

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 96, NUMBER 11

MAY 29, 1974

Measurement of the Absolute Rate Constants for Singlet Molecular Oxygen($^1\Delta_g$) Reaction with 1,3-Diphenylisobenzofuran and Physical Quenching by Ground State Molecular Oxygen

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Abstract: Singlet oxygen ($^1\Delta_g$) has been produced in Freon 113 solution by pumping the oxygen $^1\Delta_g + 1v \leftarrow ^3\Sigma_g^-$ electronic transition by 1.06 μm radiation from a continuous Nd-YAG laser or a Q-switched Nd-glass laser. The singlet oxygen thus produced was detected by reaction with the acceptor 1,3-diphenylisobenzofuran (DPBF). Comparison of the amount of DPBF concentration change with the amount of singlet oxygen produced has shown that the rate constant of reaction of DPBF with singlet oxygen obtained by Merkel and Kearns and others is an order of magnitude too high but corresponds to the total rate constant which we measure for reaction plus quenching. The rate of quenching of singlet oxygen by ground state oxygen has been measured to be $2.7 \times 10^3 \text{ l. mol}^{-1} \text{ sec}^{-1}$ in Freon 113, only twice the rate in the gas phase measured by Wayne and others.

The compound 1,3-diphenylisobenzofuran (DPBF) has been of central importance to studies of singlet oxygen ($^1\Delta_g$) reactivities in solution.²⁻⁵ It reacts more rapidly with singlet oxygen than any acceptor known up to the present.

Recently, a technique of giant pulse laser flash photolysis where a sensitizing dye is pumped by a laser flash *via* the singlet into its triplet state, which is in turn quenched by ground state oxygen to produce an instantaneous concentration of $^1\Delta_g$ oxygen in solution, has been demonstrated in several laboratories.³⁻⁵ The singlet oxygen thus produced decays with time and may be monitored by reaction with a colored acceptor which reacts to yield a colorless product. The data thus obtained were analyzed in terms of acceptor concentration and yielded the lifetime of $^1\Delta_g$ oxygen in many solvents and an estimate of the absolute reaction rate constant of DPBF with $^1\Delta_g$ oxygen. The acceptor is invariably DPBF since it is the only one

that reacts rapidly enough to make the experiment possible.

Previous studies in this laboratory have been reported^{2,6} where $^1\Delta_g$ oxygen was generated by continuous irradiation of the oxygen $^1\Delta_g + 1v \leftarrow ^3\Sigma_g^-$ electronic transition with the 1.06 μm continuous wave output of a Nd-YAG laser.

This method has the advantage of directness with no possibility of confusion by triplet sensitizer reactions but has the disadvantage that the finally worked-up data yield reaction rate constant ratios.⁶

In order to separate out rate ratios into absolute reaction rate constants we report here experiments where an effectively instantaneous concentration of $^1\Delta_g$ oxygen was obtained by irradiation of oxygen in Freon 113 (1,1,2-trifluoroethane) solution with the giant pulse output of a Q-switched Nd-glass laser. The results were analyzed in a manner similar to that for the sensitizer experiments alluded to above.

Experimental Section

The apparatus used is shown in Figure 1. Light from a 120-W tungsten strip lamp L is focused into the Bausch and Lomb high

(1) (a) University of Georgia; (b) Duke University.
(2) I. B. C. Matheson and J. Lee, *Chem. Phys. Lett.*, **7**, 475 (1970).
(3) (a) P. B. Merkel and D. R. Kearns, *Chem. Phys. Lett.*, **12**, 120 (1971); (b) *J. Amer. Chem. Soc.*, **94**, 5216 (1972).
(4) D. R. Adams and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1 (1972).
(5) R. H. Young, D. Brewer, and R. A. Keller, *J. Amer. Chem. Soc.*, **95**, 375 (1973).

(6) I. B. C. Matheson and J. Lee, *J. Amer. Chem. Soc.*, **94**, 3310 (1972).

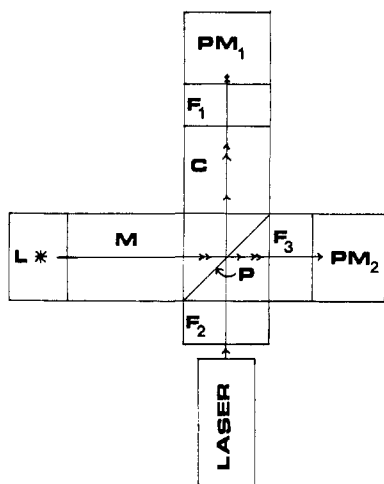


Figure 1. Schematic representation of the apparatus.

intensity monochromator M and deflected 90° by a glass microscope slide P. The visible analyzing light then passes through the sample cell C and a visible transmitter filter F_1 , Corning 4-76, to photomultiplier PM_1 , RCA 931A. The laser beam enters the apparatus *via* the filter F_2 (Kodak Wratten 88a, ir transmitting) and is largely transmitted through the slide P and is then exactly collinear with the analyzing beam with transmission to PM_1 being blocked by F_1 . A portion of the laser beam is also deflected 90° by P and is transmitted through F_3 (Kodak Wratten 88a) plus attenuating filters to PM_2 , RCA 7102. PM_2 may be used to obtain a measure of the laser energy from the Q-switched Nd-glass laser.

The continuous wave laser was a Holobeam (Paramus, N. J.) series 200 Nd-YAG which was generally operated in the 5–10-W region and its power monitored by a black body laser calorimeter (Sciencetech, Boulder, Colo.) Model 3600 disk calorimeter which could be internally calibrated by a built-in heating resistor, viewing the laser back beam. The ratio of front-to-rear power output of the laser was checked from time to time, and the estimated precision of measurement of the power entering the cell C after allowing transmission losses at F_2 and the cell window was $\pm 10\%$.

The pulse laser was a Holobeam Series 600 with a $6 \times \frac{3}{8}$ in. Nd-glass rod equipped with a Pockels cell Q-switch which delivered about 1.5 J in about 20 nsec. Its energy was measured by a calorimeter⁷ constructed of a glass container of 3.5-ml capacity holding an aqueous solution of $NiCl_3^8$ of optical density ($1.06 \mu m$) about 2. The glass container was surrounded by an insulating styrofoam jacket, and the temperature rise caused by the absorbed energy was measured by means of a thermistor which formed part of an off-balance Wheatstone bridge. This calorimeter was calibrated by irradiation with the continuous wave Nd-YAG laser operating at a known wattage for a measured time, so that both laser powers or energies are known relative to the same source, *i.e.*, the black body calorimeter. The $NiCl_3$ calorimeter was mounted for test purposes in the apparatus at the position normally occupied by C and the proportionality between the laser energy and signal generated on PM_2 per pulse obtained.

Thus in the experiments where C was present with a sample the laser energy was obtained from the signal on PM_2 and the estimated over-all precision of the procedure is $\pm 50\%$.

Three different configurations of the high-pressure cell were used, all of which were constructed of stainless steel with $\frac{3}{8}$ -in. thick quartz windows. The first cell was of 50-mm path length with a 18.4-mm internal diameter and was used for most of the continuous wave experiments. It is vital for pulse experiments that the cell aperture be equal to or less than the laser beam diameter so that the analyzing beam passes only through a cross section where reactions are taking place. Therefore, a Teflon plug was constructed to gate down the cell aperture to 6.35 mm. This did not prove satisfactory in that on two occasions violent explosions occurred on irradiation with the laser pulse blowing out the cell windows and causing extensive damage to the apparatus. The suspected reason was that in these cases the laser beam was larger

than the cell aperture and, in some cases, shock heating of fluid trapped between the Teflon and the quartz window occurred with catastrophic results. Consequently, a new cell of all stainless steel construction with a 9.5-mm aperture which matched the laser beam was constructed. The path length was cut to 18 mm so that higher DPBF concentrations could be conveniently measured. This cell has proved highly satisfactory.

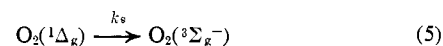
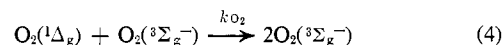
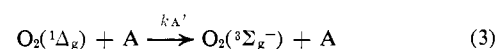
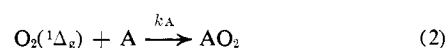
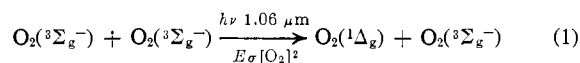
Oxygen concentrations were derived from ir absorption spectra in the continuous wave laser experiments or by measuring the oxygen pressure at which that in solution is at equilibrium, in the pulsed laser case. Data on oxygen ir absorption coefficients and Henry's law have been previously described.⁹

Data were analyzed for the continuous wave laser experiments by an on-line computer system which has been previously described.⁶ In the pulse laser experiment the signals were taken from the anodes of PM_1 and PM_2 *via* a 5 k Ω resistance load to a two-channel oscilloscope, Tektronix 564. The oscilloscope was triggered by a signal from the Pockels cell Q-switch and the stored display photographed.

Materials. 1,3-Diphenylisobenzofuran was from K & K Laboratories, Plainview N. Y., and was used as supplied. Freon 113 (1,1,2-trichlorotrifluoroethane), spectrograde, was supplied by Matheson Coleman and Bell, East Rutherford, N. J. Medical grade oxygen was used for all experiments.

Kinetic Analysis

The formation and decay of $^1\Delta_g$ oxygen in Freon solution is completely described by the following set of reactions.



Formation of $^1\Delta_g$ oxygen by absorption of E einsteins per second requires a bimolecular reaction (reaction 1). The singlet oxygen may chemically react with the acceptor A to give a product AO_2 (reaction 2). This is monitored by loss of absorbance due to A. Another process will be direct physical quenching of $^1\Delta_g$ by A (reaction 3) which leaves A unchanged. Physical quenching by molecular oxygen (reaction 4) is important at the high-oxygen concentrations used in these experiments. Finally, the solvent itself might quench $^1\Delta_g$ oxygen and this is represented by the pseudo-first-order rate constant k_s process (reaction 5).

Continuous Wave Case. When the $^1\Delta_g$ oxygen is produced continuously at a concentration represented by the symbol $[\Delta]$, a stationary state analysis yields

$$[\Delta] = \frac{\sigma E[O_2]^2}{k_s + k_{O_2}[O_2] + (k_A + k_A')[A]}$$

The rate of disappearance of A due to reaction will be given by

$$-\frac{dA}{dt} = k_A[A][\Delta] = \frac{\sigma E[O_2]^2[A]k_A}{k_s + k_{O_2}[O_2] + (k_A + k_A')[A]}$$

Generally for this type of experiment $[A]$ is chosen so that $(k_A + k_A')[A] < k_s + k_{O_2}[O_2]$ so that the expression may be simplified to

$$-\frac{dA}{dt} = \frac{\sigma E[O_2]^2[A]k_A}{k_s + k_{O_2}[O_2]} \quad (6)$$

(7) E. K. Damon and J. T. Flynn, *Appl. Opt.*, **2**, 163 (1963).

(8) B. F. Scott, *J. Sci. Instrum.*, **43**, 685, 940 (1966).

(9) I. B. C. Matheson and J. Lee, *Chem. Phys. Lett.*, **8**, 173 (1971).

It is obvious from inspection of (6) that continuous irradiation experiments can yield only k_A , the chemical reaction rate constant.

Giant Pulse Case. If E represents the number of einsteins in the 20-nsec pulse, an effectively instantaneous concentration of $[\Delta]$ will be created which initially is $[\Delta]_0 = \sigma E[O_2]^2$. This will decay with time at a rate determined by the total loss processes, *i.e.*

$$[\Delta]_t = [\Delta]_0 \exp\{-(k_s + k_{O_2}[O_2] + (k_A + k_A')[A])t\} \quad (7)$$

At any given time the $[\Delta]$ may be monitored by reaction with A, *i.e.*

$$-(dA/dt)_t = k_A[A][\Delta]_t \quad (8)$$

Solution of (7) and (8) yields

$$[A] - [A]_\infty = \frac{\sigma E[O_2]^2 k_A [A]}{k_s + k_{O_2}[O_2] + (k_A + k_A')[A]} \times \exp\{-(k_s + k_{O_2}[O_2] + (k_A + k_A')[A])t\} \quad (9)$$

or

$$\ln([A] - [A]_\infty) = -(k_s + k_{O_2}[O_2] + (k_A + k_A')[A])t + \text{const} \quad (10)$$

This is the equation used by Merkel and Kearns^{3a} but is an approximation in that it is only strictly valid for very small changes in $[A]$.⁵ The equation of Merkel and Kearns was used (with slight refinement) in this work because the typical quality of the oscilloscope photographs obtained did not justify a more sophisticated analysis. It is evident that the slope of this line as a function of $[A]$ will always yield $k_A + k_A'$, that is, the sum of the reaction and quenching rate constants.

The time-independent part of eq 9 ($t = 0$) is

$$[A]_0 - [A]_\infty = \frac{\sigma E[O_2]^2 k_A [A]_0}{k_s + k_{O_2}[O_2] + (k_A + k_A')[A]_0} \quad (11)$$

(11) in effect relates the total change in $[A]$ per pulse to the number of photons impinging on the system.

Dosimetry

It is important that the rate of $^1\Delta_g$ oxygen production be correctly estimated. The following analysis is similar to that given by Johns.¹⁰ Let σ be the cross section for the oxygen $^1\Delta_g \leftarrow ^3\Sigma_g^-$ transition; then for a path length x and sample cell volume V , the concentration of $^1\Delta_g$ oxygen produced per second will be given by

$$[\Delta] = \sigma E[O_2]^2 (x/V)$$

and cancellation of a length unit gives

$$[\Delta] = \sigma E[O_2]^2/a$$

where a is the sample cell cross-sectional area. The quantity σ/a is essential to the calibration of the apparatus so that consistent units must be used. Since mole per liter units are used in this work it is convenient to use the decimeter as the length unit. The absorbancy of oxygen in Freon 113 at 1.06 μm has been previously measured⁹ and in the appropriate units $\sigma = 3.6 \times 10^{-3} \text{ dm}^5 \text{ mol}^{-2}$. The following is σ/a as a

(10) H. E. Johns, *Photochem. Photobiol.*, **8**, 547 (1968).

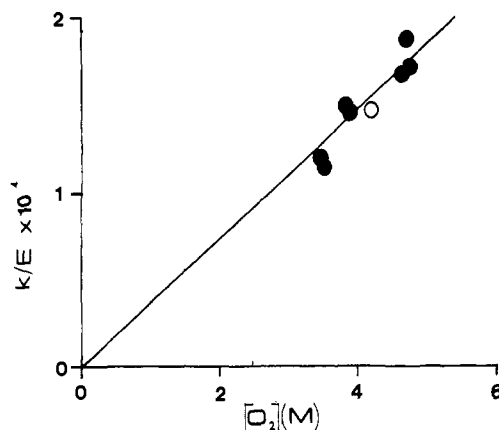


Figure 2. Variation of the experimental rate constant k as a function of pumping rate E and oxygen concentration $[O_2]$. Closed circles refer to 18.4-mm aperture cell and open circle to the 6.35-mm aperture cell.

function of cell diameter for the three configurations used.

Cell diameter, mm	σ/a , l. mol ⁻²
6.35	1.136
9.53	0.505
18.42	0.135

The light beam intensity has not been averaged over the cell path length due to the very low attenuation (a few per cent) of the laser beam by the solution; a 4% reflection loss at each air-glass optical surface has been assumed in calculating E .

A further assumption implicit in this analysis relevant to the continuous wave experiments is that the production of singlet oxygen within the 3-mm laser beam is not causing inhomogeneous concentration changes of the acceptor within the cell volume and so distorting the kinetics. This has not been observed either visually or in the results where a is varied, and thus it appears that sufficient laser beam intensity absorbed by the cell contents is dumped as heat through the agency of oxygen quenching to ensure rapid convection and adequate mixing.

Results

In Freon 113 there are good reasons to expect that $k_s < k_{O_2}[O_2]$. The semiempirical theory of Merkel and Kearns^{3b} relates the singlet oxygen lifetime in a given solvent to the solvent ir absorptions at wavelengths corresponding to the oxygen $^1\Delta_g \leftarrow ^3\Sigma_g^-$ transition and its hot bands. Since Freon 113 has an absorbance less than 0.001 A from 0.23 to $>2 \mu\text{m}$ it can be calculated that $k_s < 5 \times 10^2 \text{ sec}^{-1}$.

Thus (6) may be simplified to give

$$-\frac{dA}{dt} = \frac{\sigma E[O_2]^2 k_A [A]}{a k_{O_2}[O_2]} \quad (12)$$

which by inspection yields $d(\ln A)/dt = \sigma E[O_2] k_A / a k_{O_2} = k$, the observed pseudo-first-order rate constant.

In Figure 2, k/E is plotted as a function of $[O_2]$. This yields a straight line going through the origin within experimental error which is consistent with the supposition that k_s is negligible. Most of the data points were obtained with the 18.4-mm diameter cell but the one marked with the open circle was obtained with the 6.35-mm diameter cell and k/E was scaled down

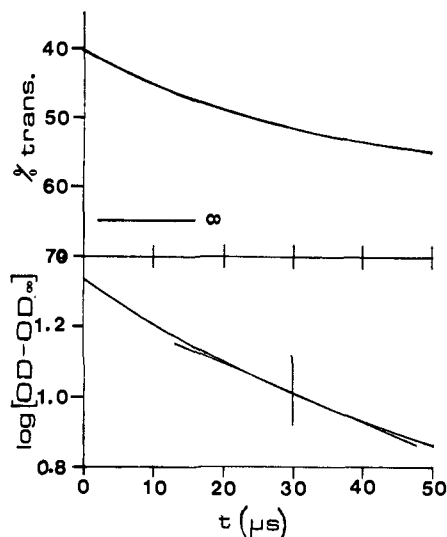


Figure 3. Upper curve: experimental result showing the variation of DPBF transmittance at 425 nm as a function of time after the Nd-YAG laser pulse ($t = 0$). The horizontal line (∞) is the final transmittance after a long time. Lower curve: same experiment where $\log(OD - OD_\infty)$ (arbitrary units) is plotted against time. The rate constant k is taken from the tangent shown at a DPBF concentration indicated by the vertical line.

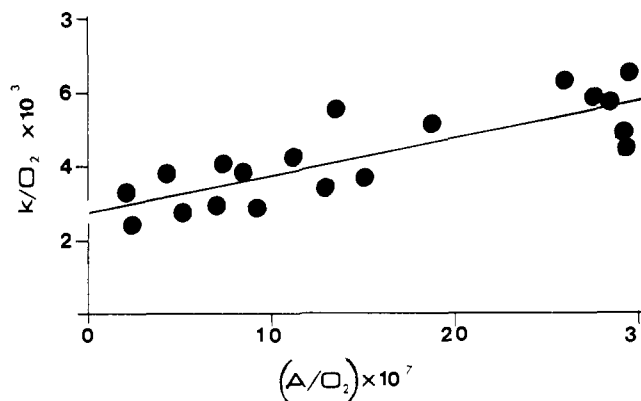


Figure 4. Collected data where k is shown as a function of $[O_2]$ and $[A]$.

in proportion to the relative areas, *i.e.*, (6.35/18.4)². This point lies satisfactorily on the line which suggests the dosimetry assumptions hold.

The similarity of the data for the different cell diameters also confirms the supposition of adequate mixing occurring in the continuous irradiation experiments.

The slope of the line is $3.71 \times 10^3 = (\sigma/a)(k_A/k_{O_2})$, which when divided by $0.135 = \sigma/a$, appropriate for the 18.4-mm diameter cell, yields $k_A/k_{O_2} = 2.8 \times 10^4$. This is as far as the data may be taken without knowledge of k_{O_2} .

A typical example of the data obtained from the Nd-glass pulse laser experiments is shown in Figure 3, where the upper curve shows per cent absorption at 425 nm ($\epsilon_{425} = 2 \times 10^4$ l. mol⁻¹ cm⁻¹ for DPBF) as a function of time. The lower curve shows a plot of $\log(OD - OD_\infty)$ as a function of time. Note the curvature of this line. The slope value, k , has been found by taking a tangent to the line at the point corresponding to the value of $[A]$. The curvature arises since $[A]$ changes appreciably during the course of the experi-

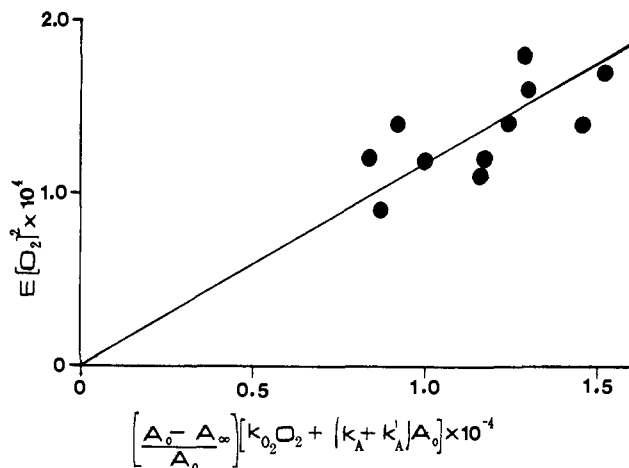


Figure 5. Relationship between the total amount of $^1\Delta_g$ oxygen produced per pulse (proportional to $E[O_2]^2$) to the total extent of reaction (proportional to $[A]_0 - [A]_\infty$).

ment and the tangent procedure will minimize errors arising from that source.

The slopes correspond to $k = k_{O_2}[O_2] + (k_A + k_{A'})[A]$ since k_s is negligible. Values of k were collected for different values of oxygen concentration, acceptor concentration, and laser energy E .

These were plotted as $k/[O_2]$ against $[A]/[O_2]$, *i.e.*

$$\frac{k}{[O_2]} = k_{O_2} + (k_A + k_{A'}) \frac{[A]}{[O_2]} \quad (13)$$

A plot of eq 13 is shown in Figure 4. This yields intercept = $k_{O_2} = 2.7 \pm 0.3 \times 10^3$ l. mol⁻¹ sec⁻¹ and slope = $k_A + k_{A'} = 1.0 \pm 0.2 \times 10^3$ l. mol⁻¹ sec⁻¹.

These results were measured using both the 6.35- and 9.51-mm cells and for some of the results using the 9.51 mm, the laser energy E was also measured and the combined results analyzed in terms of

$$E[O_2]^2 = \frac{a}{\sigma k_A} \frac{[A]_0 - [A]_\infty}{[A]_0} \{ (k_A + k_{A'})[A]_0 + k_{O_2}[O_2] \} \quad (14)$$

which is a rearrangement of (11).

The data from which the terms in (11) were calculated are shown in Table I and (11) is plotted in Figure 5. The abscissa values were calculated using the values for $k_A + k_{A'}$ and k_{O_2} obtained from the previous analysis. The points have a very great scatter around

Table I

E , J	$[O_2]$, M	$[A]_0$, μM	$[A]_\infty$, μM	$\frac{([A]_0 - [A]_\infty)}{[A]_0} (k_{O_2}[O_2] + (k_A + k_{A'}) \times [A]_0) \times 10^{-4}$	$E[O_2]^2 \times 10^4$
0.71	4.21	11.8	5.9	1.16	1.07
0.83	4.51	2.4	0	1.46	1.44
0.62	5.06	8.4	3.7	1.24	1.35
0.94	3.65	14.1	7.2	1.17	1.06
0.71	4.77	15.9	10.8	0.92	1.39
0.65	4.77	8.8	5.4	0.84	1.26
0.77	4.77	8.8	5.0	0.94	1.49
0.94	3.37	13.0	7.9	0.87	0.91
0.86	5.20	11.3	4.5	1.52	1.98
0.71	5.20	5.8	2.0	1.30	1.63
0.77	5.20	3.7	1.0	1.29	1.77

the line, which is not surprising considering the complexity of the abscissa terms and the large error of the E measurements.

The slope $1.18 \pm 0.43 \times 10^{-8} = a/(\sigma k_A)$ yields $k_A = 1.7 \pm 0.6 \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$. The k_A/k_{O_2} value from the continuous irradiation data is 2.8×10^4 which when combined with the k_{O_2} value from the pulse data yields $k_A = 8 \times 10^7 \text{ l. mol}^{-1} \text{ sec}^{-1}$, which is in rough agreement with the k_A value of $1.7 \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$ obtained from the pulsed data alone.

Discussion

The average of the two above values for k_A when weighted in inverse proportion to their standard deviations gives $k_A = 1.1 \pm 0.6 \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$. The total rate $k_A + k_A'$ of this work, $10 \pm 2 \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$, is in satisfactory agreement with the presumed reaction plus quenching rate constants in the literature, which are in the range $8\text{--}12 \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$.^{3,5}

The phenomenon of reaction and quenching occurring at the same time is not unknown in singlet oxygen studies; it has been observed for the 2,5-dimethylfuran reaction with singlet oxygen in the gas phase,¹¹ for amino acids in aqueous solution,¹² and for alkyl sulfides in solution.^{13,14} It may be that reaction and quenching occurring together is a general phenomenon for singlet oxygen acceptors and its detection requires a knowledge of absolute $[\Delta]$ oxygen concentrations which implies dosimetry measurements for optically generated $^1\Delta_g$ oxygen.

It is just possible that experiments similar to those in this work used to obtain k_A could be carried out using a pulse laser and sensitizing dyes. In the case of the experiments of Merkel and Kearns a ruby laser was used which apparently gave out enough photons per pulse to convert all the Methylene Blue sensitizer molecules present to triplets, and where $[O_2] > [\text{Methylene Blue}]$ the concentration of $^1\Delta_g$ oxygen would approximate to the Methylene Blue concentration. However, calculation of $^1\Delta_g$ oxygen concentrations might be complicated by fact that $^1\Delta_g$ can be quenched by triplet sensitizers.¹⁵ Given the $^1\Delta_g$ oxygen concentration then an equation similar to (14) could be solved for k_A .

Another possible rationalization of the present results is that $[\Delta]$ in solution is about ten times less than that supposed. The oxygen absorption at $1.06 \mu\text{m}$ and the laser power or energy are readily measured so that $^1\Delta_g + 1\nu$ oxygen concentrations can be calculated. If for some reason $^1\Delta_g + 1\nu$ decomposed to the ground state, rate k_2 in Figure 6, much more rapidly than vibrational relaxation k_1 to $^1\Delta_g$, then a situation could arise where the total $^1\Delta_g + (^1\Delta_g + 1\nu)$ concentration is much less than that predicted on the basis of $\sigma E[O_2]^2$. The extreme cases are given, where $k_2 \gg k_1$

$$[^1\Delta + 1\nu] = \sigma E[O_2]^2/k_2$$

(11) W. S. Gleason, A. D. Broadbent, E. Whittle, and J. N. Pitts, *J. Amer. Chem. Soc.*, **92**, 2068 (1970).

(12) R. Nilsson, P. B. Merkel, and D. R. Kearns, *Photochem. Photobiol.*, **16**, 117 (1972).

(13) C. S. Foote and J. W. Peters, *J. Amer. Chem. Soc.*, **93**, 3975 (1971).

(14) C. S. Foote and J. W. Peters, *Pure Appl. Chem., Suppl.*, **4**, 129 (1971).

(15) C. K. Duncan and D. R. Kearns, *Chem. Phys. Lett.*, **12**, 370 (1971).

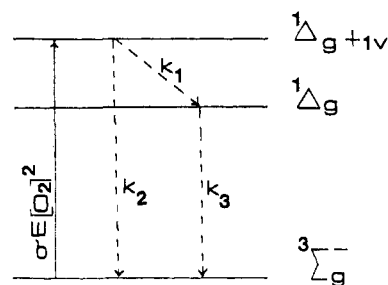


Figure 6. Scheme for the lowest energy levels of oxygen and the overall nonradiative rates (k_1 , k_2 , k_3) which connect them.

and for $^1\Delta_g$ decomposing at a rate k_3 , where $k_1 > k_2$

$$[\Delta] = \sigma E[O_2]^2/k_3$$

The relaxation of $^1\Delta_g$ ($v = 1$) has been measured recently using the ultraviolet $^1\Delta_g \rightarrow ^1\Delta_u$ transition¹⁶ and independently by a spectrophone technique.¹⁷ The results of both suggest the relaxation of $^1\Delta_g$ ($v = 1$) to $v = 0$ is extremely rapid in the presence of fluorocarbons and oxygen. Thus it appears that for the experiments described in this paper the singlet oxygen will be present as $^1\Delta_g$ ($v = 0$) and all interactions and the lifetimes refer to that state.

It would be most valuable in this regard if the ruby laser and sensitizer experiments suggested above were carried out; perhaps the data already exist.

The value for k_{O_2} obtained in this work, $2.7 \pm 0.3 \times 10^3 \text{ l. mol}^{-1} \text{ sec}^{-1}$, is interesting; it is only about a factor of 2 higher than the gas phase value¹⁸ of $1.3 \times 10^3 \text{ l. mol}^{-1} \text{ sec}^{-1}$. The small "solvent effect" on k_{O_2} may represent the fact that Freon 113 is very much a noninteracting solvent. In fact the red and infrared forbidden oxygen transitions change very little in energy, intensity, and bandwidth in going from the gas phase into solution. The k_{O_2} value of this work is in disagreement with that of $6 \pm 4 \times 10^4 \text{ l. mol}^{-1} \text{ sec}^{-1}$ reported by Stevens.¹⁹

Merkel and Kearns have given a semiempirical formula relating oxygen absorptions at 1.27 and 1.58 μm to singlet oxygen lifetimes. It is $1/\tau \mu\text{sec}^{-1} = 0.5(\text{OD}_{1.27}) + 0.05(\text{OD}_{1.58})$. Oxygen (5 M) has an absorption of $\sim 0.02/\text{cm}$ at 1.27 μm and negligible absorption at 1.58 μm . Substitution into the above formula gives $\tau = 100 \mu\text{sec}$. The value derived from k_{O_2} for 5 M oxygen is 74 μsec . The agreement is surprisingly good considering the theory was developed for purely vibrational transitions and the oxygen absorptions are due to collision-induced electronic transitions. It could possibly be improved by including a term for 1.06 μm and using Franck-Condon factors appropriate to high-pressure oxygen.

It is now possible to revise our early estimate²⁰ of 1.5×10^9 for the quenching rate constant of β -carotene acting on $^1\Delta_g$ oxygen. Use of $2.7 \times 10^3 \text{ l. mol}^{-1} \text{ sec}^{-1}$ instead of the gas phase value yields a quenching rate constant of $3.0 \times 10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$ in Freon 113. This is still an order of magnitude lower than the diffusion-controlled rate reported in the literature.²¹ Our ob-

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servations apply only to Freon 113; the rate constant may be higher in other solvents. There is some evidence that β -carotene dimerization can occur in some vents leading to an apparent lowering of the quenching rate constant,²² but we have no evidence for carotene dimerization occurring in Freon 113 at the typical experimental concentrations used.

Acknowledgment. We thank Ralph Morton and (22) D. R. Kearns, private communication.

George Fielder of the University of Georgia Instrument Shop and N. U. Curry of this department for their assistance. We also thank B. Stevens (University of South Florida) for his critical comments on this work and J. Gallagher (Georgia Institute of Technology) for his help in some of the initial experiments. This work was supported by grants from the National Science Foundation, National Institutes of Health (to J. L.), and by the Office of Naval Research (to M. L. W.).

Reaction Rate of Bilirubin with Singlet Oxygen ($^1\Delta_g$) and Its Strong Enhancement by Added Base

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Abstract: The oxidation of bilirubin by singlet oxygen produced by direct laser irradiation of the oxygen $^1\Delta_g + 1\nu \leftarrow ^3\Sigma_g^-$ electronic transition has been studied in Freon solution and in D_2O . In Freon 113 the bilirubin chemical reaction rate constant is 1.0×10^7 l. mol⁻¹ sec⁻¹ and in D_2O at pD < 7 within experimental error the same, 1.5×10^7 l. mol⁻¹ sec⁻¹. At higher pD (> 8) the reaction rate increases to 3×10^9 l. mol⁻¹ sec⁻¹. This rate constant is about 30 times higher than our recently revised value for 1,3-diphenylisobenzofuran, hitherto thought to be the most rapidly reacting singlet oxygen acceptor.

A considerable literature on singlet oxygen reactivity has been built up over the least few years.¹⁻³ Some of the reactions studied may be of biological significance, a particular case being the high quenching efficiency of singlet oxygen by β -carotenes.⁴⁻⁶ Another biological molecule worthy of study for its singlet oxygen reactivity is the bile pigment bilirubin. The mechanism of the photooxidation of bilirubin is of some importance because of the phototherapy treatment used for the condition of neonatal jaundice.⁷

There have been indications⁸⁻¹⁰ that the *in vivo* reaction may be a self-sensitized photooxidation, and there is ample evidence that bilirubin reacts with singlet oxygen produced in organic solution by external sensitizers such as Methylene Blue.⁸

The singlet oxygen reaction of bilirubin has been studied in this laboratory where the singlet oxygen was

produced directly in solution by irradiation of the dissolved oxygen $^1\Delta_g + 1\nu \leftarrow ^3\Sigma_g^-$ electronic absorption band with the 1.06 μ m output of a Nd-YAG laser.¹¹ This method avoids interference with a possible competing reaction such as the acceptor with the triplet sensitizer.

Experimental Section

The apparatus was as described in the preceding paper.¹² Bilirubin (crystalline) was from the J. T. Baker Chemical Co., Phillipsburg, N. J., and was used as supplied. Freon 113 (1,1,2-trichlorotrifluoroethane) spectrograde was supplied by Matheson Coleman and Bell, East Rutherford, N. J. D_2O , 99.8%, was supplied by the Columbia Organic Chemicals Co., Columbia, S. C. Medical grade oxygen was used in all experiments.

Results

The bilirubin reaction was studied by measurement of the pseudo-first-order decay of bilirubin absorbance at the absorption maximum 435 nm D_2O and 450 nm Freon, which occurred on irradiation of oxygenated bilirubin solutions in Freon 113 and heavy water.

Bilirubin may be made water soluble as its dianion by dissolving in water containing 2 equiv of base per equivalent of bilirubin. The laser irradiation technique is difficult to use in light water since it absorbs considerably at 1.06 μ m and solvent heating results. D_2O has an absorption of only 0.018 A cm⁻¹ at 1.06 μ m and has the added benefit that the $O_2(^1\Delta_g)$ is longer lived in D_2O than in H_2O .^{5,13}

Studies of bilirubin photooxidation are confused by

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