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Time-Resolved Measurements of Singlet Oxygen Dimol-Sensitized Luminescence

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Abstract: Using fullerenes C_{60} and C_{70} as photosensitizers, time-resolved measurements of phthalocyanine luminescence sensitized by singlet oxygen dimols have been carried out in hexafluorobenzene, benzene-d_6, and methylene chloride. The data suggest that dimol-sensitized luminescence can be observed under many different conditions. Fullerenes photosensitize formation of both monomols and dimols of singlet oxygen in solution.

Introduction

Since the first observation of photosensitized singlet oxygen luminescence in solution,[1–3] luminescence measurement has been widely used for detection and investigation of $^1O_2$ in systems of photobiological and photochemical importance.[4,5] The fundamental luminescence is at 1270–1277 nm, corresponding to radiative deactivation of the $^1\Delta_g$ state of oxygen shifted slightly by collisions with solvent molecules.[6–10] Collisions between two $^1O_2$ molecules in the gas phase have been shown to generate luminescence from $^1O_2$ "dimols", $(^1O_2)_2$, formed by "energy pooling" with principal maxima at 634 and 703 nm, twice the energy of the fundamental.[11]

The same dimol luminescence should appear upon photosensitized $^1O_2$ generation in solution. The first reported experimental attempt to observe such luminescence in air-saturated solutions used protoporphyrin as a photosensitizer.[1,3] Luminescence in the visible region was observed which was proportional to the square of the excitation power. However its intensity and spectrum were strongly dependent on the degree of porphyrin photodegradation, and it was assumed that the afterglow observed was porphyrin chemiluminescence.[3] More recent experiments with different photosensitizers showed that short-wavelength luminescence appears as a result of $(^1O_2)_2$ interaction with photosensitizers and/or products of their oxygenation. The strongest sensitizer of the dimol luminescence was tetra-*tert*-butylphthalocyanine.[12–14] However, these experiments were made using solvents (CCl_4, C_6F_6, and Freon 113) where the $^1O_2$ lifetime (τ_Δ) was in the millisecond range. Measurements were performed using mechanical phosphoroscopes, where periods of excitation and detection of the luminescence were separated by relatively long dark intervals (about 200 μs) determined by the frequency of the chopper rotation.[12–14]

We have now made time-resolved measurements of the sensitized luminescence using pulsed lasers, fast photodiodes, and signal averaging. To avoid photosensitizer fluorescence, which might overload photodetectors and make data unreliable, we used the fullerenes C_{60} and C_{70}, since they have negligible fluorescence ($\leq 10^{-4}$), generate $^1O_2$ efficiently, and are stable on strong laser excitation.[15,16] Using these photosensitizers, we performed time-resolved measurements of the dimol-sensitized light emission in phthalocyanine-containing hexafluorobenzene, benzene-d_6, and methylene chloride.

Experimental Section

Materials. Hexafluorobenzene (Aldrich 99%), methylene chloride (Fisher Scientific, reagent grade), and benzene-d_6, 99.6%, (Cambridge Isotope Laboratories) were used as received. C_{60} and C_{70} were prepared and purified as previously reported.[17,18] Tetra-*tert*-butylphthalocyanine (Pc) was synthesized and purified at the Moscow Institute of Organic Intermediates and Dyes by the procedure reported by Mikhalenko et al.[19]

$^1O_2$ Luminescence Measurements. The apparatus was a modification of that previously described.[20] C_{60} and C_{70} were excited at 355 and 532 nm by the third and second harmonics, respectively, of a QuantaRay DCR-2 Nd:Yag laser, with maximal pulse energies of 1 and 3.5 mJ. The laser pulse was filtered to remove any fundamental with a 355/532-nm pass–1060-nm reflecting mirror (Newport Corp.), followed with a KG-3 (Schott Glass) infrared absorbing filter. The 355-nm pulse was also filtered with a 355-nm pass–532-nm reflecting mirror. The near-infrared emission from $^1O_2$ was monitored at right angles to the laser beam and filtered with RG-850 (Schott Glass) and 1270-nm interference (10-nm bandpass, Institute of Physics, Belorussian Academy of Sciences) filters. The red light emission caused by energy transfer to the phthalocyanine from singlet oxygen dimols was filtered by 700- or 780-nm interference filters (10-nm bandpass, Krasnogorsk Optical–Mechanical Enterprise, Moscow). Luminescence was measured with a cryogenic germanium photodetector (North Coast Instruments, Model EO-817P, -250-V bias). The analog signal from the photodetector was sent to a digital storage oscilloscope (LeCroy 9410 Dual 150 MHz). The signal was normally averaged over 50–200 shots and then transferred to a Macintosh IIci

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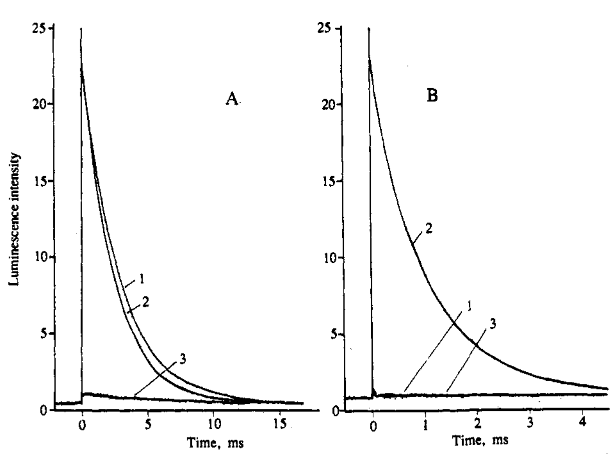

Figure 1. Photosensitized singlet oxygen luminescence at 1270 nm (A) and 700 nm (B) after 532-nm laser pulses in C_6F_6. Photosensitizer is C_{70} (2×10^{-5} M): (1) C_{70} alone; (2) C_{70} + Pc (5×10^{-7} M); (3) Pc alone, no C_{70}. Decays are averages over 50 laser shots.

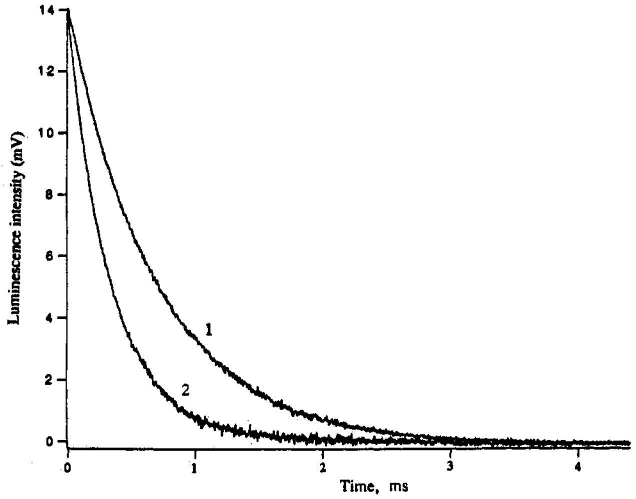

Figure 2. Photosensitized singlet oxygen luminescence at 1270 nm (1) and 700 nm (2) after 532-nm laser shots in C_6D_6. The decays were recorded with a 30-μs delay after laser pulses. The solutions contained C_{70} (10^{-5} M) and Pc (4×10^{-7} M). Decays are averages over 50 pulses.

computer with Labview software. This apparatus allowed the measurement of luminescence kinetics with 250-ns resolution, treating the data by extrapolation of exponential decays to zero time after the pulse to calculate the initial luminescence intensity. These initial intensities are proportional to the amount of singlet oxygen formed after each flash.

Results

Measurements at 1270 nm. In agreement with data reported previously,[15,16] illumination of air-saturated solutions of C_{60} and C_{70} by 532- or 355-nm laser flashes led to the appearance of luminescence at 1270 nm (Figures 1–3). This luminescence decayed exponentially with lifetimes (τ_Δ) which depended on the intensity of the laser flashes and concentrations of the photosensitizers. At the maximal C_{60} concentration (about 10^{-4} M) and low laser energy (10–20 times lower than the maximum), τ_Δ values were 95 μs in CH_2Cl_2, 780 μs in C_6D_6, and about 5 ms in C_6F_6, close to those reported previously for these solvents.[13,21,22] At the maximal laser intensity, τ_Δ decreased by no more than about 5%. This shows that formation of singlet oxygen dimols (which should increase at higher excitation energies) does not lead to appreciable quenching of the $^1O_2$ monomols.

In C_{70} solutions containing about 5×10^{-5} M photosensitizer, τ_Δ was 95 μs in CH_2Cl_2 and 780 μs in C_6D_6, but in C_6F_6, the lifetime was about 2.5 ms. After 100-fold dilution of C_{70}, τ_Δ increased to about 5 ms, suggesting that C_{70} quenches $^1O_2$ luminescence. Analysis of the data gave a rate constant for $^1O_2$ quenching by C_{70} of $(2.8 \times 0.7) \times 10^6$ M^{-1} s^{-1}, about 10 times the value reported for C_{60}.[15] Addition of tetra-*tert*-butylphthalocyanine (Pc) (10^{-7}–10^{-4} M) reduced the 1270-nm luminescence lifetimes, following the Stern–Volmer equation. The rate constant (k_q) for singlet oxygen quenching by PC is $(1.6 \pm 0.4) \times 10^8$ M^{-1} s^{-1}, slightly below the value reported previously for Pc in chloroform, 2.9×10^8 M^{-1} s^{-1}.[23]

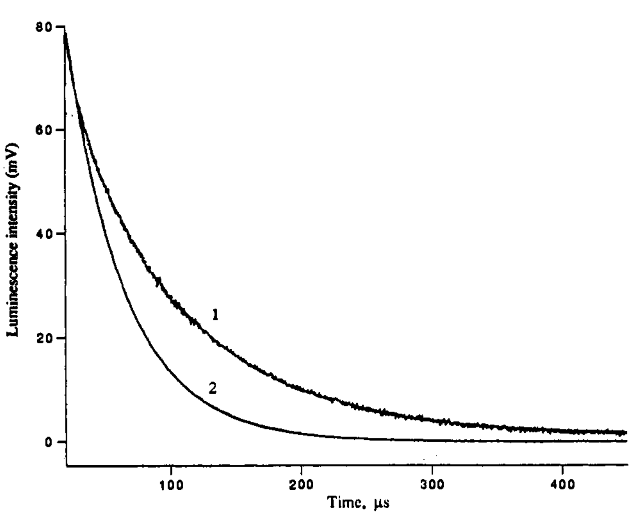

Figure 3. Photosensitized singlet oxygen luminescence at 1270 nm (1) and 700 nm (2) after 532-nm laser pulses in CH_2Cl_2. The decays were recorded with a 20-μs delay after laser shots. The solutions contained C_{70} (2×10^{-5} M) and Pc (2×10^{-6} M). Decays are averages over 50 pulses.

Measurements at 700 nm. Excitation of the photosensitizers in solutions which did not contain Pc led to a very weak luminescence at 700 nm, which could be detected only when maximal fullerene concentrations (about 10^{-4} M) and laser intensities (about 3 mJ per flash at 532 nm) were used. When 10^{-7} M Pc was added to solutions containing 5×10^{-5} M fullerenes, the 700-nm luminescence intensity (Figure 1) was higher by an order of magnitude than that without Pc. Increasing the Pc concentration caused an increase of the 700-nm luminescence. Solutions containing 10^{-7}–10^{-6} M Pc but no fullerene showed negligible luminescence (Figure 1). As reported previously, the spectrum of the delayed luminescnece in Pc-containing C_6F_6 coincides with the fluorescence spectrum of Pc, with the main maximum at 703 nm and two additional weaker bands at 740 and 780 nm.[12-14]

A small deviation from exponential decay of the luminescence was observed during the first 20 μs after laser flashes. These deviations appear to be mostly a result of a nonlinear response of the photodetector caused by overloading by the Pc fluorescence. The lifetime of the 700-nm luminescence was shorter than that of the 1270-nm luminescence by a factor of 2 (Figures 1–3). This is true under a wide variety of solvents and conditions, including where singlet oxygen is strongly quenched, even where singlet oxygen lifetimes vary over a factor of 100 (Figure 4). The intensity of the luminescence at 700 nm is proportional to the square of that at 1270 nm (Figure 5).

Figure 6 illustrates the dependence of the dimol luminescence on the concentration of Pc in C_6F_6. To obtain these data, solutions were used which contained both C_{70} and Pc. Singlet oxygen was generated by 532-nm pulses. The absorption of Pc at this wavelength was <0.01 at the maximal Pc concentration, and the absorption of C_{70} was 0.07. Hence $^1O_2$ production was largely

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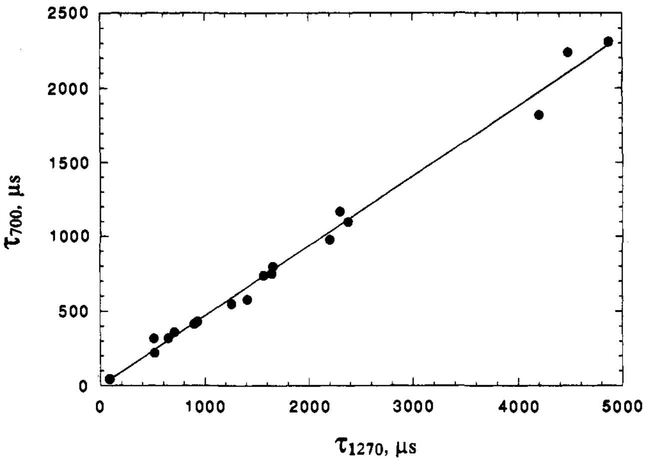

Figure 4. Dependence of the 700-nm luminescence lifetimes on those at 1270 nm in Pc-containing solutions of C_{60} and C_{70} in C_6F_6, C_6D_6, and CH_2Cl_2, summarizing data of several sets of experiments in which variable amounts of quenching occurred. The slope is 0.47 ± 0.025, showing that the lifetime of the 700-nm emission is half that at 1270 nm.

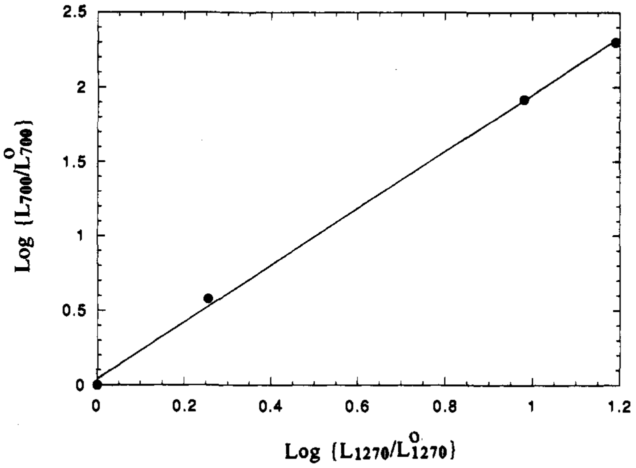

Figure 5. Double logarithmic plot for the 700-nm luminescence intensities versus those at 1270 nm in solutions containing C_{60} (4×10^{-5} M) and Pc (3×10^{-6} M). The luminescence intensity was controlled by a set of neutral filters. The superscript zero denotes the luminescence intensities at the lowest power used. The slope is 1.91 ± 0.08, which shows that the intensity of the 700-nm band is proportional to the square of that at 1270 nm.

a result of C_{70} excitation even at the highest Pc concentrations. To avoid self-absorption of the luminescence by Pc, a 2-mm cell was used and luminescnece was detected through a 780-nm interference filter, the second maximum of the Pc fluorescence. Measurements were begun using the highest Pc concentration (about 10^{-4} M); then the sample was progressively diluted with fresh C_{70} stock solution. Luminescnece intensities were calculated by extrapolating the exponential fits of the decay curves to zero time. To remove the influence of any excitation energy fluctuations, both 1270- and 780-nm emissions were measured at each Pc concentration and the ratios of the 780-nm intensities to the squares of the 1270-nm intensities were calculated (Figure 6).

Previously, using the phosphoroscope it was shown that the dimol/monomol intensity ratio increased linearly with Pc concentration from 10^{-10} to 10^{-8} M.[14] Our data indicate that this ratio is also linear in [Pc] from 10^{-7} to 10^{-4} M even though the 1270-nm lifetime decreased from 2.5 ms to 70 μs as a result of $^1O_2$ quenching by Pc at these high concentrations.

Discussion

The results of the time-resolved measurements agree well with those obtained in Pc-containing CCl_4 and C_6F_6 using mechanical phosphoroscopes.[12-14] The data are consistent with the mechanism previously proposed, in which the 700-nm luminescence is a result of energy transfer to Pc from dimols $(^1O_2)_2$ formed by collisions between two $^1O_2$ molecules, as shown in Scheme I. Two alternates are shown, 1, in which a dimol is formed, which then transfers energy to Pc, producing the fluorescent singlet, and 2, in which a complex of $^1O_2$ is formed with Pc which reacts with a second $^1O_2$ to give the fluorescent state.

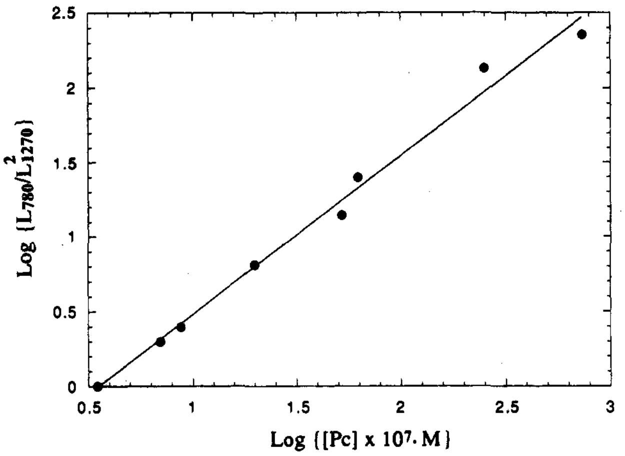

Figure 6. Double logarithmic plot for the ratio of the luminescence intensities at 780-nm to the square of the luminescence intensities at 1270 nm (L_{780}/L^2_{1270}) versus the Pc concentrations. The slope is 1.05 ± 0.1, which shows that L_{780} is a linear function of [Pc].

Scheme I[a]

$$\mathrm{S} \xrightarrow{h\nu} {}^1\mathrm{S} \longrightarrow {}^3\mathrm{S}$$

$${}^3\mathrm{S} + {}^3\mathrm{O}_2 \longrightarrow \mathrm{S} + {}^1\mathrm{O}_2$$

$${}^1\mathrm{O}_2 \longrightarrow {}^3\mathrm{O}_2 + h\nu\ (1270\ \mathrm{nm})$$

Mechanism 1

$${}^1\mathrm{O}_2 + \mathrm{Pc} \xrightarrow{k_q} {}^3\mathrm{O}_2$$

$$2\ {}^1\mathrm{O}_2 \rightleftharpoons ({}^1\mathrm{O}_2)_2$$

$$({}^1\mathrm{O}_2)_2 + \mathrm{Pc} \xrightarrow{k_q} 2\ {}^3\mathrm{O}_2 + {}^1\mathrm{Pc}$$

$${}^1\mathrm{Pc} \longrightarrow \mathrm{Pc} + h\nu_f$$

Mechanism 2

$${}^1\mathrm{O}_2 + \mathrm{Pc} \xrightarrow{k_q} {}^1\mathrm{O}_2\bullet\bullet\bullet\mathrm{Pc}$$

$${}^1\mathrm{O}_2 + {}^1\mathrm{O}_2\bullet\bullet\bullet\mathrm{Pc} \longrightarrow 2\ {}^3\mathrm{O}_2 + {}^1\mathrm{Pc}$$

$${}^1\mathrm{Pc} \longrightarrow \mathrm{Pc} + h\nu_f$$

[a] S, ^{1}S, and ^{3}S are photosensitizer in the ground and excited singlet and triplet states, $h\nu$ is singlet oxygen monomol luminescence, $h\nu_f$ is photosensitizer fluorescence, and k_q and k_{dm} are the rate constants for quenching of singlet oxygen monomols and dimols, respectively, by Pc.

Both mechanisms predict that if dimol formation does not lead to $^1O_2$ quenching and the lifetime of dimols is much less than that of monomols, the dimol-sensitized Pc luminescence should be proportional to the square of the excitation intensity, and the lifetime of the 700-nm luminescence should be equal to half that at 1270 nm. The last statement follows from the exponential decay of the $^1O_2$ concentration after the laser pulse

$$[{}^1\mathrm{O}_2] = [{}^1\mathrm{O}_2]_0 \exp(-t/\tau_\Delta)$$

where $[{}^1O_{20}$ and t are the initial $^1O_2$ concentration and the time interval after the pulse, respectively. The decay of the 1270-nm luminescence is given by the same exponential. Since dimol concentration is proportional to $[{}^1O_2]^2$, the Pc-activated dimol emission (L_{dm}) should follow the equation

$$L_{dm} = K[{}^1O_2]_0^2 \exp(-2t/\tau_\Delta)$$

where K is a proportionality constant, and lifetime of the dimol (and that of the sensitized luminescence) should be just half τ_Δ.

Note that Pc quenches singlet oxygen monomols strongly at high concentrations; however, although this decreases its lifetime, it does not affect the initial amount formed. This is precisely what is observed; several of the lifetimes in Figure 4 are strongly shortened by quenching, but the dimol lifetime is always exactly half that of the monomol, and the initial intensity is independent of quenching (data not shown).

Analysis of Figure 6 suggests that mechanism 2 is less probable than mechanism 1. According to mechanism 2, a complex $[({}^1O_2)\cdots Pc]$ is formed. In C_6F_6 at Pc concentrations $>5 \times 10^{-6}$ M, ${}^1O_2$ decay is mostly determined by ${}^1O_2$ quenching by Pc. If mechanism 2 was valid, the intensity of the 780-nm band relative to the 1270-nm band should not depend on the Pc concentrations above 5×10^{-6} M, since most of the ${}^1O_2$ is already quenched at this concentration. In fact, the dependence in Figure 6 is linear within the experimental error (±10%). This is consistent with mechanism 1 if the lifetime (τ_{dm}) of the singlet oxygen dimols in solution is very short. The linearity means that, in the presence of 10^{-4} M Pc, the dimol lifetime is not less than 80% of that at low Pc concentrations, and thus no more than 20% of the dimol can be quenched by Pc. Assuming that this 20% quenching is real and $({}^1O_2)_2$ is quenched by Pc with a diffusion-controlled rate ($k_{dq} = 10^{10}$ M^{-1} s^{-1}), from the Stern–Volmer equation, $\tau_{dm} < 200$ ns.[30] However, τ_{dm} is only a few picoseconds according to previous estimates;[24] if so, quenching should be completely negligible at all Pc concentrations.

The dissociation of $({}^1O_2)_2$ to ${}^1O_2$ must be very fast, since the singlet oxygen lifetime is not affected by laser power at the relatively low powers used in these experiments. If a significant amount of singlet oxygen were tied up as dimol, this should lead to saturation kinetics of the Pc luminescence as power increases at high Pc concentrations, which is not observed.

Pc luminescence is probably caused by efficient energy transfer from $({}^1O_2)_2$ to the excited singlet level of Pc.[13,14] Energy transfer from $({}^1O_2)_2$ to fluorescent dyes was predicted by Khan and Kasha[25] and experimentally observed in several laboratories.[26-28] This process is favored by exact coincidence between the fluorescence maximum of Pc (703 nm) and the most intense emission maximum of ${}^1O_2$ (703 nm).

However, such energy transfer is probably not the only reason for the Pc activation. An increase in the efficiency of the radiative transitions in the dimols could also be caused by $({}^1O_2)$–Pc interaction. This is apparently the case with activation of dimol luminescence by dibenzopyrenequinone, which has a high excited singlet level and cannot accept energy from the dimols.[13,14] Similar activation of the dimol luminescence by fullerenes could in principle take place. Comparison of the intensities of the 700-nm luminescence in fullerene solutions with and without Pc shows that the activation ability of fullerenes is about 4 orders of magnitude lower than that for Pc and resembles that of dibenzopyrenequinone. The exact reasons for the variable efficiencies of activation are under investigation.

Because of the complexity of this system, a numerical solution of the differential equations for Scheme I was carried out. This simulation reproduced the experimental data of Figures 1–6 remarkably closely over a wide range of rate constants for dimol formation and reversal and of other parameters in the system.

The data suggest that activated dimol luminescence is a universal phenomenon which can be observed in solvents of widely varying nature. Fullerenes can thus photosensitize formation of both monomols and dimols of singlet oxygen in solution.

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Supplementary Material Available: Mathematica simulation data may obtained on disk in Macintosh or MS-DOS formation (specify) from the authors (Mathematica required). Printouts of the simulated data (5 pages) are available as supplementary material. This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS. Ordering information is given on any current masthead page.

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(30) If $k_{dq} < 10^{10}$ M^{-1} s^{-1}, the upper limit for τ_{dm} would be higher.