ARTICLES

Photosensitized Generation of Singlet Oxygen from Vinyl Linked Benzo-Crown-Ether−Bipyridyl Ruthenium(II) Complexes

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Photophysical properties of 10 substituted methoxybenzene or vinyl linked benzo-crown-ether−2,2′-bipyridyl ruthenium(II) complexes are reported. The lifetimes of the excited triplet metal to ligand charge transfer states, ^{3}MLCT, of the complex ions are in the range 0.85 ± 0.12 μs with two exceptions where the lifetime drops to about half this value. The rate constants, k_q, for quenching in acetonitrile of the ^{3}MLCT states of these ruthenium complex ions by molecular oxygen, $O_2(^3\Sigma_g^-)$, and the variations in the efficiency, f_Δ^T, with which excited singlet oxygen, $O_2^*(^1\Delta_g)$, is thereby produced are reported. The quenching rate constants are in the range $2.2-4.2 \times 10^9$ dm^3 mol^{-1} s^{-1}, and efficiencies of singlet oxygen production are in the range 0.21−0.74. Those complexes with the highest values of k_q tend to be those with lowest f_Δ^T values; that is, k_q and f_Δ^T show a reasonable inverse correlation. The product $k_q f_\Delta^T$ gives the rate constant for oxygen quenching with energy transfer to oxygen, k_q^1, and $k_q - k_q^1$ gives the rate constant, k_q^3, for oxygen quenching by any path which does not lead to energy transfer. The values of k_q^1, k_q^3, and k_q are compared with those in the literature which are mainly available for organic sensitizers of singlet oxygen. The similarities and differences between these two classes of compounds are discussed taking into account the fact that ruthenium complex ions are likely to show enhanced intersystem crossing, due to the heavy atom effect and the likely dependence of k_q^1 and k_q^3, and thereby the efficiencies of singlet oxygen production, on the energies of the excited ^{3}MLCT states and on steric factors.

Introduction

Sixty years ago Kautsky proposed that oxygen quenching of electronically excited states could yield the singlet state of molecular oxygen and thereby account for some photosensitized oxidations.[1] Since then, there have been many attempts to elucidate the mechanism of the interactions between electronically excited states and oxygen under a variety of conditions (see for example refs 2−27). Yields of singlet oxygen $O_2^*(^1\Delta_g)$ production have been shown to depend on many factors, such as the excited-state energy, the electron configuration, the oxidation potential of the sensitizers and on the nature of the solvents, etc.[4−9,11,13,16,17,20−27] Hundreds of molecules have been shown to sensitize the production of singlet oxygen, most of which have been organic compounds; however, the inorganic complex ion ruthenium(II) tris(2,2′-bipyridine) $[Ru(bpy)_3]^{2+}$ and ions from related compounds have been shown to be good photosensitizers because they have relatively strong absorption in the visible and ultraviolet regions of the spectrum and relatively long lifetimes of the emission from the triplet metal to ligand charge transfer state, ^{3}MLCT, making these excited states susceptible to quenching by oxygen in normal aerated fluid solutions.[12,18,20−30]

Early work by Demas et al.[27] on oxygen quenching of several luminescent diimine complexes of ruthenium(II) and osmium(II) showed that the oxygen quenching rate constants, k_q, were in the range $(1.8-5.4) \times 10^9$ dm^3 mol^{-1} s^{-1} for ruthenium complexes, with singlet oxygen production efficiencies in the range 0.68 to 0.85 in methanol. Since then, many studies have been carried out using aqueous[25,26] and other solvents,[12,18,22−24,27] which confirm that direct energy transfer to oxygen with high efficiency occurs in many cases[24,25] and although oxygen quenching rate constants correlate with the oxidation potential of the ruthenium complexes,[23] there is negligible or very little production of free ions due to electron transfer to oxygen.[18]

Recently Garcia-Fresnadello et al.[18] studied oxygen quenching of the excited ^{3}MLCT state of a series of homoleptic complexes $[RuL_3]^{2+}$ (where L is 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2′-bipyrazine (bpz), 4,7-diphenyl-1,10-phenanthroline (dip), diphenyl-1,10-phenanthroline-4,7-disulfonate (dpds), and 1,10-phenanthroline-5-octadecanamide (poda)) in water and methanol. They reported oxygen quenching rate constants in D_2O and CD_3OD and found the maximum value for k_q in D_2O of 4.0×10^9 dm^3 mol^{-1} s^{-1} for $[Ru(phen)_3]^{2+}$and the lowest value of 1.7×10^9 dm^3 mol^{-1} s^{-1} for $[Ru(poda)_3]^{2+}$ in CD_3OD.

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Quantum yields of singlet oxygen production also were reported to vary between 0.22 (in D_2O for $[Ru(bpy)_3]^{2+}$) and 1.0 (in CD_3OD for $[Ru(dpds)_3]^{2+}$). These authors noted that the solvent dependence and the inverse relationship between k_q and the efficiency of singlet oxygen production during oxygen quenching follow a similar trend to that found for triplet states of naphthalene[4] and more recently of biphenyl derivatives.[9] Since considerable progress has been made in understanding charge transfer contributions which increase the rate constants for oxygen quenching of triplet states of organic compounds and reduce the efficiency of formation of singlet oxygen using a mechanism involving singlet, triplet, and quintet encounter complexes (see later), the work described here examines whether such a mechanism is applicable in the case of oxygen quenching of ^{3}MLCT states of several ruthenium(II)-substituted bipyridyl complexes, where it might be expected that the heavy atom, ruthenium, would enhance intersystem crossing between these various encounter complexes.

Experimental Section

Methods of preparation of the ruthenium complexes investigated in this work are described fully in ref 31. The complexes were designed with conjugated linkages between the 2,2′-bipyridine moiety and the macrocyclic binding sites in order to provide an efficient mechanism for recognition of group IA and IIA metal cations by the $[Ru(bpy)_3]^{2+}$ reporter group.[31] Furthermore, the presence of the vinyl linkage allows production of novel polymeric films based on the general reductive electrochemical polymerization technique.[31] We have used ruthenium(II) complexes with the ligands 2,2′-bipyridine (bpy), 4-methyl-4′-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylvinyl)- 2,2′-bipyridine L^{1a}, 4-methyl-4′-(3,4-dimethoxystyryl)-2,2′-bipyridine L^{1b}, 4,4′-bis (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopenta- oxacyclopenta-decin-15-ylvinyl)-2,2′-bipyridine L^{2a}, 4,4′-bis(3,4-dimethoxystyryl)-2,2′-bipyridine L^{2b}, 4,4′-bis(4-methoxystyryl)-2,2′-bipyridine L^{2c}, 4,4′-Bis[2-hydroxy-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13- benzopenta-oxacyclopentadecin-15-yl)ethyl]-2,2′-bipyridine L^{3a}, and several mixed ligand complexes. The structures of these ligands are shown.

The nomenclature for the complexes is as follows: if the ligand is L^2 and R is (a) the ligand is represented as L^{2a}, and three ligands of this type will contribute to a complex labeled $[Ru(L^{2a})_3]^{2+}$. The studied complexes are of two types, those with three ligands which are the same, $[Ru(bpy)_3]^{2+}$, $[Ru(L^{1b})_3]^{2+}$, $[Ru(L^{2a})_3]^{2+}$, $[Ru(L^{2b})_3]^{2+}$, $[Ru(L^{2c})_3]^{2+}$, $[Ru(L^{3a})_3]^{2+}$, and those with mixed ligand complexes, $[Ru(L^{1a})(bpy)_2]^{2+}$, $[Ru(L^{2a})(bpy)_2]^{2+}$, $[Ru(L^{2b})(bpy)_2]^{2+}$, and $[Ru(L^{3a})(bpy)_2]^{2+}$.

Acetonitrile (Aldrich, spectrophotometric grade) was dried by refluxing over calcium hydride. Acridine (Aldrich) was recrystallized from methanol. Ground-state absorption spectra were measured using a Hewlett-Packard 8453 single-beam photodiode array spectrometer. Steady-state luminescence measurements were carried out using a Spex FluoroMax spectrofluorophotometer.

For singlet oxygen luminescence measurements, the third harmonic of a Lumonics Q-switched Nd:YAG laser (HY200, 8 ns, 13mJ) was employed as a 355 nm excitation source. Time-resolved singlet oxygen luminescence at 1270 nm from air-equilibrated solutions was detected using a Judson germanium photodiode amplifier (J-16-85P-ROM5, active diameter 0.5 cm) combination as described previously.[32] The laser energies employed did not exceed 0.5 mJ per pulse. Individual luminescence traces (16 at least) were signal averaged and were fitted using a single-exponential function to yield the luminescence intensity at zero time, I_0, at different laser intensities. Plots of I_0 versus laser fluence were compared with those obtained from optically matched standards in the same solvent under identical conditions thereby yielding relative Φ_Δ values. In all cases, the rate constant, k_Δ, for singlet oxygen, $O_2^*(^1\Delta_g)$, decay was found to be $1.25 \pm 0.1 \times 10^4$ s^{-1} in acetonitrile which agrees with literature values[4,9] and demonstrates that there is negligible quenching of singlet oxygen by any of these ruthenium sensitizers.

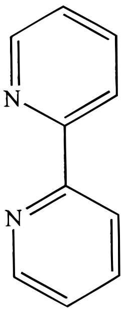
The same laser was used as the excitation source for kinetic emission measurements. Full details of the laser flash photolysis instrument used have been given previously.[33] Dilute acetonitrile solutions ($\sim 5 \times 10^{-5}$ mol dm^{-3}) were used for luminescence decay measurements of the ruthenium complexes. The laser energy was about 1.0 mJ per pulse. Ten individual luminescence traces were signal averaged and fitted using a single-exponential function to give the decay constants of samples for degassed (freeze−pump−thaw) and air-saturated solutions. Each experiment was repeated three times at least.

Cyclic voltammograms were recorded using an EG&G Princeton Applied Research (PAR) 173 potentiostat with a PAR 175 universal programmer and a PAR 179 digital coulometer. A three-compartment cell was employed with a platinum wire (0.32 cm^2 surface area) working electrode and platinum mesh counter electrode. Electrode potentials were measured with respect to a Radiometer sodium chloride saturated calomel electrode (SSCE) (NB 0.005 V lower than SCE) at 25 ± 2 °C. No IR compensation was employed. Both counter and reference electrodes were separated from the working electrode compartment of the electrochemical cell by glass frits. Platinum working electrodes were pretreated by immersion in concentrated sulfuric acid, anodization, then cathodization (2 min each at 100 mA in 0.5 mol dm^{-3} sulfuric acid), followed by washing with deionized water, then acetonitrile and finally air-dried. Measurements were carried out in deoxygenated acetonitrile solutions by purging with solvent-saturated nitrogen gas.

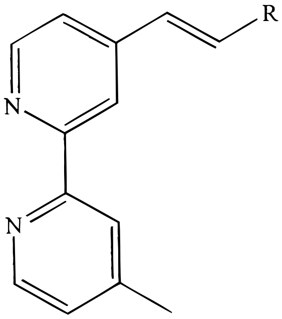
Results and Discussion

The absorption spectra of some of the ruthenium(II) complexes in dilute acetonitrile solution are shown in Figure 1a. The assignment of the bands has been discussed in detail previously.[31] It has generally been assumed that the metal to ligand charge transfer (MLCT) absorption process produces mainly an excited singlet ^{1}MLCT state which undergoes intersystem crossing populating the lowest ^{3}MLCT state with unit efficiency.[29,30,34−36] It has been found that the absorption maximum of the metal to ligand charge transfer band for all complexes are red shifted relative to $[Ru(bpy)_3]^{2+}$. An increase in the number of vinyl linked benzocrown ethers leads to increasing red shifts because of the extended conjugation within these ligands;[37] for example, the maximum absorptions occur at 458, 464, and 485 nm for compounds $[Ru(L^{1a})(bpy)_2]^{2+}$, $[Ru(L^{2a})(bpy)_2]^{2+}$, and $[Ru(L^{2a})_3]^{2+}$ where the number of extendedly conjugated benzocrown ethers present is one, two, and six, respectively. The absorption spectra of mixed ligand complexes of the type $[Ru(L^X)(bpy)_2]^{2+}$ (where X is 1a, 2a, 2b, or 3a) show the expected long wavelength MLCT bands in addition to two ligand-centered (LC) bands corresponding to the parent ligand (bpy) and the substituted ligand (L^X). Measurements of the corresponding luminescence emission maxima of the ^{3}MLCT band offers an alternative method for assessing the effect of ligand variation on excited-state energies. The emission spectra of some of the complexes are shown in

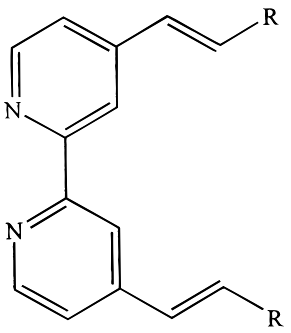
Structures and Abbreviations



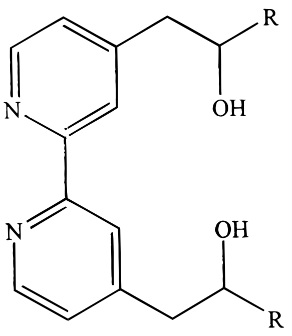
bpy



L^1

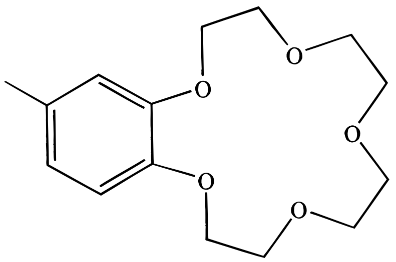


L^2

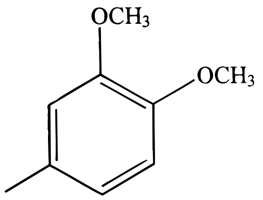


L^3

R =



a



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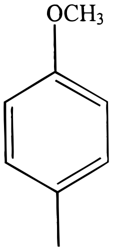


c

Figure 1b and the emission maxima, λ_{em}^{max}, are given in Table 1. These have been found to be shifted to lower energies with increasing number of vinyl linked benzocrown ethers, as observed for the ^{1}MLCT absorption maxima. The absorption and emission spectra of complexes $[Ru(L^{3a})(bpy)_2]^{2+}$ and $[Ru(L^{3a})_3]^{2+}$ are very close to those of $[Ru(bpy)_3]^{2+}$ since the side chain is reduced and extended conjugation no longer exists. It has been found that the emission maxima of complexes of the type $[RuL^X{}_3]^{2+}$ (where $X =$ 1b, 2a−c, or 3a) are red shifted relative to $[Ru(bpy)_3]^{2+}$. Complexes of the type $[Ru(L^X)(bpy)_2]^{2+}$ (where X is 1a, 2a, or 2b) show red shifts in λ_{em}^{max} relative to the parent complex, $[Ru(bpy)_3]^{2+}$ and blue shifts relative to the corresponding symmetrical complexes, $[Ru(L^X)_3]^{2+}$. The MLCT absorption and emission for $[Ru(L^{2a})_3]^{2+}$ are very similar to those for $[Ru(L^{2b})_3]^{2+}$ indicating that the mesomeric/inductive effects of the benzocrown ether are controlled mainly by the α-OCH_3 substituents, the remainder of the macrocycle having little effect.

The literature value[29] for the energy of the lowest vibrational level of the ^{3}MLCT state above the ground state, E_{00}, for $[Ru(bpy)_3]^{2+}$ in acetonitrile is 205 kJ mol^{-1}, i.e., 8 kJ mol^{-1} greater than the energy corresponding to the luminescence emission maxima for $[Ru(bpy)_3]^{2+}$. On the basis of the similarity of the shapes of the luminescence spectra of all complexes, including the parent $[Ru(bpy)_3]^{2+}$, we have assumed that E_{00} values for the complexes can be calculated by adding 8 kJ mol^{-1} to the energy corresponding to the luminescence emission maxima of the ^{3}MLCT band in all cases and E_{00} values calculated in this way are listed in Table 2.

Electrochemical measurements demonstrate that each complex

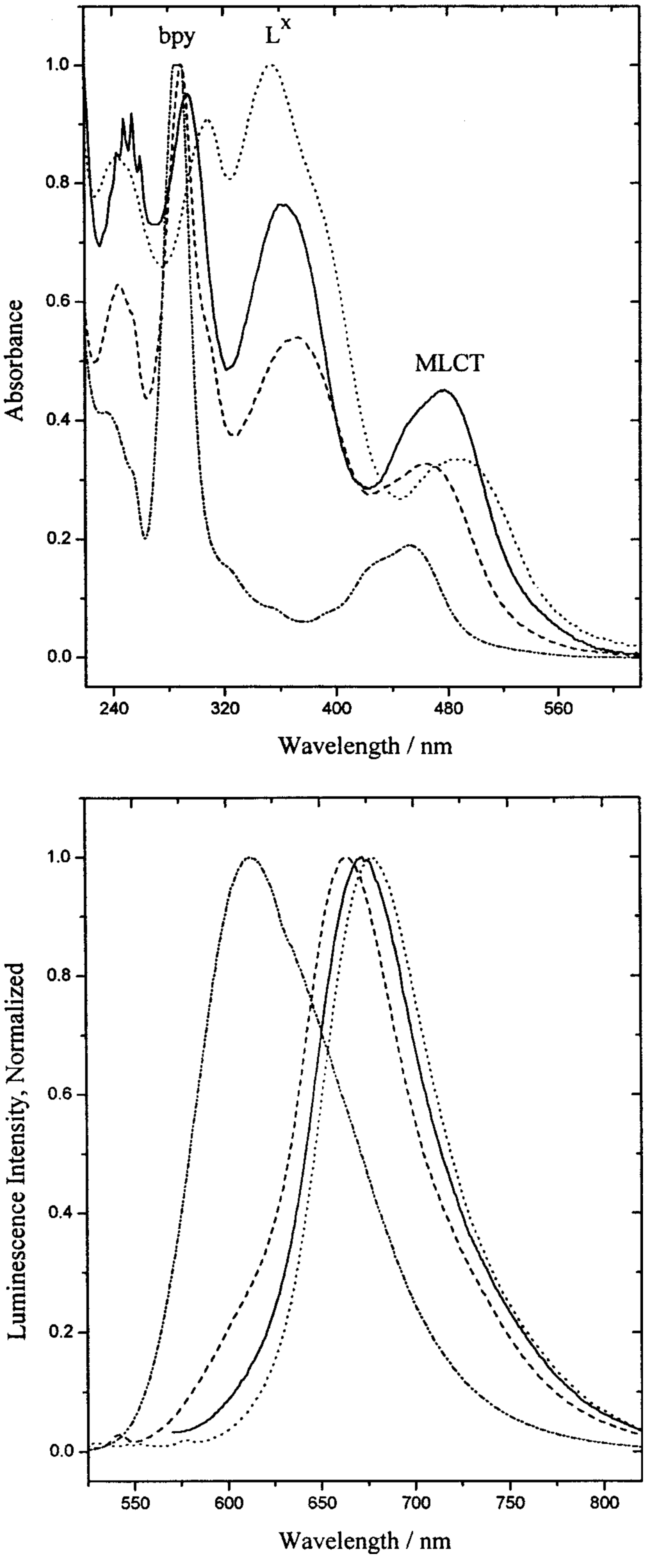


Figure 1. (a) Absorption spectra of complexes $[Ru(L^{1b})_3]^{2+}$ (—), $[Ru(L^{2a})(bpy)_2]^{2+}$ (---), $[Ru(L^{2a})_3]^{2+}$ (···), and $[Ru(L^{3a})(bpy)_2]^{2+}$ (- · · -). (b) Luminescence spectra of complexes $[Ru(L^{1b})_3]^{2+}$(—), $[Ru(L^{2a})(bpy)_2]^{2+}$ (---), $[Ru(L^{2a})_3]^{2+}$ (···) and $[Ru(L^{3a})(bpy)_2]^{2+}$ (- · · -) in acetonitrile.

undergoes one oxidation and several reduction processes. The observed waves are nearly reversible for all complexes. It is well-known that ruthenium(II) tris-2,2′-bipyridine complexes undergo an oxidation process centered on the metal and a series of three reduction waves corresponding to successive one-electron reduction of the three bidentate ligands. As can be seen from Table 2, all the complexes have higher oxidation potentials than the parent $[Ru(bpy)_3]^{2+}$ except for $[Ru(L^{1b})_3]^{2+}$ which has a slightly lower value. The $E^{OX}_{3+/2+}$ values for these complexes all lie in the range of 1.20 to 1.41 V vs SCE. The first reduction potentials are less negative than the parent $[Ru(bpy)_3]^{2+}$ except for complexes $[Ru(L^{2a})_3]^{2+}$, $[Ru(L^{3a})(bpy)_2]^{2+}$, and $[Ru(L^{3a})_3]^{2+}$ which have slightly more negative values (Table 2).

The lifetimes of the excited state of these complexes, see Table 1, all lie in the range 0.85 ± 0.12 μs, with the exception of the two mixed ligand complexes $[Ru(L^{2b})(bpy)_2]^{2+}$ and $[Ru(L^{2a})(bpy)_2]^{2+}$, where the lifetimes drop to about half this value. This can be attributed to the higher energy of the ^{3}MLCT states of these complexes relative to the corresponding $[Ru(L^X)_3]^{2+}$ complexes (i.e., complexes $[Ru(L^{2b})_3]^{2+}$ and $[Ru(L^{2a})\ _3]^{2+}$, respectively) which facilitates mixing with the metal-centered (MC) states.[38] Unfortunately, the compound $[Ru(L^{1a})_3]^{2+}$ is not available to allow comparison of its phosphorescence lifetime with that of $[Ru(L^{1a})(bpy)_2]^{2+}$. However, comparing emission lifetimes from $[Ru(L^{2b})(bpy)_2]^{2+}$ with $[Ru(L^{2b})_3]^{2+}$ and from $[Ru(L^{2a})(bpy)_2]^{2+}$ with $[Ru(L^{2a})_3]^{2+}$ and with other similar compounds[39] indicates that $[Ru(L^{1a})_3]^{2+}$ should show a longer lifetime for emission than that given for $[Ru(L^{1a})(bpy)_2]^{2+}$ in Table 1.

Luminescence decays monitored at the emission maximum for each compound in air equilibrated and in corresponding degassed solutions (freeze−pump−thaw) were used to determine the rate constants (k_q) for oxygen quenching of the lowest excited state of the ruthenium complexes. Ten single shot emission traces were signal averaged for each measurement, and excellent single-exponential fits were obtained for all the decays in either the degassed or the air equilibrated solutions. The pseudo-first-order decay constant in air-saturated solutions, k_{obs}, is given by

$$\mathrm{k}_{obs} = k_{TD} + k_q[O_2] \qquad (1)$$

where k_{TD} is the intrinsic first-order decay constant of the ^{3}MLCT state in the absence of oxygen. The k_q values listed in Table 2 were obtained using eq 1 taking the oxygen concentration in air-saturated acetonitrile[40] solution as 1.9×10^{-3} mol dm^{-3}.

The values obtained for the quenching rate constants which all lie in the range $2.2{-}4.2 \times 10^9$ dm^3 mol^{-1} s^{-1} are listed in Table 1. The highest measured rate constants in acetonitrile for oxygen quenching of the excited singlet state of biphenyl derivatives have been reported recently[10] to be $(4.3 \pm 0.6) \times 10^{10}$ dm^3 mol^{-1} s^{-1} which compares favorably with the value calculated by us[9] (4.5×10^{10} dm^3 mol^{-1} s^{-1}) for the diffusion-controlled rate constant using Smoluchowski's equation.[41] The rate constant, k_d, for diffusion-controlled reaction of $[Ru(bpy)_3]^{2+}$ with oxygen in acetonitrile calculated using Smoluchowski's equation is 2.8×10^{10} dm^3 mol^{-1} s^{-1}. However, the complexes under investigation show a wide variation in size and extent of conjugation which makes it likely that some variation in the diffusion-controlled rate constant will apply for this set of complexes. It is apparent from Table 1 that the oxygen quenching rate constants for ruthenium(II) tris(bipyridyl) complexes in acetonitrile are either close to $k_d/9$ or in several cases exceed $k_d/9$ by up to 30% if one assumes the values of k_d for all the complexes are close to the calculated value of k_d for $[Ru(bpy)_3]^{2+}$.

The quenching rate constant for $[Ru(bpy)_3]^{2+}$ is shown to be lower than for the all other complexes except for complexes $[Ru(L^{3a})(bpy)_2]^{2+}$ and $[Ru(L^{3a})_3]^{2+}$. The lower quenching rate constants for these two complexes can be understood on the

TABLE 1: Photophysical Properties of the Substituted 2,2′-Bipyridine Ruthenium(II) Complexes in Acetonitrile Including Singlet Oxygen Quantum Yield in Air Equilibrated Acetonitrile, Φ_Δ, Wavelength of Maximum Emission, λ_{em}^{max}, Lifetime of the Excited ^{3}MLCT States, τ_o, the Fraction of the ^{3}MLCT States Quenched by Oxygen, $P_T^{O_2}$, Rate Constants for Quenching of ^{3}MLCT States of Ruthenium(II) Complexes by Oxygen, k_q, and Efficiency of Singlet Oxygen Production from the ^{3}MLCT States, f_Δ^T [a]

	compound	Φ_Δ	λ_{em}^{max}/nm	$\tau_o/\mu s$	$P_T^{O_2}$	$k_q/10^9$ dm^3 mol^{-1} s^{-1}	f_Δ^T
1	$[Ru(bpy)_3]^{2+}$	0.57 ± 0.06	607	0.87	0.82	2.75	0.69 ± 0.08
2	$[Ru(L^{2c})_3]^{2+}$	0.26 ± 0.04	673	0.75	0.86	4.18	0.30 ± 0.05
3	$[Ru(L^{2b})(bpy)_2]^{2+}$	0.31 ± 0.02	664	0.48	0.78	3.82	0.40 ± 0.03
4	$[Ru(L^{2b})_3]^{2+}$	0.18 ± 0.02	677	0.92	0.88	4.02	0.21 ± 0.03
5	$[Ru(L^{1b})_3]^{2+}$	0.47 ± 0.05	673	0.72	0.81	3.03	0.58 ± 0.07
6	$[Ru(L^{1a})(bpy)_2]^{2+}$	0.36 ± 0.04	655	0.87	0.83	3.03	0.44 ± 0.06
7	$[Ru(L^{2a})(bpy)_2]^{2+}$	0.48 ± 0.06	664	0.45	0.76	3.65	0.63 ± 0.08
8	$[Ru(L^{2a})_3]^{2+}$	0.19 ± 0.03	677	0.88	0.87	3.86	0.22 ± 0.04
9	$[Ru(L^{3a})(bpy)_2]^{2+}$	0.60 ± 0.04	613	0.90	0.81	2.55	0.74 ± 0.07
10	$[Ru(L^{3a})_3]^{2+}$	0.31 ± 0.02	612	0.86	0.77	2.21	0.40 ± 0.04

[a] NB errors for $k_q = \pm 10\%$ and for $\tau_o = \pm 5\%$.

TABLE 2: Oxidation $E_{+3/+2}^{OX}$ and First Reduction $E_{+2/+1}^{red}$ Potentials of the Ruthenium Complexes in Acetonitrile, $k_q^1 = k_q f_\Delta^T$ and $k_q^3 = k_q(1 - f_\Delta^T)$, Energy of the 0−0 Transition, E_{00}, and Free Energy Change ΔG^{CT} in Acetonitrile with the *C* Term of Eq 8 Taken as Zero[a]

	compound	$E_{+3/+2}^{OX}$ /V vs SCE	$E_{+2/+1}^{red}$ /V vs SCE	k_q^1 /10^9 dm^3 mol^{-1} s^{-1}	k_q^3 /10^9 dm^3 mol^{-1} s^{-1}	E_{00} /kJ mol^{-1}	ΔG^{CT} /kJ mol^{-1}
1	$[Ru(bpy)_3]^{2+}$	1.28	−1.35	1.90	0.85	205	−6.2
2	$[Ru(L^{2c})_3]^{2+}$	1.35	−1.23	1.25	2.93	186	19.8
3	$[Ru(L^{2b})(bpy)_2]^{2+}$	1.33	−1.25	1.53	2.29	188	15.5
4	$[Ru(L^{2b})_3]^{2+}$	1.41	−1.20	0.84	3.18	185	26.7
5	$[Ru(L^{1b})_3]^{2+}$	1.26	−1.33	1.76	1.27	186	5.4
6	$[Ru(L^{1a})(bpy)_2]^{2+}$	1.31	−1.25	1.33	1.70	191	6.3
7	$[Ru(L^{2a})(bpy)_2]^{2+}$	1.31	−1.25	2.30	1.35	188	13.6
8	$[Ru(L^{2a})_3]^{2+}$	1.34	−1.36	0.85	3.01	185	19.9
9	$[Ru(L^{3a})(bpy)_2]^{2+}$	1.36	−1.37	1.89	0.66	203	3.4
10	$[Ru(L^{3a})_3]^{2+}$	1.36	−1.42	0.88	1.33	203	3.1

[a] NB errors for $E_{00} = \pm 2$ kJ mol^{-1} and for $\Delta G^{CT} = \pm 5\%$.

basis that they are electronically very similar to the parent, e.g., similar oxidation potentials and E_{00} values, but are expected to show more steric hindrance to quenching.

The quantum yield of singlet oxygen production (Φ_Δ) arising from oxygen quenching of the triplet, metal to ligand charge transfer state of the ruthenium complexes is given by[2]

$$\Phi_\Delta = \Phi_T P_T^{O_2} f_\Delta^T \tag{2}$$

where f_Δ^T is the fraction of triplet states quenched by oxygen which yield singlet oxygen $O_2{}^*({}^1\Delta_g)$. Since Φ_T the efficiency of population of the lowest excited spin forbidden ^{3}MLCT state can be taken as unity,[29−30,34−36] eq 2 becomes

$$\Phi_\Delta = P_T^{O_2} f_\Delta^T \tag{3}$$

where $P_T^{O_2}$ is the fraction of the ^{3}MLCT states quenched by oxygen and is given by

$$P_T^{O_2} = \frac{k_q[O_2]}{k_{TD} + k_q[O_2]} \tag{4}$$

For Φ_Δ measurements, acridine has been used as a standard with a reported Φ_Δ value of 0.82 in acetonitrile.[42] A typical near infrared (NIR) emission signal arising partially from singlet oxygen sensitized by $[Ru(L^{3a})(bpy)_2]^{2+}$ as a function of time is shown in Figure 2. The fast component is due to the NIR tail of the luminescence of the excited state of the ruthenium complex, while the slow component results from the luminescence of singlet oxygen $O_2{}^*({}^1\Delta_g)$. To separate the decay profile of the singlet oxygen signal from that of the fast component, fitting was carried out over the longer times where the contribution from the rapid component is minimal.

Values of Φ_Δ, are given in Table 1 along with values of f_Δ^T. It is difficult to compare these results with those reported by other authors since most measured values in the literature are for alcoholic and aqueous media.[2,24−26,43−45] The only reported[12] value of f_Δ^T in acetonitrile obtained using a different method is 0.80 ± 0.12 for $[Ru(bpy)_3]^{2+}$. This value is within experimental error of our value of $f_\Delta^T = 0.69 \pm 0.08$, measured relative to the literature value for acridine in acetonitrile as a standard.

The quantum yield, Φ_Δ, of singlet oxygen $O_2{}^*({}^1\Delta_g)$ production as a consequence of oxygen quenching of the excited ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ was first reported by Demas et al.[27] in 1977 to be 0.86 in oxygen-saturated methanol. Other values have been reported by Kenley et al.[43] as 0.90 in oxygen-saturated methanol, by Chattopadhyay et al.[44] as 0.83 in oxygen-saturated methanol and by Bhattacharyya and Das[45] as 0.81 in air-saturated methanol. Recently, quenching of the excited ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ by molecular oxygen in aqueous solution has been reported by Mulazzani et al.[25] to involve both energy and electron transfer processes, with equal bimolecular quenching rate constants. These authors reported the quantum yield of singlet oxygen production, Φ_Δ, photosensitized by $[Ru(bpy)_3]^{2+}$ to be 0.50 in D_2O relative to tetrakis(4-sulfonatophenyl) porphrine ($TPPS^{4-}$) using time-resolved near-infrared emission techniques.[25] This value has been used as a reference by others[26] to measure the quantum yield of singlet oxygen production photosensitized by $[Ru(bpy)_3]^{2+}$ in solutions with different proton concentrations and to show that singlet oxygen production is independent of pH. Tanielian et al.[12] showed recently that there is a marked solvent dependence for

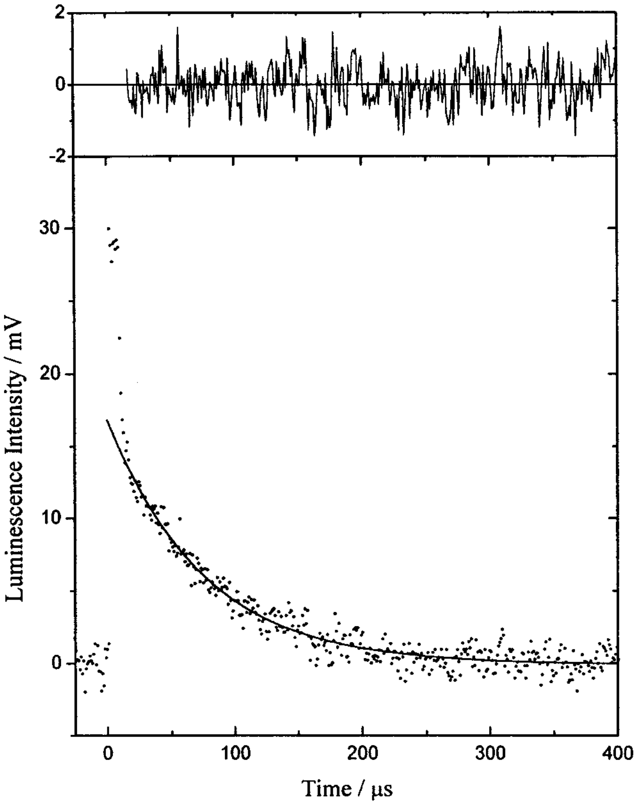


Figure 2. Time-resolved NIR luminescence trace showing long-lived emission from singlet oxygen sensitized by $[Ru(bpy)_2]^{2+}$ in air equilibrated acetonitrile.

sensitized singlet oxygen production upon excitation of $[Ru(bpy)_3]^{2+}$. These authors[12] have reported Φ_Δ in oxygen-saturated solutions ranging from 0.41 to 0.87 yielding f_Δ^T values ranging from 0.58 to 0.92 on changing solvent from water to methanol. Quantum yields of singlet oxygen production photosensitized by $[Ru(bpy)_3]^{2+}$ also have been reported by Garcia-Fresnadillo et al.[18] as 0.73 and 0.22 in CD_3OD and D_2O, respectively, relative to 1H-phenalen-1-one as a standard and with f_Δ^T values in the range 0.44 to 1.0. Where direct comparisons of literature values obtained under apparently identical conditions are possible it is apparent that considerable uncertainties exist and the reasons for variations due to change in solvent are thus difficult to discern.

Examination of the data in Table 1 demonstrates that complexes with identical tris-substituted ligands have f_Δ^T values lower than the corresponding monosubstituted ligands, which can be attributed partially to steric factors. Energy transfer requires close contact between the interacting species with orbital overlap to effect “two-electron” exchange, and therefore the presence of the bulky substituents on the ligands around the metal would be expected to reduce exchange interaction because of reduced overlap between the oxygen orbitals and the metal to ligand charge transfer orbitals of the complexes. The observation of a steric effect on f_Δ^T suggests the processes competing with energy transfer have less restrictive steric demands.

The simplest possible mechanism for the production of singlet oxygen with a yield less than unity is shown in Scheme 1.

Thus, the overall rate constant for oxygen quenching,

$$k_q = k_q^1 + k_q^3 \qquad (5)$$

where k_q^1 represents the rate constant for quenching via energy transfer resulting in singlet oxygen formation and k_q^3 the rate constant for quenching via any other pathways that lead todeactivation of the excited states of ruthenium(II)-substituted bipyridine complexes without generating singlet oxygen. It follows that

SCHEME 1

$$^3M^* + O_2\,(^3\Sigma_g^-) \xrightarrow{k_q^1} {}^1M + O_2^*\,(^1\Delta_g) \qquad (a)$$

$$^3M^* + O_2\,(^3\Sigma_g^-) \xrightarrow{k_q^3} {}^1M + O_2\,(^3\Sigma_g^-) \qquad (b)$$

$$k_q^1 = k_q f_\Delta^T \qquad (6)$$

and

$$k_q^3 = k_q(1 - f_\Delta^T) \qquad (7)$$

Values of k_q^1 and k_q^3, calculated from the experimental values for k_q and f_Δ^T, are listed in Table 2.

In Figure 3, values of k_q, k_q^3, and k_q^1 are plotted against E_{00} for the ruthenium(II) polypyridine complexes. The rate constants measured in hexane for oxygen quenching of the triplet states of aromatic hydrocarbons with E_T values in the same range[46] are also shown in Figures 3a for comparison. Bearing in mind the difference in the nature of the sensitizers and in the solvents used the values show surprisingly good agreement. Parts a and b of Figure 3 illustrate that k_q and k_q^3 show much the same inverse dependence on E_{00} for the ruthenium(II) polypyridine complexes; however, the dependence of k_q^1 on E_{00} is considerably different from that of k_q as illustrated in parts a and c of Figure 3. If the point for $[Ru(L^{3a})_3]^{2+}$, labeled 10 in Figure 3c, is ignored because it is likely to show a much larger steric factor than for the other complexes, then k_q^1 could be said to show a positive correlation with E_{00}, i.e., the opposite to that shown for k_q^3.

A more detailed mechanism for quenching of the electronically excited triplet states $^3M^*$ by molecular oxygen is given in Scheme 2 which was originally proposed by Gijzeman et al.[46] and modified by Garner and Wilkinson[47] to include charge transfer intermediates and the probability of intersystem crossing between these intermediates. In this scheme, M represents the sensitizer, the two triplet state species diffuse together and apart with diffusional rate constants k_d and k_{-d}, respectively, and quintet, triplet, and singlet encounter complexes are formed with the appropriate statistical probabilities. The involvement of charge transfer intermediates was proposed by one of us in 1977 to account for the observation of quenching rate constants higher than that of $^1/_9 k_d$ for triplet states of aromatic compounds.[47] Because of the heavy atom effect, in the case of ruthenium(II) complexes one would expect the probability of intersystem crossing to increase and possibly to occur even between the quintet, triplet, and singlet encounter complexes shown as the dotted arrows in Scheme 2. Recently, Darmanyan et al.[48] have presented strong evidence for intersystem crossing out of the quintet channel in the case of oxygen quenching of the triplet states of several amines. For naphthalene and biphenyl derivatives, the dependence of k_q on the oxidation potential of the sensitizer, M, clearly establishes the participation of charge transfer intermediates in the quenching mechanism, although the extent of intersystem crossing between these intermediates is still open to doubt.[9]

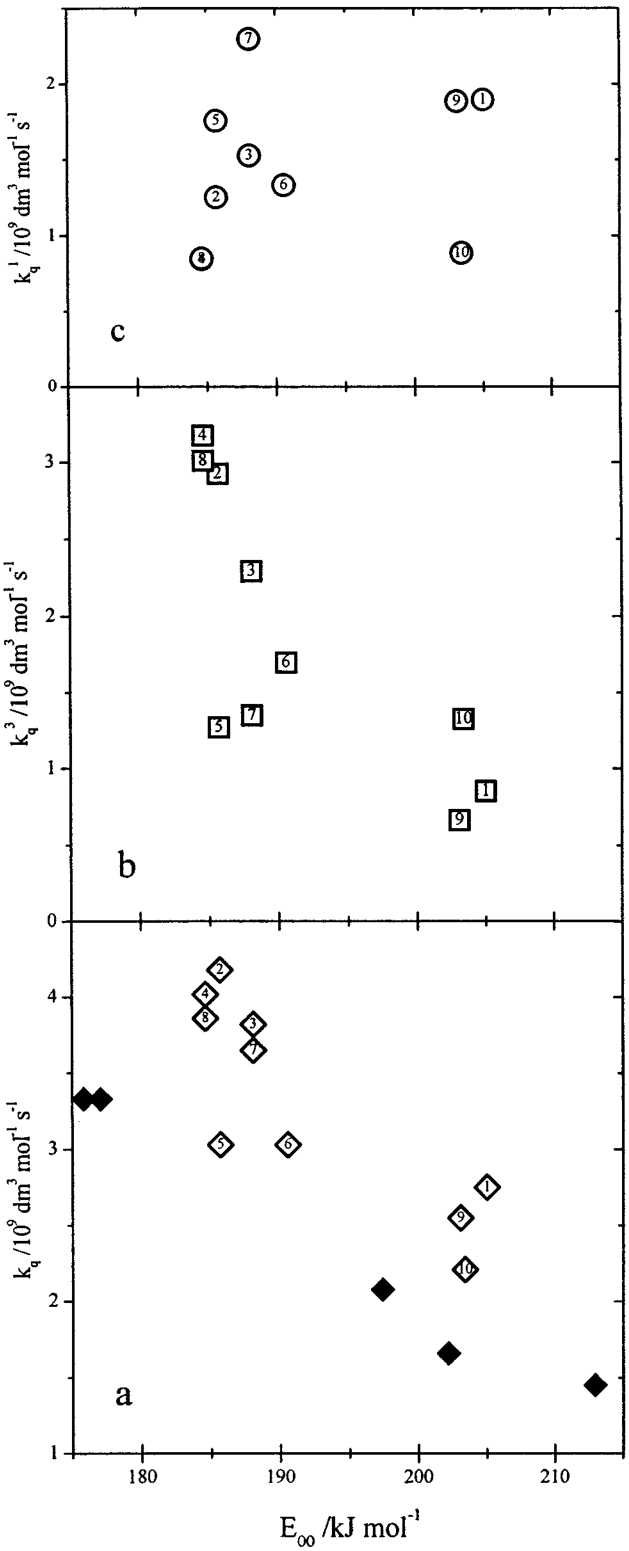


Figure 3. Dependence of the oxygen quenching rate constants of the ^{3}MLCT excited state of Ru(II) complex ions on the energy of the excited-state E_{00} in acetonitrile k_q (◇), k_q^3 (□), and k_q^1 (○). Data for oxygen quenching rate constants of triplet states of aromatic hydrocarbons with energies $E_T = E_{00}$ in *n*-hexane reported by Gijzeman et al.[46] (◆).

Scheme 2 which involves direct population of the charge-transfer states $^{1,3}(M^{+}\cdots O_2^{-})$ has been used to explain the inverse correlation between k_q and f_Δ^T that was observed recently by us for a series of naphthalene[4] and biphenyl derivatives[8,9] in various solvents (see Figure 4). However, Figure 4 also shows that if there is an inverse relationship between k_q and f_Δ^T in the case of ruthenium(II) complexes it is a much steeper curve and not as smooth as for biphenyl derivatives. This is not surprising since several factors vary for this series of Ru(II) sensitizers, for example, as discussed earlier, the steric factor for $[Ru(bpy)_3]^{2+}$ is expected to be lower than for the all other complexes especially $[Ru(L^{3a})_3]^{2+}$. It is worth noting that if the point labeled 10 in Figure 4, corresponding to $[Ru(L^{3a})_3]^{2+}$ the complex expected to show the largest steric factor, is ignored, the data presented in Figure 4 are not dissimilar to plots obtained when using a wide range of triplet states of organic sensitizers of singlet oxygen which show a similar amount of scatter [see ref 5], i.e., much greater than that for biphenyl derivatives recently obtained by us and shown in Figure 4 as filled symbols where essentially only the oxidation potential of the sensitizer was varied.[9]

The free energy for electron-transfer quenching of excited ruthenium(II) complexes by molecular oxygen is expected to depend on the redox parameters and the excitation energies of the interacting species as given by Rehm and Weller,[49] viz.,

$$\Delta G^{CT} = F[E^{ox}_{(3+/2+)} - E^{red}_{O_2}] - E_{00} + C \qquad (8)$$

where F is the Faraday constant and $E^{red}_{O_2}$ is the half wave reduction potential for oxygen taken as −0.78 V vs SCE.[50] The Coulomb term given by

$$C = qq'/\epsilon r \qquad (9)$$

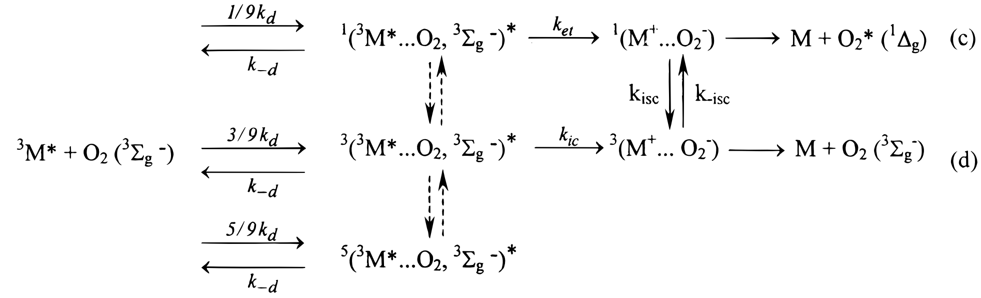
represents the electrostatic interaction energy gained by point charges separated at distance r in a solvent with static dielectric constant, ϵ, which leads to stabilization when the ions carry opposite charges. The magnitude of C to be used in eq 8 has been questioned.[51a] Often this term is neglected, especially in polar solvents such as acetonitrile, since $\epsilon = 37$. Values of ΔG^{CT} taking $C = 0$ given in Table 2 and Figure 5 show the dependence of k_q, k_q^3, and k_q^1 on ΔG^{CT} for the Ru(II) complexes compared with data from a series of biphenyl derivatives.[9] Although there appears to be an inverse correlation between ΔG^{CT} and k_q and k_q^3, respectively, for the Ru(II) complexes it is important to note that eq 8 contains the term $-E_{00}$ and this may account for the inverse relationship since some dependence on E_{00} has already been noted; see Figure 3. It is important to appreciate that for organic sensitizers of singlet oxygen a positive correlation is often observed between k_q, k_q^3, and k_q^1 and ΔG^{CT} for a series of related organic compounds,[4,5,8,9] e.g., see filled symbols in Figure 5 taken from ref 9, whereas parts a and b of Figure 5 show an inverse correlation for the Ru(II) complexes.

Suppan[51b] recently proposed what he argued was a more realistic expression for C in polar solvents when $\epsilon \geq 2$, viz.,

$$C \cong qq'/4r \qquad (10)$$

when r is the distance between the charged centers. The value of C calculated from eq 10 is about one-half of the value in nonpolar solvents, and if Suppan is correct, C cannot be neglected in the calculation of ΔG^{CT} even for highly polar solvents. The electrostatic interaction term may therefore play a role far more important in charge transfer mediated oxygen quenching than has so far been recognized. The value calculated from eq 10 using $q = 3$ and $q' = -1$ for charge separation of 6.5 Å is −225 kJ mol^{-1}, which is over 9 times greater than that calculated from eq 9 for acetonitrile. The actual value of C may well lie between the values calculated from eqs 9 and 10.

SCHEME 2



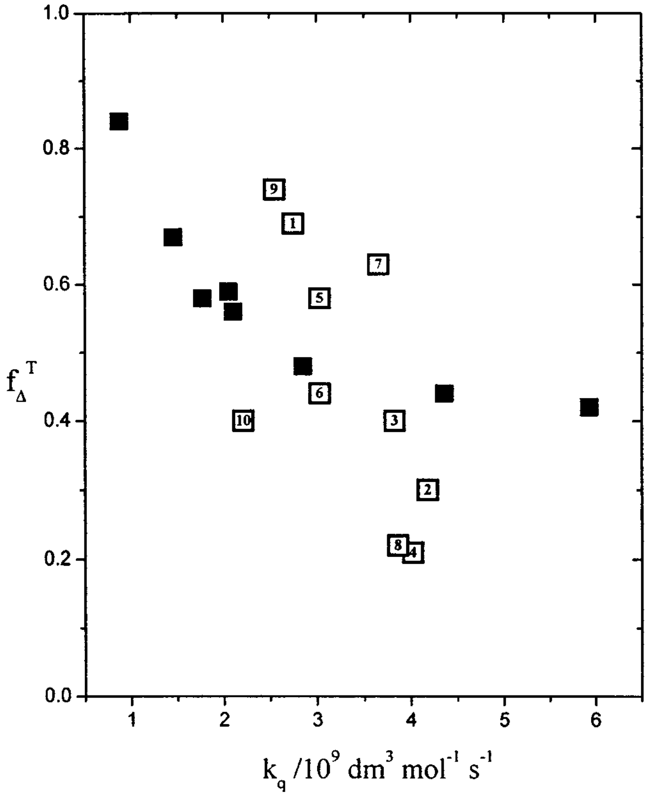


Figure 4. Dependence of the efficiencies of $O_2*(^1\Delta_g)$ production, f_Δ^T, on the rate constants for quenching of the excited ^{3}MLCT states of ruthenium complexes in acetonitrile (□). Corresponding dependence for some triplet biphenyl derivatives in acetonitrile (■) taken from ref 9.

Stabilization of ionic pairs of the type $\{[RuL_3]^{3+}\cdots O^{2-}\}$ by such a large amount (225 kJ mol^{-1}) would in many cases place the energy of such ion pairs below the energy of the separate species, O_2 and $[RuL_3]^{2+}$. This is unlikely since transient absorption measurements using nanosecond laser flash photolysis equipment give no evidence for $[RuL_3]^{3+}$or ion pairs involving the $[RuL_3]^{3+}$ ion being produced following oxygen quenching of the excited states of these $[RuL_3]^{2+}$ ions in acetonitrile.

Figure 5b shows the dependence of k_q^3 on ΔG^{CT} for data obtained for oxygen quenching of triplet biphenyl derivatives[9] as well as for the ruthenium complexes and these two classes of compounds behave very differently, although the range of rate of constants is similar. The correlation with ΔG^{CT} as mentioned earlier is negative in the case of ruthenium complexes, not positive. However, a value of $C = 0$ was substituted in eq 8, in both cases. If the stabilization energies for the ruthenium(II) complexes were more than 60 kJ mol^{-1} greater due to the greater charge on the ruthenium than on the biphenyl derivatives after charge transfer, and both eqs 9 and 10 predict it will be 3 times greater, then these results could conform to the expectations of Marcus[52] with the data for the ruthenium complexes being shifted to much more negative values of ΔG^{CT} in which case the values of k_q^3 would rise and then fall as ΔG^{CT} becomes more negative. The present data unfortunately do not give a sufficient range of changes in $E_{+3/+2}^{OX}$ and of E_{00} to firmly indicate whether charge transfer mediated catalyzed intersystem crossing is important in the case of ruthenium(II) complexes. The present authors suggest steric and energy gap dependences are most likely to explain the variations observed in k_q^1 and k_q^3 values for the ruthenium(II) complexes studied here.

The driving force for energy transfer ΔG^{EN} can be taken as the difference in the excited-state energy of the donor, D, and the acceptor, A, i.e., equal to the energy gap ΔE

$$\Delta G^{EN} = \Delta E = -(E_{D*} - E_{A*}) = -(E_{00} - E_{O_2*}) \quad (11)$$

where $E_{O_2*} = E(^1\Sigma_g{}^+) = 157$ kJ mol^{-1} or $E(^1\Delta_g) = 94$ kJ mol^{-1} depending on which excited state of oxygen is initially produced during quenching. Bodesheim et al.[16] have measured oxygen quenching rate constants for 13 organic sensitizers with triplet energies E_T in the range $140 < E_T < 309$ kJ mol^{-1} in carbon tetrachloride solution where emission from both $O_{2*}(^1\Delta_g)$ and $O_{2*}(^1\Sigma_g+)$ can be detected. They were thus able to measure the proportion of energy transfer resulting in $O_{2*}(^1\Delta_g)$ and $O_{2*}(^1\Sigma_g{}^+)$ and thereby derive the separate contributions $k_q(^1\Delta_g)$ and $k_q(^1\Sigma_g{}^+)$ to the rate constants for quenching via the single channel k_q^1 under these conditions. These authors found a similar energy gap law dependence for the values of $k_q(^1\Delta_g)$, $k_q(^1\Sigma_g{}^+)$, and for $k_q^3/3$ (NB k_q^3 is divided by 3 to allow for the spin statistical factor) for sensitizers with ΔE or $E_T < 200$ kJ mol^{-1} and their results are illustrated by the filled points in Figure 6. To compare our values for k_q^1 which equal $[k_q(^1\Delta_g) + k_q(^1\Sigma_g{}^+)]$ in acetonitrile with those of the organic triplet sensitizers in carbon tetrachloride, we have assumed that upon quenching of the exited ^{3}MLCT state of the ruthenium(II) complexes studied by us the proportion of quenching via energy transfer to give directly $O_2*(^1\Delta_g)$ and the proportion of quenching which gives $O_2*(^1\Sigma_g{}^+)$, which then undergoes a rapid decay to give $O_2*(^1\Delta_g)$ are in the same ratio as that found for organic sensitizers with the same triplet energy. This dependence on energy gap is given by the dashed curve shown in Figure 6, taken from ref 16. In this way, values of $k_q(^1\Delta_g)$ and $k_q(^1\Sigma_g{}^+)$ were estimated from our measured values of k_q^1 for ruthenium(II) complexes, and these are plotted in Figure 6. Within the typical scatter observed for organic sensitizers, our estimated values for $k_q(^1\Delta_g)$ and $k_q(^1\Sigma_g{}^+)$ fall close to the curve drawn by Bodesheim et al.[16] However, the values of k_q^3 we obtained for the ruthenium(II) complexes are at least a factor of 10 higher than the values obtained by these previous workers for triplet organic sensitizers for k_q^3 in carbon tetrachloride.

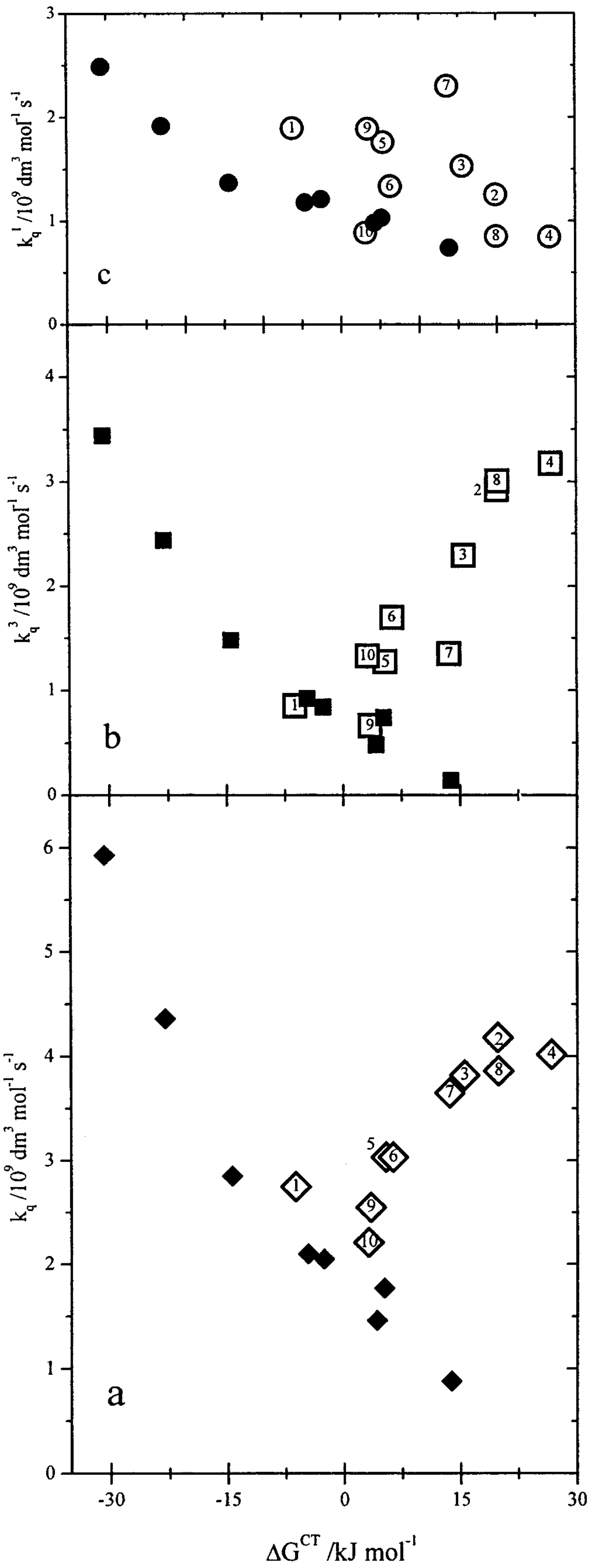


Figure 5. Dependence of the oxygen quenching rate constants of the ^{3}MLCT excited state of Ru(II) complex ions on the free energy change, ΔG^{CT}, for charge transfer from excited ruthenium complexes to $O_2(^3\Sigma_g^-)$ in acetonitrile k_q (◇), k_q^3 (□), and k_q^1 (○) together with corresponding quenching rate constants k_q (◆), k_q^3 (■), and k_q^1 (●) for biphenyl derivatives in acetonitrile.[9]

Since the dependence of k_q^1 on ΔE for the ruthenium(II) complexes in acetonitrile as a solvent is very similar to that obtained for $k_q^1 = [k_q(^1\Delta_g) + k_q(^1\Sigma_g^+)]$ for organic sensitizers in carbon tetrachloride (Figure 6), the reasons for this dependence are almost certainly the same. Bodensheim et al.[16] used the equation derived by Kearns[53] to explain their results for the rates of internal conversion of weakly bound exciplexes (labeled in Scheme 2 as k_{et} and k_{ic}),

$$k_{ic} = \frac{2\pi}{\hbar}\rho(\Delta E)F(\Delta E)\beta^2 \tag{12}$$

where $\rho(\Delta E)$ is the density of final states which are nearly degenerate with the initial state, $F(\Delta E)$ is the Frank–Condon factor, and β is the matrix element of electronic coupling between the initial and final states. These authors point out the dependence of the experimental curve for oxygen quenching rate constants, log k_q, on ΔE is much weaker than the dependence of log(ΔE) on ΔE derived by Siebrand[54] for internal conversion between potential energy curves of isolated molecules with deep minima rather than the shallow minima expected for weakly bound exciplexes.

The overall rate constants for oxygen quenching of the exited ^{3}MLCT states of ruthenium(II) complexes in acetonitrile are higher than those for aromatic hydrocarbons in carbon tetrachloride. The fact that the value for k_q^1 derived from k_q and f_Δ^T are comparable with the work of Bodensheim et al.[16] but the values for k_q^3 are much higher is probably due to increased intersystem crossing from the singlet weakly bound exciplexes (or encounter complexes) to triplet bound exciplexes in the case of the ruthenium(II) complexes in acetonitrile as shown by the dotted arrows in Scheme 2. Whether this is due to increased spin–orbit coupling due to the presence of ruthenium in the sensitizer or to the change in solvent remains to be established. Since the triplet channel represented by steps b and d in Schemes 1 and 2, respectively, is essentially a catalyzed intersystem crossing in which electronic energy is totally converted into internal energy, mainly vibrational energy, the presence of high-energy vibrations present in the solvent acetonitrile and absent in the solvent carbon tetrachloride may explain this difference in rate constants. Alternatively, it could be that charge transfer mediated catalyzed intersystem crossing is more favorable in the more polar solvent.

Conclusions

(1) Extended conjugation, within the substituted ligands in the nine Ru(II) complexes as a result of increasing the number of vinyl linked methoxybenzenes or benzocrown ethers on the 2,2′-bipyridine ligands, is responsible for the observed red shift in the phosphorescence maxima, λ_{em}^{max}, of these complexes relative to that of the parent $[Ru(bpy)_3]^{2+}$. The measured lifetimes of the excited ^{3}MLCT states of these complexes are in the range 0.85 ± 0.12 μs, except in the two cases $[Ru(L^{2b})(bpy)_2]^{2+}$ and $[Ru(L^{2a})(bpy)_2]^{2+}$, where the lifetimes drop to about half this value. These lower lifetimes can be explained as being due to the higher energies of the ^{3}MLCT states for these two complexes relative to the corresponding $[Ru(L^{2b})_3]^{2+}$ and $[Ru(L^{2a})_3]^{2+}$ which increases the probability of mixing with higher excited metal-centered states leading to more facile nonradiative deactivation of the ^{3}MLCT states.

(2) The efficiencies of singlet oxygen production, f_Δ^T, and the quenching rate constants for triplet state quenching by oxygen, k_q, have been measured for $[Ru(bpy)_3]^{2+}$ and nine Ru(II) complexes with substituted 2,2′-bipyridine ligands. An inverse

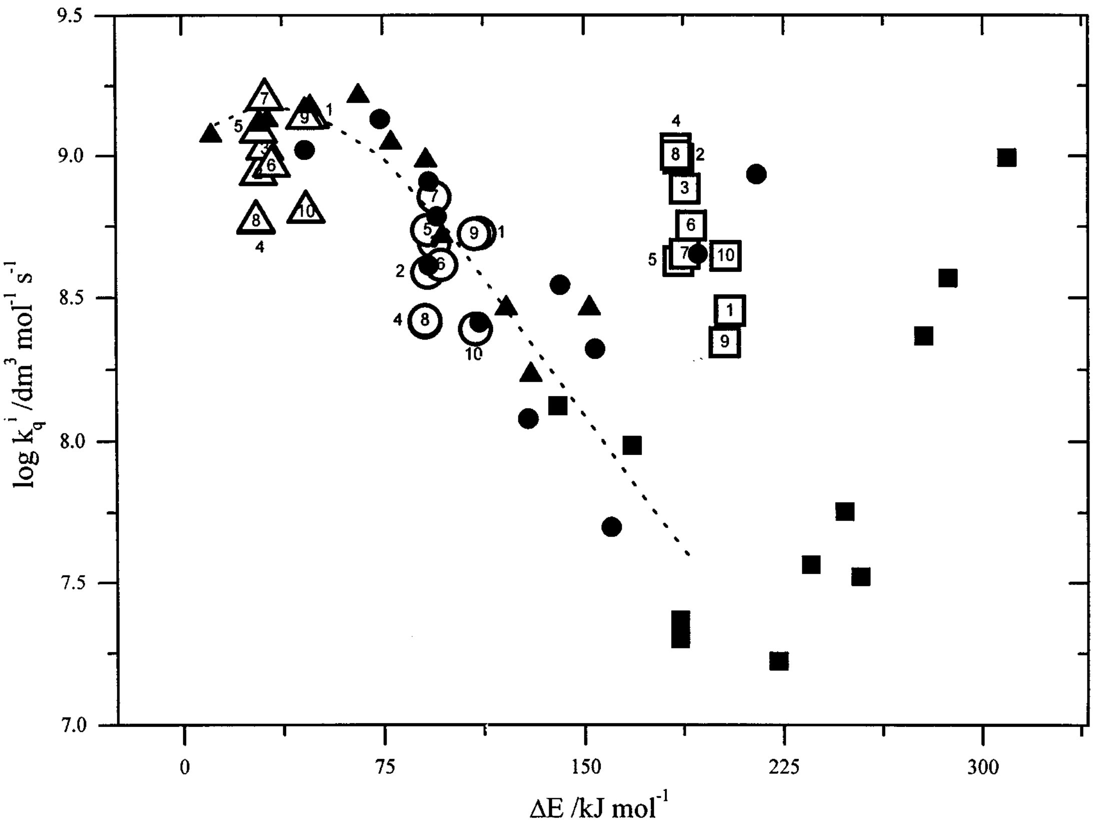


Figure 6. Dependence of the quenching rate constants k_q ($^1\Delta_g$) (○), k_q ($^1\Sigma_g$) (△), and $k_q^3/3$ (□) of the ^{3}MLCT excited state of complex ions by oxygen on the driving force for energy transfer in acetonitrile together with corresponding rate constants $k_q(^1\Delta_g)$ (●), k_q^1 ($^1\Sigma_g$) (◆), and $k_q^3/3$ (■) taken from ref 16 for aromatic hydrocarbons in carbon tetrachloride.

correlation between f_Δ^T and k_q is observed which shows more scatter and seems to be steeper than, for example, that for biphenyl derivatives because more factors, such as state energy, oxidation potential, and steric factors vary in the case of ruthenium complexes, whereas in the case of the biphenyl derivatives only the oxidation potentials change significantly. The steeper inverse correlation in the case of the ruthenium complexes is probably due to the energetic and steric factors showing a similar, and therefore amplified, dependence on the nature of the substituents.

(3) The dependence of the quenching rate constants k_q on E_{00} can be explained in terms of Frank–Condon factors, i.e., increased quenching rate constants with decreased energy gap, ΔE, between the initial and final states. The dependence of k_q^3 on E_{00} is very close to that shown by k_q; however, k_q^1 values show a much different dependence on E_{00}. The dependence of k_q^1 on ΔE for ruthenium complexes in acetonitrile are shown to be consistent with the sum $[k_q(^1\Delta_g) + k_q(^1\Sigma_g{}^+)]$ obtained for a series of aromatic hydrocarbons in carbon tetrachloride by Bodesheim et al.,[16] but k_q^3 values for the ruthenium complexes in acetonitrile are much higher than those of the aromatic hydrocarbons in CCl_4. This is attributed to increased intersystem crossing from the singlet encounter complexes to the triplet encounter complexes in the case of these Ru(II) complexes because of the presence of the ruthenium heavy atom. It also suggested that k_q^3 is likely to show a solvent dependence and to be lower when carbon tetrachloride is the solvent.

(4) It is not clear whether oxygen quenching of the phosphorescence of ruthenium complexes involves charge transfer mediated quenching. The dependence of the k_q and k_q^3 on free energy change for charge transfer, ΔG^{CT}, calculated from eq 8 is the opposite of that observed for aromatic hydrocarbons (e.g., biphenyl derivatives[9]) where charge transfer mediated quenching is firmly established.

(5) Ruthenium(II) complexes have been shown to demonstrate interesting similarities and interesting differences when compared with organic sensitizers of singlet oxygen. Further work is underway with a series of compounds which has a greater variation in E_{00} and in $E_{3+/2+}^{OX}$ and less steric variation than those reported here in order to further understanding of the quenching mechanism in the case of coordination complexes.

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