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Communications to the Editor

A Pulse Radiolysis Based Singlet Oxygen Luminescence Facility

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In this paper we report the first successful time-resolved detection of singlet oxygen, $O_2(^1\Delta_g)$, luminescence using the pulse radiolysis technique. The use of this technique (a) to produce high concentrations of solute (S) triplet states in aerated benzene (B) via a combination of channels 1–4 and (b) to subsequently form $O_2(^1\Delta_g)$ via channel 5 has already been described.[3] The method complements direct pulsed laser excitation of S in that formation of $^3S^*$, and therefore of $O_2(^1\Delta_g)$, is still efficient[4] in

$$\mathrm{B} \overset{e}{\rightsquigarrow} {}^1\mathrm{B}^*, {}^3\mathrm{B}^* \tag{1}$$

$$^1\mathrm{B}^* + \mathrm{S} \rightarrow \mathrm{B} + {}^1\mathrm{S}^* \tag{2}$$

$$^3\mathrm{B}^* + \mathrm{S} \rightarrow \mathrm{B} + {}^3\mathrm{S}^* \tag{3}$$

$$^1\mathrm{S}^* \rightarrow {}^3\mathrm{S}^* \tag{4}$$

$$^3\mathrm{S}^* + \mathrm{O}_2(^3\Sigma_g^-) \rightarrow \mathrm{S} + \mathrm{O}_2(^1\Delta_g) \tag{5}$$

those instances where intersystem crossing (channel 4) is unimportant. In the latter situation a laser-based experiment would require an additional light-absorbing sensitizer which could subsequently transfer triplet energy to high concentrations of S. Such experiments, certainly of a quantitative nature, are usually doomed to failure because of competitive light absorption problems.[7] No such problems exist with pulse radiolysis, and the high available triplet energy of $^3B^*$ (84 kcal mol^{-1})[9] ensures that virtually any solute of interest, in the $O_2(^1\Delta_g)$ context, will be efficiently promoted to its triplet state.

A major breakthrough in the time-resolved detection of $O_2(^1\Delta_g)$ came with the advent of germanium diodes which are highly sensitive in the infrared and fast, low noise, high gain amplifiers.[10,11] This allowed the observation of the extremely weak luminescence of $O_2(^1\Delta_g)$ which corresponds to the forbidden radiative (0,0) transition summarized in eq 6 and greatly enhanced

$$\mathrm{O}_2(^1\Delta_g) \rightarrow \mathrm{O}_2(^3\Sigma_g^-) + h\nu(1267\ \mathrm{nm}) \tag{6}$$

the accuracy of yield, lifetime (τ_Δ), and reactivity parameter determinations.[8,10,13] Such work has to date been restricted to laser-based systems, whereas, for reasons already emphasized, adaptation for pulse radiolytically produced $O_2(^1\Delta_g)$ would be highly desirable.[14] With the detection system used previously[15]

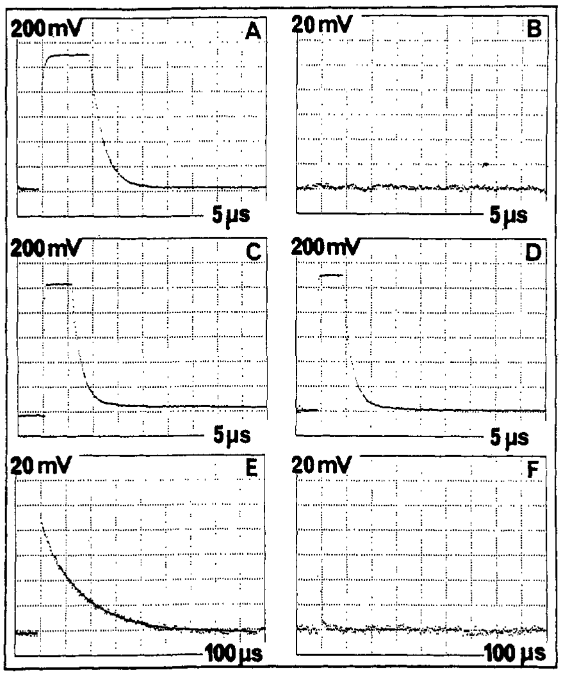

Figure 1. Transient signals measured in mV of deflection with time, each trace showing units per division of graticule, after absorption of a 100-ns electron pulse by liquid hexadeuteriobenzene containing 2-acetonaphthone (2 × 10^{-1} mol L^{-1}). (A) and (B): aerated solution with germanium detector protected from emitted light by aluminum foil, (A) inside (1 m light-guide) and (B) outside (7 m light-guide) the radiation-exposed area. (C)–(F): germanium detector exposed to emitted light and situated outside the radiation-exposed area; (C) and (E) aerated solutions with differing sensitivities and time scales; (D) and (F) corresponding experiments for nitrogen-purged solutions. In (E) the first-order fit shown corresponds to a rate constant of 6.0 × 10^3 s^{-1}.

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[1] University of Manchester.

[2] Paterson Institute for Cancer Research.

[3] Gorman, A. A.; Lovering, G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4527. In this work the bleaching of 1,3-diphenylisobenzofuran was used as an indirect monitor of the $O_2(^1\Delta_g)$ decay profile.

[4] *G* values for $^1B^*$ and $^3B^*$ are 1.4[5] and 4.2,[6] respectively.

[5] Zarnegar, D. M.; Whitten, D. G. *J. Phys. Chem.* **1972**, *76*, 198.

[6] Baxendale, J. H.; Fiti, M. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 218.

[7] In general, *selective* excitation of one compound in the presence of high concentrations (to compete effectively with oxygen quenching) of a second of lower triplet energy will be difficult or impossible. In a limited number of cases favorable S_1–T_1 splittings have made this feasible.[8]

[8] (a) Gorman, A. A.; Rodgers, M. A. J. *Chem. Phys. Lett.* **1985**, *58*, 120. (b) Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J. *Photochem. Photobiol.* **1987**, *45*, 415. (c) Gorman, A. A.; Hamblett, I.; Lambert, C.; Prescott, A. L.; Rodgers, M. A. J.; Spence, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 3091.

[9] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

[10] (a) Hurst, J. R.; McDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065. (b) Parker, J. G.; Stanbro, W. D. *J. Am. Chem. Soc.* **1982**, *104*, 2067. (c) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 2069. (d) Rodgers, M. A. J.; Snowden, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 5541.

[11] The germanium diodes exhibit enhanced sensitivity in the IR as opposed to the visible region in contrast to photomultiplier tubes used previously.[12]

[12] (a) Byteva, I. M.; Gurinovich, G. P. *J. Lumin.* **1979**, *21*, 17. (b) Salokhiddinov, K. I.; Byteva, I. M.; Dzhagarov, B. M. *Opt. Spectrosc.* **1979**, *47*, 881.

[13] (a) Rodgers, M. A. J. *Photochem. Photobiol.* **1983**, *37*, 99. (b) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423. (c) Hurst, J. R.; Schuster, G. B. *Ibid.* **1983**, *105*, 5756. (d) Rodgers, M. A. J. *Ibid.* **1983**, *105*, 6201. (e) Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J. *Ibid.* **1984**, *106*, 4679. (f) Keene, J. P.; Kessel, D.; Land, E. J.; Redmond, R. W.; Truscott, T. G. *Photochem. Photobiol.* **1986**, *43*, 117. (g) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 4599. (h) Scurlock, R. D.; Ogilby, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 640. (i) Gorman, A. A.; Hamblett, I.; Lambert, C.; Spencer, B.; Standen, M. C. *Ibid.* **1988**, *110*, 8053.

[14] In pulse radiolysis the distribution of energy is uniform throughout the reaction cell. This contrasts sharply with laser-based experiments and is a particular advantage for quantitative emission as opposed to absorption experiments.

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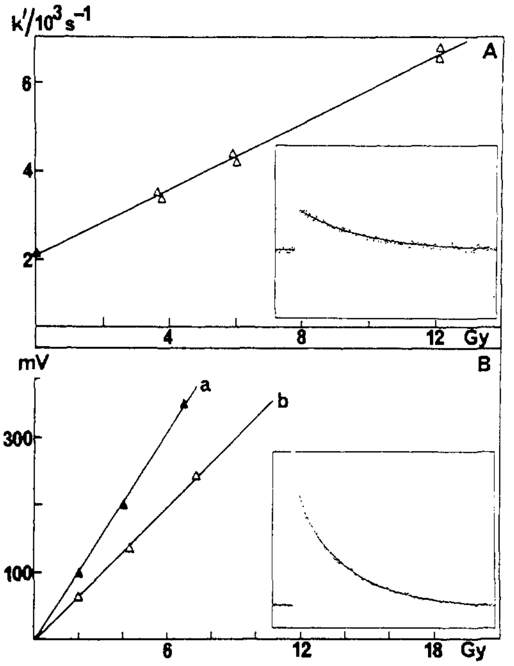

Figure 2. (A) First-order constant for $O_2(^1\Delta_g)$ luminescence decay, k', as a function of radiation dose for an aerated hexadeuteriobenzene solution of 2-acetonaphthone (2×10^{-2} mol L^{-1}). The data point at zero dose corresponds to k' determined after pulsed laser excitation (355 nm; 1 mJ) of an identical solution (cf. ref 10a,c, 13a,c). Inset: corresponding transient luminescence, with first-order fit, after absorption of a 3.65-Gy electron pulse: 20 mV/division, 100 μs/division, $k' = 3.6 \times 10^3$ s^{-1}. (B) Relative $O_2(^1\Delta_g)$ luminescence yields, measured as mV of deflection and extrapolated to time zero, as a function of radiation dose for sensitizers (2×10^{-2} mol L^{-1}) in aerated hexadeuteriobenzene: (a) naphthalene and (b) benzophenone. A small correction for the effects of ϕ_{isc} on G values gave a ratio of slopes of 1.7, to be compared with a published value of 1.9 for benzene.[8c] Inset: corresponding transient luminescence, with first-order fit, after absorption of a 6.65-Gy electron pulse with naphthalene as sensitizer: 50 mV/division, 100 μs/division.

efforts in this direction have proved fruitless due to (a) a non-light-induced signal resulting from bombardment of the germanium detector by scattered X-rays and (b) an intense IR signal due to Čerenkov emission.[16] Both signals were orders of magnitude higher in intensity than that anticipated for $O_2(^1\Delta_g)$ emission. Such problems have been overcome as detailed below.

The reaction cell and germanium detector were physically separated while remaining "close-coupled" by means of a 7-m length of fiber optic cable.[18] This allowed the detector to be situated outside the concrete-enclosed, radiation-exposed area, and the resultant loss of the scattered X-ray effect is demonstrated in Figure 1 (parts A and B). When, with this detection configuration, an aerated solution of a sensitizer, e.g., 2-acetonaphthone (2×10^{-1} mol L^{-1}), in benzene ($\tau_\Delta \sim 33$ μs)[13e] was subjected to a 100-ns pulse of 10 MeV electrons, the $O_2(^1\Delta_g)$ emission signal was virtually indiscernable from the detector response to the Čerenkov emission. However, as demonstrated in Figure 1 (parts C and E), the same experiment repeated in hexadeuteriobenzene (τ_Δ 550–700 μs)[10a,c,13a,c] allowed clear time resolution of the two signals. The $O_2(^1\Delta_g)$ emission signal from a *single shot* experiment (Figure 1E) had excellent signal-to-noise characteristics with an intensity which compared favorably to that observed on pulsed laser excitation at 355 nm (~1 mJ per pulse) of 2-acetonaphthone ($OD_{355} = 1.0$) in aerated benzene with cell and detector physically close-coupled.[19]

Several independent controls have unequivocally identified the "slow" emission of Figure 1E as that corresponding to eq 6.

(i) It disappeared completely on deaeration, but the fast Čerenkov spike was unchanged (cf. Figure 1 (parts C–F)).

(ii) Its strictly exponential decay (Figure 1E) was, as diagnosed previously for $O_2(^1\Delta_g)$,[3] linearly dependent on radiation dose (Figure 2A). Extrapolation to zero dose and zero sensitizer concentration gave a lifetime of 625 μs, in excellent agreement with published τ_Δ values for hexadeuteriobenzene.[10a,c,13a,c]

(iii) Its yield, extrapolated to time zero, was sensitizer dependent (Figure 2B). The relative values for benzophenone and naphthalene were essentially identical with those recently measured in benzene.[8c]

(iv) Its decay rate was enhanced by the efficient $O_2(^1\Delta_g)$ quencher strychnine. The routinely determined rate constant, 8.8×10^8 L mol^{-1} s^{-1}, was essentially identical with that already reported for benzene, 9.0×10^8 L mol^{-1} s^{-1}.[20]

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Registry No. O_2, 7782-44-7; Ge, 7440-56-4; C_6D_6, 1076-43-3; strychnine, 57-24-9; benzophenone, 119-61-9; naphthalene, 91-20-3; 2-acetonaphthone, 93-08-3.

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[15] The detection system used previously has been described.[13f,8c] Points to be emphasized are as follows: (a) Reaction cell and germanium detector must be close-coupled. (b) A silicon filter cuts out incident light below 1100 nm. (c) The requisite sensitivity leads to a detection system risetime of ~500 ns. (d) Single shot experiments with laser energies of ≥0.2 mJ at 355 nm lead to acceptable signal-to-noise ratios, for efficient $O_2(^1\Delta_g)$ formation, with deflection sensitivities of ≥2 mV/division. (e) Amplifier saturation occurs with emission-derived signals corresponding to slightly more than 1 V of deflection.

[16] Čerenkov emission is a consequence of the retardation of electrons which enter a medium with a velocity higher than that of light in that medium. In the context of our experiments both the cell glass (Spectrosil) and the solvent are involved.[17]

[17] Jelley, J. V. *Čerenkov Radiation and Its Applications*; Pergamon Press: London, 1958.

[18] The 10-mm cable was supplied by Optronics Ltd., Cambridge, U.K. The ~50 μm diameter fibers were of silica, and the light loss per meter was 15%.

[19] The Čerenkov emission follows the electron beam profile and only appears as a "slow" signal due to the risetime of the detection system.[15] Current experimentation is aimed at effectively grounding the diode current for several hundreds of nanoseconds followed by rapid switching of the normal load resistance into the circuitry. This is a nontrivial exercise with diodes but, if successful, will remove the problem of the Čerenkov-derived signal and allow examination of solvents with short τ_Δ values, including benzene itself.

[20] Gorman, A. A.; Hamblett, I.; Smith, K.; Standen, M. C. *Tetrahedron Lett.* **1984**, *25*, 581.

Preparation of a Discrete, Closed-Transition-Metal Boride. Characterization and Structure of *trans*-$[Fe_4Rh_2(CO)_{16}B]PPN$

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Transition-metal main-group solid-state compounds, e.g., carbides, are important materials.[1] The simplest compounds can be viewed as a metal lattice with individual main-group atoms in a set of interstitial holes. There are well-known examples of discrete molecular clusters containing electron precise (H and group 14)[2] or electron rich (groups 15[3] and 16[4]) interstitial atoms.

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[1] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; p 162.

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