Photoinduced Electron Transfer Reactions of Transition-Metal Complexes with Amines. Mechanistic Studies of Alternate Pathways to Back Electron Transfer[1c]

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Abstract: A study of the photoreduction of polypyridyl complexes of ruthenium(II) and iron(II) by amines is reported. While two of the ruthenium(II) complexes studied are found to give "permanent" reduction on irradiation in the presence of triethylamine in anhydrous media, the two iron complexes studied and $(bpy)_3Ru^{II\,2+}$ are found not to give a permanent reduction. Nonetheless, all complexes studied are found to give acetaldehyde when irradiation is carried out in the presence of water, suggesting that an irreversible oxidation of triethylamine is taking place. Studies with spin traps such as nitrosodurene also result in interception of alkyl radicals derived from triethylamine and *N,N*-dimethylaniline. The combination of spin trapping and product studies points to a mechanism in which the amine radical cation formed in the initial electron transfer quenching step rapidly reacts with a second molecule of amine to give an alkyl radical whose fate is subsequently determined by the properties and redox behavior of the specific metal complex involved.

Introduction

In recent years, there have been widespread investigations of the oxidation and reduction reactions of excited states of transition-metal complexes.[2-21] It has been well established that several transition metal complex excited states can be quenched efficiently by both electron donors and electron acceptors in one-electron transfer processes (eq 1 and 3)

$$M^{2+*} + Q \rightarrow M^{+} + Q^{+} \qquad (1)$$

$$M^{+} + Q^{+} \rightarrow M^{2+} + Q \qquad (2)$$

$$M^{2+*} + Q \rightarrow M^{3+} + Q^{-} \qquad (3)$$

$$M^{3+} + Q^{-} \rightarrow M^{2+} + Q \qquad (4)$$

where M^{2+} = metal complex and Q = quencher. Probably the most widely investigated systems to date are the polypyridyl complexes of a number of metal ions, most notably tris(2,2′-bipyridine)ruthenium(II)$^{2+}$ ($Ru(bpy)_3^{2+}$). The attraction of $Ru(bpy)_3^{2+}$, as well as analogues with osmium and iridium, is due to its strong absorption properties throughout the visible region, relatively long excited-state lifetime, and luminescence. Although quenching by electron transfer results in the production of two high-energy products, in most instances a rapidly ensuing back electron transfer reaction follows wherein the energy "stored" in the electron-transfer step is subsequently "wasted" by the regeneration of the ground states of the starting materials (eq 2 and 4).[3-5,8-12] It is clear that, in order to utilize the energy stored in the high-energy redox products, this reverse electron transfer step must be circumvented. One approach involves the design of systems whereby one of the initial products formed is rapidly converted to a redox-inactive product by an alternate pathway in competition with the back electron transfer reaction.[19,20,22,23] In some cases it has been found possible to retard quenching and/or back electron transfer steps by modification of the molecular structure of the light-absorbing substrate and/or the quencher.[1,18] Recently we reported a preliminary study of electron transfer quenching processes with hydrophobic ruthenium(II) complexes as excited substrates and tertiary amines as quencher–reductants.[1] For this system a combination of the two phenomena described above—a rapid removal of one of the redox products and a retarded back reaction—allows the efficient "permanent" production of a high-energy product, in this case the reduced metal complex. In the present paper we report a detailed study of this process, using a number of ruthenium(II) and iron(II) complexes as excited substrates and tertiary amines such as triethylamine and *N,N*-dimethylaniline as quencher reductants. The use of ESR techniques—both direct and with added "spin traps"—coupled with product studies has helped in this case to provide a rather detailed mechanistic picture. It is reasonable to anticipate that the mechanism operating in this rather general

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case should provide a prototype for developing other useful net redox processes by solution-phase light-induced electron transfer.

Experimental Section

Preparation and Purification of Materials. Spectrograde acetonitrile was distilled in a closed system over anhydrous P_2O_5 prior to use. Triethylamine was purified by distillation from potassium hydroxide pellets followed by distillation from sodium. The compounds used as spin traps (**6**–**8**) were synthesized and purified according to methods reported in the literature.[24-30] The hydrophobic complex **2** was synthesized as previously reported.[18] $Ru(bpy)_3^{2+}$ (**1**) and $Fe(bpy)_3^{2+}$ (**4**) were prepared by literature methods.[31,32] The hydrophobic complex **3** was prepared by the following procedure. 3-Picoline was refluxed over Pd/C (10%) for 5 days. The reaction mixture was added to boiling benzene, stirred, and filtered. The benzene and some of the excess picoline were evaporated. The 3,3′-dimethyl-2,2′-bipyridine crystallized out and was recrystallized from ethyl acetate. The product was then oxidized by potassium permanganate and precipitated from the aqueous solution with hydrochloric acid. The diacid was then refluxed with thionyl chloride for several hours and the reaction mixture was evaporated to dryness. An excess of 2-propanol was added and the solution was heated at reflux for 5 h. The solution was cooled and added to aqueous sodium bicarbonate. The diisopropyl ester was extracted with ether, washed several times with aqueous sodium bicarbonate, and dried over magnesium sulfate. The ether was evaporated and the ester was recrystallized from hot ether/pentane. A threefold excess of this ligand was added to a solution of ruthenium trichloride in argon-degassed 2-propanol and refluxed for 7 days. The reaction mixture was added to water and filtered. The product was precipitated out with ammonium hexafluorophosphate and filtered. The product, **3**, was purified by column chromatography and analyzed to be the desired product. The hydrophobic iron complex **5** was prepared by the following method. The ligand 4,4′-diisopropyl ester 2,2′-bipyridine was prepared as previously described. A twofold excess of this ligand was dissolved in 40 mL of reagent-grade 2-propanol. The solvent was degassed by bubbling with nitrogen for 45 min. $FeCl_2 \cdot 4H_2O$ (0.100 g) (J. T. Baker) was added to the solution and the mixture refluxed for 1 day under a nitrogen atmosphere. The solution changed in color from yellow to red-purple as the reaction proceeded. The solution was cooled and added to an excess (2:1) of water. The solution was filtered and an excess of ammonium hexafluorophosphate was added. A red-purple precipitate was formed and was filtered. The crystals were dissolved in acetone, filtered, and dried. The crystals were washed several times with anhydrous ether and analyzed as $Fe(L)_3(PF_6)_2$. Analysis was by Integral Microanalytical Laboratories, Raleigh, N.C. Anal. Calcd: C, 48.74; H, 4.51; N, 6.32. Found: C, 47.44; H, 4.34; N, 6.47.

Spectroscopy. Ultraviolet and visible spectra were recorded on a Perkin-Elmer 576ST spectrophotometer. Luminescence excitation and emission spectra were recorded on an Hitachi Perkin-Elmer MPF-2A spectrofluorimeter equipped with a red-sensitive Hamamatsu R-446 photomultiplier tube. Conventional flash photolysis experiments were performed as previously described.[3,4]

Quantum-Yield Determinations. Quantum yields were determined by irradiating samples in Pyrex test tubes in a merry-go-round apparatus. The samples were degassed by bubbling with argon for 20 min and sealed. The metal complexes were then irradiated with a Hanovia medium-pressure mercury lamp, using Corning 3-73 filters to remove ultraviolet irradiation. The incident light intensities were measured by using the Reinecke's salt actinometer.

Gas Chromatographic Analyses. The formation of products was monitored by VPC on a Hewlett-Packard 5750 research chromatograph equipped with a 10-ft column packed with 5% SF1265 on Chromosorb G. Chromatographically pure decane was used as an internal standard in quantitative irradiation experiments.

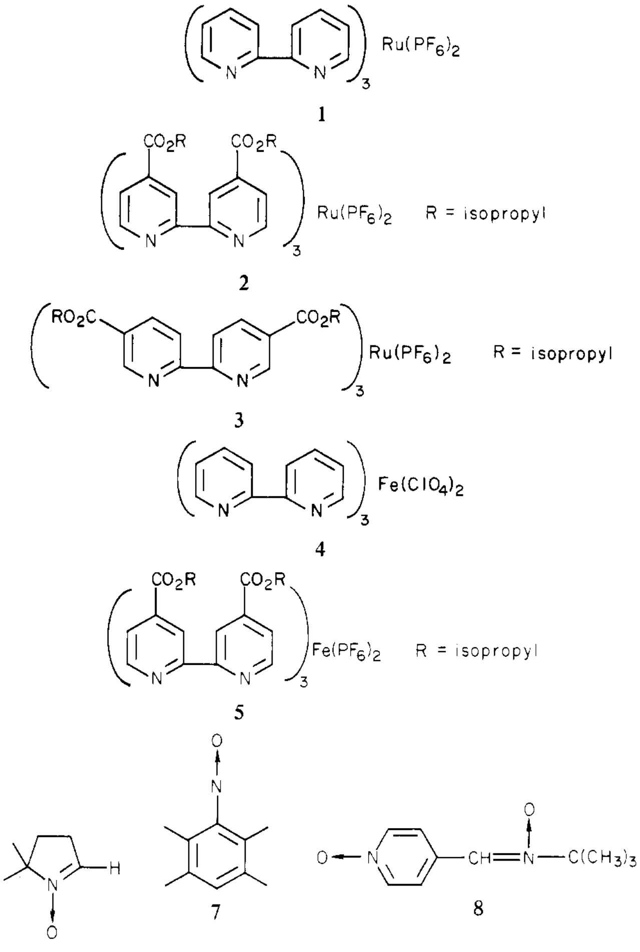
Photochemical-ESR Experiments. The solutions for investigation were placed in a test tube in the dark or diffuse room light and degassed by bubbling with argon for 10–20 min. The solutions were then transferred to a 0.1-mm quartz ESR flat cell and again deoxygenated by a slow stream of argon. The cell was then introduced into an ER-400X-RL cavity of a Bruker ER-420 spectrometer equipped with B-ST 100/700, BHN12, and B16 accessories for variable-temperature control, magnetic field calibration, and frequency measurements, respectively. The samples were irradiated in the cavity with a Hanovia 977 B0090 1000-W mercury–xenon arc lamp in a Model LH 15 1H Schoeffel lamp housing. The light was focused through quartz lenses and filtered through a 15-cm flowing-water filter and a Corning 3-73 glass filter.

Table I. Comparison of Absorption and Emission Spectra and the 2+/1+ Reduction Potential for Modified Polypyridyl Complexes of Iron and Ruthenium

complex	$\lambda_{max,abs}$[a]	$\lambda_{max,em}$[a]	$-E_{1/2}$, V[b]
$Ru(bpy)_3^{2+}$ (**1**)	450	605	1.32
2	468	625	0.90
3	505	670	0.72
$Fe(bpy)_3^{2+}$ (**4**)	522		1.35
5	544		0.92

[a] In acetonitrile. [b] In acetonitrile with 0.1 M TEAP vs. SCE.

Chart I. Structures of Metal Complexes and Spin Traps Used in These Investigations



Results and Discussion

As reported earlier, the hydrophobic ruthenium complexes of the type **2** where the ester groups are incorporated into the 4 and 4′ positions on the bipyridine ligands have absorption and emission spectra similar to those of $Ru(bpy)_3^{2+}$ (**1**) in acetonitrile.[1,18] The absorption maxima are slightly red shifted in comparison but have comparable extinction coefficients. The formal electrochemical potentials of these compounds are shifted more anodic by several hundred millivolts, making them easier to reduce than **1**. A series of analogous complexes, where carboxy ester groups are substituted at the 3 and 3′ positions of the bipyridine ligand, has also been prepared. These complexes exhibit similar changes in spectral and electrochemical properties (Table I). In addition to ruthe-

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nium complexes **1**–**3** we have also studied reductive photoprocesses involving $Fe(bpy)_3^{2+}$ (**4**) and the iron analogue of **2** (**5**). Table I lists values for the absorption and emission maxima for the various complexes together with the $E_{1/2}$ value for the 2+/1+ reduction determined by cyclic voltammetry. Chart I summarizes the structures of the metal complexes and spin traps used in these investigations.

Quenching of the luminescence of **1** concurrent with the transient observations of the one-electron reduction product $Ru(bpy)_3^+$ has been previously observed with several reducing agents including amines such as triphenylamine and *N*,*N*-dimethylaniline.[33,34] In studies with triethylamine and **1** we have found that relatively high (>3.0 M) amine concentrations are necessary to produce near-complete quenching of the luminescence; at these concentrations continuous illumination produces no permanent changes in the UV–visible spectral regions, while flash spectroscopic investigations indicate a transient formation of $Ru(bpy)_3^+$ and a rapid bimolecular back reaction.[35]

The ligand-modified complexes **2** and **3** are easier to reduce (Table I), while their excited-state energies are only slightly lower than that of **1**; consequently it is not surprising to observe that triethylamine quenches the luminescence of **2** and **3** at rates only slightly below diffusion controlled. A similar efficient quenching is also observed when *N*,*N*-dimethylaniline is used as the quencher–reductant. In contrast to the behavior observed when **1** is irradiated in the presence of triethylamine, irradiation of degassed acetonitrile solutions of **2** or **3** in the presence of 0.001–1 M triethylamine leads to "permanent" changes which can be easily followed by electronic or ESR spectroscopic techniques. For both **2** and **3** a bleaching of the original visible absorption of the complex is observed concurrent with the buildup of a new absorption at longer wavelengths of comparable breadth and intensity. In both cases the spectra produced are nearly identical with those obtained when **2** or **3** are reduced electrochemically, indicating that the product detected is the one-electron reduction product, RuL_3^+.[1] Since the parent complexes are diamagnetic, the one-electron reduction products must be paramagnetic and should consequently be detectable by ESR. In fact irradiation of deoxygenated acetonitrile solutions (22 °C) of **2** or **3** in the presence of 0.001–0.3 M triethylamine leads to a readily detectable ESR signal in each case. For solutions containing **2** the ESR spectrum produced consists of a single symmetric peak without hyperfine splitting or satellites with $g_{iso} = 1.9920 \pm 0.0002$, while for **3** a similar spectrum is obtained with $g_{iso} = 1.9979 \pm 0.0002$. The spectra and the *g* values obtained are similar to those for reduced **1**.[36,37] These values are also similar to those obtained for $Na^+Fe(bpy)_3^-$ ($g_{iso} = 2.0031$)[38] and $Fe(bpy)_3^0$ ($g_{iso} = 2.075$).[39] The value for $Fe(bpy)_3^+$ obtained by electrolytic reduction is 1.9954.[40] The low values for the g_{iso} factors in these cases have been attributed to a residence of the free electron in a low-energy π^* orbital associated mostly with the bipyridine ligand.[38-41] A similar assignment for the reduced ruthenium species in the present study appears reasonable; the variation in *g* values with ligand substitution is consistent with residence of the added electron largely in ligand orbitals.

Table II. Quantum Efficiencies for Acetaldehyde Formation in Metal Complex–Triethylamine Photolysis[a]

metal complex	$\phi_{acetaldehyde}$[b]	metal complex	$\phi_{acetaldehyde}$[b]
1	0.06	4	trace
2	0.11 ± 0.01	5	0.03 ± 0.01
3	0.09 ± 0.02		

[a] 0.3 M triethylamine, ca. 10^{-4} M complex, 10% water in acetonitrile. [b] Solutions deaerated with argon, irradiated with 436- and 546-nm lines of a 450-W mercury lamp. Reinecke's salt actinometry.

Table III. Radicals Obtained from Metal Complex–Amine Photoreactions by Use of Spin Traps

complex	amine	spin trap	properties of trapped radical
1	triethylamine	7	$a_N = 12.79$ G
2	triethylamine	7	$\alpha_\beta{}^N = 2.99$ G $\alpha_\beta{}^H = 6.16$ G $g = 2.0057 \pm 0.0002$
2	triethylamine	8	6-line spectrum $a_N = 14.83$ G $a_\beta{}^H = 1.83$ G $g = 2.0060 \pm 0.0003$
5	triethylamine	6	6-line spectrum

Since the initial quenching–electron transfer step (eq 1 and 5)

$$RuL_3^{2+*} + :NR_3 \rightarrow RuL_3^+ + \cdot NR_3^+ \qquad (5)$$

must involve generation of two paramagnetic species, the observation of only the single RuL_3^+ radical when triethylamine or *N*,*N*-dimethylaniline are used as quenchers with **2** or **3** indicates that the amine radical cation $\cdot NR_3^+$ must be reacting in subsequent steps to give nonradical products in competition with the energy-wasting back reaction (eq 2). It is expected that radical cations such as that derived from oxidation of triethylamine should be extremely reactive; reasonable paths for reaction can be initiated by hydrogen-atom abstraction from solvent (eq 6) or proton donation to a second molecule of triethylamine (eq 7).[23,42-44] Disproportionation of the radical cation (eq 8) would be possible but probably unlikely at the relatively low light intensities used in most of these studies.

$$\cdot NEt_3^+ + CH_3CN \rightarrow HN^+Et_3 + \cdot CH_2CN \qquad (6)$$

$$\cdot NE_3^+ + :NEt_3 \rightarrow CH_3\dot{C}HNEt_2 + HN^+Et_3 \qquad (7)$$

$$2\cdot NEt_3^+ \rightarrow CH_3CH{=}N^+Et_2 + HN^+Et_3 \qquad (8)$$

$$2\cdot CH_2CN \rightarrow NCH_2CCH_2CN \qquad (9)$$

$$\cdot CH_2CN + :NEt_3 \rightarrow CH_3\dot{C}HNEt_2 + CH_3CN \qquad (10)$$

$$2CH_3\dot{C}HNEt_2 \rightarrow CH_2{=}CHNEt_2 + Et_3N \qquad (11)$$

$$CH_3\dot{C}HNEt_2 + RuL_3^{2+} \rightarrow CH_3CH{=}N^+Et_2 + RuL_3^+ \qquad (12)$$

$$CH_3CH{=}N^+Et_2 + H_2O \rightarrow CH_3CHO + HNEt_2 \qquad (13)$$

$$CH_2{=}CHNEt_2 + H_2O \rightarrow CH_3CHO + HNEt_2 \qquad (14)$$

$$2CH_3\dot{C}HNEt_2 \rightarrow Et_2NCH(CH_3)CH(CH_3)NEt_2 \qquad (15)$$

Subsequent reactions of the radicals formed in eq 6 and 7 could include those given in eq 9–14. All of these reactions have analogy in other reactions involving photochemical and thermal oxidation of amines (vide infra).[45-47]

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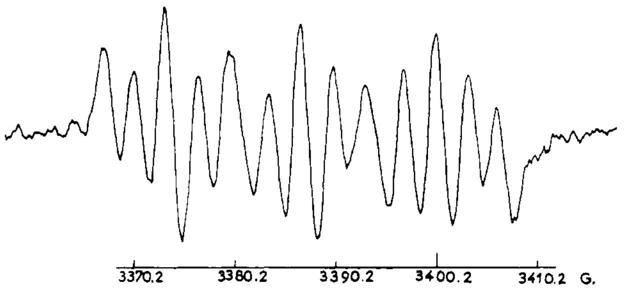
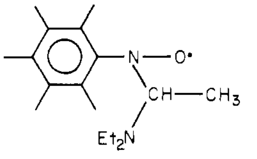


Figure 1. ESR spectrum of the photolysis of acetonitrile solution of **2** at 298 K with nitrosodurene as a spin trap: modulation amplitude 14, microwave power 62.5 mW, microwave frequency 9514 mHz, receiver gain 4 × 10^5.

Products produced from the amine radical cation generated in eq 5 were determined by irradiating complexes **1–5** for prolonged periods in the presence of 1–10% added water. Under these conditions the reduced ruthenium complex from **2** and **3** is rapidly oxidized such that a continuous photolysis is permitted.[1,48,49] Analysis of these irradiated solutions by gas chromatography indicated the presence of a very small amount of material from irradiated **2** having retention time comparable to that of succinonitrile; however, for all complexes the major product detectable by VPC was acetaldehyde, which is readily generated by hydrolysis (eq 13 and 14) of the imine or enamine formed in eq 8, 11, and 12.[45] Quantum yields for the formation of acetaldehyde under these conditions are listed in Table II. The production of acetaldehyde as a major product in the photolysis thus suggests the occurrence of reactions 11 and/or 12 as major routes for reaction of the amine radical cation formed in the initial quenching step.

Further support for steps 5, 7, and 11 (or possibly 10) as the major path for the amine-induced photoreduction comes from a study of the reaction in the presence of spin traps (**6–8**) (Table III). Thus for **2** irradiation in deoxygenated acetonitrile solution in the presence of triethylamine and the spin trap nitrosodurene (**7**) leads to a species having an ESR spectrum (Figure 1) consistent with the structure **9** in which both the nitrogen and the C–H induce hyperfine splitting. Irradiation of the same substrate–quencher combination in the presence of the trap **8** also leads to a stable trapped radical whose hyperfine splitting pattern is consistent with addition of the radical produced in eq 7 to the trap. As reported earlier, irradiation of **2** in the presence of *N*,*N*-dimethylaniline leads to reduction of the metal complex;[1] however, in this case there are side reactions which render the process irreversible and nonrecyclable. Nonetheless, irradiation of **2** and *N*,*N*-dimethylaniline in the presence of **8** leads to a trapped radical having *g* value and hyperfine splitting consistent with generation of the alkyl radical **10** in the photolysis in a reaction analogous to eq 7; the same radical has also been trapped in the reductive photoaddition of DMA to palladium porphyrins.[50] In the experiment with **2** in which the spin traps were added the reduced complexes RuL_3^+ could still be detected by ESR (with unaltered *g* values), indicating that the spin traps neither alter the course of the primary process nor interact with the reduced metal complex. The failure to trap the amine radical cation with the spin traps is not surprising due to its presumed high reactivity toward hydrogen-atom abstraction; there is little evidence to suggest that such radicals can be trapped with conventional trapping reagents. Although a precise determination of the quantum yield of radicals trapped in these experiments was not possible, a comparison of the integrated spin density obtained in these studies with those in which known yields are generated indicates the efficiency of trapped radicals to be $\phi \sim 0.1$, indicating that the radicals trapped are major intermediates in the reaction sequence.



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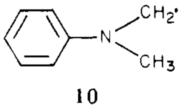

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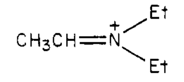
Both the product studies with **1–5** and the spin trapping results with **2** and **5** point to the intermediacy of radical **11** and imine **12** in the photoreaction; not surprisingly, the same type of intermediates have been indicated or suggested as being involved in other photoreductions involving amines.[45–47] That **11** should be able to reduce a second metal complex in a dark process (eq 12) appears reasonable in view of estimates that the potential for the oxidation, $E_{1/2}(\mathbf{11}/\mathbf{12})$, should be ca. 1.0 V.[43,51] This predicts, in analogy with the photoreduction of ketones by amines,[43] that the limiting quantum yield for reduction of RuL_3^{2+} should be 2; although we have studied reaction of **2** in a variety of solvent systems, the highest value obtained thus far is obtained in dry acetonitrile, where $\phi = 0.35$. The quantum yield for production of acetaldehyde should have a limiting value of 1 (or lower depending on the importance of steps such as 8, 11, and 15) according to the overall reaction

$CH_3\dot{C}HNEt_2$

11



$CH_3CH{=}\overset{+}{N}Et_2$

12

$$RuL_3^{2+*} + 2Et_3N + RuL_3^{2+} \rightarrow 2RuL_3^+ + HN^+Et_3 + CH_3CH{=}N^+Et_2 \quad (16)$$

$$CH_3CH{=}N^+Et_2 + H_2O \rightarrow CH_3CHO + H_2N^+Et_2 \quad (17)$$

However, values obtained for all complexes studied thus far are substantially lower and probably reflect inefficiencies in the dark reaction (eq 17) under the photolysis conditions as well as the occurrence of other reactions involving **11**. The lower than limiting values obtained for reduction of **2** and **3** probably reflect inefficiency in the initial electron-transfer step; other studies have suggested that quenching of similar ruthenium(II) complexes by net electron transfer to form separated ions occurs with a net efficiency in the range 0.1–0.3.[52] However, in at least one case a quenching of **1** by Fe^{3+} in aqueous solution has been indicated to occur with an efficiency near unity.[53]

While identification of the reduced metal complex as a permanent product has been established only with the ruthenium complexes **2** and **3**, it is interesting to note that both the parent ruthenium complex **1** and the hydrophobic iron complex **5** show evidence through the spin traps and acetaldehyde formation of participating in photoreactions giving net chemical change. For **1** this is not particularly surprising since flash-photolysis studies (vide supra) indicate that reaction 5 occurs but is followed by back electron transfer in dry acetonitrile.[35] The trapping of radical **11** with nitrosodurene indicates that there is some reaction via eq 7 even though no permanent products from the reduced complex RuL_3^+ are detected in dry acetonitrile. This could reflect a relatively low "leakage" to permanent products in the case of **1** or a different sequence beyond reaction 10. Since acetaldehyde is formed with an efficiency only moderately lower than for **2** and **3** where the buildup of RuL_3^+ is observed, it appears reasonable that relatively efficient reaction through eq 10 occurs but that

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(48) Under these conditions no quenching of the luminescence of **2** or **3** by water occurs so it can be assumed that the primary photoreaction (eq 5) remains the same.

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reaction 12 proceeds with difficulty or not at all in anhydrous media. This appears reasonable in view of the fact that it is more difficult to reduce **1** than **2** or **3** by some 400-600 mV. Thus, in anhydrous media radical **11** could participate in a net back electron transfer process

$$RuL_3^+ + Et_3NH^+ + CH_3\dot{C}HNEt_2 \rightarrow RuL_3^{2+} + 2Et_3N \quad (18)$$

in which it functions as an oxidizing agent. In aqueous solution it has been found that reduced **1** and **2** can react with water in net redox processes[49] and the present results may indicate that a scavenging of the reduced **1** in competition with back electron transfer results in net chemistry via reactions 7, 8, and 17 in this case as well. Here, rapid reaction of **12** with water may divert the net reaction via reactions 16 and 17. Alternatively, **11** may participate in water reduction in aqueous media[43,49,51] (vide supra).

The observation of analogous products for the iron complex **5** is perhaps of even greater interest since **4** and **5** have relatively short-lived nonluminescent excited states. However, although no luminescence has been detected for **4** or **5**, indirect studies have suggested that the excited-state lifetime of **4** in solution is sufficiently long (1-23 ns)[54,55] to permit its participation in bimolecular reactions in solution. In recent investigations we have found that **4** and **5** participate in oxidative photoreactions analogous to their ruthenium(II) counterparts.[56] When solutions of **4** and **5** are irradiated in the presence of triethylamine and in dry acetonitrile, there is no direct evidence for buildup of a reduced FeL_3^+ species; however, the finding that irradiation of **5** in the presence of triethylamine results both in the trapping of radical **11** and in generation of acetaldehyde indicates that the same net photochemistry must be occurring with the iron as for the ruthenium complexes. However, studies with the simple bipyridine derivative **4** led to no detectable trapped radicals and to very low yields of acetaldehyde. In this case there is evidently insufficient generation of amine radical cation to permit the formation of a trappable concentration of **11**. The relatively small differences in efficiency of acetaldehyde formation between the corresponding iron and ruthenium complexes (**5** and **2**, respectively) suggest that analogous reactions such as water reduction[49] should be observable for a number of related metal complexes.

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Intramolecular Proton Transfer and Excited-State Relaxation in 2-(2-Hydroxyphenyl)benzothiazole

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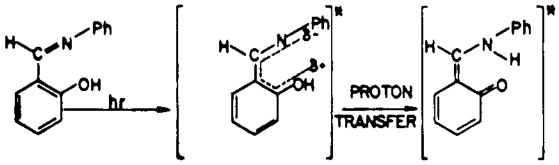
Abstract: The excited state vibrational and conformational relaxation of 2-(2-hydroxyphenyl)benzothiazole in solution has been studied as a function of temperature by means of picosecond spectroscopy, using a streak camera with <5-ps resolution. Three distinct relaxation processes were identified: (a) intramolecular proton transfer producing a cis-keto tautomer occurring within 5 ps from $T = 4$ to 300 K; (b) vibrational energy redistribution and/or relaxation into the medium at a rate of 10^{11} s^{-1} at 4 K and increasing rapidly with temperature; (c) radiationless decay (10^2-10^3 ps) induced by large amplitude torsional motion in solution at $T > 200$ K.

Introduction

Recently we have investigated the picosecond kinetics of intramolecular proton transfer in the lowest $^1\pi-\pi^*$ state of salicylidenaniline (SA).[1] The enol form of this molecule was found to tautomerize (eq 1) into a cis-keto form with a rate of $k \geq 2 \times 10^{11}$ s^{-1} following Franck-Condon excitation at 355 nm. The time-resolved fluorescence emitted from the cis-keto product was monitored by a streak camera with <5-ps resolution. We have shown that this molecule tautomerizes within 5 ps at temperatures above 4 K in both protic and aprotic solvents. We also observed that the kinetics were unchanged when the phenolic proton was deuterated. The fluorescence of the cis-keto form was found to be biexponential at 4 K. A variety of experiments led us to conclude that the excited cis-keto conformer must undergo vibrational or conformational relaxation on the ~10-ps time scale. This is a novel observation because energy decay from vibrational levels of large molecules is normally thought to be a much faster process.

Equation 1 shows that SA may undergo several different torsional motions. Torsional relaxation naturally occurs on the picosecond and longer time scales in fluid environments, and might possibly influence the decay rates even in frozen solutions. Torsional relaxation in SA is complicated owing to the existence of at least three different torsional normal modes: two rotations about different C-N single bonds and rotation about the C_1-C_7 bond. We have now investigated the decay kinetices of a similar molecule, 2-(2-hydroxyphenyl)benzothiazole (HBT), which has only the C_1-C_7 torsional degree of freedom shown in Scheme I.



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