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## A Pulse Radiolysis Study of the Triplet Sensitized Production of Singlet Oxygen: Determination of Energy Transfer Efficiencies

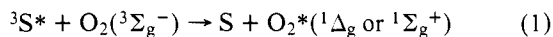
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**Abstract:** The technique of pulse radiolysis has been used to produce aromatic and aromatic carbonyl triplet states in liquid benzene. The quenching of such triplets by  $\text{O}_2(^3\Sigma_g^-)$  leads to the production of singlet oxygen ( $^1\Delta_g$ ), the subsequent reactivity of which has been followed by time-resolved observation of the bleaching of diphenylisobenzofuran (DPBF). Measurement of quenching rate constants together with sensitizer triplet and DPBF bleaching yields has allowed the efficiency of the process for energy transfer to oxygen to be determined. This efficiency varies considerably from sensitizer to sensitizer and appears to be inversely related to the sensitizer intersystem crossing efficiency.

### Introduction

Singlet oxygen  $\text{O}_2(^1\Delta_g)$  is now accepted as an important participant in the overall process termed photodynamic action. It seems likely that the major process by which it is formed in biological systems involves energy transfer from a triplet sensitizer ( $^3\text{S}^*$ ) according to



and indeed this process is the most common means of its production in the laboratory. It has been generally assumed that this process takes place with unit efficiency; i.e., for each triplet quenching act a molecule of  $\text{O}_2(^1\Delta_g \text{ or } ^1\Sigma_g^+)$  is produced and in solution any  $^1\Sigma_g^+$  states produced rapidly decay to  $\text{O}_2(^1\Delta_g)$ . A systematic investigation of the validity of this overall picture has so far been lacking. We have established a method for the investigation of  $\text{O}_2(^1\Delta_g)$  reactivity based on the pulse radiolysis technique and have addressed ourselves to the particular question of the efficiency of step 1.

The interaction between ground-state molecular oxygen and the electronically excited triplet states of organic molecules has been the subject of a number of recent studies.<sup>2-7</sup> In the quenching by oxygen of aromatic hydrocarbon triplets<sup>6</sup> the highest rate constants observed were for those sensitizers

having triplet energies close to but greater than the singlet energy of  $\text{O}_2(^1\Delta_g)$ . Further, the maximum rate constant measured was only some 10% of the diffusion-limited value in the liquid matrix. An encounter complex between  $\text{O}_2(^3\Sigma_g^-)$  and a triplet state can have either singlet, triplet, or quintet multiplicity.<sup>8</sup> The quintet encounter complex can only decay to starting materials and hence the maximum attainable quenching rate constant should be  $1/5$  of the diffusion-controlled value. That values of  $1/5$  of diffusion control or lower were found led to the conclusion<sup>6</sup> that the major decay route was from the singlet complex, the products of which are ground-state (singlet) aromatic and excited singlet oxygen. This conclusion supported the suggestion of Algar and Stevens,<sup>3</sup> based on a photooxidation study, that all of the quenched sensitizer triplets give rise to  $\text{O}_2(^1\Delta_g)$ . In addition, Stevens<sup>9</sup> names the encounter complex an "oxicplex" and assigns structural and spectroscopic properties to it.

In this work we have made direct measurements of the decay kinetics and yield of  $\text{O}_2(^1\Delta_g)$  in benzene solution as a function of sensitizer. Triplet sensitizer states have been generated by energy transfer from matrix triplet and singlet states produced by pulse radiolysis.

When a high energy electron beam is incident on a target

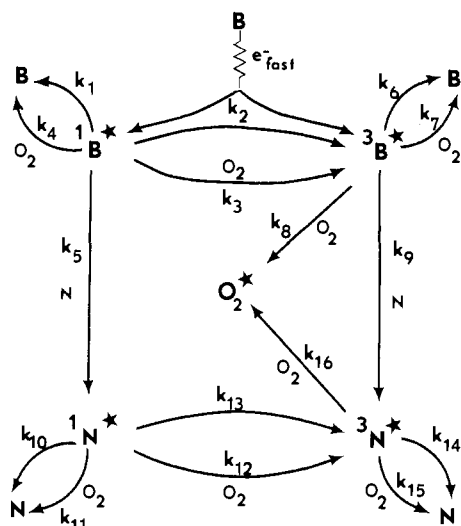


Figure 1. Kinetic scheme for  $O_2^*(^1\Delta_g)$  formation in aerated benzene (B) solutions containing naphthalene (N) irradiated by ionizing radiation.

Table I. Literature Rate Constant Values Pertinent to Figure 1

Unimolec constants, $s^{-1}$	Bimolec constants, $L \text{ mol}^{-1} s^{-1}$
$k_1, 1.6 \times 10^7$ <sup>a</sup>	$k_3, 9.0 \times 10^{10}$ <sup>f</sup>
$k_2, 2.3 \times 10^7$ <sup>b</sup>	$k_5, 3.8 \times 10^{10}$ <sup>g</sup>
$k_6, 3.0 \times 10^8$ <sup>c</sup>	$k_8, 3.0 \times 10^9$ <sup>h</sup>
$k_{10}, 2.0 \times 10^6$ <sup>a</sup>	$k_9, 3.8 \times 10^{10}$ <sup>g</sup>
$k_{13}, 7.0 \times 10^6$ <sup>d</sup>	$k_{12}, 3.0 \times 10^{10}$ <sup>i</sup>
$k_{14}, 4.0 \times 10^4$ <sup>e</sup>	$k_{16}, 2.2 \times 10^9$ <sup>j</sup>

<sup>a</sup> J. B. Birks, "Photophysics", Wiley-Interscience, New York, N.Y., 1970. <sup>b</sup> Deduced from  $k_1$  and a  $\phi_{\text{triplet}}$  value of 0.6; R. B. Cundall and W. Tippet, *Trans. Faraday Soc.*, **60**, 114 (1964). <sup>c</sup> J. H. Baxendale and M. Fiti, *J. Chem. Soc., Faraday Trans. 2*, **68**, 218 (1972). <sup>d</sup> F. Wilkinson in "Organic Molecular Photophysics", Vol. 2, Wiley, London, 1975, Chapter 3. <sup>e</sup> R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, **67**, 1904 (1971). <sup>f</sup> G. L. Braga, M. D. Lumb, and J. B. Birks, *ibid.*, **60**, 114 (1964). <sup>g</sup> J. H. Baxendale and P. Wardman, *ibid.*, **67**, 2997 (1971). <sup>h</sup> It is possible that the value of one-ninth of diffusion control taken is an underestimate owing to the matrix effect on the energy-transfer process. This does not affect the result of the calculations. <sup>i</sup> C. S. Parmenter and J. D. Rau, *J. Chem. Phys.*, **51**, 2242 (1969). <sup>j</sup> A. Aamer and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 2*, **72**, 1010 (1976).

of liquid benzene (B) or other aromatic, a high yield of bound excited states of the matrix molecules are rapidly formed. Yields are measured as  $G$  values, the number of molecules produced per 100 eV of absorbed radiation, and primary yields (those resulting from radiation-induced events prior to any photophysical interconversion) have been measured as  $G(^3B^*)_p = 4.2^{10}$  and  $G(^1B^*)_p = 1.4$ ,<sup>11</sup> i.e., a total excited state yield of 5.6 molecules per 100 eV absorbed. Free radical yields are only  $1/10$  of the excited state yield and escaped ions<sup>12</sup> (molecular cations and electrons) amount to <1% of the excited-state yield.

The ion recombination and internal conversion processes leading to thermalized excited-state formation are extremely rapid and in an experiment using a pulsed electron beam of, say, 20-ns half-width, they will be completed during the falling edge of the pulse. In our experiments radiation doses normally ranging from 1–4 krad ( $0.6\text{--}2.5 \times 10^{20} \text{ eV L}^{-1}$ ) were delivered in a single pulse to benzene which, based on the above  $G$  values, produced some  $6\text{--}25 \times 10^{-6} \text{ L}^{-1}$  of excited benzene states by the end of the pulse. The presence of added solutes at low enough concentration to avoid significant direct excitation allows subsequent energy-transfer processes to be studied by time-resolved spectrophotometry.

The intrinsic lifetimes of the benzene states in neat liquid are extremely short<sup>13</sup> ( $^3B^* \sim 2 \text{ ns}$ ;  $^1B^* \sim 12 \text{ ns}$ ) preventing efficient energy transfer to dissolved oxygen to equilibrium with air ( $2 \times 10^{-3} \text{ mol L}^{-1}$ ).<sup>14</sup> This situation can be improved by incorporating a sufficient concentration ( $\sim 10^{-2} \text{ mol L}^{-1}$ ) of an energy interceptor to take up the majority of the benzene excitation. The most useful interceptors (sensitizers) are molecules having a long-lived triplet state ( $\sim 1 \mu\text{s}$  or more) and a high intersystem-crossing quantum efficiency. For example, with naphthalene (N) as sensitizer at  $10^{-2} \text{ mol L}^{-1}$ , oxygen quenching of both  $^3B^*$  or  $^3N^*$  can produce  $O_2^*(^1\Delta_g)$ . The total reaction scheme for such a case is shown in Figure 1, analysis of which leads to the following equation governing the yield of  $O_2^*(^1\Delta_g)$

$$G(O_2^*) = G(^1B^*)_p \alpha \beta \delta' + \{G(^3B^*)_p + G(^1B^*)_p \delta\} \{\alpha \gamma + \gamma'\} \quad (2)$$

where

$$\alpha = k_{16}[O_2]/(k_{16}[O_2] + k_{14})$$

$$\beta = k_{12}[O_2]/(k_{10} + k_{13} + k_{12}[O_2])$$

$$\gamma = k_9[N]/(k_6 + k_8[O_2] + k_9[N])$$

$$\gamma' = k_8[O_2]/(k_6 + k_8[O_2] + k_9[N])$$

$$\delta = (k_2 + k_3[O_2])/(k_1 + k_2 + k_3[O_2] + k_5[N])$$

$$\delta' = k_5[N]/(k_1 + k_2 + k_3[O_2] + k_5[N])$$

These coefficients have been derived by assuming (i) that the interaction between  $O_2(^3\Sigma_g^-)$  and  $^1B^*$  or  $^1N^*$  results only in intersystem crossing and not in quenching to ground states<sup>15</sup> ( $k_3 \gg k_4$ ,  $k_{12} \gg k_{11}$ ); (ii) that the interaction between  $O_2(^3\Sigma_g^-)$  and  $^3B^*$  or  $^3N^*$  produces  $O_2^*(^1\Delta_g)$  stoichiometrically ( $k_8 \gg k_7$  and  $k_{16} \gg k_{15}$ ). This is not necessarily true (see later), but such an assumption allows estimation of the maximum possible singlet oxygen yield.

The literature values of  $k_1 \rightarrow k_{16}$  in Figure 1 are collected in Table I and lead to  $\alpha = 0.99$ ,  $\beta = 0.97$ ,  $\gamma = 0.55$ ,  $\gamma' = 0.009$ ,  $\delta = 0.34$ ,  $\delta' = 0.63$  whence  $G(O_2^*) = 3.5$ . This is the maximum  $G$  value attainable at  $10^{-2} \text{ mol L}^{-1}$  naphthalene. In the absence of an energy interceptor we obtain  $\alpha = 0.99$ ,  $\beta = 0.97$ ,  $\gamma' = 0.02$ ,  $\delta = 0.93$ ,  $\gamma = \delta' = 0$  which gives  $G(O_2^*) = 0.1$ . Thus the presence of  $10^{-2} \text{ mol L}^{-1}$  naphthalene in aerated benzene could in principle increase the singlet oxygen yield some 35 times. The extremely small contribution of oxygen to the total electron fraction in the mixtures prevents any significant direct population of upper oxygen levels.

The lack of any physical property to make direct observation of the production and decay kinetics of singlet oxygen in condensed media led us to follow others<sup>5,7,16</sup> and utilize the chemical reactivity of this species toward diphenylisobenzofuran (DPBF). The resultant bleaching of the absorption of this substrate ( $\lambda 415 \text{ nm}$  ( $\epsilon_{415} 2.21 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ )) may be conveniently followed using kinetic absorption spectrophotometry as the CRO trace in Figure 2a shows.

## Experimental Section

**1. Pulse Radiolysis.** Experiments were performed at the Christie Hospital and Holt Radium Institute, Manchester, using the Vickers 10-MeV linear accelerator which will generate electron pulses of 5-ns to 5- $\mu\text{s}$  duration. Kinetic absorption spectrophotometry measurements were made using the apparatus designed by Keene.<sup>17</sup> The time dependence and final extent of bleaching of DPBF absorption at 415 nm were displayed as CRO traces of voltage waveforms at the anode of an EMI 9558 QA photomultiplier tube. The use of a 10-K $\Omega$  load resistor gave signal risetimes of  $\sim 100 \text{ ns}$ . The faster sensitizer triplet decay was monitored using an EMI 9783 R photomultiplier tube coupled to a 50- $\Omega$  load resistance; this system gave a minimum rise time of  $\sim 5 \text{ ns}$ . Irradiation cells were of high purity quartz with optical

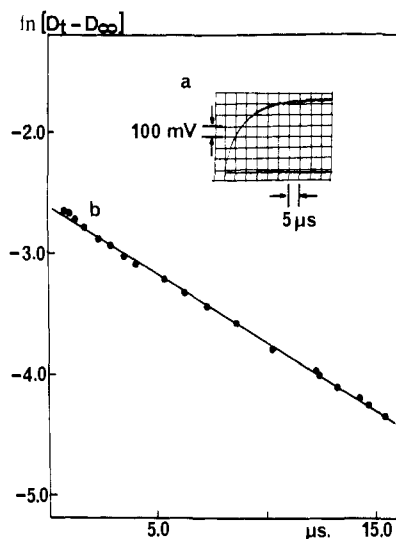


Figure 2. (a) Time-dependence of DPBF bleaching measured at 415 nm after absorption of a 20-ns electron pulse by aerated liquid benzene containing naphthalene ( $10^{-2}$  mol  $\text{L}^{-1}$ ) and DPBF ( $2.5 \times 10^{-5}$  mol  $\text{L}^{-1}$ ). (b) Semilogarithmic plot of  $(D_t - D_\infty)$  vs. time for the above experiment ( $D$  = optical density).

path lengths of either 3 or 25 mm. All irradiation experiments were carried out at room temperature and except where stated solutions were aerated (oxygen concentration =  $2 \times 10^{-3}$  mol  $\text{L}^{-1}$ ).<sup>14</sup>

Owing to the photosensitivity of DPBF, special precautions were taken to keep the monitoring light from the 250-W xenon arc at negligible levels during the experiments since the normal operating mode requires a shutter to open and stay open for  $\sim 1$  s before the electron pulse is triggered. The amount of light reaching the target system during this period was found to be excessive. This was overcome by interposing neutral density and haze filters between the lamp and target cell such that  $\sim 10\%$  of the continuous beam was incident on the target cell. A high current pulse increased the arc intensity some 100-fold for 1 ms<sup>18</sup> and the accelerator was triggered on the flat top of this pulse after 750  $\mu\text{s}$ . These precautions eliminated DPBF photolysis in the target system (see later).

The dose delivered to the sample cell was measured by a secondary emission chamber, which had been calibrated using one of two chemical dosimeters. (a) The yield of solvated electrons ( $G = 2.7$ )<sup>19</sup> in pure argon-saturated water was determined by monitoring their transient absorption at 550 nm ( $\epsilon$  9490). (b) Oxidation by OH radicals ( $G = 3.2$ )<sup>20</sup> of potassium ferrocyanide ( $5 \times 10^{-3}$  M), in oxygen saturated aqueous solution, was monitored by observation of the absorption due to the ferricyanide product at 420 nm ( $\epsilon$   $10^3$ ).<sup>21</sup> A simple density factor was employed to calculate the dose delivered to a hydrocarbon solvent.

**2. Materials.** Anthracene, naphthalene, *p*-terphenyl, 2-acetonaphthone, and benzophenone were the best available and used as supplied. Biphenyl (EtOH), benzil (hexane), and acridine (EtOH/ $\text{H}_2\text{O}$ ) were recrystallized. Diphenylisobenzofuran (Aldrich) was twice recrystallized from methanol-water and stored in the dark. Benzene (AnalaR) was washed with sulfuric acid, water and sodium bicarbonate and distilled from  $\text{P}_2\text{O}_5$ . Toluene (AnalaR grade) was refluxed with lithium aluminum hydride and fractionated under nitrogen.<sup>12</sup>

## Results and Discussion

**1. Determination of Rate Parameters.** Having been produced by energy transfer from sensitizer triplet species,  $\text{O}_2^*(^1\Delta_g)$  can decay via the following channels, the rate parameters for which depend on medium and solutes present:

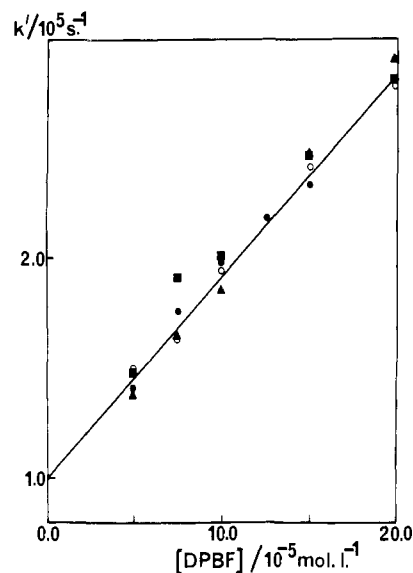
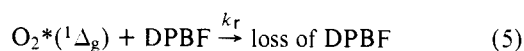
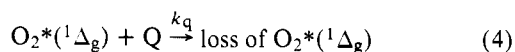
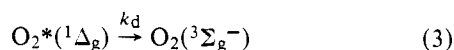


Figure 3. Dependence of first-order constant for bleaching of DPBF,  $k'$ , on DPBF concentration for aerated benzene solutions containing naphthalene (O), anthracene (●), benzophenone (▲) and benzil (■),  $10^{-2}$  mol  $\text{L}^{-1}$  in each case.

When the initial concentration of  $\text{O}_2^*(^1\Delta_g)$  is small compared with the initial concentrations of DPBF and Q, the rate of loss of DPBF is given by

$$\frac{d(-[\text{DPBF}])}{dt} = k_r[\text{DPBF}][\text{O}_2^*]_0 \exp(-\{k_d + k_r[\text{DPBF}] + k_q[\text{Q}]\}t) \quad (6)$$

where Q is a quencher molecule which may act via chemical or physical action, and  $[\text{O}_2^*]_0$  is the concentration of singlet oxygen at the end of the electron pulse. It is readily shown that a plot of  $\ln(D_t - D_\infty)$  against time will be linear with a slope  $k' = k_d + k_r[\text{DPBF}] + k_q[\text{Q}]$  where  $D_t$  and  $D_\infty$  are, respectively, the DPBF optical densities at time  $t$  and at completion of the bleaching event. Typical results are shown in Figure 2. The rate parameters  $k_d$ ,  $k_r$ , and  $k_q$  can be evaluated from plots of  $k'$  against (i) DPBF concentration for  $k_d$  and  $k_r$  and (ii) quencher concentration (at fixed DPBF) for  $k_q$ . When solutions were deaerated by argon bubbling, no significant bleaching was observed. In addition, the exposure of the oxygenated target solution to the monitoring light flash in the absence of an electron beam failed to produce a bleaching signal. Thus photolytic change by the monitoring light was not significant under the conditions employed.

**2. Evidence for  $\text{O}_2^*(^1\Delta_g)$  Production in Pulse Radiolysis of Aerated Benzene.** Although triplet states of benzene and sensitizer are produced in high yield under pulse radiolysis conditions and the presence of oxygen was shown to be necessary for DPBF bleaching, these facts alone do not constitute unequivocal proof for the intermediacy of  $\text{O}_2^*(^1\Delta_g)$ . To obtain further evidence experiments were performed in which  $k'$  was measured over a range of DPBF concentrations using a number of energy interceptors (sensitizers). Representative plots are shown in Figure 3 where it can be seen that all  $k'$  values for different sensitizers used fall about a single line, i.e., the species responsible for DPBF has  $k_d$  and  $k_r$  values independent of sensitizer. Were the reacting species not identical in each experiment but, say, a complex of sensitizer with oxygen, such sensitizer-independent behavior would be extremely unlikely. Additionally the measured  $k_r$  value from Figure 3 was  $9.4 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$  in close agreement with literature values<sup>5,7,16</sup> for the reaction between DPBF and  $\text{O}_2^*(^1\Delta_g)$ .

Further evidence was obtained from measurements of the

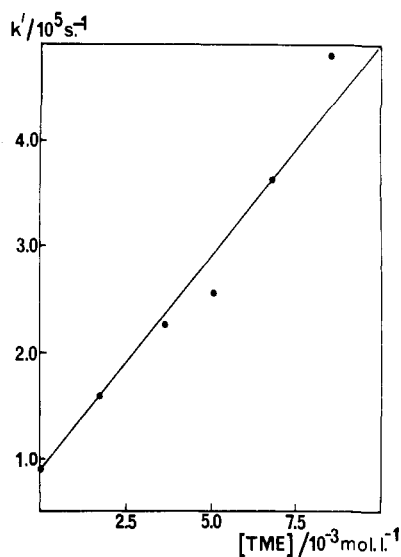


Figure 4. Dependence of first-order constant for DPBF bleaching,  $k'$ , on TME concentration of aerated benzene containing naphthalene ( $10^{-2}$  mol  $L^{-1}$ ) and DPBF ( $2.5 \times 10^{-5}$  mol  $L^{-1}$ ).

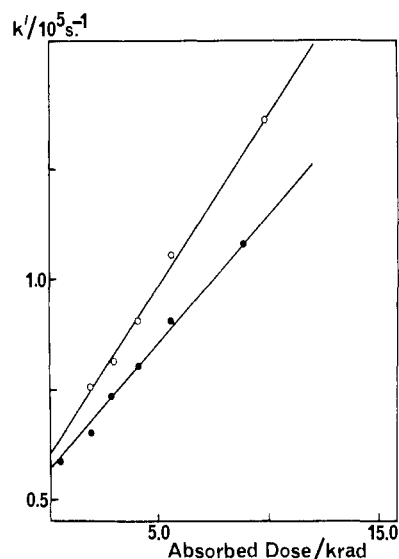


Figure 5. Dependence of first-order constant for DPBF bleaching,  $k'$ , on the absorbed radiation dose for oxygenated benzene ( $\bullet$ ) and toluene ( $\circ$ ) solutions containing naphthalene ( $10^{-2}$  mol  $L^{-1}$ ) and DPBF ( $2.5 \times 10^{-5}$  mol  $L^{-1}$ ).

rate of DPBF removal in the presence of added substances known to quench singlet oxygen. For example, Figure 4 shows a plot of  $k'$  measured over a range of tetramethylethylene (TME) concentrations at fixed DPBF concentration ( $2.5 \times 10^{-5}$  mol  $L^{-1}$ ) in aerated toluene containing naphthalene ( $10^{-2}$  mol  $L^{-1}$ ). The slope of Figure 4 leads to a value for  $k_q$  of  $4.2 \times 10^7$  L mol $^{-1}$  s $^{-1}$  which is in excellent agreement with the value of  $4.0 \times 10^7$  L mol $^{-1}$  s $^{-1}$  obtained using a laser photolysis method for  $O_2^*(^1\Delta_g)$  production.<sup>7</sup> Several other quenching rate constants have been measured using the pulse radiolysis technique and all compare favorably<sup>22</sup> with literature values where available. We conclude that free  $O_2^*(^1\Delta_g)$  is the species responsible for the bleaching of DPBF in the pulse radiolysis experiments described. That such high yields of  $O_2^*(^1\Delta_g)$  are formed as a result of depositing the energy from ionizing radiation into an  $O_2$ -containing system may be of importance to understanding the enhancement by oxygen of the biological effects of ionizing radiation.<sup>28</sup>

### 3. Effect of Radiation Intensity of Singlet Oxygen Lifetime.

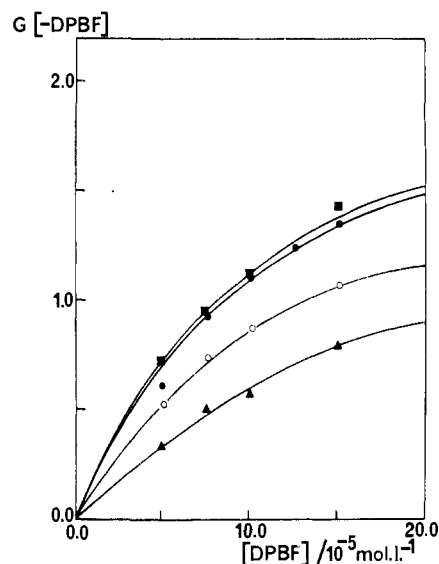


Figure 6. Dependence of DPBF bleaching yield,  $G(-DPBF)$  on DPBF concentration for aerated benzene solutions containing naphthalene ( $\circ$ ), anthracene ( $\bullet$ ), benzophenone ( $\blacktriangle$ ) and benzil ( $\blacksquare$ ),  $10^{-2}$  mol  $L^{-1}$  in each case (cf. Figure 3).

Although the data presented in the preceding section show that the active species produced in these experiments is indeed  $O_2^*(^1\Delta_g)$ , the intercept in Figure 3 gave a  $k_d$  value of  $1.0 \times 10^5$  s $^{-1}$  which corresponds to a lifetime in benzene for this molecule of 10  $\mu$ s. This is significantly lower than that of 25–26  $\mu$ s obtained previously<sup>7</sup> and it was found that the  $O_2^*(^1\Delta_g)$  lifetime was dependent on the radiation intensity. In Figure 5 are shown plots of  $k'$  at  $2.5 \times 10^{-5}$  mol  $L^{-1}$  DPBF in oxygenated benzene and toluene containing  $5 \times 10^{-2}$  mol  $L^{-1}$  naphthalene, the measurements being made over a range of 0.5–10 krad per pulse. It is observed that  $k'$  increases linearly with absorbed intensity in both benzene and toluene. Extrapolation to zero dose gives  $k'$  values which correspond to lifetimes of 27  $\mu$ s in benzene, in good agreement with previous work, and 25  $\mu$ s in toluene for which no published data is available.<sup>23</sup> The observed first-order kinetics indicate that the one or more dose-dependent species responsible for the quenching of  $O_2^*(^1\Delta_g)$  are not destroyed in the quenching act. Paramagnetic quenching by radicals or conceivably a radical chain reaction would accommodate the experimental facts. The slope of the plot for benzene in Figure 5 is  $5.8 \times 10^3$  krad $^{-1}$  s $^{-1}$ . The known radical yield ( $G = 0.8$ )<sup>24</sup> allows conversion to a rate constant for radical quenching of  $7 \times 10^9$  L mol s $^{-1}$ . A similar value is obtained for toluene.

**4. Effect of Sensitizer on the Singlet Oxygen Yield.** The oscilloscope traces used to obtain the values of  $k'$  shown in Figure 3 have been used together with absorbed dose measurements to produce values for  $G(-DPBF)$  as a function of DPBF concentration. The data obtained in aerated benzene are shown in Figure 6 where it is seen that at any given DPBF concentration the efficiency of its removal depends on the sensitizer used. These differences must, at least in part, be due to differing sensitizer triplet yields. In order to examine this effect more closely we carried out the following series of experiments. (i)  $G(^3S^*)$  was determined in argon-saturated benzene solutions containing  $10^{-2}$  mol  $L^{-1}$  sensitizer, by measuring the optical density at  $\lambda_{max}$  of the T-T absorption spectrum immediately after the electron pulse. Extinction coefficients published by Bensasson and Land<sup>25</sup> were used. (ii) The fraction of sensitizer triplets undergoing oxygen quenching in oxygen-saturated benzene solutions was determined by measuring the first-order rate constant of sensitizer triplet decay at several oxygen concentrations from which the bimolecular rate con-

**Table II.** Yields of Singlet Oxygen Compared with Yields of Sensitizer Triplets

Sensitizer	$G(^3S^*)^a$	Rate constants for O <sub>2</sub> quenching		$G(O_2^*)^b$	$S_\Delta$	$\phi_{isc}$	$(E_T - IP)/eV$
		in benzene, 10 <sup>9</sup> L mol <sup>-1</sup> s <sup>-1</sup>					
<i>p</i> -Terphenyl	2.18	1.20		1.99	0.9	0.11 <sup>e</sup>	5.77
Acridine	3.30	1.81		2.39	0.7	0.76 <sup>e</sup>	
Anthracene	3.30	2.47	(2.78) <sup>e</sup>	2.29	0.7	0.75 <sup>f</sup>	5.61
Biphenyl	2.79	1.40		1.53	0.6	0.81 <sup>f</sup>	5.41
2-Acetonaphthone	3.76	1.54	(1.60) <sup>d</sup>	1.95	0.5	0.84 <sup>f</sup>	
Naphthalene	3.57	1.54	(1.85) <sup>d</sup>	1.85	0.5	0.82 <sup>f</sup>	5.48
Benzophenone	3.74	1.84	(2.53) <sup>d</sup>	1.55	0.4	1.00 <sup>f</sup>	6.41

<sup>a</sup> Difference between  $G(^3S^*)$  and  $G(Q)$  ignored (see text). <sup>b</sup> From Table III. <sup>c</sup> Reference 6. <sup>d</sup> Reference 26. <sup>e</sup> Reference 27. <sup>f</sup> Reference 28.

**Table III.** Experimental Data<sup>a</sup> for Determination of Singlet Oxygen  $G$  Values

Sensitizer <sup>a</sup>	10 <sup>2</sup> $\Delta D^b$	$G(-DPBF)$	10 <sup>-5</sup> $k'/s^{-1}$	$G(O_2^*)$
<i>p</i> -Terphenyl	5.14	1.18	1.57	1.99
Acridine	6.21	1.42	1.46	2.39
Anthracene	5.94	1.36	1.59	2.29
Biphenyl	3.96	0.91	1.58	1.53
2-Acetonaphthone	5.07	1.16	1.56	1.95
Naphthalene	4.69	1.10	1.57	1.85
Benzophenone	3.46	0.79	1.59	1.55

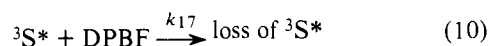
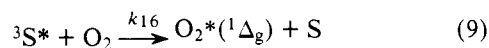
<sup>a</sup> Obtained at 10<sup>-2</sup> mol L<sup>-1</sup> sensitizer and 10<sup>-4</sup> mol L<sup>-1</sup> DPBF in oxygen-saturated benzene. <sup>b</sup>  $\Delta D$  = overall change in optical density at 415 nm owing to loss of DPBF.

stants for oxygen quenching were obtained for all sensitizers (Table II). These experiments led us to conclude that, in oxygen-saturated solutions, >95% of all sensitizer triplets were quenched by oxygen. (iii)  $G(O_2^*)$  values were determined by observing  $G(-DPBF)$  and  $k'$  for bleaching at 1 × 10<sup>-4</sup> mol L<sup>-1</sup> DPBF in oxygen-saturated benzene solutions each containing 1 × 10<sup>-2</sup> mol L<sup>-1</sup> sensitizer. Singlet oxygen yields (Table III) were then calculated from the relationship

$$G(O_2^*) = G(-DPBF) \frac{k_d + k_r[DPBF]}{k_r[DPBF]} \quad (7)$$

Values of  $G(O_2^*)$  and  $S_\Delta = G(O_2^*)/G(Q)$  are collected in Table II where  $G(Q)$  is the yield of sensitizer triplets quenched by oxygen (approximately equal to the value for  $G(^3S^*)$  determined in the absence of oxygen).<sup>29</sup>

It is necessary to consider the possibility of reaction between <sup>3</sup>S\* and DPBF (physical quenching, energy transfer, etc.) as such a process would reduce  $G(O_2^*)$ . Based on the following reaction scheme



the yield of sensitizer triplets quenched by oxygen is given by

$$G(Q) = G(^3S^*)k_{16}[O_2](k_{16}[O_2] + k_{14} + k_{17}[DPBF]) \quad (11)$$

At  $[O_2] = 1 \times 10^{-2}$  mol L<sup>-1</sup> and  $[DPBF] = 1 \times 10^{-4}$  mol L<sup>-1</sup> and assuming  $k_{17} = 7 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>, the optimum triplet energy-transfer value in benzene,<sup>30</sup> then

$$G(Q) = 0.97G(^3S^*) \quad (12)$$

i.e., nonoxygen quenching decay modes are insignificantly small.

In Table II it is clear that the values of  $S_\Delta$ , i.e., the fraction of oxygen quenchings which lead to  $O_2^*(^1\Delta_g)$ , depart seriously from unity for most quenchers used. Only in the case of *p*-terphenyl does the value approach the maximum; hence the reaction described by eq 1 does not generally proceed with unit efficiency, contrary to the suggestion of Algar and Stevens<sup>3</sup> and conclusions derived from quenching rate constants.<sup>6</sup>

## Conclusions

All of the sensitizers investigated have triplet energies high enough to produce <sup>1</sup>Δ<sub>g</sub> and/or <sup>1</sup>Σ<sub>g</sub><sup>+</sup> via an exothermic energy transfer process and as expected our  $S_\Delta$  values show no correlation with triplet energies.

Garner and Wilkinson have recently reported a study of the quenching of aromatic ketone and amine triplets by oxygen;<sup>26</sup> they found that in some cases the quenching rate constants exceeded 1/9 diffusion control. In particular, for *N*-methylindole triplet the rate constant was measured as 1.4 × 10<sup>10</sup> L mol<sup>-1</sup> s<sup>-1</sup>, which is close to the 4/9 fraction of that expected for diffusion control if both singlet and triplet encounter complexes are decaying to products very efficiently. Garner and Wilkinson<sup>26</sup> have suggested that encounter complexes involving high energy triplets of carbonyl and amine molecules with O<sub>2</sub> can have a degree of charge-transfer character which allows the complex to reach the ground-state surface. In support they note, without giving details, that quantum yields of <sup>1</sup>Δ<sub>g</sub> of less than unity have been observed. Our findings that the efficiency of process 1 can be significantly less than unity and varies with sensitizer clearly agree with their comment concerning yields.<sup>31</sup> However, in contrast, none of our rate constants for triplet quenching by oxygen exceed one-ninth of diffusion control.

In an attempt to examine our data according to the Garner and Wilkinson<sup>26</sup> proposal, we have included a column headed  $(E_T - IP)$  in Table II. If a charge-transfer state of sensitizer and oxygen does exist, its energy will be related to the sensitizer ionization potential. The  $E_T - IP$  term then governs the ease with which the complex can reach the charge-transfer state given the energy of the sensitizer triplet. The larger the energy gap, the less easily the transition can be made, the more readily the encounter complex decays via the  $O_2^*(^1\Delta_g)$  route. That benzophenone fails to fit, and the correlation for the remainder is only poor leads us to conclude that the charge-transfer mechanism is unlikely to be a significant contributor here.

Gijzeman et al. have concluded<sup>6</sup> that aromatic triplet states react with oxygen with a rate constant of ~1/9 of diffusion control to produce a singlet encounter complex, and for triplets of intermediate energy (10 000–15 000 cm<sup>-1</sup>) the complex breaks down with unit efficiency to give singlet oxygen (<sup>1</sup>Δ<sub>g</sub> or <sup>1</sup>Σ<sub>g</sub><sup>+</sup>) and ground-state aromatic. For higher energy triplets the decay of complex to reactants becomes significant and lower values for the experimental quenching rate constant are obtained. Our measured quenching rate constants are typically ~1/9 of the diffusion controlled value and we therefore conclude

that in these cases quenching only proceeds via the singlet encounter complex. Gijzeman et al.<sup>6</sup> assumed that intersystem crossing within the singlet complex was insignificant with respect to spin-allowed dissociative processes. This assumption is not necessarily valid and we have considered the possibility that the inefficient production of  $^1\Delta_g$  which we have observed is in fact a result of such an intersystem crossing. In this event it is possible that the efficiency of intersystem crossing within the singlet encounter complex reflects that within the free sensitizer singlet; i.e.,  $S_\Delta$  should decrease with an increase in  $\phi_{isc}$ . The data in Table II clearly show this to be the case. It would therefore appear that the factors which influence sensitizer intersystem crossing efficiencies may also influence the mode of decay of the corresponding singlet encounter complexes with oxygen. Further studies on this hypothesis are proceeding.

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- (31) A referee points out that Garner and Wilkinson's data for  $O_2^*(^1\Delta_g)$  yields sensitized by naphthalene and benzophenone are 1.05 and 0.56, respectively, different from the values of 0.5 and 0.4 found by us. He comments that the discrepancies may arise from insufficiently precise literature data for triplet-triplet extinction coefficients either for the sensitizers used by us or  $\beta$ -carotene used by Garner and Wilkinson. We agree with this observation but emphasize that, in both works, the ketone-derived yield was lower.

## Carbon Acidity. 56. Equilibrium Acidities of 4-Methyl-, 4-Ethyl-, and 4-Isopropylbiphenyls with Cesium Cyclohexylamide<sup>1</sup>

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**Abstract:** *p*-Methylbiphenyl whose  $pK_{CsCHA}$  was reported previously to be 38.7 has been found to be incompletely converted to carbanion by cesium cyclohexylamide (CsCHA). The extinction coefficient for *p*-biphenylmethylcesium in CHA has been determined and the revised  $pK_{CsCHA}$  is 38.95. The same procedure applied to *p*-ethylbiphenyl and *p*-isopropylbiphenyl gives  $pK_{CsCHA}$  values of 38.8 and 38.6, respectively (all values statistically corrected). *p*-Methylbiphenyl had been used as an indicator for thiophene and methylthiathiane and to provide an extrapolated acidity for toluene. The revised  $pK_{CsCHA}$  values are 38.2, 37.8, and 41.2, respectively.

*p*-Methylbiphenyl (pMB) occupies an important place in the scale of equilibrium hydrocarbon acidities. Its  $pK$  measurement<sup>3</sup> with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA),  $pK_{CsCHA}$ , represents the least acidic hydrocarbon whose equilibrium acidity is measured directly. As such, it is an important indicator that has been used for acidity measurements of some heterocyclic molecules (e.g., thiophene<sup>4</sup> and methylthiathiane<sup>5</sup>). It forms a vital point in the Brønsted correlation of kinetic acidities with lithium cyclo-

hexylamide<sup>6</sup> to provide an extrapolated  $pK_{CsCHA}$  of toluene. pMB is an indicator for that crucial region of the acidity scale accessible in the CsCHA system that lies beyond the observable realm of the Me<sub>2</sub>SO system. We now report that our previous measurement of the  $pK_{CsCHA}$  of this compound is in error because of an unrecognized solvent-leveling effect. pMB is sufficiently close to solvent CHA in equilibrium acidity with the CsCHA base that it is incompletely converted to its cesium salt. We report corrected values together with the equilibrium