Oxygen Quenching of Electronically Excited Hexanuclear Molybdenum and Tungsten **Halide Clusters**

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Quenching of the electronically excited $[M_6X_8]Y_6^{2-}$ (M = Mo^{II}, W^{II}; X, Y = Cl, Br, I) ions by molecular oxygen has been investigated. Stern-Volmer analysis of emission intensity and lifetime data reveals that the rate constants for oxygen quenching of the $[M_6X_8]Y_6^{2^-}$ ions are similar $(k_q^{obs} = 8.1 (37) \times 10^7 M^{-1} s^{-1})$ with the exception of the $[W_6I_8]Y_6^{2^-}$ clusters, which exhibit significantly greater quenching rates $(k_q^{obs} = 2.1 (5) \times 10^9 M^{-1} s^{-1})$. Photosensitized oxidation of 1-methylcyclohexene and 1,2-dimethylcyclohexene by all $[M_6X_8]Y_6^{2^-}$ clusters yields products expected for the reaction of the olefins with singlet oxygen. No evidence of radical autooxidation products were detected. However, the measured quantum yields for the photooxidation of 2,3-diphenyl-p-dioxene by only the $[M_6X_8]Y_6^{2-}$ ($M \neq W$; $X \neq I$) clusters are in agreement with the values calculated from a kinetic scheme involving the exclusive production of singlet oxygen by direct energy transfer; observed quantum yields of [W₆I₈]Y₆²⁻-photosensitized reactions are not consistent with this scheme. One explanation for the enhanced oxygen quenching rates of the $[W_6I_8]Y_6^{2-}$ excited states ($[W_6I_8]Y_6^{2-*}$) and anomalous observed quantum yields is the contribution of an electron-transfer pathway to the quenching reaction. Transient absorption spectra for the reaction between $W_6I_{14}^{2-4}$ and oxygen, however, do not display transients attributable to electron-transfer products. Accordingly, we ascribe the enhanced quenching rate of $[W_6I_8]Y_6^{2-*}$ by oxygen to greater adiabaticity of the energy-transfer reactions of these ions as compared to their homologous cluster counterparts. The absence of an electron-transfer contribution to the $[M_6X_8]Y_6^{2-}$ cluster photosensitized production of ${}^{1}O_{2}$ ([M₆X₈]Y₆^{2-*} + O₂ \rightarrow [M₆X₈]Y₆²⁻ + O₂ \rightarrow [M₆X₈]Y₆²⁻ + ¹O₂) parallels the results observed for the photosensitized production of ${}^{1}O_{2}$ by RuL₃²⁺ (L = polypyridyl) systems, which also produce singlet oxygen exclusively by energy transfer despite the existence of potential electron-transfer pathways.

Introduction

Reactions between oxygen and molecules in electronic excited states typically proceed by electron or energy transfer to yield unique primary photoproducts of oxygen. Transfer of a single electron from an electronic excited state results in the direct¹⁻³ or indirect⁴⁻⁹ production of superoxide ion, O_2^- , whereas energy exchange leaves oxygen in its lowest energy singlet excited state, ${}^{1}O_{2}$. The formation of ${}^{1}O_{2}$ can be alternatively explained

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by postulating secondary reactions of photoinduced electrontransfer products. Specifically, several investigations during recent years have described the formation of ${}^{1}O_{2}$ by the oxidation of O_{2}^{-} with transition-metal complexes^{26,27} and organic peroxides.²⁸ Such chemiluminescence reactions may play an especially important role in photochemical ¹O₂ schemes involving the former because the back reaction between superoxide and a one-electron photooxidized metal complex, produced as the primary photoproducts of electron-transfer quenching, often occurs with sufficient exergonicities to directly populate the lowest energy singlet excited state $({}^{1}\Delta_{g})$ of oxygen. For example, the energetics of the Ru-(bpy)₃²⁺ (bpy = 2,2'-bipyridine)/O₂ system, which has served as the prototype for transition-metal sensitization of ${}^{1}O_{2}$, 29,30 are such that singlet oxygen can be formed in principle by electron transfer between $Ru(bpy)_3^{2+*}$ and O_2 followed by cage recombination of the primary photoproducts (i.e., $Ru(bpy)_3^{3+} + O_2^- \rightarrow Ru(bpy)_3^{2+}$ + $^{1}O_{2}$). Kinetics studies employing chemical traps initially suggested the quantitative production of singlet oxygen from $Ru(bpy)_3^{3+}/O_2^{-}$ reaction.³¹ However, the failure to directly detect

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infrared luminescence at 1.27 μ m, corresponding to the ${}^{1}O_{2} \rightarrow {}^{3}O_{2}$ transition, provides strong evidence against the chemiluminescent production of singlet oxygen.³² That the importance of an electron-transfer pathway to photosensitized ${}^{1}O_{2}$ production has come under dispute, even for this well-examined system, underscores the difficulties associated with precisely defining the photochemistry of transition-metal complexes with O_{2} .

Early in our studies of the excited-state reactivity of the d⁴ $[M_6X_8]Y_6^{2-}$ (M = Mo^{II}, W^{II}; X, Y = Cl, Br, I) ions, we observed that the intense luminescence, which characterizes these complexes, is efficiently quenched by oxygen. The spin-triplet nature of the luminescent $[M_6X_8]Y_6^{2^-}$ excited state, originally inferred from the long lifetimes of these complexes,^{33,34} has been confirmed by experiments employing conventional organic energy-transfer acceptors such as azulene and anthracene.³⁵ On this basis, O_2 quenching of $[M_6X_8]Y_6^{2-}$ excited states by an energy-transfer mechanism is a viable reaction pathway. Additionally, $[M_6X_8]Y_6^{2-}$ excited-state complexes possess a rich oxidation-reduction chemistry, and we have recently demonstrated the propensity of $[M_6X_8]Y_6^{2-}$ ions to undergo electron-transfer reactions along highly energetic chemiluminescence pathways.³⁶ These results in conjunction with the energetics of the $[M_6X_8]Y_6^{2-}$ excited state suggest that electron and energy transfer are potential contributing pathways to the photooxygenation reactivity of this class of compounds.

We now report a detailed kinetics analysis of the reactions of electronically excited $[M_6X_8]Y_6^{2-}$ ions with O_2 . For a given metal core, the energy and oxidation potential of the excited state can be tuned with the ligating halides, thereby allowing us to systematically examine the photooxygenation chemistry of these cluster ions over a wide range of electron- and energy-transfer driving forces.

Experimental Section

Materials. The tetrabutylammonium salts of $M_6 X_{14}^{2-}$ and the mixed-halide molybdenum and tungsten clusters $[M_6X_8]Y_6^{2-}$ were prepared and purified by previously described methods.^{37,38} Clusters were analyzed by fast atom bombardment mass spectrometry (FABMS) at the NIH/MSU Mass Spectrometry Facility. The purity of the cluster system was confirmed by the presence of a single-parent ion cluster peak in FABMS spectra.³⁹ Ethylene glycol dibenzoate and 2,3-diphenyl-p-dioxene were prepared and purified by literature methods.^{40,41} Tetracyanoethylene (TCNE) was obtained from Aldrich Chemical Co., recrystallized from chlorobenzene, and twice sublimed. Tetrabutylammonium hexafluorophosphate (Southwestern Analytical Chemicals) was dissolved in ethyl acetate, dried over MgSO₄, recrystallized from pentane-ethyl acetate solution, and dried in vacuo for 12 h at 60 °C. Acetonitrile, acetone, and dichloromethane, obtained from Burdick and Jackson Laboratories (distilled-in-glass grade), were used as received for electrochemical and photochemical experiments. For quenching and transient absorption studies, these solvents were subjected to seven freeze-pump-thaw cycles and vacuum distilled onto 4-Å molecular sieves (3-Å molecular sieves were used for acetonitrile) contained in a 1-L flask equipped with a high-vacuum Teflon valve.

Instrumentation and Methods. Absorption spectra were measured on a Cary 17D or a Varian 2300 spectrometer. Steady-state and time-resolved luminescence spectra were recorded with a previously described emission spectrometer and a DCR1 Nd:YAG laser (λ_{exc} = 355 nm, fwhm = 8 ns) system.^{36b,42} Transient absorption measurements were made with the pulseprobe technique. The excitation source was a Quanta Ray DCR2-A Nd:YAG laser whose fundamental frequency can be doubled or tripled with a Quanta Ray HG-2 harmonic generator. For the experiments described herein, the third harmonic, which was employed as the excitation pulse, was separated from the second harmonic and fundamental frequencies with three ESCO dichroic mirrors. The laser excitation beam intercepted a white light probe beam generated from a 150-W pulsed OSRAM Xe arc lamp (XBO150/S) mounted in a Photon Technology International (PTI) A1000 lamp housing and driven with a PTI LPS1000 power supply. The excitation and probe beams were nearly collinear with an incidence angle of 11°. The probe beam passed through a Uniblitz 23X mechanical shutter and a Schott WG-360 cutoff filter before it was focused onto the sample (0.2 cm path length) by an f/7.0 lens. The lamp was pulsed (2 Hz repetition rate) to ~ 12 A for a duration of 5 ms. The triggering of the Nd:YAG laser, pulsing of the lamp, and opening and closing of the shutter were orchestrated by synchronization electronics designed and built by Martin Rabb, Electronics Design Engineer, Chemistry Department, Michigan State University. The light transmitted by the sample was collimated by an f/7.0 lens and focused by a second lens (f/4.0) through a 399-nm (Schott KV-399) cutoff filter onto the entrance slit of a SPEX 1680A monochromator. The signal obtained from a Hamamatsu R928 photomultiplier tube was amplified by using a LeCroy 6103 dual amplifier/trigger. The amplifier output was passed into a LeCroy TR8828D transient recorder, and the digitized signal was stored in two MM8104 memory modules arranged in a series configuration. The amplifier, digitizer, memory modules, and a LeCroy 6010 GPIB interface were housed in a LeCroy 8013A minicrate. Data acquired and processed by a Compaq 386 computer equipped with a 40-megabyte hard disk, were typically averaged over 1000 pulses.

The light source used in photooxidation studies was a 1000-W Hanovia Hg/Xe lamp (f/3.0 housing). The excitation beam of light was passed through an iris with a 10-mm aperture onto the photolysis reaction cell, which was a standard Schlenk tube capped with a serum cap. The Schlenk tube was housed in a cell compartment thermostated at 20.0 \pm 0.2 °C. Photolyzed solutions were continually saturated with oxygen which entered the cell through the side arm of the Schlenk tube. Aliquots were removed from the Schlenk tube with a 1.00-mL Hamilton syringe during the course of photolysis. Photochemically generated products were identified by GC/MS (Hewlett-Packard 5985 GC/MS equipped with a HP5 capillary column) and ¹H NMR spectroscopy (Bruker WM-250). Once the photoproducts had been identified, their formation during photolysis reactions was monitored with a 5890 Hewlett-Packard GC equipped with a flame ionization detector, a 25-m GB-1 Foxboro capillary column, and integrator. Hexadecane was used as an internal standard.

Electrochemical measurements were performed with a PAR Model 173 potentiostat, Model 175 programmer, and a Model 179 digital coulometer. The output of the PAR 179 was fed directly into a Houston Instrument Model 2000 X-Y recorder. A Pt button and gauze were employed as working and auxiliary electrodes, respectively, and a Ag wire served as a reference electrode by using ferrocene as an internal standard. Potentials

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TABLE I: Cluster Lifetimes and Oxygen Quenching Rate Constants

	$[M_6X_8]Y_6^{2-}$ ions	$\tau_0/\mu s^a$	$k_{g}^{obs}/M^{-1} s^{-1 b,c}$
1	[MosClo]Cls2-	180	3.5×10^{7}
2	[Mo ₆ Cl ₈]1 ₆ ²⁻	86	5.6×10^{7}
3	Mo ₆ Cl ₈ Br ₆ ²⁻	140	3.9×10^{7}
4	[Mo ₆ Br ₈]Br ₆ ²	120	1.2×10^{8}
5	$[Mo_6Br_8]I_6^{2-}$	71	5.0×10^{7}
6	$[Mo_6Br_8]Cl_6^{2-}$	190	8.2×10^{7}
7	[W ₆ Cl ₈]Cl ₆ ²⁻	2.2	8.4×10^{7}
8	$[W_6C_{18}]I_6^{2-}$	5.6	6.6×10^{7}
9	$[W_{6}Cl_{8}]Br_{6}^{2-}$	4.4	5.9×10^{7}
10	$[W_6Br_8]Br_6^{2-}$	15	1.4×10^{8}
11	$[W_6Br_8]Cl_6^{2-}$	15	1.0×10^{8}
12	$[W_6Br_8]I_6^{2-}$	19	1.4×10^{8}
13	$[W_6I_8]I_6^{2-}$	25	2.7×10^{9}
14	$[W_{6}I_{8}]Br_{6}^{2-}$	27	1.7×10^{9}
15	[W ₆ I ₈]Cl ₆ ²⁻	16	1.9×10^{9}

^aLifetimes measured in acetone with $\lambda_{exc} = 355$ nm (Nd:YAG, fwhm = 8 ns). ^bRate constant for the quenching of $[M_6X_8]Y_6^{2-}$ luminescence by oxygen. $c \pm 15\%$.

were related to the SCE reference scale by using a ferroceniumferrocene couple of 0.31 V vs SCE.43

Quantum Yields. Absolute quantum yields for the $[M_6X_8]Y_6^{2-}$ -photosensitized oxidation of 2,3-diphenyl-p-dioxene in acetone at room temperature were measured at 436 nm with a ferrioxalate actinometer.44,45 The excitation wavelength was isolated with 10-cm CuSO₄ and NaNO₂ solution filters and an Oriel 56450 narrow band-pass interference filter. Lamp intensities at 436 nm were typically 2.5×10^{-5} einsteins min⁻¹. The disappearance of 2,3-diphenyl-p-dioxene and the appearance of the photooxidized product, ethylene glycol dibenzoate, were monitored by gas chromatography and NMR spectroscopy. Reported quantum yields are averages of three experimental runs.

Product Distribution Studies. The photooxidations of 1methylcyclohexene $(2 \times 10^{-2} \text{ M})$ and 1,2-dimethylcyclohexene $(2 \times 10^{-2} \text{ M})$ were carried out with Mo₆Cl₁₄²⁻ $(1 \times 10^{-5} \text{ M}, \lambda_{exc})$ \geq 436 nm), W₆I₁₄²⁻ (1 × 10⁻⁵ M, $\lambda_{exc} \geq$ 436 nm), and Rose Bengal $(1 \times 10^{-3} \text{ M}, \lambda_{\text{exc}} \ge 590 \text{ nm})$ as the photosensitizers in acetone and acetonitrile. Photolyzed solutions were treated with excess triphenylphosphine, which reduced the initially formed hydroperoxide to its corresponding alcohol. Products were analyzed by gas chromatography and GC/MS. As had previously been reported for Rose Bengal,46 product analysis could be facilitated by immobilizing the photosensitizers to polymer supports, owing to the ease with which the photosensitizer could be isolated from photolyzed solutions. This was particularly useful for the Rose Bengal and $Mo_6Cl_{14}^{2-}$ photosensitized oxidations because oils typically formed during the work-up of the photoproducts. The measured product ratios of photolysis were the same (within our experimental error of $\pm 15\%$) whether the photosensitizer was immobilized on the polymer support or dissolved in homogeneous solution.

Results

Excited-state lifetimes of $M_6X_{14}^{2-}$ and $[M_6X_8]Y_6^{2-}$ cluster ions in rigorously deoxygenated acetone at 23.0 ± 0.5 °C are listed in Table I; all decays were exponential over four half-lives. The lifetime and luminescence intensity of the cluster ions are attenuated significantly by oxygen. Observed rate constants (k_{a}^{obs}) for O_2 quenching, also given in Table I, were determined by Stern-Volmer analysis of the emission intensity and lifetime quenching data; measured rate constants were independent of the experimental method and the rates reported in Table I represent

TABLE II: Electronic Origin of Lowest Energy Excited State, Reduction Potentials, and Energy- and Electron-Transfer Driving Forces

	$[M_6X_8]Y_6^{2-}$ ion	$\Delta E_{0,0}/\mathrm{eV}^a$	$E_{1/2}/V^{b}$	$\Delta G_{ m en}/{ m V}$ c	$\Delta G_{\rm et}/{ m V}^{d}$
1	[Mo6Cl8]Cl62-	1.79	1.46	-0.81	+0.55
2	$[Mo_6Cl_8]I_6^{2-}$	1.75	1.47	-0.77	+0.60
3	$[Mo_6Cl_8]Br_6^{2-}$	1.80	1.46	-0.82	+0.54
4	$[Mo_6Br_8]Br_6^{2-}$	1.79	1.20	-0.81	+0.29
5	$[Mo_6Br_8]I_6^{2-}$	1.70	1.23	-0.72	+0.41
6	$[Mo_6Br_8]Cl_6^{2-}$	1.70	1.20	-0.72	+0.38
7	[W ₆ Cl ₈]Cl ₆ ²⁻	1.83	1.06	-0.85	+0.11
8	$[W_6C_{18}]I_6^{2-}$	1.93	1.11	-0.95	+0.06
9	$[W_6Cl_8]Br_6^{2-}$	1.86	1.11	-0.88	+0.13
10	$[W_6 Br_8] Br_6^{2-}$	1.91	0.93	-0.93	-0.10
11	$[W_6Br_8]Cl_6^{2-}$	1.89	0.91	-0.91	-0.10
12	$[W_6Br_8]I_6^{2-}$	1.92	0.92	-0.94	-0.12
13	$[W_6I_8]I_6^{2-}$	2.08	0.67	-1.10	-0.53
14	$[W_6 I_8] Br_6^{2-}$	2.07	0.71	-1.09	-0.48
15	[W ₆ I ₈]Cl ₆ ²⁻	2.07	0.69	-1.09	-0.50

^a Estimation of the 0-0 energy of the emissive excited state of the $[M_6X_8]Y_6^{2-}$ ions from low temperature (77 K) luminescence spectra. ^bAs reduction potentials for the $[M_6X_8]Y_6^{-/2-}$ couple vs SCE. ^cStandard free energy change for the energy-transfer reaction between $[M_6X_8]Y_6^{2-*}$ and ${}^{3}O_2$; $\Delta G_{en} = -\{E_{0,0}([M_6X_8]Y_6^{2-*}) - E({}^{1}O_2({}^{1}\Delta_8))\}$. [M₆X₈] Γ_6^{-1} and O_2 , $\Delta O_{en} = \neg \mathcal{L}_{0,0}(\Gamma_{106},\kappa_8) \Gamma_6 = \mathcal{L}_{0,2}(\neg \mathcal{L}_{g}) \mathcal{L}_{0}$ ^d Standard free energy change for the electron-transfer reaction be-tween [M₆X₈] Y_6^{-2*} and ³O₂ to produce [M₆X₈] Y_6^{-} and superoxide ion; $\Delta G_{et} = -\{E_{1/2}([M_6X_8]Y_6^{-/2-*}) - E(O_2/O_2^{-})\}.$

the averages of at least three experimental runs. Stern-Volmer plots were linear over the O_2 concentration range 10^{-5} – 10^{-2} M and intercepts were unity.

The mechanism of the quenching reaction is intimately related to the thermodynamic driving forces of the excited-state energy-transfer (reaction 1) and electron-transfer (reaction 2) pathways. Free energies for reactions 1 and 2 depend directly on the

$$[M_6X_8]Y_6^{2-*} + O_2 \rightarrow [M_6X_8]Y_6^{2-} + {}^{1}O_2$$
(1)

$$[M_6X_8]Y_6^{2-*} + O_2 \rightarrow [M_6X_8]Y_6^{-} + O_2^{-}$$
(2)

formal reduction potential and the free energy content of the hexanuclear cluster excited state. This latter energy is determined directly from low-temperature emission spectra. Spectroscopic studies of transition-metal complexes in recent years have demonstrated that the free energy content of the excited state is primarily enthalpic and possesses only a small entropic contribution.^{47,48} Consequently, the excited-state free energies of the hexanuclear cluster ions are approximated by the 0-0 energies of the luminescent excited state; Table II lists 0-0 energies which were estimated from the high-energy tail of the low-temperature luminescence bands of the respective cluster ions.⁴⁹ From these energies, the $[M_6X_8]Y_6^{-/2-}$ excited-state couple can be ascertained from the simple thermodynamic relation $E_{1/2}([M_6X_8]Y_6^{-/2-*}) =$ $\Delta E_{0,0} - E_{1/2}([M_6X_8]Y_6^{-/2-})$. This expression requires explicit knowledge of the $E_{1/2}([M_6X_8]Y_6^{-/2-})$ formal reduction potential. Accordingly, cyclic voltammograms of the hexanuclear cluster ions in acetone were recorded. The clusters, whose redox potentials are shown in Table II, undergo simple one-electron oxidation. Plots of anodic and cathodic peak currents ($i_{p,a}$ and $i_{p,c}$, respectively) vs [scan rate]^{1/2} were linear with an intercept of zero and $i_{p,a}/i_{p,c}$ = 1.02 ± 0.02. Anodic to cathodic peak separations (ΔE_p) were greater than 59 mV, but were comparable to that measured for ferrocene, thereby establishing that deviations of ΔE_p from the theoretical limit are primarily due to uncompensated cell resistance.

Foote and co-workers have shown that substituted cyclohexenes react with oxygen radicals and ¹O₂ to yield characteristic products and product distributions.⁵⁰ Reaction of 1-methylcyclohexene,

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TABLE III: Products of Reaction (%) of 1-Methylcyclohexene (1) and 1,2-Dimethylcyclohexene (2) with Oxygen under Photosensitized and Radical Oxidation Conditions^a

	products of 1		products of 2			
photosensitizer	3	4	5	6	7	8
Mo ₆ Cl ₁₄ ^{2-b}	77	23	0	85	15	0
$W_{6}I_{14}^{2-c}$	64	24	2	90	10	0
Rose Bengal ^d	41	45	14	89	11	0
Rose Bengal ^e	45	41	14	86	14	0
radical autooxidation/	36	12	40	7	39	54

^a Products designated 3-8 are defined in eqs 3-6. ^b Irradiated ($\lambda_{exc} \ge 436 \text{ nm}$) O₂-saturated acetone solutions containing [Mo₆Cl₁₄²⁻] = 1 × 10⁻⁵ M and [olefin] = 2 × 10⁻² M. ^c Irradiated ($\lambda_{exc} \ge 436 \text{ nm}$) O₂-saturated acetone solutions containing [W₆I₁₄²⁻] = 1 × 10⁻⁵ M and [olefin] = 2 × 10⁻² M. The photosensitized reaction of 1 yielded 10% unidentified products. ^d Product distributions reported in ref 50. Radical autooxidation of 1 yields 12% unidentified products. ^e Polymer-bound sensitizer in O₂-saturated acetone solutions containing [olefin] = 2 × 10⁻² M. ^f Product distributions reported in ref 50.

1 and 1,2-dimethylcyclohexene, 2, with ${}^{1}O_{2}$ yields products 3–7, derived from allylic hydroperoxide intermediates (ene reaction^{51,52})



Conversely, reactions of 1 and 2 with superoxide ion yield oxygenated products 5 and 8 corresponding to the radical autooxidation of the olefin. For 2, the ene products (6 and 7) are distinct from the product generated by radical autooxidation (8)



Table III reproduces the product distributions for the photooxidation of 1 and 2 sensitized by $Mo_6Cl_{14}^{2-}$, $W_6I_{14}^{2-}$, and Rose Bengal, and also lists the previously reported product distributions measured by Foote et al. for the radical oxidation and Rose Bengal sensitized photooxidations of 1 and 2.

Efficiencies for the overall production of ${}^{1}O_{2}$ for cluster-sensitized photoreactions can be deduced with quantum yield measurements of substrate photooxidation. Although 2 is a suitable trapping reagent of ${}^{1}O_{2}$, quantum yield measurements were performed by employing 2,3-diphenyl-*p*-dioxene, 9, as a trapping substrate because the reaction of this compound with ${}^{1}O_{2}$ is well documented and efficient.⁴⁶ Oxidation of 9 by ${}^{1}O_{2}$ in nonaqueous solution yields the carbonyl containing product, ethylene glycol dibenzoate (10), at a rate of $1.5 \times 10^{7} \text{ M}^{-1} \text{ s}^{-1}$.⁵³



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Figure 1. The tetrabutylammonium salt of $Mo_6Cl_{14}^{2-}$ -photosensitized conversion of 9 to 10 in acetone- d_6 as monitored by ¹H NMR spectroscopy at various irradiation ($\lambda_{exc} \ge 436$ nm) time intervals. Upon photosensitized reaction, the 4.4 ppm resonance of the methylene protons of 9 are shifted to 4.9 ppm for 10 and the phenyl ring proton resonance located at 7.3 ppm in 9 is split and shifted downfield in 10. Peaks arising from the tetrabutylammonium cation and solvent lie between 0.9 and 3.5 ppm.

TABLE IV: Quantum Yields for the $[M_6X_8]Y_6^{2-}$ -Sensitized Photooxidation of 9 in Acetone

	Φ _p		
photosensitizer ^a	obsd	calcd ^c	
[Mo ₆ Cl ₈]Cl ₆ ²⁻	0.80	0.91	
Mo ₆ Cl ₈]I ₆ ²⁻	0.77	0.91	
Mo ₆ Cl ₈]Br ₆ ²⁻	0.84	0.91	
[Mo ₆ Br ₈]Br ₆ ²⁻	0.79	0.91	
$[Mo_6Br_8]I_6^{2-}$	0.72	0.90	
[Mo ₆ Br ₈]Cl ₆ ²⁻	0.84	0.91	
$[W_6Br_8]Br_6^{2-}$	0.96	0.86	
$[W_6Br_8]Cl_6^{2-}$	0.92	0.86	
$[W_6Br_8]I_6^{2-}$	0.77	0.87	
$[W_{6}I_{8}]I_{6}^{2-}$	0.76	0.04 ^d	
$[W_{6}I_{8}]Br_{6}^{2-}$	0.65	0.04 ^d	

^a The absorbance of oxygenated solutions containing $[W_6Cl_8]Y_6^{2-}$ clusters significantly increased during photolysis thereby suggesting a competing reaction pathway. Therefore, quantum yields are not reported for these complexes. ^bQuantum yield for the $[M_6X_8]Y_6^{2-}$ sensitized photoproduction of 10 from 9. ^c Evaluated from eq 11 where τ_0 's are given in Table I, k_3 's $(=k_q^{obs})$ are given in Table II, $k_4 \le 10^5$ $M^{-1} s^{-1}$ for all clusters, $k_5 = 1.5 \times 10^7 M^{-1} s^{-1}$ (ref 53), and $k_6 = 1.95 \times 10^4 s^{-1}$ (ref 20, Vol. 1, p 183). The oxygen concentration in acetone at saturation is 1.14×10^{-2} M (Whilhelm, E.; Battino, R. Chem. Rev. 1973, 73, 1–9) and the concentration of 9 was 1.47×10^{-2} M. ^d Calculated by using eq 13 with $k_3 = k_q^{em} = 8.1 \times 10^7 M^{-1} s^{-1}$, $k_7 = 2.1 \times 10^9 M^{-1} s^{-1}$, and k_8 is negligibly small.

Furthermore, as evidenced by extremely small quenching rate constants $(k_q(9) \le 10^5)$, 9 does not react with electronically excited $M_6 X_{14}^{2-}$ ions. The NMR spectra, recorded at various time intervals of a photolyzed solution containing $Mo_6 Cl_{14}^{2-}$ (6 × 10⁻³ M) and 9 (2 × 10⁻¹ M) and saturated with oxygen, are displayed in Figure 1. Inspection of these spectra reveal the quantitative conversion of 9 to 10, thereby establishing that the photooxidation reaction is catalytic in cluster complex. Indeed, solutions of the $Mo_6 Cl_{14}^{2-}$ cluster ion are indefinitely stable and no appreciable diminution in photoreactivity is observed over a period of months. The measured quantum yields for this and other $[M_6 X_8]Y_6^{2-}$ photosensitized oxidations of 9 are summarized in Table IV.

Discussion

The product distributions of cluster-photosensitized oxidations of 1 and 2 parallel those of Rose Bengal (Table III), which is known to be an efficient ${}^{1}O_{2}$ generator. Distributions characteristic of radical autooxidation chemistry are not observed. For 1, addition of ${}^{1}O_{2}$ to the olefinic bond, with subsequent abstraction of

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the sterically accessible allylic hydrogen, produces the appropriate hydroperoxide, which undergoes ensuing decomposition to give 3 and 4 in highest yields. Owing to the steric congestion of the "ene" transition state, 5 is produced in the lowest yield. This result is noteworthy because 5 is the autooxidation product of 1, therefore suggesting that the photochemically generated oxidant is ${}^{1}O_{2}$ and not O_2^- . Along this line, photooxidation studies employing 2 as a chemical trap are even more compelling. The symmetric disposition of the methyl groups about the double bond in 2 is manifested in the generation of only two products, 6 and 7, from the ene reaction; production of 8 is unique to the radical autooxidation pathway. As summarized in Table III, the products formed in the cluster-photosensitized oxidation of 2 can exclusively be accounted for by 6 and 7, and 8 is not detected as an oxidation product. Although these trapping studies clearly establish $^{1}O_{2}$ as the principal oxidant generated from the reaction between electronically excited $[M_6X_8]Y_6^{2-}$ cluster ions and O₂, this observation does not necessarily imply that ${}^{1}O_{2}$ is the primary photoproduct. As described above, the cluster excited states are sufficiently strong reducing agents to produce superoxide ion. Recombination of oxidized cluster ion $[M_6X_8]Y_6^-$ and O_2^- by electron transfer is sufficiently energetic to leave oxygen in either its ${}^{1}\Delta_{g}$ or ${}^{1}\Sigma_{g}$ excited states.

Insight into the nature of the primary photoprocess for the reaction of electronically excited $[M_6X_8]Y_6^{2-}$ ions with oxygen is provided by analysis of the free energy dependence of the quenching rate constants for reactions 1 and 2. We begin by considering the electron-transfer pathway. The classical theory of outer-sphere electron-transfer predicts that the rate of quenching of an electronically excited molecule by an oxidant or reductant, k_q^{et} , at modest free energy driving forces, ΔG_{et} , is given by the Marcus expression⁵⁴

$$\ln k_{q}^{\text{et}} = \left\{ \ln \left[\frac{2H_{AB}^{2}}{\hbar} \left(\frac{\pi^{3}}{\lambda k_{B}T} \right)^{1/2} \right] - \frac{\lambda}{4k_{B}T} \right\} - \frac{1}{2} \frac{\Delta G_{\text{et}}}{k_{B}T}$$
(8)

where H_{AB} is the electronic coupling matrix element and λ is the sum of the inner- and outer-sphere reorganizational energies. For a homologous series of molecules, which are electronically and structurally related, H_{AB} and λ will be constant;⁴⁸ and eq 8 predicts that a plot of the RT ln (k_q^{et}) vs ΔG_{et} should be linear with a slope -0.5 and an intercept given by the argument of the logarithm on the right-hand side of eq 8. A slope of -0.09 and a poor linear correlation of this plot (ΔG_{et} 's are given in Table II) for the one-electron reduction of oxygen by the homologous series of $[M_6X_8]Y_6^{2-}$ cluster ions are clearly incompatible with a quenching mechanism proceeding exclusively by electron transfer.

Conversely, the observed quenching rate constants are better correlated to the driving force for energy transfer (reaction 1). Ignoring the $[W_6I_8]Y_6^{2-}$ cluster ions for the moment, inspection of kinetics data in Table I reveals that the observed quenching rates of the $[M_6X_8]Y_6^{2-}$ (M = Mo, W; X = Cl, Br) are relatively independent of the energy-transfer driving force. Acknowledging small differences in rates among the $[M_6X_8]Y_6^{2-}$ (M \neq W; X \neq I) series, which we attribute to minor differences in the electronic structures of the $[M_6X_8]$ core, a constant value of k_q^{obs} = 8.1 (37) × 10⁷ M⁻¹ s⁻¹ is observed for this cluster series. This result can be understood within the context of current energytransfer theories. Specifically, Balzani and co-workers have shown⁵⁵ that the quenching rate constant for energy transfer, k_q^{en} , between an electronically excited donor D and acceptor A

$$D^* + A \xrightarrow[k_{-d}]{k_{-d}} D^* \cdots A \xrightarrow[k_{-m}]{k_{-m}} D \cdots A^* \xrightarrow[k_{-d}]{k_{-d}} D + A^* \qquad (9)$$

is obtained directly from coupling Agmon and Levines' free energy relationship⁵⁶ to absolute rate theory, and is given by

$$k_{q}^{en} = k_{d} \left[1 + \exp\left(\frac{\Delta G_{en}}{k_{B}T}\right) + \frac{\lambda G_{en}^{*}(0)}{\ln 2} \ln\left[1 + \exp\left(-\frac{\Delta G_{en} \ln 2}{\Delta G_{en}^{*}(0)}\right)\right] \right]_{h}$$

$$\frac{k_{-d}}{k_{en}^{0}} \left\{ \frac{\Delta G_{en} + \frac{\Delta G_{en}^{*}(0)}{\ln 2} \ln\left[1 + \exp\left(-\frac{\Delta G_{en} \ln 2}{\Delta G_{en}^{*}(0)}\right)\right]}{k_{B}T} \right\}_{(10)}$$

In the above expression ΔG_{en} is the free energy driving force for energy transfer, $\Delta G^{*}_{en}(0)$, which is the free energy of activation for the energy transfer process with $\Delta G_{en} = 0$, is the sum of the inner- and outer-sphere reorganizational energies associated with relaxation of D* to ground state and promotion of A to its excited state, and $k_{\rm en}^{0}$ is the usual preexponential factor given by $\kappa_{\rm en}^{-1}$ $(k_{\rm B}T/\hbar)$ where the transmission coefficient $\kappa_{\rm en}$ is the product of nuclear and electronic factors. Parallel to electron-transfer kinetics schemes, k_d , k_{-d} , k_{en}^0 , and $\Delta G^*_{en}(0)$ are constant for the reaction between a quencher and a homologous series of electronically and structurally related excited states. In this case, two limiting regimes follow directly from eq 10: at large ΔG_{en} , ln (k_q^{en}) will be constant and equal to either k_d for $k_{en}^0 \gg k_d$ or equal to $k_{en}^0(k_d/k_{-d})$ for $k_{en}^0 < k_{-d}$; and for small ΔG_{en} , ln (k_q^{en}) will linearly increase with a slope of $(1/k_BT)$ as ΔG_{en} increases. These two limiting regimes are interconnected by a monotonic increase of $\ln (k_q^{en})$ with ΔG_{en} as described by eq 10. This nonlinear regime will span a larger range of ΔG_{en} with increasing $\Delta G^{*}_{en}(0)$. Thus the functional dependence of the energy-transfer quenching rate constant on the free energy driving force of a given system can be ascertained simply with knowledge of $\Delta G^*_{en}(0)$. In contrast to electron-transfer reactions, the outer-sphere contribution to the activation free energy is typically negligible because the net charges of the reactants are not changed upon energy transfer. Consequently, $\Delta G^*_{en}(0)$ only reflects the energy associated with the inner-sphere reorganizations of the donor and acceptor molecules. For reaction 1, inner-sphere reorganizational energies arise from the exchange of electrons among the frontier orbitals of the cluster core and oxygen. Spectroscopic^{33a} and theoretical^{57,58} results establish the HOMO and LUMO oribtals to be primarily metal in character and to possess e_g and a_{2g} molecular symmetries, respectively. In this regard, the cluster ion is brought to ground state during collisional energy transfer by the simultaneous removal of an electron from the antibonding a_{2g} orbital and population of the bonding eg level. Oxygen is promoted to its lowest energy singlet state by spin-pairing the electrons residing in the $p\pi$ orbital. For the latter process, the oxygen bond length increases by <0.01 Å.⁵⁹ For the former, crystal structure⁶⁰ and EPR data^{33a} of M_6X_{14} ions reveal few structural differences from that of the parent dianion; electron-transfer measurements show an innersphere reorganizational energy of ≤ 1500 cm⁻¹ for the $M_6X_{14}^{2-}/M_6X_{14}^{3-}$ exchange,⁶¹ which involves the interchange of an electron between the a_{2g} metal-based molecular orbitals. On this basis, the upper limit for the total reorganizational energy of reaction 1 is $\leq 1500 \text{ cm}^{-1}$ and thus the free energy of activation, as is typical of most energy-transfer processes involving transition-metal complexes, will be small $(\Delta G^*_{en}(0) \sim 1500 \text{ cm}^{-1})$. According to eq 10, the large free energies of reaction 1 (Table

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Figure 2. Free energy dependence of the rate constant for energy transfer calculated by evaluating eq 10 with $k_d = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{-d} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{en}^0 = 9.4 \times 10^7 \text{ s}^{-1}$, T = 298 K, and $\Delta G^*_{en}(0) = 1500 \text{ cm}^{-1}$. The solid line is the theoretical fit to the experimental data (\odot). The numbering scheme for different clusters is given in Tables I and II.

II) as compared to this relatively small $\Delta G^*_{en}(0)$ will be manifested in quenching rate constants that are independent of ΔG_{en} . Indeed, this predicted behavior is observed. Figure 2 shows a plot of ln (k_q^{en}) vs ΔG_{en} as determined from eq 10 for the homologous cluster series by employing the upper limit of $\Delta G^*_{en}(0) \sim 1500 \text{ cm}^{-1}$. As described above, for lesser activation energies, the overall fit remains the same but the nonlinear regime spans a smaller range of ΔG_{en} . The observed quenching rate constants for the $[M_6X_8]Y_6^{2-}$ cluster ions $(M \neq W, X \neq I)$ are identical within the experimental error of our Stern-Volmer measurements to the theoretical curve. The best fit of the experimental data to eq 10 yields an asymptotically limiting value of $k_q^{en} = 8.0 \times 10^7 \text{ M}^{-1}$ s⁻¹. The good agreement between the observed quenching rate constants and eq 10 suggests that the primary photoprocess between oxygen and the electronically excited $[M_6X_8]Y_6^{2-}$ (M \neq W, X \neq I) cluster ions is direct energy transfer. It is important to note that the energy-transfer rates of the $[M_6X_8]Y_6^{2-}$ and $[W_6I_8]Y_6^{2-}$ ions cannot be related by a unique fit to a single curve described by eq 10. If this were the case, the energy-transfer rates of the $[M_6X_8]Y_6^{2-}$ ions would be activated. However, owing to the large driving forces of the energy-transfer reactions of the $[M_6X_8]Y_6^{2-}$ series, activation-controlled energy-transfer rates will be only observed if $\Delta G^*_{en} > 12\,000 \text{ cm}^{-1}$. Because such large activation energies are without precedence in the energy-transfer chemistry of transition-metal complexes and more importantly entirely inconsistent with the reorganizational energies of these cluster compounds, the anomalous behavior of the $[W_6I_8]Y_6^{2-1}$ series cannot reasonably be ascribed to activated energy transfer. Thus the order of magnitude increase in the quenching rate constant of the $[W_6I_8]Y_6^{2-}$ ions presages either a more efficient energy-transfer quenching mechanism for these ions or a contributing quenching pathway in addition to energy transfer (vide supra).

The analysis of the quenching rate constants by classical electron- and energy-transfer models is supported by the kinetics of cluster-sensitized photooxidation of olefins such as 2,3-diphenyl-p-dioxene (9). Scheme I shows the excited-state decay pathways and reactions for $[M_6X_8]Y_6^{2^-}$ in the presence of oxygen and 9. Internal conversion to the long-lived triplet, which characterizes these $[M_6X_8]Y_6^{2^-}$ complexes, is fast and hence reaction from the initially prepared singlet excited state of the cluster ion need not be considered. In Scheme I, bimolecular rates for oxygen and substrate quenching, k_3 and k_4 , respectively, are directly competitive with the unimolecular rates for intrinsic nonradiative (k_1) and radiative (k_2) decay. The overall kinetics for the appearance of oxidized olefin 10 will be mediated by the trapping efficiency of 9 with respect to unimolecular conversion of 10 ground state (defined by rate constants k_5 and k_6 , respectively). By using steady-state approximations, the overall

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quantum yield for the cluster-sensitized production of 10, $\Phi_{\rm p}(10),$ is derived to be

$$\Phi_{p}(10) = \left(\frac{k_{3}[{}^{3}\mathrm{O}_{2}]}{(1/\tau_{1}) + k_{3}[{}^{3}\mathrm{O}_{2}] + k_{4}[9]}\right) \left(\frac{k_{5}[9]}{(1/\tau_{2}) + k_{5}[9]}\right)$$
(11)

where $\tau_1 = (k_1 + k_2)^{-1}$ and τ_2 , equal to k_6^{-1} , is the lifetime of singlet oxygen in acetone. In the above expression, the observed quenching rate constant is defined by k_3 . Inasmuch as the rate constants in eq 11 are known, $\Phi_p(10)$ can be explicitly calculated. Table IV lists the observed quantum yields for photosensitized production of 10 as well as the values calculated from eq 11. The observed quantum yields for $[M_6X_8]Y_6^{2-}$ -sensitized (X \neq I) reactions are in good agreement with those expected for an exclusive singlet oxygen quenching mechanism whereas the $[W_6I_8]Y_6^{2-}$ ions, parallel to Stern-Volmer quenching results, exhibit anomalous behavior.

An obvious explanation for the behavior of the $[W_6I_8]Y_6^{2-}$ system is that the quenching reaction does not proceed solely by energy transfer but also includes an additional contribution from electron transfer. In this case, Scheme I should be expanded to include electron-transfer quenching of the $[W_6I_8]Y_6^{2-}$ excited state as well as the back reactions between the primary photoproducts to yield oxygen in its excited singlet (reaction 12a) and ground triplet (reaction 12b) states. Inclusion of reactions 12a and 12b

$$[W_{6}I_{a}]Y_{6}^{2-*} + {}^{3}O_{2} \xrightarrow{k_{7}} [W_{6}I_{a}]Y_{6}^{2-} + {}^{1}O_{2} \quad (12a)$$
$$[W_{6}I_{a}]Y_{6}^{-} + O_{2}^{-} \xrightarrow{k_{8}} [W_{6}I_{a}]Y_{6}^{2-} + {}^{3}O_{2} \quad (12b)$$

in Scheme I modifies the expression for the overall observed quantum yield as follows

$$_{p}(10) =$$

Φ

$$\left\{\frac{k_3[{}^{3}\mathrm{O}_2] + \left(\frac{k_7k_8}{k_8 + k_9}\right)[{}^{3}\mathrm{O}_2]}{(1/\tau_1) + (k_3 + k_7)[{}^{3}\mathrm{O}_2] + k_4[9]}\right\} \left(\frac{k_5[9]}{(1/\tau_2) + k_5[9]}\right) (13)$$

where k_q^{obs} is now equal to the sum of the energy- and electrontransfer rate constants $(k_3 + k_7)$. The partitioning of the back electron-transfer reaction between chemiluminescent and ground-state pathways (i.e., the chemiluminescence efficiency = $k_8/(k_8 + k_9)$) can be calculated directly from eq 13 with knowledge of the energy- and electron-transfer rate constants. Assuming for the moment that the energy-transfer quenching rate constant of the $[W_6I_8]Y_6^{2-}$ clusters is the same as that for the remaining members of the homologous series (from Figure 2, $k_q^{en} = 8.0 \times$ $10^7 M^{-1} s^{-1}$), an electron-transfer rate of $2.1 \times 10^9 M^{-1} s^{-1}$ is determined from the $k_q^{obs}([W_6I_8]Y_6^{2-})$'s listed in Table I. Solving eq 13 for $k_8/(k_8 + k_9)$ yields a chemiluminescence efficiency of 83%. On this basis, quenching is predicted to proceed predominantly by electron transfer and therefore nearly exclusive production of $[W_6I_8]Y_6^{-}$ and O_2^{-} should be observed.

Yet transient absorption experiments do not show any evidence of the $[W_6I_8]Y_6^-$ ion. The transient absorption spectrum of oxygenated solutions of $W_6I_{14}^{2-}$ is representative of those for each



Figure 3. Transient difference spectra for $W_6I_{14}^{2-}$ in deoxygenated CH₃CN (O), $W_6I_{14}^{2-}/TCNE$ (tetracyanoethylene) in deoxygenated CH₃CN (\Box), and $W_6I_{14}^{2-}$ in oxygenated CH₃CN (Δ), recorded with 355-nm excitation. All difference spectra were recorded 50 ns after the excitation pulse. The concentration of $W_6 I_{14}^{2-}$ in CH₃CN was 8×10^{-4} M and that of TCNE was 4×10^{-3} M. Deoxygenated and oxygen-saturated solutions were prepared by bubbling with N2 and O2, respectively.

of the $[W_6I_8]Y_6^{2-}$ ions. Figure 3 compares the spectra of transients produced upon excitation of deoxygenated CH₃CN solutions containing $W_6I_{14}^{2-}$ and $W_6I_{14}^{2-}/TCNE$ to a CH₃CN solution of $W_6I_{14}^{2-}$ saturated with oxygen. We initially consider the transient spectrum of $W_6 I_{14}^{2-}$ in the absence of oxygen. The appearance of an intense transient absorption feature at 490 nm is consistent with the expected red shift of the lowest energy ligand-to-metal charge-transfer transition upon excited-state production.⁶² It is noteworthy that the spectrum of $W_6 I_{14}^{2-}$ in its excited state is spectroscopically distinct from the transient profile produced upon electron-transfer quenching of the excited state. The transient spectrum of $W_6 I_{14}^{2-}$ in the presence of TCNE, which is known to be an efficient one-electron quencher of $[M_6X_8]Y_6^{2-}$ excited states,^{33a} is dominated by bands at 435 and 610 nm and a shoulder at 550 nm. The 435-nm feature is characteristic of the TCNE anion $(\lambda_{max} = 435 \text{ nm} (\epsilon = 7100 \text{ M}^{-1} \text{ cm}^{-1}))^{63}$ whereas the absorptions to the red of the TCNE⁻ band are those of the W₆I₁₄⁻ ion. The important issue of interest here is that the transient spectrum of $W_6 I_{14}^{2-}$ in the presence of oxygen is identical with that of $W_6 I_{14}^{2-*}$, and no evidence of the electron-transfer product, W_6I_{14} , is observed. In our experiment, the relative intensity of the transient absorption for $W_6 I_{14}^{2-*}$ is such that the electrontransfer contribution, if any, to the quenching pathway must be less than 30%. These transient absorption results establish that oxygen quenching proceeds primarily by energy transfer and that our assumption of similar energy-transfer rates across the $[M_6X_8]Y_6^{2-}$ series is invalid for the $[W_6I_8]Y_6^{2-}$ cluster species, with the latter exhibiting more efficient energy-transfer reactivity.

These results suggest that the quenching rates of the $[M_6X_8]Y_6^{2-}$ ions are governed by the transmission coefficient. By using $k_d = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, and determining $k_{-d} = 1.2 \times 10^{10} \text{ M}^{-1}$ s⁻¹ from the Eigen equation,⁶⁴ a value of $k_{en}^{0} = 9.4 \times 10^{7} \text{ s}^{-1}$ for the $[M_6X_8]Y_6^{2-}$ (M \neq W; X \neq I) cluster ions follows directly

from the limiting observed quenching rate (Figure 2). This transmission coefficient is 5 orders of magnitude smaller than that calculated for the adiabatic limit $(k_{en}^{0} = k_{B}T/\hbar)$. Low values of k_{en}^{0} have been observed previously for both organic^{52,65-67} and inorganic^{68,69} energy-transfer reactions; because k_{en}^{0} directly reflects the electronic matrix coupling element, these low values of k_{en}^{0} have been attributed to poor orbital overlap between the donor/acceptor pair. Such an explanation for the very low k_{en}^{0} of the $[M_6X_8]Y_6^{2-}$ cluster series is particularly appropriate because energy transfer involves the overlap of localized orbitals of the metal core. The aforementioned e_g HOMO and a_{2g} LUMO orbitals, which are the crucial orbitals involved in the energytransfer process, are constructed from linear combinations of d_{xy} orbitals of adjacent metal atoms.⁵⁷ As indicated by the pictorial representation, the molecular orbitals are confined to a cube that



inscribes the octahedral metal atoms of the cluster unit. These orbitals are masked by the eight face-bridging atoms situated at the vertices of the cube and the six axial halides juxtaposed over the faces of the cube. Photophysical and spectroscopic studies of the Mo₆ clusters indicate little mixing between these metal-based orbitals^{33a,70} and the ligating halides and hence the HOMO and LUMO orbitals are effectively shielded from interactions with exogenous substrates. Similarly, the axial ligands of the W_6 clusters shield the metal core and insignificantly perturb the electronic structure. However, steady-state and time-resolved emission studies indicate that the metal-based orbitals are mixed with the face-bridging ligands.⁷¹ To this end, the simultaneous overlap of the cluster's HOMO and LUMO with the oxygen acceptor orbitals will be enhanced and therefore k_{en}^{0} will be increased. Consequently the energy-transfer quenching rate constant will also increase. In agreement with previous spectroscopic studies, our quenching results suggest that this increase is most important for the tungsten clusters possessing face-bridging iodides. The enhanced energy-transfer rates of the $[W_6I_8]Y_6^2$ clusters can be accounted for with an increase of k_{en}^{0} from 9.4 $\times 10^{7}$ s⁻¹ for the $[M_6X_8]Y_6^{2-}$ (M \neq W and X \neq I) to 2.4 $\times 10^{9}$ s⁻¹ for the $[W_6I_8]Y_6^{2-}$ species. It is noteworthy that despite this increase, k_{en}^{0} has not attained the adiabatic limit.

Concluding Remarks

Thus electronically excited $[M_6X_8]Y_6^{2-}$ ions react with oxygen exclusively by energy transfer to produce singlet oxygen. Generation of singlet oxygen by energy transfer between one-electron-oxidized cluster and superoxide ion is efficiently circumvented by the competitive energy-transfer process despite the high free energy driving forces associated with the former pathway. That

⁽⁶²⁾ The lowest energy LMCT transitions of the cluster ions in their ground state formally involve the promotion of electrons from ligand-based orbitals to the a_{2g} LUMO. Because excitation promotes an electron from the e_g HOMO to the a_{2g} LUMO, the LMCT's of the hexanuclear clusters in their lowest energy excited state will shift to the red owing to transitions corresponding to the promotion of electrons from ligand-based orbitals to the depopulated eg level

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the quenching rates of the $[M_6X_8]Y_6^{2-}$ (M = Mo, W; X = Cl, Br) ions are small and similar is entirely consistent with a highly nonadiabatic exchange resulting from poor overlap of the oxygen acceptor orbitals with the sterically shielded frontier orbitals of the cluster core. The anomalous behavior of the $[W_6I_8]Y_6^{2-1}$ clusters is in accordance with increased electronic coupling arising from mixing between the orbitals of the metal core and the face-bridging iodides. The absence of an electron-transfer contribution to the $[M_6X_8]Y_6^{2-}$ -cluster-photosensitized production of ${}^{1}O_{2}$ parallels the results of RuL₃²⁺ (L = polypyridyl) systems^{32,72} and contributes to the emerging trend that reaction of electronically excited transition-metal complexes with oxygen will proceed

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by energy transfer even in the presence of potentially competitive exergonic electron-transfer pathways.

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Double-Selective Excitation Techniques as a Means of Delineating Dynamics of Protein-Bound Small Molecules

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A method for delineation of dynamics of protein-bound ligands is presented that relies on measuring ¹H NMR spin-lattice relaxation rates upon double-selective excitation of dipolarly connected ligand resonances. Dipolar interaction energies of proton pairs are obtained in the free and bound states. For protons at fixed distances such dipolar energies are interpreted in terms of motional correlation times of relaxation vectors. As an example the reorientational correlation time of the indole moiety was evaluated at 23.5 ps for L-tryptophan in water solution and at 27.0 ns for L-tryptophan bound to human serum albumin.

Introduction

The interaction between small bioactive ligands with proteins has long been acknowledged as one of the main topics of molecular biology. Most significant events referred to in any biological activity imply in fact binding to adequate protein structures. Small flexible active molecules exist in solution in a number of equally probable conformations, whereas it can be reasonably assumed that only a single conformation occurs in the complex with the protein. Thus the formation of the complex involves a process of conformational selection that affets both kinetics and energetics of the association process.

Among several physical techniques, it is perhaps true to say that only NMR is potentially capable of determining dynamic and/or geometric features of small molecules bound to macromolecular sites, especially in cases where the macromolecule contains intrinsic or extrinsic paramagnetic centers.¹⁻³ In diamagnetic systems clear-cut information on the bound site is much more difficult to obtain, due to the small effects on J couplings, chemical shifts, or spin-lattice relaxation rates. Some information has been gained in some diamagnetic systems by measuring the T_1/T_2 ratio⁴ or the transferred nuclear Overhauser effect (trNOE).5,6

Here we show that double-selective excitation of any two dipolarly connected ¹H NMR resonances allows us to measure the dipolar interaction energy of any proton pair within the bound ligand, wherefrom dynamics of the bound state can be delineated. The method is just an extension of double-selective relaxation rate measurements^{7,8} to exchanging systems such as any ligandmacromolecule complex at exceeding ligand concentrations. The interaction between L-tryptophan (L-trp) and human serum albumin (HSA) was considered to test the method since this complex formation (i) has long been characterized^{9,10} and (ii) is of great biological relevance.11

Experimental Section

L-trp and HSA were purchased from Sigma Chemical Co. and used without further purification. Solutions were made in D₂O (99.9% from Merck) buffered at pH = 7.0 (pH meter reading) and carefully deoxygenated by bubbling nitrogen. Concentrations of HSA were determined spectrophotometrically.

NMR measurements were carried out on a Varian VXR-200 NMR spectrometer at the fixed temperature of 294 ± 1 K. Chemical shifts were referred to internal TSP- d_4 (sodium trimethylsilyl)tetradeuteriopropanesulfonate).

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