

Registry No. $[Ru(bpy)_3]Br_2$, 15388-41-7; $Ru(bpy)_2Br_2$, 23377-85-7; $[Ru(bpy)_2(DMF)Br]^+$, 73663-67-9; $[Ru(bpy)_3]Cl_2$, 14323-06-9; $[Ru(bpy)_3]^{2+}$, 15158-62-0.

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Rate of Electron Self-Exchange between the Delocalized Clusters $[Ru_3O(CH_3CO_2)_6(py)_3]^{+/0}$

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Rate constants for electron self-exchange between the delocalized clusters $[Ru_3O(CH_3CO_2)_6(py)_3]^{+/0}$ at a series of temperatures were determined by analysis of line broadening observed for the acetate ^1H NMR resonances in solutions containing both clusters. At 24 °C, a rate constant of 1.1×10^8 M^{-1} s^{-1} was obtained for the self-exchange reaction, and kinetic parameters characterizing the reaction were determined from the temperature dependence of the rate constant: ΔH^*_{obsd}(exptl) = 4.4 kcal/mol and ΔS^*_{obsd}(exptl) = −7 cal/(mol deg). The results obtained from the self-exchange study are discussed in terms of a mechanism involving preassociation of the reactants, electron transfer within the association complex, and dissociation of the successor complex. The observed rate constant is then the product of a preequilibrium constant, K_A $(=\exp(-\Delta G_A/RT))$, and the rate constant for electron transfer within the association complex, k_{et} $(=\nu_{et}\exp(-G^*/RT))$, $k_{obsd} = K_A k_{et}$. Theoretical calculations for the equilibrium constant and for the electron-transfer rate constant are presented and calculated kinetic parameters are compared to the experimental results. A statistical thermodynamic calculation of the preequilibrium constant results in a better agreement with the experimental results than that obtained by using the Eigen–Fuoss equation. Attempts to measure the rate of intramolecular electron transfer within the "mixed-valence" ligand-bridged dimer $[(py)_2Ru^I_3O(CH_3CO_2)_6(1,4\text{-}pz)Ru^0_3O(CH_3CO_2)_6(py)_2]^+$ (1,4-pz is 1,4-pyrazine) using the NMR technique were unsuccessful but allowed an estimate of $k_{et} > 7 \times 10^4$ s^{-1} at −70 °C to be made.

Introduction

Recent experimental and theoretical advances have led to a more precise description of the microscopic events which occur during an electron-transfer process. In terms of theory, the earlier semiclassical treatments of Hush[1] and Marcus[2] have been reinforced and extended by more comprehensive quantum mechanical treatments.[3] One of the more important experimental advances has been based on the observation of intervalence transfer (IT) or metal–metal charge transfer (MMCT) absorption bands in specially designed mixed-va-

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