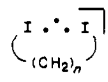
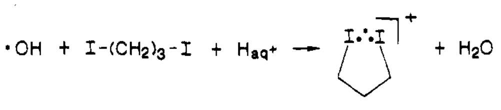
Table I. Properties of *Intra*molecular Radical Cations of Type **1**[a]

 **1**	λ_{max}, nm	$t_{1/2}$, μs	G, per 100 eV	ϵ, M^{-1} cm^{-1}
$n = 6$	455	75	0.6	5500
$n = 5$	445	85	1.7	4500
$n = 4$	435	120	2.1	4700
$n = 3$ (**1a**)	405	150	2.9	4400
$n = 2$	(550)		(<0.3)	

[a] Experimental conditions: pulse radiolysis of N_2O saturated, pH 3, aqueous solutions of 2×10^{-5} M 1,*n*-diiodoalkanes. Error limits: ±5 nm for λ_{max}, ±50 nm for $n \approx 2$; ±10% for $t_{1/2}$, G, and ϵ, ±20% for $n = 6$.

•OH-induced oxidation of monoiodoalkanes, i.e., the radical cations are only formed at low pH (<5). The extinction coefficient of the transient is calculated to 4400 M^{-1} cm^{-1}.

The absorption is assigned to the *intra*molecular radical cation **1a** formed in the overall process



(2)

1a

The alternative possibilities, namely a molecular radical cation without iodine–iodine interaction, $I(CH_2)_3{-}I^{\bullet+}$, or a bimolecular complex of type **2**, can be excluded. The former is unlikely because all other $RI^{\bullet+}$ in aqueous solution have been found to absorb around 315 nm.[5] The dimer species, on the other hand, showed a pronounced dependence on the solute concentration with hardly any detectable yield ($G < 0.2$) at the concentration of 2×10^{-5} M used in our present experiment.[5] Low solubilities ($\lesssim 5 \times 10^{-5}$ M) unfortunately precluded the study of such a concentration dependence for the diiodo alkanes. A most important argument in support of **1a** is its lifetime which exceeds that of $RI^{\bullet+}$ and $(RI{\therefore}IR)^+$ by almost one order of magnitude. The high stability of **1a** can, of course, be rationalized by its sterically most favorable five-membered ring structure.

Compatible results have been obtained in the oxidation of a number of other 1,*n*-diiodoalkanes. The measured data are summarized in Table I. It can be seen that an increasing chain length between the two iodine atoms and thus an increasing ring size of **1** is accompanied by a red-shift in λ_{max} and a decrease in lifetime and yield. All this matches with corresponding observations for numerous *intra*molecular S∴S-bonded radical cations generated in the oxidation of organic dithia compounds.[1] The underlying rationale is a lower degree of hetero atom p-orbital overlap in the larger ring system.

A geometry situation which is even less favorable would exist in strained three- or four-membered ring structures as has been demonstrated in the oxidation of various sulfur compounds.[1,9] In our present case the oxidation of 1,2-diiodoethane would represent such an example. In fact, only a very small yield of radical cations seems to be formed ($G < 0.3$ according to conductivity measurements) besides a larger yield of neutral, as yet unidentified radicals. The observable UV-absorption in a pulsed aqueous 1,2-diiodoethane solution shows, however, a long tailing with a shoulder around 500 ± 50 nm. Assignment of such a red-shifted band to an *intra*molecular radical cation would be reasonable since the optical transition energies for $2\sigma/1\sigma^*$ species are a direct function of orbital overlap.[1,2] It needs to be mentioned that a relatively fast hydrolysis of the 1,2-diiodoethane leaves, however, some ambiguity about this last result.

Acknowledgment. This work has been supported by the International Bureau of the KfA Jülich within the terms of an agreement on scientific cooperation between the Federal Republic of Germany and the Republic of India. H.M. has been on deputation from Bhabha Atomic Research Center, Bombay.

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(9) Bonifačić, M.; Asmus, K.-D. *J. Org. Chem.* **1986**, *51*, 1216.

The Photosensitized Production of Singlet Molecular Oxygen ($^1\Delta_gO_2$) in a Solid Organic Polymer Glass: A Direct Time-Resolved Study

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Received April 6, 1987

The photosensitized production of singlet molecular oxygen ($^1\Delta_gO_2$) has long been a subject of scientific study.[1-6] Recently, direct evidence for the presence of $^1\Delta_gO_2$ in thin (10–30 μm) polymer films was obtained by Byteva et al.[7,8] who detected $^1\Delta_gO_2$ phosphorescence ($^3\Sigma_g{}^-O_2 \leftarrow {}^1\Delta_gO_2$: 1270 nm) in a steady-state photosensitized experiment. In a time-resolved study, $^1\Delta_gO_2$ has also been observed in a heterogeneous ionomer system (Nafion powders) in which the $^1\Delta_gO_2$ sensitizer was apparently located at the surface of solvent filled or dessicated cavities.[9] We now report that $^1\Delta_gO_2$ phosphorescence can be detected in a time-resolved photosensitized experiment from a homogeneous, solid polymethylmethacrylate (PMMA) glass. As in the solution phase,[10-26] we expect this technique will become an indispensable

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(1) *Singlet Oxygen: Reactions with Organic Compounds and Polymers*, Ranby, B., Rabek, J., Eds.; Wiley: New York, 1978; and references cited therein.

(2) *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; and references cited therein.

(3) *Singlet Oxygen*; Frimer, A. A., Ed.; Vols. I–IV, CRC Press, Inc.: Boca Raton, Fl, 1985; and references cited therein.

(4) Ranby, B.; Rabek, J. F. in ref 1, pp 211–223, and references cited therein.

(5) Kaplan, M. L.; Trozzolo, A. M. in ref 2, pp 575–595, and references cited therein.

(6) Rabek, J. F. in ref 3, Volume IV, pp 1–90, and references cited therein.

(7) Byteva, I. M.; Gurinovich, G. P.; Golomb, O. L.; Karpov, V. V. *Opt. Spektrosk.* **1984**, *56*, 923–925.

(8) Byteva, I. M.; Gurinovich, G. P.; Golomb, O. L.; Karpov, V. V. *Zhur. Prik. Khim.* **1984**, *57*, 2081–2086.

(9) Lee, P. C.; Rodgers, M. A. J. *J. Phys. Chem.* **1984**, *88*, 4385–4389.

(10) (a) Salokhiddinov, K. I.; Byteva, I. M.; Dzhagarov, B. M. *Opt. Spectrosk.* **1979**, *47*, 487–490. (b) Salokhiddinov, K. I.; Dzhagarov, B. M.; Byteva, I. M.; Gurinovich, G. P. *Chem. Phys. Lett.* **1980**, *76*, 85–87.

(11) Hurst, J. R.; McDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065–2067.

(12) Parker, J. G.; Stanbro, W. D. *J. Am. Chem. Soc.* **1982**, *104*, 2067–2069.

(13) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 2069–2070.

(14) Rodgers, M. A. J.; Snowden, P. T. *J. Am. Chem. Soc.* **1982**, *104*, 5541–5543.

(15) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423–3430.

(16) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 5756–5760.

(17) Rodgers, M. A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6201–6205.

(18) Scurlock, R. D.: Ogilby, P. R. *J. Phys. Chem.*, in press.

(19) Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 1611–1617..

(20) Dobrowolski, D. C.; Ogilby, P. R.; Foote, C. S. *J. Phys. Chem.* **1983**, *87*, 2261–2263.

(21) Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1984**, *106*, 4679–4682.

(22) Gurinovich, G. P.; Salokhiddinov, K. I. *Chem. Phys. Lett.* **1982**, *85*, 9–11.

(23) Krasnovskii, A. A. *Zh. Prik. Spektrosk.* **1980**, *32*, 852–856.

(24) Keene, J. P.; Kessel, D.; Land, E. J.; Redmond, R. W.; Truscott, T. G. *Photochem. Photobiol.* **1986**, *43*, 117–120.

(25) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.*, submitted for publication.

0002-7863/87/1509-4746$01.50/0

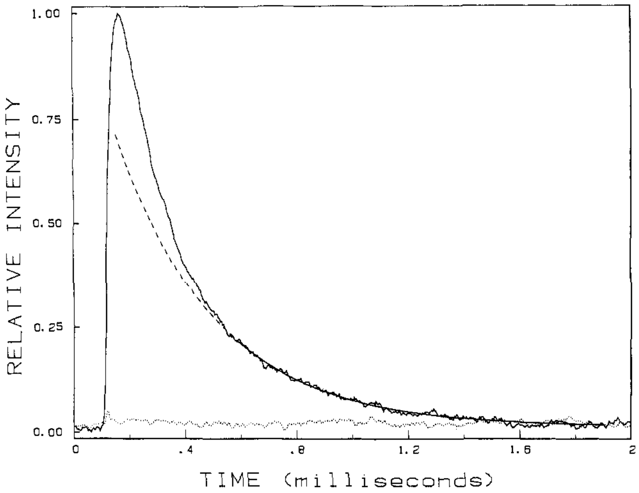

Figure 1. The time-resolved, near IR luminescence signal observed subsequent to irradiation of acridine (9.3×10^{-4} M, 355 nm, 1.0 mJ pulse^{-1}) in an aerated, 22 °C, PMMA glass (solid line). The data shown are an average of 16 independent signals. Under these conditions, the half-life for $^1\Delta_gO_2$ decay is approximately 240 μs. A single exponential function has been applied to the latter portion of the signal. A substantial deviation from first-order decay kinetics is apparent. Near IR luminescence was not observed from a similar polymer sample prepared in the absence of oxygen (dotted line). The latter data are an average of 128 independent signals.

tool in studies of $^1\Delta_gO_2$ photophysics and photochemistry. In particular, the role of $^1\Delta_gO_2$ in the photooxidation and photodegradation of solid polymers has been a focus of debate.[4-6] Since we directly monitor molecular oxygen, this experimental approach also provides a unique method to accurately quantify oxygen diffusion in a polymer.[27-30]

PMMA samples[31] were prepared containing one of five different sensitizers. $^1\Delta_gO_2$ was identified as the carrier of the observed signal[32] (Figure 1) on the basis of the following points: (1) λ_{max} of luminescence was ~1270 nm, in agreement with previous $^1\Delta_gO_2$ assignments.[7,8,15,16,34] (2) A sample prepared in the absence of oxygen failed to give a signal upon irradiation (Figure 1).[35] (3) Irradiation of a sensitizer free, oxygenated PMMA sample failed to yield a signal. (4) Samples prepared with the known $^1\Delta_gO_2$ quencher, 1,4-diazabicyclo[2.2.2]octane (DABCO), led to an increased rate of signal decay.[36] (5) Polymer samples stored under air gave rise to a signal whose peak intensity was less than that observed for identical samples stored under atmospheres with a larger partial pressure of oxygen. More importantly, the rate of both signal appearance and disappearance increased as the oxygen concentration in the sample increased. We suggest that these observations reflect, respectively, an increased rate of sensitizer quenching by oxygen[19] and the contribution of an oxygen-induced $^1\Delta_gO_2$ deactivation channel.[36]

The time-resolved $^1\Delta_gO_2$ signals were characterized by three general features: (1) A substantial deviation from first-order decay kinetics was observed in each case, (2) the rate of $^1\Delta_gO_2$ decay was dependent both on the sensitizer and the sensitizer concentration, and (3) The half-lives ($\tau_{1/2}$) for $^1\Delta_gO_2$ decay and rise in air-saturated samples (~300 and ~10 μs, respectively) were approximately an order of magnitude larger than the corresponding values in an appropriate liquid phase PMMA monomer model, methyl propionate. As in the case of other liquid phase organic solvents,[10-19] the $^1\Delta_gO_2$ decay in methyl propionate followed first-order kinetics ($\tau_{decay} = 38\ \mu$s).[26,32,36] In an attempt to quantify the PMMA data, we have applied a single exponential function to portions of the decay signal (Figure 1). This approach indicates clearly the extent to which $^1\Delta_gO_2$ deactivation is determined by mixed-order kinetics. For the five sensitizers examined, the rate of $^1\Delta_gO_2$ decay decreased in the order phenazine ($\tau_{1/2}$ ~110 μs) > acridine ($\tau_{1/2}$ ~225 μs) > fluoranthene and 1,12-benzoperylene ($\tau_{1/2}$ ~260 μs) > 2′-acetonaphthone ($\tau_{1/2}$ ~425 μs).[37] These rates reflect the relative efficiency with which the sensitizers quench $^1\Delta_gO_2$ in solution.[36]

At this juncture, our results may be interpreted to support several different models. The kinetics of $^1\Delta_gO_2$ appearance and disappearance, and the rate of signal change subsequent to a perturbation in the ambient atmosphere,[35] indicate that physical displacement of molecular oxygen in the polymer host, in the period defined by the $^1\Delta_gO_2$ lifetime (~100 μs), is substantially less than the displacement allowed by diffusion in the solution phase.[35,38] As a result, $^1\Delta_gO_2$ may encounter several different environments within its lifetime, each characterized by a unique set of $^1\Delta_gO_2$ quenching conditions. For example, upon formation in a photosensitized process, $^1\Delta_gO_2$ will necessarily be adjacent to the sensitizer which, in turn, may act as a quencher.[15] Diffusion of $^1\Delta_gO_2$ will change both the oxygen-sensitizer distance and relative geometric orientation and may expose $^1\Delta_gO_2$ to a slightly different bulk polymer environment.[27-28] $^1\Delta_gO_2$ may also encounter a photoinduced transient (e.g., a sensitizer triplet state[39] or a polymer-derived intermediate) which, in turn, could give rise to a time dependent quenching channel.[26,40] Within the period of ~100–200 μs, therefore, the relative probability of $^1\Delta_gO_2$ quenching will change, and a deviation from first-order decay kinetics will result.[41] Alternatively, since a biexponential function can be used to fit the $^1\Delta_gO_2$ decay, we must also consider a model for which evidence has been presented in the literature:[46-48] Small gas molecules dissolved in the polymer may be sorbed in two distinct modes, ordinary dissolution and adsorption in microvoids. Experiments currently in progress in our laboratory are designed to further characterize $^1\Delta_gO_2$ kinetics in the solid phase.

Acknowledgment. This work was supported by the National Science Foundation under Grant no. CHE-8501542 (P.R.O. and K.K.I.) and by the U.S. Department of Energy under contract number DE-AC04-76DP00789 (R.L.C.). We thank Michael Malone (Sandia) for his assistance is sample preparation.

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(26) In, K.-K.; Ogilby, P. R. *J. Phys. Chem.*, submitted for publication.

(27) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985; and references cited therein.

(28) Shaw, G. *Trans. Faraday Soc.* **1967**, *63*, 2181–2189.

(29) MacCallum, J. R.; Rudkin, A. L. *Eur. Polymer. J.* **1978**, *14*, 655–656.

(30) *Diffusion in Polymers*; Crank, J.; Park, G. S., Eds.; Academic Press: London, 1968.

(31) Details of sample preparation will be forthcoming. The samples were polished disks ~1.5 cm in diameter and 0.5-cm thick in which the sensitizer (3×10^{-4} M–5.7×10^{-3} M) was distributed as a solute.

(32) $^1\Delta_gO_2$ sensitizers were irradiated with a pulsed laser at 355 nm (1.5 mJ/pulse) (ref 19, 25, 26, 33).

(33) Iu, K.-K.; Scurlock, R. D.; Ogilby, P. R. *J. Photochem.* **1987**, *37*, 19–32.

(34) Khan, A. U. in ref 3, Vol. I, pp 39–79, and references cited therein.

(35) The time required for our signal amplitude to change under different ambient oxygen concentrations coincides with the expected rate of oxygen diffusion (ref 38) into the bulk polymer. This result, and other evidence (ref 36), indicates that $^1\Delta_gO_2$ phosphorescence originates primarily from the sample interior.

(36) Details will be forthcoming.

(37) [sensitizer] ~5.4×10^{-3} M (ref 31).

(38) By using published values for the oxygen diffusion coefficient (D) in PMMA (ref 28 and 29), we calculate a mean oxygen displacement of ~200 Å in 100 μs (ref 36). D in a liquid phase solvent is approximately three orders of magnitude larger (ref 27, pp 57–58).

(39) Since the rate constant for $^1\Delta_gO_2$ appearance ($\tau_{1/2}$ ~10 μs, air saturated sample) must equal the total rate constant for the disappearance of its precursor (ref 19), the excited state sensitizer lives long enough to influence the $^1\Delta_gO_2$ decay.

(40) Gorman, A. A.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1986**, *108*, 5074–5078.

(41) Mixed order phosphorescence decay kinetics for an organic molecule in the solid phase has recently been discussed in terms of a "fractal-like" energy-transfer process (ref 42–45).

(42) Klafter, J.; Blumen, A. *J. Chem. Phys.* **1984**, *80*, 875–877.

(43) Yang, C. L.; Evesque, P.; El-Sayed, M. A. *J. Phys. Chem.* **1985**, *89*, 3442–3444.

(44) Lin, Y.; Nelson, M. C.; Hanson, D. M. *J. Chem. Phys.* **1987**, *86*, 1586–1592.

(45) Even, U.; Rademann, K.; Jortner, J.; Manor, N.; Reisfeld, R. *Phys. Rev. Lett.* **1984**, *52*, 2164–2167.

(46) Stannett, V. T. *Polym. Eng. Sci.* **1978**, *18*, 1129–1134.

(47) Koros, W. G.; Paul, D. R. *Polym. Eng. Sci.* **1980**, *20*, 14–19.

(48) Vieth, W. R.; Howell, J. M.; Hsieh, J. H. *J. Membrane Sci.* **1976**, *1*, 177–220.