Radiationless Decay of Singlet Molecular Oxygen in Solution. II. Temperature Dependence and Solvent Effects

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Abstract: A laser flash photolysis technique has been used to study the radiationless decay of singlet ($^1\Delta$) molecular oxygen in solution. In accord with a previous theoretical treatment of the decay process, we find that the lifetime of singlet oxygen changes by only ~50% over a 100° temperature range in $CHCl_3$. Several solvents in which the lifetime of singlet oxygen approaches the millisecond range have been studied. The variation of the lifetime of $^1\Delta$ in mixtures of benzene and CS_2 was measured and found to correlate in a regular manner with the mole fraction of composition of the solution. These results show that the anomalous photooxidation results obtained with this solvent system are not due to any unexpected variation of the singlet oxygen lifetime.

Several years ago we developed a laser flash photolysis method for determining the lifetime of electronically excited singlet ($^1\Delta$) oxygen molecules in solution.[1] Contrary to expectations based on measurements of photooxidation rates in solution, we found that the lifetime of singlet oxygen varied over a tremendous range (2 μsec to msec) and that there was a correlation between the lifetime and ir spectral properties of the solvent (particularly in the overtone and combination band region near 12,700 Å).[2-4] This led to the development of a simple first-order theoretical treatment of the relaxation of singlet oxygen molecules by a mechanism involving electronic-to-vibrational intermolecular energy transfer, and the following expression for the quenching rate constant[3]

$$k_q \simeq \frac{2\pi\tau_{vib}}{\hbar^2}\left|\beta_{el}'\frac{\beta_{so}}{\Delta E}\right|^2 \sum_{m,n} F_m \left|M_n\right|^2$$

where τ_{vib} = vibrational relaxation time of solvent molecules, β_{cl}' = solvent-induced electrostatic matrix element coupling $^1\Sigma$ and $^1\Delta$ states, β_{so} = spin-orbit coupling matrix element between $^3\Sigma$ and $^1\Delta$, ΔE = 7,880 cm^{-1}, F_m = Franck-Condon factor for O_2 transition, M_n = infrared transition moment for the $0 \rightarrow n$ transition of solvent.

As the above expression indicates, the total quenching rate constant should be summed over all possible vibronic transitions of oxygen including the $0 \rightarrow 0$, $0 \rightarrow 1$, etc., bands. In solvents such as water and alcohols, it appears that the $0 \rightarrow 0$ transition is the most important one, but in solvents such as carbon tetrachloride where the overtone and combination bands are extremely weak in the near ir, contributions from the $0 \rightarrow 3$, $0 \rightarrow 4$, and perhaps even the $0 \rightarrow 5$ transitions of oxygen may be important in the relaxation.[3]

There were various aspects of the simple theory which had not been fully tested. First of all, the theory provided a simple criterion for selecting solvents in which the lifetime of singlet oxygen would be especially long or short. Since we and others have, unsuccessfully, attempted to observe the $^1\Delta \rightarrow {}^3\Sigma$ emission from singlet oxygen dissolved in solution we hoped it might be possible to find a solvent where the lifetime would be particularly long. We also were interested in finding chemically inert molecules which might be used to more effectively relax singlet oxygen than even water, and therefore could be used as a quencher of singlet oxygen. The temperature dependence of the singlet oxygen decay was another aspect of the theory which was not explored, but which we have examined in this paper. Finally, there were the interesting observations of Foote et al.[5] on the rate of the sensitized photooxidation of anthracene in the mixed solvent of benzene and CS_2. Rather surprisingly they observed that the photooxidation rate passed through a maximum at about 25 mol % benzene (see Figure 1) and suggested that the singlet oxygen lifetime might be anomalous in the 25% solution as compared with the lifetime in either of the pure solvents.[5] We have now carried out measurements of the singlet oxygen lifetime in various benzene-CS_2 solutions to test this intriguing possibility.

Experimental Section

Chemicals. Chloroform, benzene, and carbon disulfide were Matheson Coleman and Bell spectroquality. Freon 11 (CF_3Cl), from Matheson Gas Products, was passed twice through a 6-ft alumina column to remove some unknown green fluorescing substance. Hexafluorobenzene from Aldrich was used as received. Deuteriochloroform was standard NMR grade solvent from Mallinckrodt used as received. Aldrich 1,4-diphenylisobenzofuran (DPBF) was recrystallized twice (in the dark) from methanol-water mixtures. Methylene Blue was from Matheson Coleman and Bell stated 90% pure.

Methods. The laser flash photolysis method which we have used to measure singlet oxygen lifetimes is described elsewhere.[1,3] The same apparatus was used in the present experiments. The apparatus was modified slightly to provide for an electromagnetic shutter to turn on the analyzing light a few milliseconds before the laser pulse arrived. This was necessary in the longer lived solvents because of the rapid decay of DPBF under the illumination of the intense analyzing light. In this method a small amount of Methylene Blue (MB) (~10^{-5} *M*) and varying small amounts (10^{-5} to 10^{-4} *M*) of the singlet oxygen acceptor 1,4-diphenylisobenzofuran (DPBF) are added to the solution of interest. The Methylene Blue is then excited with a Q-switched ruby laser and the disappearance of the DPBF due to reaction with singlet oxygen is monitored at 410 nm. By a series of kinetic calculations[3] the lifetime of $^1\Delta_g$ can be extracted from the DPBF decay curve. In some solvents there is a problem due to the low solubility of the MB (this includes benzene, C_6F_6, CCl_3F, CS_2–C_6H_6 mixtures) and this was overcome by adding in about 1–2% methanol. The effect of the methanol is then subtracted out during the kinetic calculations. For the temperature dependence experiments the sample was cooled in a slush of frozen xylene at approximately −58°. The sample was in cuvette (in the dark) and the cuvette was surrounded by a test tube of methyl Cellosolve. The methyl Cellosolve provided adequate cooling and had the convenient property of not clouding the windows at these temperatures. The cuvette was withdrawn, wiped clean, and rapidly placed in the sample compartment and flashed within a couple of seconds. The sample compartment was purged with dry N_2 to prevent frost from forming on the cuvette windows.

Results and Discussion

(1) Temperature Dependence of the Singlet Oxygen Lifetime in $CHCl_3$. The variation of the lifetime of singlet oxygen in $CHCl_3$ with temperature is shown in Figure 2. Although the data are rather limited, there is an approximate-

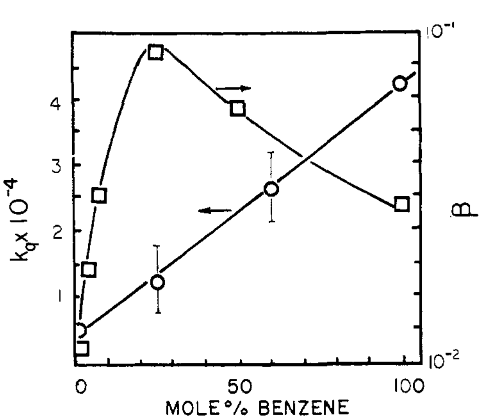

Figure 1. Variation in β, the rate of the sensitized photooxidation of anthracene in mixtures of CS_2 and benzene, and k_q, the rate constant for decay of singlet oxygen in these same mixtures.

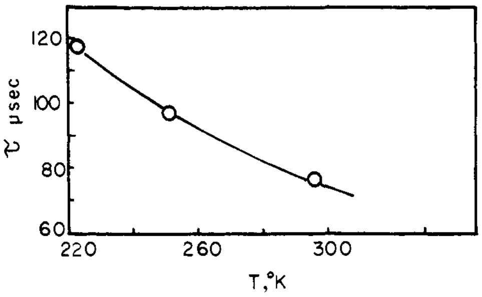

Figure 2. Variation of the lifetime of singlet oxygen with temperature in $CHCl_3$ solvent.

ly 50% decrease in the lifetime on going from −50 to +25°. According to the simple quenching theory, no *significant* temperature dependence is expected so in this sense there is agreement between theory and experiment. The small temperature dependence which is observed could be due to any one or a combination of different effects including subtle changes in the intensity of some of the ir overtone bands of the solvent and an increase in β_{el}' due to harder O_2–solvent collisions at the higher temperatures. Because of the low absorption intensity in the appropriate spectral region we were unable to determine whether or not there are changes in the near ir spectrum of $CHCl_3$ with temperature.

In the course of calculating the singlet oxygen decay rates, it was first necessary to determine the rate constant for the reaction of DPBF with singlet oxygen at various temperatures and these results are shown in Figure 3 where the log of the rate constant has been plotted as a function of $1/T$. Over the 100° change in temperature there is about a twofold increase change in the rate constant. Although the rate constant is less than the diffusion-controlled value (10^{10}) this does not appear to be due to a large activation energy for the reaction, since the data shown in Figure 3 indicate that the activation energy is only about 1 kcal. The apparent lack of reactivity must be attributed to other factors, and the observed small temperature dependence of the rate constant could easily be due to change in viscosity of the $CHCl_3$ with temperature.

(2) Search for Long Lived Solvents. One strong prediction of the simple theory was that molecules which have only low frequency vibrations should be good solvents for favoring long singlet oxygen lifetimes. We previously explored some of these solvents and have now examined several additional ones, and these results are shown in Table I. Although the approximate two-term expression which we used to account for the variation of a singlet oxygen lifetime in the hydrocarbon solvents would predict extraordinary long lifetimes for singlet oxygen in solvents such as CCl_4, Freon 11, and C_6F_6, experimentally the lifetime is not longer than about 1 msec. This clearly indicates that relaxation of the electronically excited oxygen can, if necessary, proceed via transitions to very high vibrational states of the ground electronic state oxygen, and terms representing these processes were knowingly omitted in our initial simplified theoretical treatment, since they were not important in the case of hydrocarbon solvents.[3] There was also the difficulty of obtaining Franck-Condon factors for the various oxygen transitions. A measurement of the emission spectrum of oxygen dissolved in solution would have provided the needed data, but these experiments have not been successful. As an alternative approach, we have measured the absorption spectrum of oxygen dissolved under high pressure in various solvents but again were unable to detect the 3′ ← 0 or 4′ ← 0 transitions.[6] We, therefore, do not have an independent measure of the appropriate oxygen Franck-Condon factors so that a more rigorous test of this aspect of the theory is not feasible at this time. This aspect notwithstanding, the results which have been presented here have uncovered some solvent systems in which the lifetime of singlet oxygen can approach 1 msec and these may prove to be useful in other studies of the physical and chemical properties of singlet oxygen.

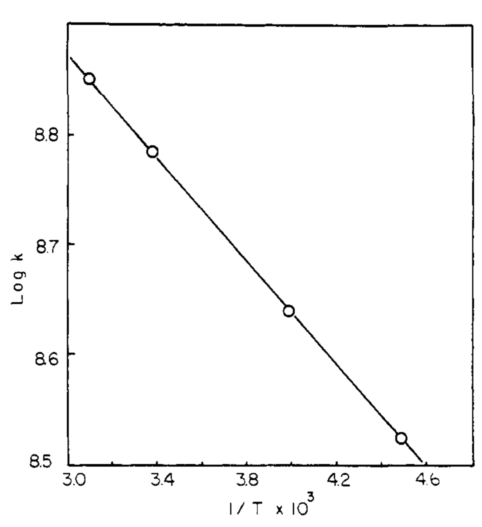

Figure 3. Temperature dependence of the rate constant, k, for the reaction of singlet oxygen with DPBF in $CHCl_3$.

Table I. Singlet Oxygen Lifetimes in Various Solvents

Solvent	Lifetime, μsec	Solvent	Lifetime, μsec
$CHCl_3$	60 ± 15	C_6F_6	600 ± 200
CS_2	200 ± 60	CCl_4	700 ± 200
$CDCl_3$	300 ± 100	Freon 11	1000 ± 200

(3) Variation of Singlet Oxygen Lifetimes in the Benzene–CS_2 Mixed Solvent System. Foote has carried out a study of the sensitized photooxygenation of anthracene in a solvent system consisting of a mixture of benzene and CS_2 and obtained the results shown in Figure 1 where β, the ratio of singlet oxygen decay rate (k_D) to the rate of reaction of singlet oxygen with the acceptor (k_A), is plotted as a function of the percent benzene in the solution.[5] Rather surprisingly, he found that there was a pronounced maximum at about 25 mol % benzene. This raised the intriguing possibility that the lifetime of singlet oxygen might be abnormally short in the mixed solvent system, as compared with the lifetime in either of the pure solvents. To test this and other possibilities, we have carried out a series of measurements of the singlet oxygen lifetime in this mixed solvent system, and the results of this measurement are also shown in Figure 1. As the data show, the lifetime of singlet oxygen varies in a very simple fashion with the percent benzene and the lifetime for any mixture can be computed simply from the solvent composition and the lifetimes in each of the pure solvents. We, therefore, conclude that the anomalous behavior of the sensitized photooxygenation of anthracene cannot be attributed to anomalies in the lifetime of singlet oxygen. Rather, we conclude that it is the rate of reaction of singlet oxygen with the acceptor which is responsible for the anomaly. In this regard we should point out that only 1% methanol was needed to solubilize the MB in the 25 mol % benzene solution, whereas 1.7% methanol had to be added to the 7 and 60 mol % benzene solutions to dissolve the MB. Even then, we noticed spectral evidence for the dimerization of the MB and precipitation after the solutions had been exposed to light for say 15 min. This may or may not be relevant, but it suggests that the photooxygenation reaction should be reinvestigated.

The results which we have presented in this paper show that there are no important discrepancies between theory and experiment with regard to the variation of the lifetime of singlet oxygen with solvent or temperature. There is a small temperature dependence to the decay of a singlet oxygen in $CHCl_3$, but a number of small effects may account for this. We were able to find some solvent systems in which the lifetime of singlet oxygen approaches 1 msec, but we were unable to discover any "super solvent". The anomalous behavior of benzene-CS_2 mixtures as a solvent system for carrying out sensitized photooxygen reactions is shown not to be due to anomalies in the singlet oxygen lifetime.

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References and Notes

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The Chemical Dynamics of Symmetric and Asymmetric Reaction Coordinates

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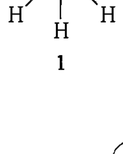
Abstract: The question has been posed as to whether a rotation-inversion process that results in the interconversion of two enantiomeric or identical species can be described by a unique asymmetric reaction coordinate. It is shown that the methods of classical kinetics and reaction dynamics are unable to solve this problem rigorously. A quantum mechanical analysis, employing the symmetry properties of the reaction surface, has therefore been developed, and applied to two cases: case I, in which one transition state separates reagents and products; and case II, in which a stable intermediate appears on the reaction coordinate. It is found that no unique path exists for the case I situation, *i.e.*, that all asymmetric reaction coordinates are indistinguishable. This conclusion holds under equilibrium conditions, under nonequilibrium conditions, and under photochemical excitation. The analysis developed to describe the equilibrium situation of case I constitutes a quantum mechanical demonstration of the principle of microscopic reversibility. For the case II situation, it is found that distinguishable asymmetric paths can exist under nonequilibrium conditions. These are related to each other in a diastereomeric sense, in contrast to case I, in which various reaction paths differ in an enantiomeric sense.

In the course of our theoretical studies[3] of the properties of systems of type L-MH_2, in which the ligand L is CH_3, CH_2^-, CH_2F, NH_2, PH_2, OH, SH, SHO, and SHO_2, and M is a tricoordinate atom such as C^-, N or P, we became interested in the topomerization[4] of these species. To treat this problem, it was necessary to obtain energy surfaces corresponding to rotation about the L-M bond and pyramidal inversion at the atom M. Topomerization then refers to the process in which structures corresponding to energy minima of such surfaces interconvert. For the case of $^-CH_2CH_3$, the rotation-inversion surface associated with the interconversion of the two minima **1** and **1'** was found to have the form shown in Figure 1. It is evident that there exist three modes of topomerization, a symmetric mode from **1** *via* **2** to **1'**, and two asymmetric modes from **1** *via* **3** or **3'** to **1'**.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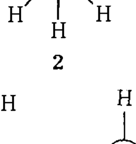
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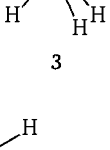
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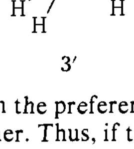
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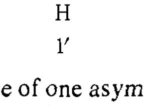
1'

Subsequently it occurred to us that the initial portions of the two asymmetric reaction paths could be sufficiently different to result in the preference of one asymmetric reaction path over the other. Thus, if the path **1** *via* **3** to **1'** were to be preferred in the forward process, then the path **1'** *via* **3'** to **1**