Notes

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Flash Photolysis of a Photoactive Ruthenium Complex Mixture

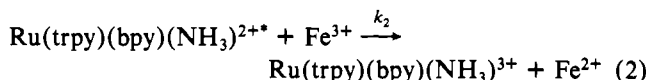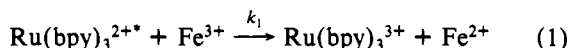Jeffrey K. Nagle*[1a] and Thomas J. Meyer[1b]

Homogeneous photoredox systems require the presence of at least one light-absorbing species capable of undergoing an excited-state reaction. Most systems studied so far have involved a single photoactive species. Perhaps the most thoroughly investigated example is $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine).

A drawback to these systems is that only a small portion of the solar spectrum is utilized. If more than one photoactive species were present, a broader range of light energy could be absorbed and transformed into chemical energy. Recently, two approaches related to this problem have been reported. The first system involves a mixture of $Ru(bpy)_3^{2+}$ and UO_2^{2+}, in which cross-quenching of the excited states by the ground states is known to occur.[2] Both quenching reactions lead to the same redox products, and the net effect is an enhanced absorption of light relative to a solution containing only one photoactive species. The second system uses a mixture of $Ru(bpy)_3^{2+}$ and 9-anthracenecarboxylate (AA^-) and leads to the sole production of the triplet excited state of 9-anthracenecarboxylate ($^TAA^-$) by both direct light excitation and the quenching of $Ru(bpy)_3^{2+*}$ by AA^-. This is followed by reaction of $^TAA^-$ with methylviologen (MV^{2+}) to give $AA\cdot$ and $MV^+\cdot$.[3]

An alternative approach illustrated here is to use a mixture of two excited states that does not result in cross-quenching. In this case both excited states are quenched in electron-transfer reactions by a single, nonabsorbing quencher. The sequence of reactions that follows the quenching steps can readily be studied by simple flash photolysis techniques. In this note such an experiment is described, which involves $Ru(bpy)_3^{2+}$ and $Ru(trpy)(bpy)(NH_3)^{2+}$ (trpy is 2,2',2''-terpyridine) as photoactive species and Fe^{3+} as quencher.

Both $Ru(bpy)_3^{2+}$ and $Ru(trpy)(bpy)(NH_3)^{2+}$ emit light in aqueous 1.0 M $HClO_4$ (τ = 0.62 and 0.43 μs, respectively)[4] and both are quenched by Fe^{3+} at nearly diffusion-controlled rates.[4,5] Therefore, upon flash photolysis of an aqueous solution containing $Ru(bpy)_3^{2+}$, $Ru(trpy)(bpy)(NH_3)^{2+}$, and Fe^{3+}, the following reactions are expected to occur:

$$Ru(bpy)_3^{2+*} + Fe^{3+} \xrightarrow{k_1} Ru(bpy)_3^{3+} + Fe^{2+} \quad (1)$$

$$Ru(trpy)(bpy)(NH_3)^{2+*} + Fe^{3+} \xrightarrow{k_2}$$
$$Ru(trpy)(bpy)(NH_3)^{3+} + Fe^{2+} \quad (2)$$

where $k_1 = 2.8 \times 10^9$ M^{-1} s^{-1}[5] and $k_2 = 3.1 \times 10^9$ M^{-1} s^{-1}.[4] Since the formal potentials for the redox couples $Ru(bpy)_3^{3+/2+}$ and $Ru(trpy)(bpy)NH_3^{3+/2+}$ are 1.30 V[6] and 1.08 V[7] (NHE, 1.0 M $HClO_4$) respectively, the equilibrium

$$Ru(bpy)_3^{3+} + Ru(trpy)(bpy)NH_3^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}}$$
$$Ru(bpy)_3^{2+} + Ru(trpy)(bpy)(NH_3)^{3+} \quad (3)$$
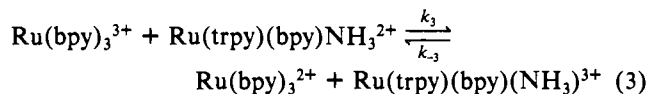
favors the formation of $Ru(trpy)(bpy)(NH_3)^{3+}$ ($K = 1.7 \times 10^4$) immediately following the electron-transfer quenching reactions (eq 1 and 2).

This approach is an extension of that used previously in which mixtures of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ were photolyzed in the presence of Fe^{3+} as quencher.[8]

Experimental Section

$[Ru(trpy)(bpy)(NH_3)](ClO_4)_2$ was obtained from Dr. T. R. Weaver. $[Ru(bpy)_3](ClO_4)_2$ was prepared as described previously.[9] $Fe(ClO_4)_3 \cdot 6H_2O$ (G. F. Smith Co.) was used as received, and $Fe(ClO_4)_2 \cdot 6H_2O$ (Alfa) was recrystallized from aqueous $HClO_4$. Water was deionized and distilled twice from $KMnO_4$.

All solutions were 1.0 M in $HClO_4$. The concentrations of $Ru(bpy)_3^{2+}$, $Ru(trpy)(bpy)(NH_3)^{2+}$, and Fe^{3+} were determined spectrophotometrically by using molar absorptivities of 1.39×10^4 M^{-1} cm^{-1} (450 nm), 9.55×10^3 M^{-1} cm^{-1} (480 nm), and 4.16×10^3 M^{-1} cm^{-1} (240 nm),[10] respectively. The concentration of Fe^{2+} was determined spectrophotometrically from an aliquot as the $Fe(phen)_3^{2+}$ complex with a maximum absorbance at 510 nm ($\epsilon = 1.11 \times 10^4$ M^{-1} cm^{-1}).

Flash photolysis experiments were performed by using an apparatus described previously.[8,11,12] A cell of 12-cm path length containing N_2-degassed solutions was used in all cases. Corning 3-73 UV filters limited the photolysis light to the visible region.

Kinetic analysis of the flash photolysis data was accomplished by using the standard expression for a second-order reaction involving unequal initial concentrations[13]

$$\frac{1}{a-b} \ln \left[\frac{b(a-x)}{a(b-x)} \right] = kt \quad (4)$$

which is rearranged to give, in terms of the extent of reaction x

$$x = a[1 - e^{(a-b)kt}]/[1 - (a/b)e^{(a-b)kt}] \quad (5)$$

(a and b represent the initial concentrations of the reactants). This is combined with the equation relating the absorbance changes (ΔA) to the extent of reaction

$$x = (\Delta A/l(\Delta\epsilon)) + b \quad (6)$$

(l = cell path length, cm; $\Delta\epsilon = \epsilon_{A^+} - \epsilon_A + \epsilon_B - \epsilon_{B^+}$ where ϵ_{A^+}, ϵ_A, ϵ_B,

(1) (a) Bowdoin College. (b) The University of North Carolina.
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Table I. Concentrations of Species Present at Various Times following Flash Photolysis of a Mixture of $Ru(bpy)_3{}^{2+}$, $Ru(trpy)(bpy)(NH_3)^{2+}$, Fe^{3+}, and Fe^{2+} and Molar Absorptivities at the Two Wavelengths Monitored

	concn × 10⁶, M				$10^{-3}\epsilon$, M⁻¹ cm⁻¹	
	$t = 0$ s	$t = 80$ μs	$t = 1$ ms	$t = 1$ s	450 nm	480 nm
$Ru(trpy)(bpy)(NH_3)^{2+}$	3.48	2.46	1.60	3.48	8.1	9.55
$Ru(trpy)(bpy)(NH_3)^{3+}$	0.00	1.02	1.88	0.00	1.69	0.15
$Ru(bpy)_3{}^{2+}$	5.64	4.78	5.64	5.64	13.9	5.39
$Ru(bpy)_3{}^{3+}$	0.00	0.86	0.00	0.00	0.45	0.14
Fe^{2+}	52.5	54.4	54.4	52.5	0.0	0.0
Fe^{3+}	4200	4200	4200	4200	0.0	0.0

and ϵ_{B^+} represent the molar absorptivities of the relevant reactants and products in eq 3 and 9) to give

$$\Delta A = l(\Delta\epsilon)(a - b)/[1 - (a/b)e^{(a-b)kt}] = -\log(1 + \Delta I/I_0) \quad (7)$$

This rearranges finally to give

$$\Delta I = I_0 e^{2.303l(\Delta\epsilon)(a-b)/[(a/b)e^{(a-b)kt}-1]} - I_0 \quad (8)$$

Since values of l, $\Delta\epsilon$, I_0, and $a - b$ are independently determined, the nonlinear least-squares data analysis involves a two-parameter fit to yield values of a/b and k.

All reported uncertainties in the kinetic results represent the standard deviations obtained from the nonlinear least-squares data analyses.

Results

In order to produce nearly equal concentrations of Ru-$(bpy)_3{}^{3+}$ and $Ru(trpy)(bpy)NH_3)^{3+}$ (eq 1 and 2) and to provide an excess of Fe^{2+} (eq 9), a 1.0 M $HClO_4$ solution con-

$$Ru(trpy)(bpy)(NH_3)^{3+} + Fe^{2+} \xrightarrow{k_b}$$
$$Ru(trpy)(bpy)(NH_3)^{2+} + Fe^{3+} \quad (9)$$
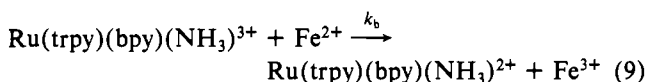
taining 5.64 × 10⁻⁶ M $Ru(bpy)_3{}^{2+}$, 3.48 × 10⁻⁶ M Ru-$(trpy)(bpy)(NH_3)^{2+}$, 4.2 × 10⁻³ M Fe^{3+}, and 5.25 × 10⁻⁵ M Fe^{2+} was investigated by flash photolysis in the visible region. At the absorption maxima for both $Ru(bpy)_3{}^{2+}$ (450 nm) and $Ru(trpy)(bpy)(NH_3)^{2+}$ (480 nm), rapid (100 μs/division) transient intensity changes followed by slower ones (100 ms/division) were observed (Figure 1). Immediately following the flash, a decrease in the absorbance was observed at both 450 nm and 480 nm (Figure 1a,b). This is accounted for by eq 1 and 2 in which $Ru(bpy)_3{}^{2+*}$ and $Ru(trpy)(bpy)(NH_3)^{2+*}$ are both oxidized by Fe^{3+}. As predicted by eq 3, at 480 nm on the microsecond time scale the absorbance continued to decrease (Figure 1a), while at 450 nm the absorbance increased slightly (Figure 1b). This increase did not completely restore the absorbance to the original value (before photolysis) because $Ru(trpy)(bpy)(NH_3)^{2+}$ also significantly absorbs at this wavelength ($\epsilon = 8.1 \times 10^3$ M⁻¹ cm⁻¹). Analysis of the kinetic data according to eq 8 yields values for k_3 of (2.58 ± 0.11) × 10⁹ M⁻¹ s⁻¹ at 450 nm and 2.82 ± 0.08) × 10⁹ M⁻¹ s⁻¹ at 480 nm. The rate constant for this intervening reaction is nearly diffusion controlled[8] as expected on the basis of the rapid self-exchange rates of the reactants[18] and the large thermodynamic driving force for the reaction ($\Delta E^{\circ\prime} = 0.22$ V[6,7]).

Since the sequence of events given above results in the net production of $Ru(trpy)(bpy)(NH_3)^{3+}$ and Fe^{2+}, it is logical that the back-reaction shown in eq 9, for which $\Delta E^{\circ\prime} = 1.82$ V,[7,14] should correspond to the slow, millisecond absorbance changes at 450 and 480 nm (Figure 1c,d). Values for k_b of (3.11 ± 0.03) × 10⁴ M⁻¹ s⁻¹ at 450 nm and (3.12 ± 0.04) × 10⁴ M⁻¹ s⁻¹ at 480 nm are obtained from an analysis of the data according to eq 8. These are in excellent agreement with the values of (3.13 ± 0.21) × 10⁴ M⁻¹ s⁻¹ [15] and (3.0 ± 0.2) × 10⁴ M⁻¹ s⁻¹ [16] obtained by stopped-flow experiments under similar conditions.

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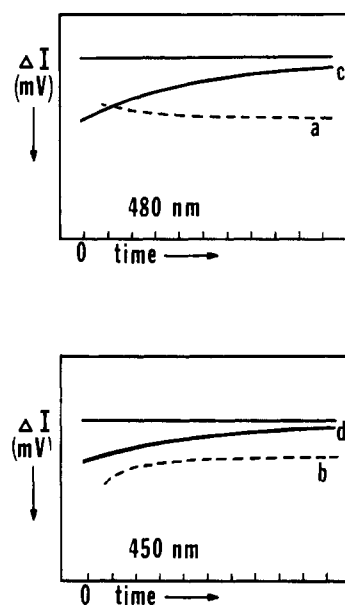
Figure 1. Light intensity changes at 480 nm (a, c) and 450 nm (b, d) following visible flash photolysis of a 1.0 M $HClO_4$ solution containing $Ru(bpy)_3{}^{2+}$, $Ru(trpy)(bpy)(NH_3)^{2+}$, Fe^{3+}, and Fe^{2+}. The dashed lines represent intensity changes on the 100 μs/division time scale (a, b) and the solid lines represent intensity changes on the 100 ms/division time scale (c, d). These tracings of photographs of the actual oscilloscope displays give an indication of the signal-to-noise ratios obtained. No useful data prior to 80 μs were obtained owing to interference from the flash pulse.

Evidence that the slow absorbance decay at 450 nm is due to eq 9 and does not involve $Ru(bpy)_3{}^{3+}$ comes from the kinetic data. The reaction between $Ru(bpy)_3{}^{3+}$ and Fe^{2+} is known to proceed with a rate constant of 6.5 × 10⁵ M⁻¹ s⁻¹,[5,17] 20 times greater than the rate constant observed here. This is presumably a reflection of the faster self-exchange rate for $Ru(bpy)_3{}^{3+/2+}$ compared to that of $Ru(trpy)(bpy)-(NH_3)^{3+/2+}$.[18] Furthermore, an analysis of the absorbance changes at 1 ms combined with known molar absorptivities for the various species is not consistent with a reaction involving $Ru(bpy)_3{}^{3+}$.

By measuring absorbance changes at both wavelengths at 80 μs and 1 ms and combining these with known molar absorptivities and the values of a/b obtained from the kinetic data, we have calculated values for the concentrations of all species at these times following photolysis, which are listed in Table I. Note that the net efficiency of converting both $Ru(bpy)_3{}^{2+}$ and $Ru(trpy)(bpy)(NH_3)^{2+}$ into $Ru(trpy)-(bpy)(NH_3)^{3+}$ (light excitation followed by eq 1–3) is 21%.

Discussion

The most notable feature of these results is that *both* metal complex excited states are used to produce $Ru(trpy)(bpy)-(NH_3)^{3+}$ as the sole oxidation product of the quenching reactions (eq 1 and 2 followed by eq 3). In addition, the possibility of observing and measuring rate constants for different types of rapid redox reactions in a simple flash photolysis experiment is well demonstrated. In contrast, a stopped-flow

experiment of this same mixture would provide evidence for the back-reaction only (eq 9) and could not reveal the actual sequence of events leading to this final step. A variety of redox products can be produced by electron-transfer quenching of more than one excited-state molecule. Judicious adjustment of the concentrations of photosensitizers and quenchers can be used to vary the relative amounts of these redox products.

Note the distinction between the system described here using a nonabsorbing quencher (Fe^{3+}) and those described previously in which quenching occurs via the ground state of a photoactive partner.[1-3] In the present case, the rapid intervening reaction (eq 3) results in the exclusive production of only two redox products, $Ru(trpy)(bpy)(NH_3)^{3+}$ and Fe^{2+}, which undergo a relatively slow back-reaction (eq 9).

The important point to be made is that the oxidized photoactive species with the lower reduction potential is produced in the intervening reaction (eq 3). Therefore, in the design of light energy conversion schemes based on this approach, the reduction potentials of *all* photoactive species should be large enough to produce the desired reaction. Regardless of the details of the reactions, a common feature of all the schemes involving photoactive mixtures described so far is the production of only two redox products. (An exception to this statement is the special case of the $Ru(bpy)_3^{2+}/Ru(phen)_3^{2+}$ mixture,[8] in which both photosensitizers have the same reduction potential (1.30 V) for the $RuL_3^{3+/2+}$ couple).

There has been a report in which a mixture of three photoactive species was used.[19] In that case MV^{2+} was photoreduced by a mixture of tris(4,7-dimethyl-1,10-phenanthroline)ruthenium(II), (tetraphenylporporphyrinato)zinc(II), and hematoporphyrin. Assuming only MV^{2+} quenching of the excited states and hematoporphyrin to be the most easily oxidized of the three photoactive species, the net redox products should be MV^+· and oxidized hematoporphyrin.[20] A flash photolysis experiment of the type described here would enable this prediction to be tested.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(trpy)(bpy)(NH_3)^{2+}$, 58452-44-1.

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Contribution from the Department of Chemistry,
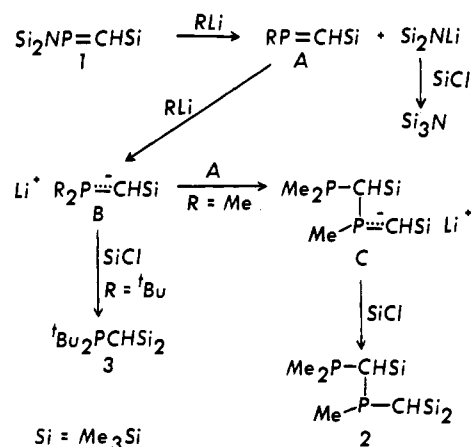Texas Christian University, Fort Worth, Texas 76129

Substitution and Addition Reactions of a Methylenephosphine with Alkyllithium Reagents

Bei-Li Li and Robert H. Neilson*

Many recent reports have dealt with the preparative chemistry of methylenephosphines $RP{=}CR'_2$ as well as their structural and bonding characteristics.[1] Moreover, some relatively clear and consistent patterns of reactivity of such compounds are now emerging. The types of reactions of methylenephosphines reported thus far include: (1) addition

(1) For a general review, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731.

Scheme I

of polar electrophilic reagents to the P=C bond;[2] (2) oxidation to 3-coordinate P(V) derivatives;[3] (3) complexation of transition metals to the phosphorus lone pair or to the P=C π bond;[4] (4) various cycloaddition processes such as Diels–Alder reactions.[5] In another general mode of reactivity, we find that these coordinatively unsaturated phosphorus compounds will also react smoothly with nucleophiles.[6] We report here some novel examples involving both substitution and addition reactions of a bis[(trimethylsilyl)amino]-substituted methylenephosphine with alkyllithium reagents.

Treatment of [bis(trimethylsilyl)amino][(trimethylsilyl)methylene]phosphine[2c] (**1**) in Et_2O at -78 °C with MeLi, followed by quenching with Me_3SiCl, does not yield the expected[7] phosphine $(Me_3Si)_2NP(Me)CH(SiMe_3)_2$. Instead, the reaction takes a much more complicated course, forming the novel bis(phosphino)methane derivative **2** (eq 1). The product
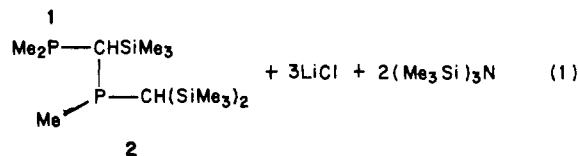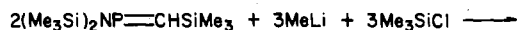
2 is isolated as a colorless liquid in 88% yield by fractional

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