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Energy Transfer from Luminescent Transition Metal Complexes to Oxygen

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Abstract: A study of the O_2 quenching of 16 luminescent diimine complexes of Ru(II), Os(II), and Ir(III) is reported. Decay times, bimolecular quenching constants, and sensitized photooxidation yields are presented. With the charge-transfer (CT) excited states of the Ru(II) and Os(II) species, singlet O_2 ($^1O_2$) is formed with efficiencies of 0.68–0.85 per quenching encounter. $^1O_2$ formation is attributed to simple energy transfer, but a chemical generation by electron transfer processes cannot be ruled out. Possible sources of the subunity yields are discussed. The π-π^* triplet states of the Ir(III) complexes appear to produce $^1O_2$ with high efficiency, but photochemistry of the complexes prevents an unambiguous interpretation. Quantitative photooxygenation studies are shown to be a powerful tool for evaluating the spectroscopic and sensitization properties of metal complex sensitizers. Solvation effects appear important in varying the bimolecular quenching constants. Two of the complexes have longer fluid solution lifetimes (>5 μs) than the widely used luminescent sensitizer tris(2,2′-bipyridine)ruthenium(II) ion has in a rigid glass at 77 K.

Although the subject of O_2 quenching of excited states of organic molecules has been studied extensively,[1-4] relatively little is known concerning the interactions of excited inorganic complexes and O_2. The ligand field doublet states of Cr(III) complexes are quenched by O_2, presumably by energy transfer,[5] and some Co(II) and Ni(II) complexes are good $^1O_2$ quenchers.[6] We have reported earlier that the charge-transfer (CT) excited states of Ru(II) and Os(II) complexes and the ligand localized $^3(\pi$-$\pi^*)$ states of Ir(III) complexes transfer energy to O_2 with high efficiency.[7,8]

Studies on O_2 quenching of luminescent metal complexes provide useful fundamental information about the excited states of metal complexes. Further, these studies also provide a simple method of evaluating new luminescent inorganic photosensitizers which are proving particularly useful in mechanistic inorganic and organic photochemistry as well as showing great promise in solar energy conversion.[9-16]

We report here details and an expansion of our earlier work as well as the first quantitative study of the efficiencies and mechanisms of energy transfer between metal complexes and O_2. Also six previously unreported and potentially very useful luminescent Ru(II) photosensitizers are presented.

Experimental Section

The complexes studied and their abbreviations are given in Table I. The preparations of the $[Ir(bpy)_3]^{3+}$ and $Ru(bpy)_2(CN)_2$ have been given elsewhere.[17,18] The $[Ru(bpy)_3]Cl_2$ was from G. Frederick Smith and was used either directly or after recrystallization from water; both samples were equivalent. The syntheses of the other complexes will be given elsewhere.[19,20] The rose bengal from Fischer and the tetramethylethylene (TME), trimethylethylene, and thiourea (TU) from Aldrich were used without further purification.

The experimental apparatus, absolute bolometer, and procedures for the measurement of absolute O_2 uptake yields and for the intensity quenching studies are given elsewhere.[21-23] For the Ru(II) and Os(II) complexes the irradiation source was usually the 488-nm laser line (~0.5 W) from a Coherent Radiation CR5 ionized Ar laser. For $[Ir(bpy)_3]^{3+}$ and $[Ir(phen)_3]^{3+}$, a Coherent Radiation CR2 ionized Kr laser with UV optics was used at 350.7 and 356.4 nm (~0.1 W). For the photooxygenations using trimethylethylene, a pair of 500-W projection lamps was usually used with the Os(II) complexes, while the lasers were used with the Ru(II) and Ir(III) species. Decay times, τ's, were measured using a 1-kW pulsed N_2 laser system.[24]

All photooxidations were in absolute methanol. With TME and trimethylethylene, the initial concentration of olefin was ~0.12 M. With thiourea, the concentration was varied over the range 0.06–0.6 M. Generally, 5–25 μmol of sensitizer in 100–150 mL of solution was used and uptakes were usually ≥1 mmol.

The analysis of the reaction products for the photooxygenations of the trimethylethylene was as follows. After photooxygenation (carried out to ~50–75% completion), excess $NaBH_4$ was added and the solution was allowed to stand for ~0.5 h at room temperature to reduce the two hydroperoxides to alcohols. The products after addition of water were extracted into ether. The ether layer was dried over a molecular sieve (4-Å pore) and analyzed by gas chromatography on a Varian Aerograph A 90-P3 equipped with a 12 ft 20% Carbowax 20 M column operated at 150 °C. The two product peaks overlapped somewhat with each other and with the solvent tail, which precluded using the integrator for comparing ratio of products. Further, peak shape was dependent on sample size. We were, however, only interested in showing that the product distribution was the same as for $^1O_2$ oxidation, and the following procedure was adopted. It was found that for the rose bengal sensitized photooxidation of trimethylethylene using different runs and sample sizes that a smooth reproducible curve was obtained if the interpolated solvent baseline was first subtracted and the ratio of second to first peak heights was plotted vs. the first peak height. The ratio varied from ~1 to 2. Since rose bengal is a clean, efficient $^1O_2$ generator,[1,3] this curve represented the standard against which the complexes were compared.

Table I. Photosensitizers and Photooxygenation Characteristics

Complex[a]	τ_0,[b] μs	K_{sv},[b] M^{-1}	$k_2 \times 10^{-9}$,[c] $M^{-1}\ s^{-1}$	ϕ_0,[d] TME
$[Ru(bpy)_3]^{2+}$	0.765[e]	1 400[f]	1.8	0.855[f]
$[Ru(phen)_3]^{2+}$	0.313[e]	1 045	3.3	0.744, 0.750
$[Ru(Clphen)(phen)_2]^{2+}$	0.947	2 170	2.3	0.808, 0.815
$[Ru(Brphen)(phen)_2]^{2+}$	0.989	2 300	2.3	0.792, 0.804
$Ru[(SO_3Ph)_2phen](phen)_2$	3.98	7 310	1.8	0.818, 0.824
$[Ru(Ph_2phen)(phen)_2]^{2+}$	2.56	6 700	2.6	
$[Ru(Ph_2phen)_3]^{2+}$	5.34	13 600	2.5	
$[Ru[(SO_3Ph)_2phen]_3]^{4-}$	5.52	10 600	1.9	
$Ru(bpy)_2(CN)_2$	0.40	2 000	5.0	0.790, 0.795
$Ru(phen)_2(CN)_2$	1.58	8 600	5.4	0.678, 0.676
$[Os(bpy)_3]^{2+}$	0.049[g,h]	220	4.5	
$[Os(phen)_3]^{2+}$	0.183[g,h]	1 040	5.7	0.760, 0.751
$[Os(Ph_2phen)(phen)_2]^{2+}$	0.212[g,h]	980	4.6	0.774, 0.780, 0.792
$Os[(SO_3Ph)_2phen](phen)_2$	0.093[g,h]	630	6.8	0.736, 0.749
$[Ir(bpy)_3]^{3+}$	2.37[g]	820	0.34	~1[i]
$[Ir(phen)_3]^{3+}$	2.60[g]	720	0.28	~1[i]
Rose bengal		~250 000[j]		0.799, 0.807

[a] bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; Xphen (X = Cl, Br) = 5-halo-1,10-phenanthroline; Ph_2phen = 4,7-diphenyl-1,10-phenanthroline; $(SO_2Ph)_2phen^{2-}$ = disulfonated 4,7-diphenyl-1,10-phenanthroline. [b] Accuracy ~±5–10%. [c] Accuracy ~10–20%. [d] Accuracy ~5%. [e] From ref 23. [f] From ref 21 and 22. [g] From ref 8. [h] From ref 24. [i] See text. [j] Estimated from data in ref 1.

Results

Table I gives the decay times of the metal complexes in deoxygenated methanol, τ_0's; all decays were exponential over 2-3 half-lives. The Ru(II) and Os(II) complexes were not detectably quenched (< 1-2%) by ~0.12 M TME or by thiourea at ~0.6 M. The Ir(III) complexes were not quenched by TME, but were essentially totally quenched by thiourea even at ~0.06 M.

The intensity Stern–Volmer plots ($(\theta_0/\theta) - 1$) vs. $[O_2]$) were linear in all cases; θ_0 and θ are the emission intensities in the absence and presence of O_2, respectively. The Stern–Volmer quenching constants, K_{sv}'s, equal the slope of these plots, and the bimolecular quenching constants, k_2's ($= K_{sv}/\tau_0$), are given in Table I.

With Ru(II) or Os(II) complexes the limiting quantum yields, ϕ_0's, for O_2 consumption in photosensitized oxidations of TME at infinite O_2 and TME concentrations are also given in Table I. See Discussion for method.

For the thiourea scavenging experiments with $[Ru(bpy)_3]^{2+}$ as the sensitizer, the plot of $\overline{K_{sv}}/\phi'_{obsd}$ vs. $1/[TU]$ is shown in Figure 1. $\overline{K_{sv}}$ corrects the yields to an infinite O_2 concentration or total O_2 quenching of $*[Ru(bpy)_3]^{2+}$ (see Discussion).[22] The linear least-squares fit yields a slope of $(2.49 \pm 0.17) \times 10^{-2}$ M and an intercept of 1.050 ± 0.016. Indicated errors are standard deviations.[25]

For the trimethylethylene $^1O_2$ scavenging experiments, $[Ru(bpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$, $Ru(phen)_2(CN)_2$, $[Os(bpy)_3]^{2+}$, $[Os(phen)_3]^{2+}$, $[Os(Ph_2phen)(phen)_2]^{2+}$, and $Os[(SO_3Ph)_2phen](phen)_2$ were used as the donors. For all complexes the ratio of the two alcohols formed by product reduction was identical within experimental error (~±10%) to that formed in the rose bengal sensitized photooxidations of trimethylethylene.

For $[Ir(phen_3)]^{3+}$ and $[Ir(bpy)_3]^{3+}$ we were unable to obtain reproducible O_2 uptake yields with TME. Using the smallest possible uptakes (5-10 mL of O_2 with 10-20 mg of complex in 75-100 mL of solution), initial ϕ_0's were usually around 1.0 (±15%), although a value of ~1.6 was obtained with $[Ir(phen)_3]^{3+}$ in one experiment. In all cases the initial nearly colorless solutions developed a pale pinkish-orange color, indicating some photodecomposition of the complex; we have also seen decomposition in the spectrofluorimeter without any quenchers present. On continuing photolysis, yields sometimes fell in an experiment, but usually rose to above unity (generally 1.1-1.2). Because of insufficient material, we have been unable to pursue these experiments.

With $[Ir(bpy)_3]^{3+}$ one experiment was carried out with trimethylethylene as the $^1O_2$ scavenger. The solution turned greenish-blue on addition of $NaBH_4$. Some of this color was extracted into the ether layer. On standing, the aqueous layer turned pink. The ether layer lost its green color; if water droplets were still present a pink color was found in them. The GC analysis yielded two peaks of comparable intensities, which indicated a distribution similar to that of $^1O_2$ oxidation, but the peaks were quite broad, unlike those found in the other experiments, and quantitative analysis was not possible. The sequence of color changes seen could qualitatively be duplicated on unphotolyzed methanolic solutions of $[Ir(phen)_3]^{3+}$ or $[Ir(bpy)_3]^{3+}$ with or without added TME.

Discussion

Photochemically Generated Oxidant. We begin by showing that, at least with the Ru(II) and Os(II) sensitizers, the principal photochemically generated oxidant is probably $^1O_2$. Oxidation of trimethylethylene gives two possible hydroperoxide products, and the ratio is extremely sensitive to the nature of the oxidant.[3] In our photooxidations of trimethylethylene, the product ratios were the same regardless of whether the sensitizers were the $^1O_2$ generator rose bengal[3] or Ru(II) and Os(II) complexes. Further, our earlier work showed that the Ru(II) complex sensitized photooxidations of TME or 1,3-cyclohexadiene proceeded with the exact 1:1 olefin–oxygen stoichiometry of $^1O_2$ oxidations and that the products were the same as in $^1O_2$ oxidation.[7] These combined results leave little doubt that $^1O_2$ is the principal oxidant.

The oxidizer formed by the Ir(III) photosensitizers is less clear. O_2 uptakes are definitely catalytic (>12 mol of O_2 consumed per mole of sensitizer). Also, beyond the equilibration time following irradiation (~10-15 min), there is no thermal oxidation. Initial photooxidation yields center around unity, and the single $[Ir(bpy)_3]^{3+}$ experiment with trimethylethylene suggests normal $^1O_2$ oxidation. It remains unclear, however, whether sensitizer decomposition or the nature of the primary sensitization process is responsible for the erratic yields. An unstable catalyst for the thermal oxidation of the olefins might be formed photochemically; if the catalyst survives only a few minutes, our experiments could not differentiate catalyzed thermal oxidation from normal photooxidation.

Alternatively, if excited-state electron transfer yielded some Ir(IV) and O_2^-, the resultant radical oxidation could be sensitive to uncontrollable impurities and the yields might exceed unity. Because the behavior of the Ir(III) systems does approach that of $^1O_2$ sensitizations, we favor $^1O_2$ as the dominant oxidizing agent, with side reactions producing the erratic results. Further experiments are, however, necessary.

Kinetics. Kinetically our data can be described by the following mechanism:

$$D \xrightarrow[\phi']{h\nu} {*D} \tag{1}$$

$$*D \xrightarrow{k_1} D + h\nu \text{ or heat} \tag{2}$$

$$*D + O_2 \xrightarrow{k_2} D + O_2\,(1 - \phi_{et}) + {^1O_2}\,(\phi_{et}) \tag{3}$$

$$^1O_2 \xrightarrow{k_1^{C2}} O_2 + \text{heat} \tag{4}$$

$$^1O_2 + A \xrightarrow{k_{rx}} AO_2 \tag{5}$$

$$^1O_2 + A \xrightarrow{k_q^A} O_2 + A + \text{heat} \tag{6}$$

D is the donor, *D is the excited donor in its long-lived emitting state, and A is the $^1O_2$ scavenger (TME, trimethylethylene, or TU), ϕ' is the efficiency of generation of *D per photon absorbed by D, ϕ_{et} is the efficiency of production of $^1O_2$ per quenching encounter of O_2 with *D, and k_2 is the observed bimolecular quenching constant for deactivation of *D by O_2. Quenching of *D by A was absent in the systems that were studied quantitatively and is omitted. The detailed mechanisms for $^1O_2$ generation will be discussed later.

The sensitizing states of the Ru(II) and Os(II) complexes are all CT in character.[26-28] Crosby et al.[26] have shown that these Ru(II) CT excited states are neither singlets nor triplets, but must be classified as strongly mixed singlet–triplet spin-orbit states. Because of the even greater spin-orbit coupling of Os, their emitting CT states must also be classified as spin-orbit states rather than as singlets or triplets. The Ir(III) sensitizing states have been assigned as predominantly π–π^* triplets; the decay times appear shortened by an intermolecular heavy-atom effect.[17,19] The high atomic number of Ir, however, might make a spin-orbit classification necessary here also. Therefore, except possibly for the Ir(III) complexes, ϕ' is not a normal intersystem crossing yield. To avoid an incorrect and misleading symbolism, we replace the previously used ϕ'_{isc}[27] or ϕ_{isc} with ϕ'.

For TME as the scavenger, AO_2 is a hydroperoxide.[3] With a thiourea scavenger, the initial product is a sulfinic acid,[1] but the system is probably more complicated than a simple 1:1 product would imply (see below).

This scheme of reaction 1–6 yields the following:

$$\phi'_{obsd} = \phi_0\overline{\beta}\overline{K_{sv}} \tag{7}$$

$$\overline{\beta} = [\overline{A}]/(\beta + [\overline{A}])$$

$$\overline{K_{sv}} = K_{sv}[\overline{O_2}]/(1 + K_{sv}[\overline{O_2}])$$

$$\phi_0 = \phi'\phi_{rx}\phi_{et},$$

$$\phi_{rx} = k_{rx}/(k_{rx} + k_q{}^A)$$

$$\beta = k_1{}^{O_2}/k_{rx}$$

$$K_{sv} = k_2/k_1$$

ϕ_0 is the limiting photooxygenation yield at infinite O_2 and A concentrations, ϕ'_{obsd} is the observed yield of O_2 uptake for a photolysis run, and $[A]$ and $[O_2]$ are the average concentrations of A and O_2 during the run. The procedures for evaluating $[\overline{A}]$ and $[\overline{O_2}]$ are given elsewhere.[22] ϕ_{rx} is the probability of reaction of $^1O_2$ with A per quenching encounter.

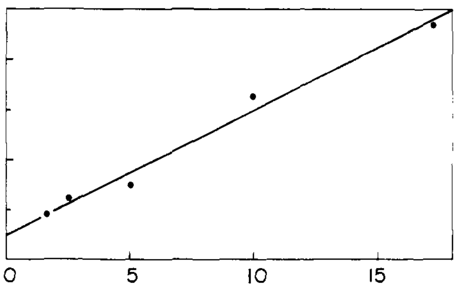

Figure 1. Photochemical plot for $[Ru(bpy)_3]^{2+}$ photosensitized oxidation of thiourea. ϕ'_{obsd} is observed O_2 consumption yield, and $\phi'_{obsd}/\overline{K}_{sv}$ is corrected to $[O_2] = \infty$ or total quenching of $*[Ru(bpy)_3]^{2+}$: slope $(2.49 \pm 0.17) \times 10^{-2}$ M; intercept = 1.050 ± 0.016.

With TME β is very small and could not be evaluated by our experiments. We used $\beta = 0.0027$ M.[3] ϕ_0's evaluated from eq 7 are summarized in Table I.

Equation 7 predicts that a plot of $\overline{K_{sv}}/\phi'_{obsd}$ vs. $1/[\overline{A}]$ will be linear with a slope of β/ϕ_0 and an intercept of $1/\phi_0$; the slope to intercept ratio equals β. Figure 1 shows that the $[Ru(bpy)_3]^{2+}$ sensitized oxidation of TU fits the equation well and gives $\beta = 0.0237 \pm 0.0017$ M and $\phi_0 = 0.952 \pm 0.015$.

Sensitizer Characteristics. The ϕ_0's for the TME scavenging experiments supply useful fundamental data on the sensitizers. Since $\phi' \geqslant \phi_0$, on excitation all of the complexes relax with very high efficiencies to their long-lived sensitizing states. Their high ϕ''s coupled with their intense emissions in room temperature fluid solutions should permit them to join $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ as extremely useful photosensitizers.[9-16]

Particularly noteworthy for practical application of these photosensitizers is their high ϕ_0's and ϕ'_{obsd}'s. ϕ'_{obsd}'s for TME photooxidation were > 0.6, which makes these complexes more efficient $^1O_2$ generators than methylene blue (~0.5).[29] Similar to methylene blue, the Os(II) complexes give a good spectral match to incandescent light sources and readily form optically dense solutions for $\lambda \leq 700$ nm. Under 1 atm of O_2, $[Ru(bpy)_3]^{2+}$, $[Ru(Clphen)(phen)_2]^{2+}$, $[Ru(Brphen)(phen)_2]^{2+}$, $Ru[(SO_3Ph)_2phen](phen)_2$, and $Ru(bpy)_2(CN)_2$ generate $^1O_2$ with yields of 0.75–0.81, which compare well with 0.80 for the widely used $^1O_2$ generator rose bengal.[1,30,31] This work has already led to the development of a quantum flat $[Ru(bpy)_3]^{2+}$ sensitized actinometer for use with high power lasers ($\lambda \leq$ ~530 nm); Os(II) complexes promise to extend the range to ~700 nm.[21,22]

For the design of new sensitizers, Ph_2phen and $[(SO_3Ph)_2phen]^{2-}$ ligands have very beneficial effects on the τ_0's of Ru(II) complexes. $[Ru(Ph_2phen)_3]^{2+}$, $[Ru[(SO_3Ph)_2phen]_3]^{4-}$, $[Ru(Ph_2phen)(phen)_2]^{2+}$, and $Ru[(SO_3Ph)_2phen](phen)_2$ have substantially longer τ_0's than have previously been reported for CT excited states in fluid solution,[32] which suggests their use as laser dyes. $[Ru[(SO_3Ph)_2phen]_3]^{4-}$ and $[Ru(Ph_2phen)_3]^{2+}$ have longer τ_0's at room temperature than $[Ru(bpy)_3]^{2+}$ does at 77 K.[27]

Energy Transfer Efficiencies. The failure of ϕ_0 to be unity implies ϕ', ϕ_{rx}, and/or ϕ_{et} are less than unity. We address ourselves to the source(s) of this inefficiency.

First, ϕ_{rx} is probably unity. Gollnick et al. determined the limiting yields for rose bengal sensitized photooxidations of TME and 2,5-dimethylfuran in methanol to be 0.78–0.83 and 0.80–0.83, respectively;[31] they equated this value to the dye's intersystem crossing efficiency. This inference seems likely. Photooxidation of these two substrates is chemically so different that the yields would probably not be the same unless both substrates chemically scavenged ${}^1O_2$ with ϕ_{rx}'s of unity. Thus, we assume ϕ_{rx} for TME is unity,[33] and ϕ' or ϕ_{et} must be less than unity.

The spectroscopic evidence is compelling that ϕ' is unity for at least several model Ru(II) and Os(II) complexes. $[Ru(bpy)_3]^{2+}$ in methanol at room temperature and in a methanol-ethanol glass at 77 K showed no variation in luminescence quantum yield with varying excitation wavelength; excitation spanned the very weak absorptions inverse to the emission and the highly allowed upper CT states.[27] Similar results were obtained for $[Os(terp)_2]^{2+}$ (terp = 2,2′,2″-terpyridine), a typical Os(II) CT emitter, in methanol.[27] Recent room temperature experiments with $[Ru(bpy)_3]^{2+}$ in water and in methanol, $[Ru(phen)_3]^{2+}$ in methanol, and $Ru(phen)_2(CN)_2$ and $Ru(bpy)_2(CN)_2$ in water and in methanol reveal no experimentally significant variation in yield with wavelength.[35,36] The most reasonable interpretation is that ϕ' is quite close to unity. Thus, $\phi_0 = \phi_{et}$.

That $\phi' = 1$ for $[Ru(bpy)_3]^{2+}$ has recently been questioned, and a flash photolysis value of $\phi' = 0.5 \pm 0.1$ has been claimed.[37,38] This result cannot be correct. A growing body of data shows primary sensitization yields much closer to unity (>0.8).[13,15a,39] Further, the $[Ru(bpy)_3]^{2+}$ sensitized photooxidation of TME gives $\phi_0 = 0.85 \pm 0.05$,[22] which makes $\phi' \geqslant 0.80$.

Mechanism of ${}^1O_2$ Generation. There are two basic mechanisms for photosensitized ${}^1O_2$ generation: simple energy transfer of the type accepted for organic compounds (eq 8-10)[4,40] and a variant of the excited-state electron-transfer mechanism proposed by Lin and Sutin[12c,15a] (eq 11-13)

$$*D + O_2 \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} *(DO_2) \qquad (8)$$

$$*(DO_2) \xrightarrow{k_{et}} D + {}^1O_2 \qquad (9)$$

$$\xrightarrow{k_q} D + O_2 \qquad (10)$$

$$*D + O_2 \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} *D|O_2 \xrightarrow{k_3} D^+|O_2^- \qquad (11)$$

$$D^+|O_2^- \xrightarrow{k_{et}} D|{}^1O_2 \longrightarrow D + {}^1O_2 \qquad (12)$$

$$\xrightarrow{k_q} D|O_2 \longrightarrow D + O_2 \qquad (13)$$

$*(DO_2)$ is the donor-oxygen exciplex. Species separated by a | denote cage encounter pairs. Both mechanisms yield

$$\phi_{et} = k_{et}/(k_q + k_{et}) \qquad (14)$$

although the significance of the rate constants differs between the two models. The observed k_2's for the energy transfer and the electron transfer cases are given by eq 15 and 16, respectively.

$$k_2 = k_d \left[\frac{(k_q + k_{et})}{(k_q + k_{et}) + k_{-d}}\right] \qquad (15)$$

$$k_2 = k_d \left[\frac{k_3}{k_3 + k_{-d}}\right] \qquad (16)$$

For all donors energy transfer to O_2 is allowed, highly exothermic, and must be considered as a possible mechanism. The excited-state electron-transfer mechanism requires some justification. Reaction 12 is thermodynamically highly allowed for $[Ru(bpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$, $Ru(bpy)_2(CN)_2$, $[Os(bpy)_3]^{2+}$, and presumably for the remaining Ru(II) and Os(II) species.[12e,f,15a,41] The reaction $*D + O_2 \rightarrow D^+ + O_2^-$ is energetically favored by ~0.3-0.4 eV for $[Ru(phen)_3]^{2+}$, $[Ru(bpy)_3]^{2+}$, $[Os(bpy)_3]^{2+}$, and $Ru(bpy)_2(CN)_2$.[12e,f,15a,41] Although electrochemical data are not available for the Ir(III) complexes, their high excited-state energies might permit generation of ${}^1O_2$ by the electron-transfer pathway. The absence of significant formation of D^+ and O_2^- in our experiments would be explained by very rapid back electron transfer in the cage pair.[42]

The only direct evidence supporting formation of the $D^+|O_2^-$ intermediate of the electron-transfer scheme is the demonstration that O_2 quenching of $*[Ru(bpy)_3]^{2+}$ in concentrated aqueous H_2SO_4 produces $[Ru(bpy)_3]^{3+}$ and HO_2^- [44] The authors interpreted these data as showing 100% efficient production of $D^+|O_2^-$ followed by reactions 12 and 13 unless H^+ scavenged O_2^- from the cage pair.[44] An alternative interpretation is that $D^+|O_2^-$ is formed on only 6% of the quenching encounters, and that H^+ can scavenge O_2^- from the cage with high efficiency; the remainder of the quenching encounters follow reactions 8-10. Another reasonable possibility is that the scanvengeable species is not $D^+|O_2^-$, but a charge-transfer stabilized exciplex;[44] all ${}^1O_2$ production would then be by the normal energy-transfer paths of eq 8-10.

We favor simple energy transfer as the dominant mode for ${}^1O_2$ production. For the electron-transfer mechanism to dominate, the excited-state electron-transfer rate in the encounter pair must far exceed the highly allowed energy-transfer rate, and the back electron transfer reaction to form ${}^1O_2$ (eq 12) must proceed with very high efficiency (≥0.7). Chemical generation of excited states is frequency inefficient,[45] and we are unaware of any direct evidence that oxidation of O_2^- gives ${}^1O_2$ with such high yields, although ferricinium ion oxidizes O_2^- to ${}^1O_2$ with an efficiency of 0.04.[41] We feel that a consistent 70-85% efficient generation of ${}^1O_2$ by reaction 12 is excessively high in view of the structural, spectroscopic, and electrochemical variations in the donors. Further work is, however, in progress.

A detailed interpretation of our data rests on confirmation of one of the two models for ${}^1O_2$ generation. Several observations are, however, relevant. There are significant and variable inefficiencies in the generation of ${}^1O_2$ per quenching encounter. In the energy-transfer model, radiationless relaxation of $*(DO_2)$ before it can dissociate to ${}^1O_2$ is the most likely cause. We know of no direct evidence for such a process in an oxygen organic compound exciplex. Exciplexes in general can undergo efficient radiationless deactivation,[40] and $*(DO_2)$ should be no exception, especially if charge-transfer stabilization increases its lifetime. In the electron-transfer scheme, subunity ϕ_{et}'s would arise from inefficient utilization of chemical energy in the chemical generation of ${}^1O_2$; such inefficiencies are common.[45]

Quenching Constants. Several Ru(II) and Os(II) complexes have k_2's larger than $3.3 \times 10^9\ M^{-1}\ s^{-1}$, the theoretical upper limit for O_2 quenching of triplet states.[46] In the energy-transfer model for quenching, such large k_2's can be explained, since the quenched states are not singlets or triplets, but spin-orbit states; the spin statistical factor is thus no longer valid, and the maximum k_2 can exceed $3 \times 10^9\ M^{-1}\ s^{-1}$. In the electron-transfer model, there is no spin-statistical factor, and the k_2's need only be less than the diffusional limit as is observed.

Charge factors also appear important in controlling the quenching rates, especially with the Ir(III) complexes. The emitting states of the Ir(III) complexes are largely ${}^3(\pi\text{-}\pi^*)$ in character and should show the normal k_2's of $1\text{-}3 \times 10^9\ M^{-1}\ s^{-1}$ for triplet quenching.[4,40] Observed k_2's are, however, an order of magnitude smaller than expected for energy transfer.[48] We attribute this result to the large charges on the complexes which give tight solvation spheres that retard penetration of O_2 to an effective quenching distance. A similar effect of charge on k_2's was observed in the deactivation of organic triplets by Cr(III) complexes of varying charges: $[Cr(CN)_6]^{3-}$, $[Cr(urea)_6]^{3+}$, and $[Cr(en)_3]^{3+}$ quenched anthracene 10–100 times less effectively than $Cr(acac)_3$.[49] The somewhat smaller effects seen with the Ir(III) complexes and O_2 may arise because of the Ir(III) complex's larger size and thus greater isolation of the charge center and solvation sphere from each other.

Surprising is the apparent absence of any steric effect on k_2. We had hoped and expected that the bulky phenyl or sulfonated phenyl groups on 1,10-phenanthroline would shield the excited portion of the complexes. In the absence of any consistent pattern of decrease in k_2 on replacing phen's by Ph_2phen's or by $[(SO_3Ph)_2phen]^{2-}$'s, however, we conclude that shielding of O_2 by these ligands is of minimal importance. This result probably arises either because O_2 is small enough to fit between the shielding groups or because the phenyl groups are so strongly coupled to the CT excited states that excitation extends spacially over the phenyl rings and quenching can occur even at the periphery.[50]

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References and Notes

(1) K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968).
(2) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).
(3) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
(4) D. O. L. Gijzeman, F. Kaufman, and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **69**, 708 (1973).
(5) A. Pfeil, *J. Am. Chem. Soc.*, **93**, 5395 (1971).
(6) D. J. Carlsson, G. D. Mendenshall, T. Suprunchuk, and D. M. Wiles, *J. Am. Chem. Soc.*, **94**, 8960 (1972).
(7) J. N. Demas, D. Diemente, and E. W. Harris, *J. Am. Chem. Soc.*, **95**, 6864 (1973).
(8) J. N. Demas, E. W. Harris, C. M. Flynn, Jr., and D. Diemente, *J. Am. Chem. Soc.*, **97**, 3838 (1975).
(9) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **93**, 1800 (1971).
(10) P. Natarajan and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 3635 (1972).
(11) M. Wrighton and J. Markham, *J. Phys. Chem.*, **77**, 3042 (1973).
(12) (a) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974); (b) *ibid.*, **97**, 2909 (1975); (c) A. Juris, M. T. Gandolfi, M. F. Manfrin, and V. Balzani, *ibid.*, **98**, 1047 (1976); (d) C. Creutz and N. Sutin, *Inorg. Chem.*, **15**, 496 (1976); (e) C. T. Lin, W. Böttcher, M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **98**, 6536 (1976); (f) F. Bolletta, M. Maestri, and V. Balzani, *J. Phys. Chem.*, **80**, 2499 (1976).
(13) G. S. Laurence and V. Balzani, *Inorg. Chem.*, **13**, 2976 (1974).
(14) (a) H. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 8238 (1972); (b) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974); (c) H. Gafney and A. W. Adamson, submitted for publication.
(15) (a) C. Lin and N. Sutin, *J. Phys. Chem.*, **80**, 97 (1976); (b) G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 2337 (1976).
(16) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).
(17) C. M. Flynn, Jr., and J. N. Demas, *J. Am. Chem. Soc.*, **96**, 1959 (1974).
(18) J. N. Demas, T. F. Turner, and G. A. Crosby, *Inorg. Chem.*, **8**, 674 (1969).
(19) C. M. Flynn, Jr., and J. N. Demas, manuscript in preparation.
(20) J. N. Demas, M. Weiss, C. M. Flynn, Jr., D. Diemente, and A. McNutt, manuscript in preparation.
(21) J. N. Demas, R. P. McBride, and E. W. Harris, "Lasers in Physical Chemistry and Biophysics," J. Joussot-Dubien, Ed., Elsevier, Amsterdam, 1975, p 477.
(22) J. N. Demas, R. P. McBride, and E. W. Harris, *J. Phys. Chem.*, **80**, 2248 (1976).
(23) J. N. Demas and J. W. Addington, *J. Am. Chem. Soc.*, **98**, 2434 (1976).
(24) J. N. Demas and C. M. Flynn, Jr., *Anal. Chem.*, **48**, 353 (1976).
(25) Y. Beers, "Theory of Error", Addison-Wesley, Reading, Mass., 1957.
(26) (a) R. W. Harrigan and G. A. Crosby, *J. Chem. Phys.*, **59**, 3468 (1973); (b) R. W. Harrigan, G. D. Hager, and G. A. Crosby, *Chem. Phys. Lett.*, **21**, 487 (1973); (c) G. D. Hager and G. A. Crosby, *J. Am. Chem. Soc.*, **97**, 7031 (1975); (d) G. D. Hager, R. J. Watts, and G. A. Crosby, *ibid.*, **97**, 7037 (1975), (e) K. W. Hipps and G. A. Crosby, *ibid.*, **97**, 7042 (1975).
(27) J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 2841 (1971).
(28) (a) D. M. Klassen and G. A. Crosby, *J. Chem. Phys.*, **48**, 1853 (1968); (b) G. A. Crosby, D. M. Klassen, and S. L. Sabath, *Mol. Cryst.*, **1**, 375 (1966); (c) B. Pankuck, Ph.D. Thesis, University of New Mexico, 1970.
(29) N. Nemoto, H. Kokubun, and Koizumi, *Bull. Chem. Soc. Jpn.*, **42**, 2464 (1969).
(30) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).
(31) K. Gollnick, T. Franken, G. Schade, and G. Dörhöfer, *Ann. N.Y. Acad. Sci.*, **171**, 89 (1970).
(32) A τ_0 of 4.7 μs has recently been reported for $[Ru(Ph_2phen)_3]^{2+}$ in water.[12e] We find this complex to be so insoluble in water as to have limited use as a sensitizer in this solvent. In contrast the Ru(II) mixed-ligand complexes containing Ph_2phen and $(SO_3Ph)_2phen$ as well as $[Ru[(SO_3Ph)_2phen]_3]^{4-}$ have adequate to high solubilities, making them suitable as sensitizers in water.
(33) There is an apparent discrepancy between the $[Ru(bpy)_3]^{2+}$ sensitized oxidations of TME and of TU: $\phi_0 = 0.85$ for TME and 0.95 for TU, which is a statistically significant difference. Since only ϕ_{rx} is different, this seems to imply that ϕ_{rx} for TME is 0.90. The photooxidation of TU is not as simple as that of TME, however, and the related allylthiourea has dye-sensitized photooxidation yields well in excess of unity,[34] apparently due to side reactions.[3] We attribute the higher yield for TU in our experiments to a small component of a side reaction.
(34) R. Livingston and K. E. Owens, *J. Am. Chem. Soc.*, **78**, 3301 (1956).
(35) (a) D. G. Taylor, M. S. Thesis, University of Virginia, 1976; (b) D. G. Taylor and J. N. Demas, unpublished results.
(36) (a) S. H. Peterson and J. N. Demas, *J. Am. Chem. Soc.*, **98**, 7880 (1976). (b) S. H. Peterson and J. N. Demas, manuscript in preparation.
(37) R. Bensassen, C. Salet, and V. Balzani, *J. Am. Chem. Soc.*, **98**, 3722 (1976).
(38) A footnote in ref 12f states that ϕ^r is in fact probably unity, but no experimental results are given. Reference 12f sets ϕ' for $[Ru(phen)_3]^{2+}$ at 0.65, however.
(39) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **95**, 5159 (1973).
(40) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970.
(41) E. A. Mayeda and A. Bard, *J. Am. Chem. Soc.*, **95**, 6223 (1973).
(42) In water, the reaction $[Ru(bpy)_3]^{3+} + O_2^- \rightarrow [Ru(bpy)_3]^{2+} + O_2$ has a high rate constant ($\gg 3 \times 10^5$ M^{-1} s^{-1}),[43] which suggests that back electron transfer in $D^+|O_2^-$ might compete with dissociation.
(43) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2858 (1975).
(44) J. S. Winterle, D. S. Kliger, and G. S. Hammond, *J. Am. Chem. Soc.*, **98**, 3719 (1976).
(45) R. Bezman and L. R. Faulkner, *J. Am. Chem. Soc.*, **93**, 3565 (1971); **94**, 6324 (1972); **94**, 6331 (1972).
(46) The diffusion-limited rate constant in methanol is 3×10^{10} M^{-1} s^{-1} based on the observed fluorescence oxygen quenching constants for similarly sized organic species.[40,47] For triplet quenching, theory, supported by experiment, reduces this maximum value by a factor of 9.[4,40]
(47) W. R. Ware, *J. Phys. Chem.*, **66**, 455 (1962).
(48) If part or all of the quenching is by electron transfer, then the prohibition against energy transfer is even greater.
(49) H. F. Wasgestian and G. S. Hammond, *Theor. Chim. Acta*, **20**, 186 (1971).
(50) The potentials for $D^+ + e \rightarrow {}^*D$ are very nearly the same for $[Ru(Ph_2phen)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$; we presume $(SO_3Ph)_2phen^{2-}$ also has little effect on the excited-state reduction potential. Therefore, even if quenching is by electron transfer, we would expect little intrinsic difference in the rates of electron-transfer quenching except for those caused by steric effects.