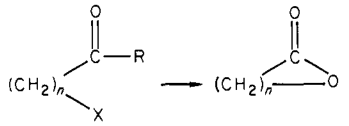
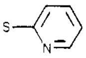
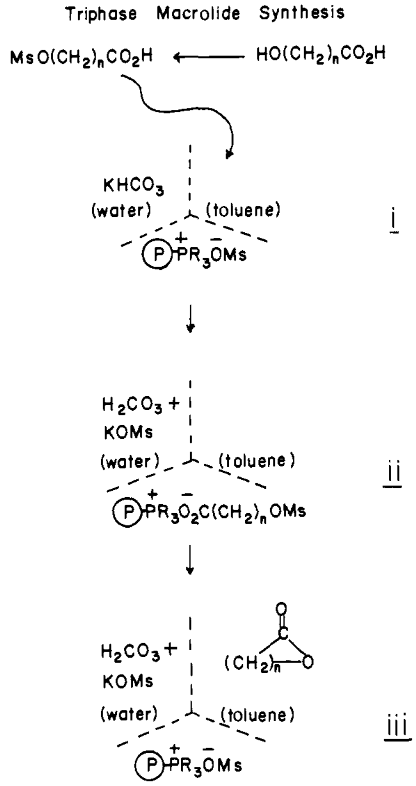
Table II. Yields of Lactone (%)[a]



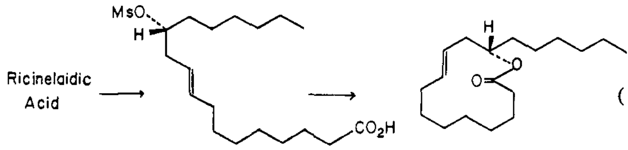
			Corey-Nicolaou[c]	
n	ring size	triphase cyclization[b] (R = OH, X = OMs)	R = , X = OH	Kruizinga-Kellog[d] (R = OH, X = I)
7	9	0	25	
10	12	47	64	33
11	13	66	76	62
		68[e]	66[e]	
12	14	76	79	77
14	16	72	88	83

[a] Yields determined by GLC. [b] Same reaction conditions as described in Table I. [c] Reference 8. [d] Reference 7. [e] Isolated Yield.

Scheme I



Since naturally occurring macrolides are often closed at a secondary hydroxyl group, it was of interest to evaluate the effectiveness and stereochemistry of a triphase cyclization taking place at a secondary carbon. For this purpose, ricinelaidic acid was converted to the corresponding mesylate and subjected to the cyclization conditions described above (see eq 1).[7,10] Preparative



(1)

layer chromatography afforded a 40% isolated yield of ricinelaidic acid lactone having $[\alpha]^{21}_{D}$ −38°. Comparison with the optically pure *R* form of the macrolide having $[\alpha]^{20}_{D}$ +42° indicates that the displacement proceeds with predominate inversion of configuration.[7]

Further applications of this new methodology to macrocyclic synthesis are in progress.

Registry No. 11-(Methylsulfonyloxy)undecanoic acid, 80907-73-9; 12-(methylsulfonyloxy)dodecanoic acid, 80907-74-0; 13-(methylsulfonyloxy)tridecanoic acid, 80907-75-1; 15-(methylsulfonyloxy)tetradecanoic acid, 80907-76-2; 11-hydroxyundecanoic acid lactone, 1725-03-7; 12-hydroxydodecanoic acid lactone, 947-05-7; 13-hydroxytridecanoic acid lactone, 1725-04-8; 15-hydroxytetradecanoic acid lactone, 106-02-5; ricinelaidic acid, 540-12-5; ricinelaidic acid mesylate, 78773-30-5; ricinelaidic acid lactone, 69651-29-2.

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(9) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95.

(10) Sigma Chemical Co., $[\alpha]^{20}_{D}$ +6.6° (*c* 1, C_2H_5OH), mp 50.5–52 °C.

Lifetime of Singlet Oxygen in Solution Directly Determined by Laser Spectroscopy

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The properties of singlet oxygen (${}^1\Delta_g$, ${}^1O_2$) are of profound importance to the understanding of its role in physical, chemical, and biological transformations.[1,2] In consideration of its important position there have been numerous studies of this reactant in the gaseous and in the condensed phases. Until recently these studies have been hampered by the unavailability of suitable methods for unambiguously detecting ${}^1O_2$ or for directly measuring its lifetime in solution. Recently phosphorescence characteristic of ${}^1O_2$ at 1270 and 1580 nm has been observed in solution[3-6] and has been used to determine directly its lifetime in a variety of solvents.[7,8] We have also been engaged in an effort to determine directly the properties of ${}^1O_2$ generated through dye sensitization by monitoring the phosphorescent emission characteristic of this state (eq 1).

$$\text{Sens} \xrightarrow{h\nu} {}^1(\text{Sens*}) \rightarrow {}^3(\text{Sens*}) \xrightarrow{{}^3O_2} {}^1O_2 \rightarrow h\nu \text{ (1270 nm)} \quad (1)$$

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(1) (a) "Singlet Molecular Oxygen"; Schaap, A. P., Ed.; Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1976. (b) "Singlet Oxygen, Reactions with Organic Compounds and Polymers"; Ranby, B., Rabek, J. F., Eds.; Wiley: New York, 1978. (c) "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979.

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(4) Krasnovsky, A. A., Jr. *Photochem. Photobiol.* **1979**, *29*, 29.

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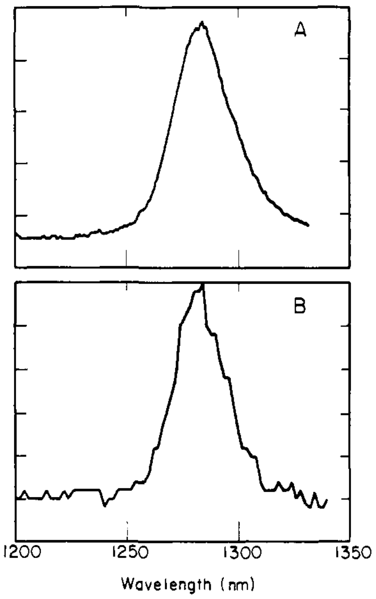

Figure 1. (a) Emission spectrum of $^1O_2$ generated from thermolysis of triphenylphosphite ozonide. (b) Emission spectrum of $^1O_2$ recorded 100 μs after pulse irradiation of tetraphenylporphyrin in oxygen-saturated $CDCl_3$. The observed emission maximum is apparently shifted from 1270 to 1284 nm by the nonlinearity of the detector and monochromator.

Herein we report the results of our investigation, which show in part that the rate of the radiative and nonradiative decay paths for $^1O_2$ in solution depends upon the nature of the solvent. Also, we find that perdeuteration of the solvent results invariably in a considerable decrease in the rate of the nonradiative decay path of $^1O_2$ without measurably altering the rate of the radiative route. Finally, our findings show that no theoretical model yet proposed can account quantitatively for the effect of solvent on the lifetime of $^1O_2$.

We have detected infrared emission of $^1O_2$ generated either by triphenylphosphite ozonide decomposition[9] (Figure 1a) or by irradiation of an appropriate sensitizer with the output of a frequency-doubled Nd-YAG laser (Figure 1b). In the latter case the emission was monitored 100 μs after the excitation pulse and resolved with a Jarrell-Ash 0.25-m monochromator equipped with a grating blazed at 1000 nm. The detector used is a germanium photodiode[10] (Judson Infrared Inc., J-16-5, 2-mm diameter) in a fast, high-gain amplifier circuit (schematic diagram of the amplifier, Figure 4, is available as supplementary material to this paper). The photodiode and first-stage amplifiers are operated at liquid-nitrogen temperature to reduce thermal noise. Two methods were used to verify the suitability of the detector-amplifier to measure transient signals. First, the response time of the apparatus was shown to be 10 μs by fitting the edge of a square wave generated with an infrared light emitting diode (IRLED, Motorola MLED900) with an exponential function. Second, the detector was shown to reproduce faithfully an exponential decay function which was used to power the IRLED.

Table I

solvent	τ ($^1O_2$), μs[a]	lit value	k_{rad}^{rel}	$10^{17}\times$ overlap,[b] cm^3
CCl_4	900[c,f]	26 000,[7] 700[13b]		
$CHCl_3$	265,[c] 240[d]	250,[7] 60[13b]	1.000	4.3
$CDCl_3$	640[c]	840[7]	0.75	1.7
CH_2Cl_2	100[c]	91[7]	1.2	18
CH_3CN	61,[e] 68[d]	30[13b]	(1.00)[h]	620
CD_3CN	440[e]		(0.98)[h]	120
$(CH_3)_2CO$	51,[c] 40,[e] 39[d]	51,[7] 26[13b]	(1.00)[h]	760
$(CD_3)_2CO$	640[c]	26[13b]	(1.03)[h]	490
C_6H_6	32[c]	30,[7] 24[13b]	1.9	360
C_6D_6	700[c]		1.8	40
C_6H_5Cl	45[c]	42[7]	1.9	105
C_6H_5Br	43[c]		2.1[g]	87
C_6H_5I	27[c]		2.7[g]	147
p-dioxane	25[c]		0.9	1910
CH_3OD	37[d]			990
D_2O	58[d]	20[13b]		
THF	20[c]	30[7]	1.0	1957

[a] This work. The reproducibility of the measured $^1O_2$ lifetime for completely independent samples is about ±10%. [b] Integrated overlap of the phosphorescence of $^1O_2$ with the absorptions of the solvent according to the proposal of Salokhiddinov et al.[7] [c] The sensitizer is tetraphenylporphyrin adjusted so that its optical density is ca. 0.6 at 531 nm, the laser wavelength. [d] The sensitizer is methylene blue adjusted so that its optical density is ca. 0.6 at 531 nm. [e] The sensitizer is rose bengal adjusted so that its optical density is ca. 0.6 at 531 nm. [f] The observed extrapolated lifetime depends greatly on the origin of the CCl_4 and on the history of each individual sample. [g] These values represent a lower limit to the relative radiative rate since the quantum yield of fluorescence of TPP is reduced in these solvents compared to 11% in benzene.[21] If the reduced fluorescence is due to quenching of singlet TPP, then the actual relative radiative rate constant in these solvents will be larger than that reported. [h] Due to the virtual insolubility of TPP in this solvent, these relative radiative rate constants are not directly comparable to the others. However, they do show that there is no change on solvent deuteration.

The rate of decay of the infrared phosphorescence provides a direct measure of the lifetime of $^1O_2$. We have determined this decay rate under a variety of experimental conditions and have found that its value depends in some cases on the details of the experiment. In particular, in halogenated solvents the measured lifetime of $^1O_2$ depends upon the power of the laser pulse used to excite the sensitizer. This most reasonably results from a secondary interaction between excited sensitizer and the solvent to generate a physical quencher of $^1O_2$.[11] This observation explains the discrepancy between the earlier indirect measurements of $^1O_2$ lifetimes in chlorinated solvents,[12,13] the recent direct measurements,[7,8] and our results reported below. With some sensitizers in polar solvents the lifetime measured again exhibits a power dependency. For these cases the effect of laser power may be a consequence of the simultaneous generation by electron transfer from excited sensitizer of a small amount of superoxide ($O_2^-\cdot$)[14] which is a rapid quencher of $^1O_2$.[15] To avoid these problems we report lifetimes that are extrapolated to the limit of zero laser power. This procedure gives reliable and reproducible estimates of the lifetime of $^1O_2$.

Figure 2 shows a typical plot of the time dependency of the infrared emission from $^1O_2$ following pulse excitation fit to a first-order rate law.[16] Even at the highest laser powers available (80 mJ) the decay remains first order, thus eliminating from consideration the proposed rapid singlet-oxygen self-annihilation reaction.[8]

The lifetimes of $^1O_2$ that we have determined as well as the relative radiative rates in several solvents are shown in Table I. We determined the latter parameters by comparing the relative intensities of the observed infrared emission in various solvents

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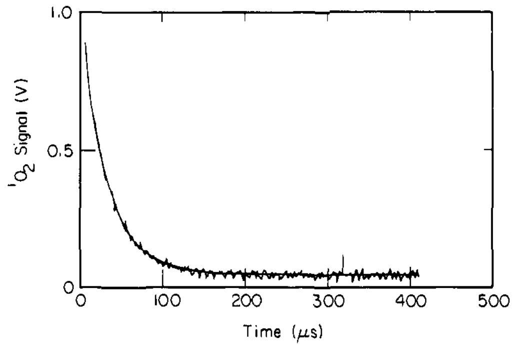

Figure 2. Observed decay of the transient infrared emission following pulse irradiation of tetraphenylporphyrin in benzene. The solid line through the data is the least-squares fit to a first-order decay.

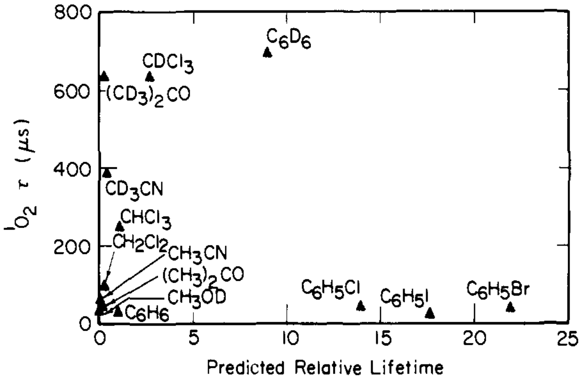

Figure 3. Comparison of the observed lifetime of $^1O_2$ in various solvents to the relative lifetime predicted by the equation used by Salokhiddinov et al.,[7,22] which is based on the overlap of the solvent absorptions with the oxygen emission and various physical properties of the solvent.

under identical conditions at extrapolated time equals zero.

The radiative lifetime of $^1O_2$ in the gas phase at extrapolated zero pressure has been calculated to be 45 min.[17,18] The lifetime of $^1O_2$ in condensed phase is reduced by interaction with the medium. By comparing the intensity of tetraphenylporphyrin (TPP) fluorescence to that of the observed $^1O_2$ emission, Krasnovsky[5] has recently reestimated the quantum efficiency of the phosphorescence of $^1O_2$ in CCl_4 to be ca. 4.4×10^{-3}. Thus it is evident that the rates of the radiative as well as the nonradiative processes are influenced by solvation.

An important factor for understanding the influence of the solvent on the rates of decay of $^1O_2$ is the remarkable increase in lifetime when the solvent is deuterated.[13] Our findings indicate that the effect of deuteration is universal. Indirect determination of the lifetime of $^1O_2$ in acetone and acetone-d_6 by Merkel and Kearns[19] showed no isotope effect. However, our results confirm the recent report by Foote and Ogilby[20] of an isotope effect of 18 ± 4 in this solvent.

A theoretical model advanced by Kearns[19] to explain the effect of solvent on the lifetime of $^1O_2$ assumed an intermolecular electronic-to-vibrational energy transfer which was supported by an apparent empirical correlation of the lifetime with the intensities of the solvent infrared absorptions at 1269 and 1592 nm. Our data, especially the solvent isotope effect in acetone, indicate essentially no correlation with the suggested solvent absorption intensities. Recently Salokhiddinov and co-workers[7] suggested a modification of Kearn's correlation in which the overlap of the complete infrared phosphorescence spectrum of $^1O_2$ with the solvent absorption spectrum and certain other physical properties of the solvent were claimed to predict the relative lifetime of $^1O_2$. Our findings also disagree with the predictions made by this modified approach as is shown in Table I and Figure 3.

Solvation of $^1O_2$ apparently increases the rate of the radiative as well as the nonradiative decay paths. The recent report by Krasnovsky[5] indicates that the radiative rate is independent of the nature of the solvent. This is approximately correct for many of the solvents we have studied. In particular, we find that there is no measurable effect of solvent deuteration on the radiative process. However, when the solvent is an aromatic compound there is an effect on the radiative rate. The data in Table I show that for benzene, deuteriobenzene, and the halogenated benzenes the radiative rate is approximately twice that in the other solvents. While we do not yet have a precise explanation for this effect, it does appear to be related to the polarizability of the sovlent. This observation may indicate the formation of contact complexes between $^1O_2$ and the solvent. If so, these complexes may also affect the nonradiative rate.

In sum, we have developed a procedure to determine reliably the lifetime of $^1O_2$ in solution. Our measurements of the lifetime under a variety of conditions have revealed properties of this system. We are continuing to probe the variables that control the lifetime of $^1O_2$ in solution.

Acknowledgment. We thank Charles Hawley and James Wehmer of this department for their valuable help in selection of the detector, construction of the amplifier, and operation of the laser system. This work was supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Oxygen, 7782-44-7.

Supplementary Material Available: Schematic diagram of the amplifier used with the germanium photodiode (1 page). Ordering information is given on any current masthead page.

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(22) The equation put forth by Salokhiddinov et al.[7] is

$$\tau = cn^4R^6d\Big/\left(\mu\int I\alpha\nu^{-4}\,d\nu\right)$$

where τ = lifetime of $^1O_2$, n = refractive index of the solvent, R = mean radius of the solvent molecule, d = density of the solvent, μ = molecular weight of the solvent, I = intensity of $^1O_2$ emission as a function of ν, α = optical density of the solvent as a function of ν, ν = frequency, and c = a proportionality constant.

Optical Determination of the Collisional Lifetime of Singlet Molecular Oxygen $[O_2(^1\Delta_g)]$ in Acetone and Deuterated Acetone

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Received November 2, 1981

Recently Ogilby and Foote[1] have carried out an investigation of the effect of solvent deuteration on the collisional lifetime of singlet molecular oxygen in acetone, acetonitrile, benzene, and chloroform and have observed an order of magnitude increase in all cases. The earlier work of Merkel and Kearns[2] also indicated an order of magnitude lengthening of lifetimes with solvent deuteration for H_2O and chloroform; however, in the case of acetone, a lifetime of 26 μs was obtained for both. These data were consistent with a theory developed by them that related the $O_2(^1\Delta_g)$ quenching rates to infrared absorption of the solvent, primarily at 1.27 and 1.59 μm corresponding to (0,0) and (0,1) $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transitions. Importance of the (0,1) transition was a consequence of the assumption that the associated Franck-

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