

head positions ( $H_b$ ,  $H_c$ ) were established from the decoupling experiments on the cyclobutanones, the stereochemical relationships between  $H_a$  and  $H_b$  in the alcohols allowed the assignment of the relative configurations at all four asymmetric carbon atoms. It is of course necessary to assume that the reduction of the carbonyls took place from the least-hindered side of the molecules, *i.e.*, the side opposite the bulky *tert*-butyl group. As a result, the *tert*-butyl substituent is *trans* to  $H_a$  and *cis* to the adjacent methylene in both alcohols **9** and **10**. Therefore, *tert*-butylcyanoketene reacts with alkenes in complete analogy to other ketene cycloadditions.

The results reported above for the reaction of **1** with **2** are of particular interest in view of the current investigations into the mechanism of cumulene cycloadditions. Allene dimerizations, for example, have been studied in some detail.<sup>12-17</sup> The high stereoselectivity of these dimerizations is consistent with a concerted [ $\pi 2_s + \pi 2_a$ ] cycloaddition in which the allene functions as both the suprafacial and antarafacial components. However, a recent kinetic secondary deuterium isotope effect study on the dimerization of allene itself shows this to be a two-step process.<sup>17</sup> Ketenes on the other hand react with alkenes in a concerted manner, and, as shown above, *tert*-butylcyanoketene (**1**) is no exception. An important unresolved question existing prior to the results reported here concerned the concertedness of the ketene plus allene cycloadditions. A sweeping generalization to the above question cannot yet be made. However, the observed optical activity in both cyclobutanones **5** and **6** from the reaction involving optically active allene **2**, the fact that the major product **5** has a *cis* relationship between the *tert*-butyl and the adjacent  $CH_2$ , and the propensity of *tert*-butylcyanoketene to react with C=C double bonds in a concerted fashion all suggest that the cycloaddition of cyanoketene **1** to the cyclic allene **2** is a one-step synchronous reaction.

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$J_{ae}$  coupling to be appreciably larger than  $J_{ee}$  coupling in nonplanar cyclobutanols.

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Walter Weyler, Jr., Larry R. Byrd  
Marjorie C. Caserio, Harold W. Moore\*

Department of Chemistry, University of California, Irvine  
Irvine, California 92664

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### Remarkable Solvent Effects on the Lifetime of $^1\Delta_g$ Oxygen<sup>1</sup>

Sir:

Knowledge of the lifetime of singlet oxygen in solution plays an important role in interpreting many of the

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photooxidation studies now being carried out. There now appears to be a widespread belief that the lifetime of singlet oxygen ( $^1\Delta_g$ ) is approximately solvent independent.<sup>2-7</sup> This is based on experimental observations that the " $\beta$ " value for a given oxygen acceptor, the ratio of the rate of the decay of singlet oxygen to the rate of reaction with the acceptor, does not depend strongly on the nature of the solvent. In most of the recent collections of data we find that  $\beta$  values for some of the common acceptors vary by at most a factor of 4 in different solvents.<sup>2,3,5</sup> In contrast to these more recent findings, Bowen<sup>7</sup> and Livingston and Owens<sup>8</sup> found relatively large solvent effects on the *rate* of photooxidation of anthracene (and hence presumably on its  $\beta$  value), but the significance of these observations was questioned because of the possible solvent effects on the fluorescence of anthracene.<sup>2</sup>

Recently we developed a spectroscopic method which has permitted us to directly measure the lifetime of singlet oxygen in solution.<sup>9</sup> We have used this method to measure the lifetime of singlet oxygen in some of the solvents which are commonly used in photooxidation studies. Contrary to previous conclusions, we find that the lifetime of singlet oxygen is remarkably sensitive to the nature of the solvent.

In our experiments singlet molecular oxygen ( $\sim 5 \times 10^{-5} M$ ) was generated in  $\sim 10^{-7}$  sec by energy transfer from methylene blue triplets which were excited by a 20-nsec ruby laser pulse.<sup>9</sup> Singlet oxygen was then monitored spectroscopically by following its reaction with the colored acceptor, 1,3-diphenylisobenzofuran, to form a colorless product.

The results of these experiments, which are presented in Table I, demonstrate that the lifetime of  $^1\Delta_g$  varies by

Table I. Solvent Effects on the Lifetime of  $^1\Delta_g$

Solvent	Viscosity, cP <sup>a</sup>	Dielectric constant <sup>a</sup>	$\tau^1\Delta_g$ , $\mu$ sec
H <sub>2</sub> O	0.80 <sup>b</sup>	80	2
CH <sub>3</sub> OH	0.51	33	7
C <sub>6</sub> H <sub>6</sub>	0.56	2.2	24
CH <sub>3</sub> C(=O)CH <sub>3</sub>	0.29	~20	26
CS <sub>2</sub>	0.35	2.6	200

<sup>a</sup> "Handbook of Chemistry and Physics," 35th ed, Chemical Rubber Publishing Co., Cleveland, Ohio. <sup>b</sup> Extrapolation based on data using 1:1 H<sub>2</sub>O-CH<sub>3</sub>OH.

a factor of 100 in going from water to CS<sub>2</sub>. It is not surprising that there are large solvent effects on the  $^1\Delta_g$  lifetime since it represents a good example of what Robinson<sup>10</sup> and others,<sup>11-13</sup> would classify as a small

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molecule in their theoretical treatments of radiationless transitions in molecules. The solvent-dependent quenching of  $^1\Delta_g$  oxygen to its ground state is to be contrasted with the somewhat analogous relaxation of triplet state organic molecules which (aside from heavy atom effects) is relatively independent of solvent because large molecules have sufficiently large numbers of internal vibrational modes to act as their own heat sinks.<sup>10</sup>

Even at this preliminary stage of investigation it is clear that certain solvent properties are unimportant in affecting the lifetime of singlet oxygen. The fact that the lifetime is shortest in water might suggest that the dielectric constant or dipole moment of the solvent molecules is an important parameter, but this possibility is eliminated by the fact that the lifetime is almost the same in both benzene and acetone. Comparison of the data in Table I further demonstrates that there is no correlation between viscosity and lifetime. Foote has also arrived at similar conclusions.<sup>2</sup>

Our observation that the lifetime of singlet oxygen is quite sensitive to the nature of the solvent appears to be at variance with conclusions reached by other workers, and it is worthwhile to see how this discrepancy might have arisen. Many of the previous studies of dye-sensitized photooxidation involved mixed solvents, and using the numbers in Table I we compute that the lifetime of  $^1\Delta_g$  in a 4:1 mixture of benzene and methanol (a common mixture)<sup>2,6</sup> would be 16  $\mu\text{sec}$ . This is considerably reduced from the lifetime in neat benzene, so it is easy to see that incorporation of small amounts of methanol in various solvents would prevent observation of large solvent effects on the lifetime of  $^1\Delta_g$ . Furthermore, reaction rate constants of certain acceptors may be solvent dependent (the rate constant for 1,3-diphenylisobenzofuran in  $\text{CS}_2$  is about one-half its value in methanol) and therefore obscure lifetime changes.

We are continuing our investigation of the various factors which influence the lifetime of  $^1\Delta_g$  in solution, and a more detailed experimental and theoretical analysis of these observations follows.<sup>14</sup>

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Paul B. Merkel, David R. Kearns\*

Department of Chemistry, University of California  
Riverside, California 92502

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## Deuterium Effects on Singlet Oxygen Lifetimes in Solutions. A New Test of Singlet Oxygen Reactions

Sir:

Work during the past 6 years has clearly established the central role which singlet oxygen plays in a number of dye-sensitized photooxidation reactions of simple organic acceptors.<sup>1-6</sup> On the basis of this work singlet oxygen has also been proposed as the reactive intermediate in a variety of other reactions, including the

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ozone phosphite oxidations<sup>7,8</sup> and the photooxidation of amines<sup>6,9,10</sup> and amino acids and nucleic acids.<sup>11,12</sup> However, because of a variety of problems (solubility, lack of volatility, possible reaction with excited sensitizers,<sup>13</sup> sensitivity of acceptors to peroxide and radical oxidation)<sup>8,14,15</sup> it has been very difficult to determine whether or not these reactions involve singlet oxygen. In view of these difficulties we felt that it was essential to have additional criteria to determine whether or not an oxidation reaction involves singlet oxygen and which could be used in a wide range of solvents and would not be susceptible to the limitations of the  $\beta$ -carotene<sup>16,17</sup> or azide quenching test.<sup>18</sup> In this communication we report the development of a simple diagnostic test for singlet oxygen reactions which appears to be free of most of these limitations.

The basis of this test follows directly from our recent discovery that the lifetime of singlet oxygen is extremely sensitive to the nature of the solvent<sup>19,20</sup> and that there is a direct correlation between the lifetime of singlet oxygen and the intensity of the infrared absorption of the solvent.<sup>20</sup> This correlation, which has now been confirmed in a number of different solvents, has permitted us to derive the following approximate expression relating the two quantities<sup>20</sup>

$$\frac{1}{\tau} (\mu\text{sec}^{-1}) \simeq 0.5(\text{OD}_{1270}) + 0.05(\text{OD}_{1590}) + \dots$$

where  $\text{OD}_{1270}$  and  $\text{OD}_{1590}$  are the optical densities of 1 cm of solvent at 1270 and 1590 nm, respectively, and additional terms may be neglected for most solvents where  $\tau \lesssim 40 \mu\text{sec}$ . Since much of the solvent absorption intensity in this region is due to OH or CH vibrations (overtones and combinations), it was immediately apparent that there could be large changes in the singlet oxygen lifetime in going from a normal solvent to a perdeuterated solvent. For photosensitized oxidation reactions this carries with it the additional prediction that the " $\beta$ " value for a given acceptor (the ratio of the rate of decay of singlet oxygen to the reaction rate with singlet oxygen) should show a similar variation, since reaction rate constants are not expected to be altered significantly upon solvent deuteration. In fact, we have shown that for DPBF rate constants do not vary greatly even with large changes in solvent character.<sup>20</sup>

We recently developed a direct method for measuring the lifetime of singlet oxygen and have now used this to examine the effect of solvent deuteration on singlet oxygen lifetimes.<sup>19-21</sup> In these experiments the singlet

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