We associate the highest energy transition (39 530 cm^{-1}, $\epsilon \sim$ 23 500 L mol^{-1} cm^{-1}) with a d metal to π^* CO charge-transfer absorption on the basis of its invariance with substitution at the X, L, or R positions and the similarity between the energy of this transition and that identified as d metal $\rightarrow \pi^*$ CO in $[W(CO)_6]$.[12] This assignment is also consistent with the reported molecular orbital calculation carried out for the $[XCr(CO)_4(CPh)]$ analogue.[7] The absorption at 30 580 cm^{-1} (ϵ = 13 000 L mol^{-1} cm^{-1}) is assigned to the conjugated alkylidyne–phenyl $\pi \rightarrow \pi^*$ transition on the basis of the spectra of free benzene and its derivatives.[15]

Substitution of a *tert*-butyl group for the phenyl group of the complex causes this peak to shift up in energy (λ_{max} = 33 330 cm^{-1}) and decrease by an order of magnitude in intensity (ϵ = 1400 L mol^{-1} cm^{-1}), consistent with the destruction of the alkylidyne conjugation and removal of the corresponding bathochromic effect. Whether or not this assignment accounts for all of the absorbance in this portion of the spectrum is still under investigation.

Finally we note, concomitant with the observed luminescence, there appears to be a bimolecular photochemical reaction channel, consistent with the relatively long excited-state lifetime. The nature of this photochemistry is currently under investigation along with a more detailed analysis of the nature of the luminescent excited state.

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(15) (a) Free benzene[15b] exhibits a $\pi \rightarrow \pi^*$ transition at 37 200 cm^{-1} with a molar extinction coefficient of 11 L mol^{-1} cm^{-1} while free acetylene[15c] absorbs at 42 200 cm^{-1} to the extent of 7 L mol^{-1}cm^{-1}. Conjugation of these two systems in diphenylacetylene[15b] shifts the $\pi \rightarrow \pi^*$ transition to 33 900 cm^{-1} raising the molar extinction coefficient to 29 000 L mol^{-1} cm^{-1}. (b) "DMS Atlas of Organic Compounds"; Butterworths: London, 1966; Vol. I and II. (c) Nakayama, T.; Watanabe, K. *J. Chem. Phys.* **1964**, *40*, 558-561.

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Quantitative Generation of Singlet Dioxygen via the Reaction of Tris(bipyridine)ruthenium(III) with Superoxide Ion in Aqueous Solution

Sir:

Although there is a great deal of interest in the possible generation of singlet dioxygen by the one-electron oxidation of superoxide ion,[1] the available evidence suggests that this is a rare occurrence both in aqueous solution[2] and in nonaqueous solvents.[1] In the few cases where there appears to be unequivocal proof of the production of singlet dioxygen by the reaction of O_2^- with one-electron oxidants, the yields are very small (~4% in the reaction between ferrocenium ion and superoxide ion in acetonitrile[3] and ~11% in dimethylformamide[4]) and/or are unspecified.[4,5] The reaction between $Ru(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) and O_2^- and the possible generation of singlet dioxygen as a reaction product has been postulated by several authors,[6-12] but kinetic studies of the reaction or experimental evidence for the formation of singlet dioxygen has not been published. In one case,[12] an estimate of the rate constant for electron transfer in the postulated cage $Ru(bpy)_3^{3+}|O_2^-$ has been advanced.

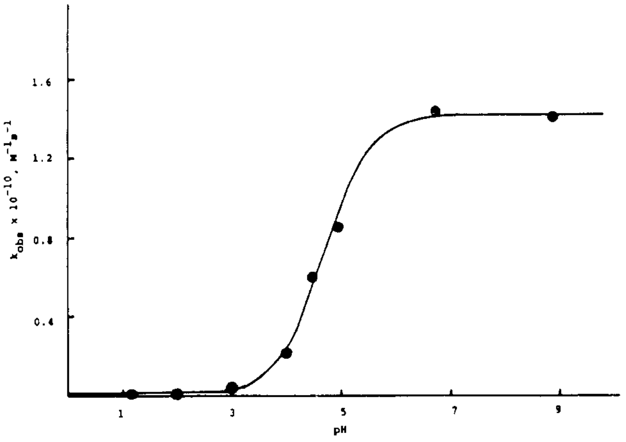

Figure 1. Observed second-order rate constant for the $Ru(bpy)_3^{3+}$–O_2^- reaction vs. pH: (circles) observed values; (solid line) values calculated from eq 7 with the parameters given in the text.

We report herein a useful photochemical method for the aqueous generation of superoxide ion, the kinetics of its oxidation by $Ru(bpy)_3^{3+}$ as a function of pH, and the quantitative production of singlet dioxygen in the title reaction. The method is based on the reported[13] formation of hydrogen peroxide in a photoelectrochemical cell consisting of $Ru(bpy)_3^{2+}$, *N,N′*-dimethyl-4,4′-bipyridinium (hereinafter referred to as methylviologen, MV^{2+}), and dioxygen, the known[14] reaction of the radical MV^+ with dioxygen, and the popular[15] sensitizer $Ru(bpy)_3^{2+}$.

When aqueous solutions (pH 2-9, ionic strength 0.10 M maintained with LiCl, 23 °C) of $Ru(bpy)_3^{2+}$ (~5×10^{-5} M), MV^{2+} (~0.01 M), and dioxygen ((0.70-10) × 10^{-4} M) are subject to flash photolysis (300-ns pulse from a Phase-R DL1100 dye laser, Coumarin 460), following excitation three reactions proceed in sequence (eq 1-3). Under our usual experimental conditions,

$$^*Ru(bpy)_3^{2+} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^+ \quad k_1 \qquad (1)$$

$$MV^+ + {}^3O_2 \rightarrow MV^{2+} + O_2^- \quad k_2 \qquad (2)$$

$$Ru(bpy)_3^{3+} + O_2^- \rightarrow Ru(bpy)_3^{2+} + {}^1O_2 \quad k_{obsd} \qquad (3)$$

the first reaction is too rapid to be detected ($k_1 = 1.0 \times 10^9$ M^{-1} s^{-1};[15,16] with $[MV^{2+}]$ = 0.010 M, the lifetimes of $^*Ru(bpy)_3^{2+}$ are ~90 and ~86 ns in D_2O and H_2O, respectively) and results in the "instantaneous" bleaching of the $Ru(bpy)_3^{2+}$ absorption at 452 nm and the appearance of the 605- and 395-nm absorption

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(16) Our value of k_1 is $(1.0 \pm 0.2) \times 10^9$ M^{-1} s^{-1} at 23 °C and 0.10 M ionic strength and was obtained by lifetime measurements in the absence of dioxygen and at very low $[MV^{2+}]$. We also carried out flash photolysis measurements in the absence of dioxygen and obtained a value of 4.0×10^9 M^{-1} s^{-1} (23 °C, μ = 0.10 M, pH 1.18-6.7) for the recombination reaction between the $Ru(bpy)_3^{3+}$ and MV^+ produced in the quenching step (eq 1).

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maxima characteristic of MV^+. The second reaction is accompanied by first-order decreases in absorbance at 395 or 605 nm. The observed first-order rate constants depend linearly on $[^3O_2]$ ($(0.70–2.1) \times 10^{-4}$ M) and yield $k_2 = (8.1 \pm 0.7) \times 10^8\ M^{-1}\ s^{-1}$ (23 °C, $\mu = 0.10$ M, pH 6.72 or 1.18) in excellent agreement with the value $(8.0 \pm 0.3) \times 10^8\ M^{-1}\ s^{-1}$ obtained by pulse radiolysis.[14] Finally, the third reaction is accompanied by the second-order recovery of the 452-nm absorbance of $Ru(bpy)_3^{2+}$. The second-order rate constants, k_{obsd}, were found to vary with pH as depicted in Figure 1 (circles).[17] The proposed mechanism is given by eq 4–6, which yield eq 7. The experimental values of k_{obsd} were fitted

$$HO_2 \rightleftharpoons H^+ + O_2^- \quad K_a \tag{4}$$

$$Ru(bpy)_3^{3+} + O_2^- \rightarrow Ru(bpy)_3^{2+} + {}^?O_2 \quad k_5 \tag{5}$$

$$Ru(bpy)_3^{3+} + HO_2 \rightarrow Ru(bpy)_3^{2+} + {}^?O_2 + H^+ \quad k_6 \tag{6}$$

$$k_{obsd} = \frac{k_5K_a + k_6[H^+]}{K_a + [H^+]} \tag{7}$$

to eq 7 by keeping K_a as a constant parameter equal to $2.04 \times 10^{-5}\ M^{-1}$ [18] and floating k_5 and k_6. The nonlinear least-squares computation yielded $k_5 = (1.43 \pm 0.03) \times 10^{10}\ M^{-1}\ s^{-1}$ and $k_6 = (7 \pm 23) \times 10^7\ M^{-1}\ s^{-1}$. The latter parameter is not significantly different from zero, and we conclude that HO_2 is unreactive as a reductant toward $Ru(bpy)_3^{3+}$. In contrast, O_2^- reduces $Ru(bpy)_3^{3+}$ at a diffusion-controlled rate.[19,20] The large difference in reactivity between HO_2 and O_2^- toward $Ru(bpy)_3^{3+}$ is not unexpected. One-electron oxidation of HO_2 would produce the thermodynamic unstable species HO_2^+, and therefore such a process would be rather unfavorable,[21] whereas one-electron oxidation of O_2^- yields the correct state of protonation of the product.

From the reduction potentials of $Ru(bpy)_3^{3+/2+}$ (1.26 V)[15] and $^3O_2/O_2^-$ (−0.16 V, 1 M $^3O_2$),[22] the exoergonicity of eq 5 when $^3O_2$ is formed is 1.42 eV. Since the lowest state of singlet dioxygen ($^1\Delta_g$, hereinafter referred to as $^1O_2$) is 0.98 eV above the triplet,[23] it follows that the oxidation of O_2^- to $^1O_2$ by $Ru(bpy)_3^{3+}$ is also exoergonic (0.44 eV). Therefore, it is important to determine experimentally[24] the multiplicity of the dioxygen produced in eq 5. This was done by utilizing the water-soluble singlet oxygen trap 9,10-anthracenedipropionate[25] (hereinafter referred to as ADPA). The measurements were carried out by steady-state irradiation at 450 nm of D_2O[26] solutions (pH 6.9, 22 °C, $\mu = 0.10$ M) of $Ru(bpy)_3^{2+}$ ($(3–5) \times 10^{-5}$ M), MV^{2+} (~0.01 M), $^3O_2$ (2.7×10^{-4} M), and ADPA ($(2–4) \times 10^{-5}$ M). The bleaching of the 378.5-nm absorption ($\lambda_{max} = 1.15 \times 10^4\ M^{-1}\ cm^{-1}$) of ADPA was monitored as a function of time. Blank experiments with solutions containing all the components except $^3O_2$ showed that the bleaching of the ADPA amounted to less than 1% of the bleaching observed in the presence of $^3O_2$. According to the sequence of reactions given by eqs 8, 9, 1, 2, 5, 10, and 11, the absorbance

$$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^*Ru(bpy)_3^{2+} \quad I_{abs} \tag{8}$$

$${}^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu' + \text{heat} \quad k_9 \tag{9}$$

$$^1O_2 \rightarrow {}^3O_2 + h\nu'' + \text{heat} \quad k_{10} \tag{10}$$

$$^1O_2 + ADPA \rightarrow (ADPA)O_2 \quad k_{11} \tag{11}$$

at 378.5 nm depends on time and the various rate constants according to eq 12. A_t, A_0, and A_∞ are the absorbances at time

$$k_{10} \ln \frac{A_0 - A_\infty}{A_t - A_\infty} + k_{11}\frac{A_0 - A_t}{\epsilon l} = \frac{\phi_1\phi_{cs}I_{abs}k_1k_{11}[MV^{2+}]t}{(k_9 + k_1[MV^{2+}])V} \tag{12}$$

t, 0, and ∞, respectively; l is the path of the cell, V is the volume of the solution, I_{abs} is the number of einsteins per second absorbed by $Ru(bpy)_3^{2+}$, ϕ_1 is the yield of $^1O_2$ produced in eq 5, and ϕ_{cs} is the cage separation yield for $Ru(bpy)_3^{3+}|MV^+$. Values of k_{10} and k_{11} in D_2O are $(1.8 \pm 0.2) \times 10^4\ s^{-1}$ [27] and $(8.2 \pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$.[25] Plots of the left-hand side of eq 12 vs. time were linear for about 50% reaction (at longer times some upward curvature obtains), and the slopes of the lines give the value 24.3 ± 2.1 (average of three experiments). I_{abs} was measured by ferrioxalate actinometry, $k_9 = (9.8 \pm 0.5) \times 10^5$,[28] $\phi_{cs} = 0.21 \pm 0.02$,[29] and $k_1 = 9.1 \times 10^8\ M^{-1}\ s^{-1}$.[30] From the above values, the calculated slope in eq 12 is $\phi_1(20.1 \pm 2)$. Comparison between calculated and experimental slopes yields $\phi_1 = 1.2 \pm 0.2$, and therefore we conclude that singlet dioxygen is quantitatively produced in the $Ru(bpy)_3^{3+} - O_2^-$ reaction. Since the formation of $^3O_2$ is thermodynamically more favorable, the quantitative formation of $^1O_2$ suggests that the $Ru(bpy)_3^{3+}–O_2^-$ reaction pathway that leads to $^3O_2$ is nonadiabatic or, because of the high exoergonicity of this pathway, that it lies in the inverted region.

We have also measured the yield of $^1O_2$ produced in the $^*Ru(bpy)_3^{2+}–{}^3O_2$ reaction[31,32] in D_2O and found a value of 1.0 ± 0.1.[33] A comparison between the yields of singlet dioxygen produced in the $Ru(bpy)_3^{3+}–O_2^-$ and $^*Ru(bpy)_3^{2+}–{}^3O_2$ reactions could, in principle, resolve the question of the mechanism of the latter reaction. Both energy transfer[31,32] and electron transfer followed by cage recombination between the $Ru(bpy)_3^{3+}$ and O_2^- produced in the quenching event[7] have been proposed as possible mechanisms. Unfortunately, since the yield of $^1O_2$ in both reactions is essentially quantitative, no distinction is possible.

Since the chloride salts of $Ru(bpy)_3^{2+}$ and MV^{2+} are soluble in nonaqueous solvents, the present method of generation of

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(17) At $[H^+] > 1 \times 10^{-2}$ M, the reaction is not fully reversible: H_2O_2 and $Ru(bpy)_3^{3+}$ are produced in a 1:2 ratio. The quantum yield for H_2O_2 production at $[H^+] = 6.6 \times 10^{-2}$ M is ~0.1. These observations are consistent with the reported[8,9,12] formation of H_2O_2 when solutions of $Ru(bpy)_3^{2+}$ are irradiated in the presence of dioxygen in sulfuric acid solution. Presumably, HO_2 (formed by protonation of O_2^-), because of its lack of reactivity toward $Ru(bpy)_3^{3+}$, undergoes disproportionation to peroxide and dioxygen or is reduced to peroxide by $Ru(bpy)_3^{2+}$. But note that, in 0.5 M HCl, irradiation of $Ru(bpy)_3^{2+}$ and dioxygen is reported[10] not to produce H_2O_2.

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(33) From the rate constants for the $^*Ru(bpy)_3^{2+}–MV^{2+}$ ($1 \times 10^9\ M^{-1}\ s^{-1}$) and $^*Ru(bpy)_3^{2+}–{}^3O_2$ ($3 \times 10^9\ M^{-1}\ s^{-1}$) reactions and the concentrations of MV^{2+} (1.0×10^{-2} M) and $^3O_2$ (2.7×10^{-4} M) utilized in the $^1O_2$ yield measurements, we estimate that less than 10% of the $^1O_2$ observed in the $Ru(bpy)_3^{3+}–O_2^-$ reaction comes from quenching of $^*Ru(bpy)_3^{2+}$ by $^3O_2$.

aqueous O_2^- is also useful for nonaqueous solvents. Moreover, by adding reductants that compete with O_2^- for $Ru(bpy)_3^{3+}$, it is possible to study the oxidation of O_2^- by other reagents. Such studies are in progress.

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Note Added in Proof. After this work was completed, the rate constant for the $Ru(bpy)_3^{3+}$–O_2^- reaction was reported as 3.5×10^{10} M^{-1} s^{-1} at $\sim 1 \times 10^{-3}$ M ionic strength, in good agreement with our value 1.4×10^{10} M^{-1} s^{-1} at a higher (0.10 M) ionic strength: Sassoon, R. E.; Aizenshtat, Z.; Rabani, J. *J. Phys. Chem.* **1985**, *89*, 1182.

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Stopped-Flow and Rapid-Scan Spectral Examination of the Iron(III)-Acetohydroxamic Acid System

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Kinetic and thermodynamic parameters for the hydrolysis of tris- and bis(acetohydroxamato)iron(III) complexes at $I = 2.0$ M and 25 °C have been obtained by stopped-flow and rapid-scan spectral methods. Hydrolyzed iron(III) species are not believed to be involved. The results are compared with those already available for the hydrolysis of the mono(acetohydroxamato)iron(III) complex. The rate constants for reaction of $FeA_2(H_2O)_2^+$, $FeA(H_2O)_4^{2+}$, and $FeOH^{2+}$ with acetohydroxamic acid (HA) are very similar, all $\sim 2 \times 10^3$ M^{-1} s^{-1}, and an I_d mechanism is preferred.

Microbial iron transport is mediated by low-molecular-weight multidentate ligands termed siderophores, which have been extensively studied.[3] The naturally occurring siderophore desferrioxamine B is currently used as a drug ("Desferal") for the treatment of chronic iron poisoning, which can result from repeated massive blood transfusions (as with patients suffering from the genetic disease known as Cooley's anemia).[4] The interaction of iron(III) with desferrioxamine has been thoroughly investigated,[5-9] and the results are important in advancing an understanding of the molecular basis for iron availability in microorganisms, as well as the mechanisms for siderophore-mediated microbial iron transport[10,11] and siderophore chelation therapy.

The synthetic hydroxamic acids, $R_1C(O)N(OH)R_2$, are excellent model ligands for the siderophores, and their interaction with iron(III) has been well-studied.[3-5,12-19] The mono(hydroxamate)–iron(III) complexes have been the subject of several kinetic investigations.[12-14,16,17,19] We report in this paper equilibria and kinetic data for the formation and hydrolysis of bis- and tris(acetohydroxamato)iron(III) cations in perchlorate and chloride media. Because of the lability of the system, the use of rapid-scan stopped-flow spectrophotometry has proved very useful for measuring the spectrum of the bis species and for determining the hydrolysis constants of the three stages of complex formation. The results can be used for probing the intimate mechanism of ligand substitution in iron(III)[20] and for understanding the decidedly more complicated ferrioxamine–iron(III) system and iron(III) interchange kinetics involving ferrioxamine B[21] and tris(acetohydroxamato)iron(III).[22,23]

Experimental Section

Reagents were chemically pure. Acetohydroxamic acid was recrystallized from ethyl acetate. Ferric perchlorate solutions were standardized with use of a molar extinction coefficient of 4.16×10^3 M^{-1} cm^{-1} at 240 nm.[24] Perchloric acid solutions were obtained by dilution of 70% perchloric acid. In all experiments, the solvent was water containing NaCl or $NaClO_4$ to produce a final ionic strength of 2.0 M. For the determination of the hydrolysis constants, ferric perchlorate (0.2–0.5 mM) and acetohydroxamic acid (10–100 mM) were equilibrated at pH 6.0 and mixed in a rapid-scan stopped-flow apparatus with the sodium perchlorate solution containing various concentrations of perchloric acid (0–16 mM for tris → bis; 6–400 mM for bis → mono, and 0.2–2.0 M for mono → Fe^{3+}). In each case, a spectrum was recorded that corre-

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