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Solvent-Induced Deactivation of Singlet Oxygen: Additivity Relationships in Nonaromatic Solvents

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Abstract: Time-resolved measurements of the decay of the infrared luminescence from aerated solutions of porphyrins have led to determinations of the natural lifetime (τ_Δ) of $O_2(^1\Delta_g)$ in many solvent systems. Excitation was by an 11-ns pulse of 532-nm light. Conversion of τ_Δ into bimolecular rate constants (k_Δ) using the solvent molarity leads to linear relationships between k_Δ and the number of methylene groups in the carbon skeleton of normal alkanes and normal alcohols. In general it appears that the value of k_Δ is built up additively from individual factors for the various atomic groupings, CH_3, CH_2, CH, OH, etc. By use of such additivity factors, values of k_Δ and τ_Δ have been calculated and compared with experimental values. In many cases, good correspondence is found.

Prior to the use of pulsed lasers for the determination of the intrinsic lifetime of the electronically excited state of oxygen, $O_2(^1\Delta_g)$, it had become apparent from relative rate measurements (β values) that photooxidation reactions of organic compounds showed marked solvent effects.[1] Around 1970, several investigators employed Q-switched and flashlamp pumped lasers for rapidly generating a relatively high concentration (10^{-6} M and above) of singlet oxygen in liquid systems by energy transfer from photoexcited sensitizer molecules added to absorb the generating light.[2-4] In the presence of an oxidizable solute, the kinetic properties of $O_2(^1\Delta_g)$ could be monitored by observing the rate of bleaching of the optical absorption of the solute after the excitation flash. Manipulation of the data allowed both intrinsic lifetimes (τ_Δ) and bimolecular reaction rate constants of $O_2(^1\Delta_g)$ to be determined.[2-4] In analogous experiments it was later shown[5] that in some cases pulsed electron beams could replace laser beams and that the kinetic spectrophotometric method for obtaining absolute rate parameters for $O_2(^1\Delta_g)$ was also applicable to microheterogeneous media such as aqueous micelles, reverse micelles, and vesicles.[6] Oxidizable solutes used in this way have been 1,3-diphenylisobenzofuran,[2-6] bilirubin,[7] anthracenedipropionic acid,[8] and crocetin.[9]

Although yielding absolute rate constants and lifetimes, the above method is not direct; i.e., a physical property (absorbance) of an additive is monitored over time and not a property of the entity being studied, i.e., $O_2(^1\Delta_g)$. Further, the method for τ_Δ evaluation suffers from inaccuracies, relying, as it does, on an extrapolation of rate data to zero solute concentration. Nevertheless, a compilation[10] of τ_Δ in many different liquids, largely obtained by this method, demonstrates a marked solvent dependence and an unprecedented isotope effect.

The radiative transition $O_2(^3\Sigma_g^-) \leftarrow O_2(^1\Delta_g)$ being spin, symmetry, and parity forbidden contributes very weakly to the decay in solution phase. Furthermore, the intramolecular nonradiative step is difficult owing to the paucity of ground-state vibrational oscillators in O_2 and weak Franck–Condon factors.[11] These considerations led Merkel and Kearns[11] to postulate that $O_2(^1\Delta_g)$ in solution finds that its most effective pathway for reaching the ground state is by transferring its electronic energy to vibrational oscillators in the adjacent solvent molecules. That one solvent species can have different accessible energy levels from another provides a qualitative rationale for the variation among the various liquids. Merkel and Kearns[11] proposed that the nonradiative rate parameter is related to a linear combination of the solvent near-IR absorbances of the solvent at 7880 cm^{-1} and 6280 cm^{-1} corresponding to the $V^1 = 0$ to $V = 0$ and $V^1 = 0$ to $V = 1$ vibronic gaps in O_2. This expression showed promise with the τ_Δ values available in 1972; in particular the large isotope effect in water seemed understandable. Since that time more τ_Δ values have become available,[10] and this wider availability of data has tended to undermine the quantitative aspects of this correlation.

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In the last few years, careful observations using sensitive detection equipment demonstrated that near-infrared radiation (1269 nm) arising from the weak radiative component of the $^3\Sigma_g^- \leftarrow {}^1\Delta_g$ transition in oxygen could be detected[12,13] during CW photoexcitation of sensitizers in aerated fluid solutions. Subsequently the use of high intensity laser pulses and high-gain, wide-band amplifiers allowed this IR luminescence to be time resolved.[14–17] Recently, the time response of this method was reduced to less than 1 μs, thereby allowing the observation[18] of infrared luminescence from $O_2(^1\Delta_g)$ in liquid H_2O, leading to the measurement of τ_Δ = 4.2 μs, the shortest intrinsic lifetime known for this species.

The IR luminescence method monitors the time evolution of a population of singlet oxygen molecules directly and only a single (repeated) experiment is required for evaluation of τ_Δ. The method is therefore rapid, straightforward, accurate, and convenient; indirect photobleaching, etc., methods are obsolete and IR luminescence becomes the method of choice not only for τ_Δ measurements[19] but also for determinations of bimolecular rate constants of $O_2(^1\Delta_g)$ with substrates.

This report describes the results of an experimental survey of τ_Δ values in an array of liquids. When the values are converted into bimolecular rate constants, some interesting trends are noted. Additivity factors have been extracted which allow comparisons to be made with very recent data from the laboratory of G. B. Schuster.[20]

Experimental Section

Materials. The most frequently used sensitizer was hematoporphyrin dimethyl ester (HPDME, Porphyrin Products), which proved to be soluble in a large variety of solvents, sometimes with gentle heating and stirring. In alkanes tetraphenylporphine (TPP, Aldrich Chemical) was used. In H_2O and D_2O, tetrakis(4-sulfatophenyl)porphine (TPPS, Porphyrin Products) was employed. Organic solvents were either spectroscopic or reagent grade and used as supplied.[21] D_2O (99.8 atom %) from Aldrich Chemical was used as supplied. Millipore reagent-grade H_2O was prepared in the laboratory.

Apparatus. A Quantel Nd:YAG Q-switched laser with KDP harmonic generator delivering ca. 250 mJ in an 11-ns pulse at 532 nm was the excitation source.

The samples were contained in a 10 mm × 10 mm fluorimetry cuvette held in a specially designed holder to ensure reproducible excitation and emission geometry. The laser beam was not focussed and measured ca. 8 mm in diameter at the incident face. Where necessary, attenuation was accomplished by interposing metal gauze screens upstream from the cuvette. The laser output area and beam separation optics were enclosed in a light-tight box to prevent the large component of scattered 1064-nm laser fundamental from reaching the detector. The output port through which the 532-nm beam passed was protected with a heat-absorbing filter. In this way scattered IR radiation from the laser was reduced to insignificant levels.

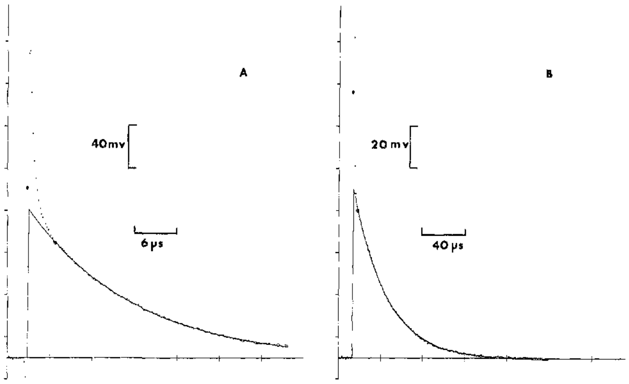

Figure 1. Computer-filled luminescence intensity (ordinate) vs. time (abscissa) profiles for singlet oxygen in methanol (A) and hexane (B). Each curve is an average of six individual shots. The dotted curve is the experimental data processed by the digitizer (10 digitizer channels per dot); the full curve is the exponential function that most closely fits the dotted curve after the initial fast change. This latter probably arises from the residual porphyrin fluorescence that has leaked through the filters. It has a time constant of ca. 0.4 μs equal to the e^{-1} fall time of the diode-amplifier configuration.

Table I. Measured τ_Δ Values for a Series of Normal Alkanes

solvent	[S]/M	τ_Δ/μs	k_Δ/ ($M^{-1}\ s^{-1}$)	N_{CH_2}
n-pentane	8.8	34.6	3280	3
n-hexane	7.7	31.4	4140	4
n-heptane	6.8	29.5	4990	5
n-nonane	5.6	23.7	7520	7
n-decane	5.1	27.6	7110	8
n-undecane	4.7	25.2	8420	9
n-dodecane	4.5	24.7	9080	10
n-tetradecane	3.8	24.7	10630	12
n-hexadecane	3.4	24.3	12020	14

Table II. Measured τ_Δ Values for a Series of Normal Alcohols

solvent	[S]/M	τ_Δ/μs	k_Δ/ ($M^{-1}\ s^{-1}$)	N_{CH_2}
methanol	24.7	10.4	3890	0
ethanol	17.2	15.3	3800	1
1-propanol	13.4	16.3	4590	2
1-butanol	10.9	17.5	5240	3
1-pentanol	9.3	17.8	6060	4
1-hexanol	8.0	17.9	6980	5
1-heptanol	7.1	18.1	7770	6
1-octanol	6.4	18.5	8430	7
1-nonanol	5.7	18.6	9450	8
1-decanol	5.3	17.8	10600	9

Infrared radiation emitted from the cuvette was detected by a Judson J16 germanium photodiode (5 mm^2) closely coupled to the cuvette in right-angle geometry. The only elements between the cuvette face and diode cover plate were a 5-mm thick (2-in. diameter) piece of AR-coated silicon metal (II-IV Inc.) and a Kodak Wratten gelatin 87A filter (cut-on near 900 nm). The photodiode output current was amplified with a Judson 000 50-dB amplifier with a 50-Ω resistor connected across its +15-V pin and ground in order to effectively reverse bias the diode. The output from the amplifier was fed into the 50-Ω input of a Biomation 8100 transient recorder via a Comlinear 150-MHz, 20-dB amplifier used largely as an impedance match. Details of the computerized experiment control, data acquisition, and analysis have been published.[22] The e^{-1} fall time of light flashes of effective δ-pulse duration was determined to be 0.4 μs, a factor of 2 improvement on that described earlier.[18]

Sample Conditions. All samples were prepared such that their absorbance at 532 nm was in the range 0.4–0.5 wherever possible. Solubility problems precluded this in the case of TPP in the alkanes, and A_{532} of 0.2 to 0.3 was used. All solutions were air-saturated and the experimental temperature was 22 °C except for cyclohexanol (35 °C), which otherwise tended to freeze. Binary solvent mixtures were prepared by making up stock solutions of sensitizer in each component and making the requisite mixtures volumetrically. For all systems, typically six individual shots were given, and the data were stored on disk and subsequently averaged prior to kinetic analysis to improve the signal to noise ratio. Representative data traces and the computer fits are shown in

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(19) The photobleaching method is, however, capable of yielding accurate data when proper precautions are taken. This is exemplified by comparing τ_Δ values for some of the solvents obtained here with DPBF photobleaching values of Young and Brewer (in: Råby, B.; Rabek, J. F. "Singlet Oxygen; Reaction with Organic Compounds and Polymers"; Wiley: Chichester, 1976; Chapter 6).

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Table III. Effects of Isotopic Substitution

solvent	τ_Δ	[S]/M	k_Δ/ (M^{-1} s^{-1})	k_Δ- (*h*/*d*)
water-h_2	4.2	55.5	4290	
water-d_2	55.0	55.5	330	13
acetonitrile-h_6	58.3	19.2	890	
acetonitrile-d_6	621	19.2	80	11
methanol-h_4	10.4	24.7	3890	
methanol-d_4	227	24.7	180	22
acetone-h_6	50.5	13.6	1460	
acetone-d_6	585	13.6	130	11
benzene-h_6	31.2	11.3	2840	
benzene-d_6	628	11.3	140	20

Figure 1. Lifetimes presented here are estimated to have error limits of ±5%.

Results and Discussion

The lifetime of $O_2(^1\Delta_g)$ in a wide range of solvents was measured by directly observing the decay of the IR luminescence following excitation by a pulse of 532-nm radiation. In all solvents except alkanes, HPDME was used as sensitizer ($A_{532} \sim 0.5$). This was not possible for alkanes because of solubility problems; TPP ($A_{532} \sim 0.2$) was used in such cases. Lifetime data for the normal alkanes and normal alcohols studied herein are listed in Tables I and II, respectively. Table III compares τ_Δ values in perprotio and perdeuterio variants of the same solvent.

A major premise in what follows is that the nonradiative deexcitation of $O_2(^1\Delta_g)$ results from collisions between itself and individual molecules of the medium that, for one reason or another, have a finite probability of inducing deactivation. In other words, the first-order rate constant observed, k_d ($= 1/\tau_\Delta$), is given by

$$k_d = k_0 + k_\Delta[S] \qquad (1)$$

where k_0 is an intrinsic rate, probably identical with the radiative rate and negligible in the liquids used here, [S] represents the solvent concentration in moles per liter, and

$$[S] = 1000\rho/(\text{formula})$$

The parameter k_Δ is the bimolecular rate constant for solvent molecule induced deexcitation. Then, when k_0 is very small,

$$k_\Delta = k_d/[S] = (10^6/\tau_\Delta)[S] \qquad (2)$$

The experimental k_Δ parameters are also listed in the tables.

Support for this premise comes from the effect of composition of binary mixtures of liquids on k_d. In carbon disulfide–benzene mixtures[23] and in H_2O/D_2O mixtures,[18] k_d was shown to be a linear function of composition. To examine this further a series of mixtures of acetone-h_6/acetone-d_6 and benzene-h_6/acetone-d_6 were prepared containing HPDME at $A_{532} = 0.45$. The first-order rate constants for $O_2(^1\Delta_g)$ decay are plotted against mixture composition in Figure 2 where it is seen that excellent linear behavior holds for both systems. In the relatively few systems studied, therefore, it appears that the decay of $O_2(^1\Delta_g)$ is properly described by eq 1 and that the interaction of $O_2(^1\Delta_g)$ with molecules of a pure liquid is governed by homogeneous kinetics. Hence eq 2 can be used to evaluate k_Δ. This has been assumed to be valid for all the liquids reported here.

Homologous Series Effects. Hurst and Schuster[20] investigated the effect of a series of halogenated arenes on τ_Δ and showed that $1/\tau_\Delta$ was a linear function of the concentration of H atoms in the liquid (i.e., the number of C–H bonds in the solvent molecule multiplied by the solvent molarity). A similar plot (with a lesser slope) was found for a series of fully deuterated halobenzenes. They concluded that the solvent parameter governing $O_2(^1\Delta_g)$ decay is an additive quantity; i.e., it can be obtained by summing together the contributions from C–H, C–D, OH, O–D, etc., bonds in the molecule. This turns out to be an extremely valuable contribution. Refinement, however, is apparently necessary since Hurst and Schuster[20] produce a quenching constant that is an average of all C–H bonds in a molecule irrespective of whether the bond is in methyl, methylene, methyne, or aromatic functions. A cursory glance at the experimental τ_Δ values for isomeric liquids (e.g., normal and branched alcohols) indicates that structural features are apparently important. This is examined further below.

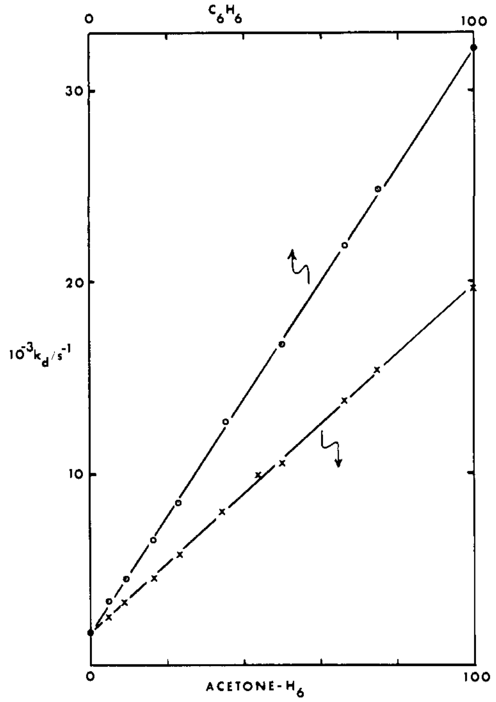

Figure 2. Effect of mixture composition on the first-order decay constant of $O_2(^1\Delta_g)$. Upper line: acetone-d_6 + C_6H_6 mixtures. Lower line: acetone-d_6 + acetone-h_6 mixtures. Compositions expressed as volume percent.

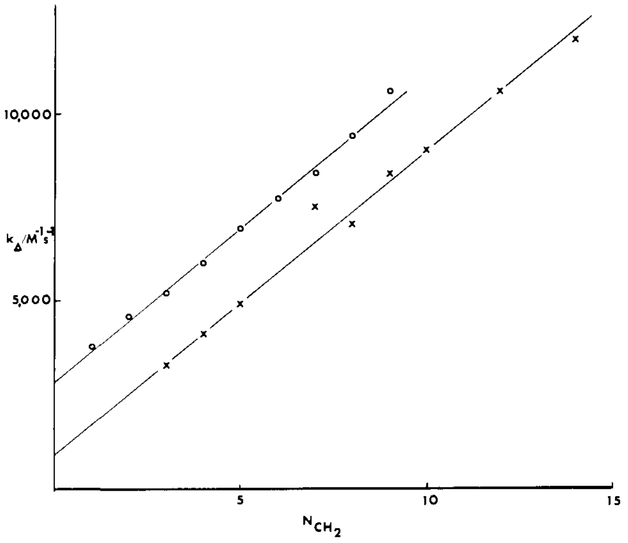

Figure 3. Effect of number of methylene groups on k_Δ for *n*-alkanes (×) and *n*-alcohols (O).

Normal Alkanes and Normal Alcohols. Figure 3 shows plots for a series of *n*-alkanes (C_5–C_{16}) and normal alcohols (C_2–C_{10}) in which k_Δ is plotted against the number of methylene groups (N_{CH_2}) in the molecule. N_{CH_2} is used instead of N_H (as in Hurst and Schuster[20]) since such a plot recognizes that normal alkanes contain two terminal methyl groups and all normal alcohols contain one methyl and one hydroxyl terminus. The slopes are 831 M^{-1} s^{-1} (alkanes) and 795 M^{-1} s^{-1} (alcohols), and the intercepts are 1100 M^{-1} s^{-1} (alkanes) and 2840 M^{-1} s^{-1} (alcohols). Thus, within experimental error, the lines are parallel with a mean slope of 813 M^{-1} s^{-1}. This is taken to be the additivity number for methylene groups (Δ_{CH_2}).

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Table IV. Additivity Numbers for Bond Groupings

residue	Δ, M^{-1} s^{-1}
CH_3	550 (420[a,b])
CD_3	15 (17[a,b])
CH_2	813
CH[c]	90
OH	2290 (2000[a])
OD	165 (150[a])
C=O	100
C≡N	65

[a] Hurst and Schuster's values.[20] [b] For an "average" CH bond, including aromatics. [c] Nonaromatic.

The intercept of the normal alkane line at $N_{CH_2} = 0$ is the k_Δ value for ethane, i.e., a normal alkane having two methyl groups but no methylene groups. Thus

$$2\Delta_{CH_3} = 1100\ M^{-1}\ s^{-1}$$

or

$$\Delta_{CH_3} = 550\ M^{-1}\ s^{-1}$$

Similarly, the intercept of the normal alcohol line at $N_{CH_2} = 0$ (2840 M^{-1} s^{-1}) corresponds to contributions from one CH_3 and one OH residue or

$$\Delta_{OH} = 2840 - \Delta_{CH_3} = 2290\ M^{-1}\ s^{-1}$$

Finally, Δ_{CH} was obtained by recognizing that for 2-propanol

$$k_\Delta = 2\Delta_{CH_3} + \Delta_{CH} + \Delta_{OH} = 3840\ M^{-1}\ s^{-1}$$

whence

$$\Delta_{CH} = 90\ M^{-1}\ s^{-1}$$

Other Δ values can be obtained from a consideration of the data presented in Table III on isotope effects. For H_2O the experimental k_Δ value (4290 M^{-1} s^{-1}) is close to twice Δ_{OH} (2290 M^{-1} s^{-1}). With the assumption that this continues through into the deuterio analogues, k_Δ for D_2O can also be divided; thus

$$\Delta_{OD} = 165\ M^{-1}\ s^{-1}$$

and from $k_\Delta(CD_3OD) = 180\ M^{-1}\ s^{-1}$, then

$$\Delta_{CD_3} = 15\ M^{-1}\ s^{-1}$$

Finally, by use of the k_Δ values for acetone-d_6 and acetonitrile-d_6:

$$\Delta_{C=O} = 100\ M^{-1}\ s^{-1}$$

$$\Delta_{C\equiv N} = 65\ M^{-1}\ s^{-1}$$

The additivity numbers for all the atomic arrangements obtained here are collected in Table IV. All except Δ_{CH_3}, Δ_{CH_2}, and Δ_{OH} are from single point determinations and therefore suffer from a higher degree of uncertainty.

The linear relationships for homologous series of normal alkanes and normal alcohols (Figure 3) constitute additional evidence that collisional processes are important. The additive nature of the CH_2 increments points out that the CH_2 group contributes to the quenching process and the amount of contribution depends directly on the number of CH_2 groups in a solvent molecule. Thus the probability of an $O_2(^1\Delta_g)$ molecule being quenched by a member of the series depends on the concentration of methylene groups present, which is governed by the number in the chain. The same argument is applicable to all the different kinds of atomic groupings.

In both the alkane and alcohol homologous series, increases in molecular weight cause increases in viscosity—about an order of magnitude in both series. This viscosity increase will lower the rate constant for molecular encounters as N_{CH_2} increases. This is not significant in the quenching processes being observed here since the magnitudes of k_Δ are in the range 10^3–10^4 M^{-1} s^{-1} whereas the diffusion-controlled values are in the 10^{10}–10^8 M^{-1} s^{-1} range and thus only 1 in 10^4 collisions (or less) results in quenching. The rate-determining step is thus clearly the quenching interaction and not viscosity-controlled diffusion.

Calculated vs. Experimental k_Δ Values. In addition to the solvents presented in Tables I and II, a variety of other liquids was studied. Table V compiles the τ_Δ and k_Δ values obtained and compares the experimental parameters with those calculated by using the Δ_x values in Table IV and also with calculated k_Δ values using Hurst and Schuster's[20] factors, which are also listed in Table IV for comparison. Inspection of Table V reveals the following points:

(i) A majority of the calculated k_Δ values are closer approximations to the experimental ones when the Δ_x values derived in this work are applied.

(ii) This is particularly true for molecules containing branched alkyl chains (the isomeric butanols, octanes, pentanols, and 3-methylpentane). In such cases the use of Hurst and Schuster's approach[20] severely overestimates k_Δ.

(iii) Where the only carbon–hydrogen bonds are present in methylenic groupings (cyclohexane, cyclohexanol, dioxane, methylene chloride), the two methods appear to be equally good. This arises from the fortuitous circumstance that Δ_{CH_2} has approximately twice the value of the average C–H contribution

Table V. Comparison of Measured and Calculated Values of k_Δ

		experiment	calculated	
solvent	[S]/M	k_Δ (τ_Δ)[a,b]	k_Δ (τ_Δ)[a,b]	k_Δ(τ_Δ)[a,c]
2-propanol	13.1	3480 (22.1)		4950 (15.4)
2-butanol	10.8	4710 (19.7)	4290 (21.4)	5790 (15.9)
2-methyl-1-propanol	10.9	4340 (21.1)	4290 (21.4)	5790 (15.9)
2-methyl-2-propanol	10.7	3040 (30.8)	3940 (23.7)	5790 (15.9)
2,4,4-trimethylpentanol	6.3	6550 (24.2)	6200 (25.6)	9160 (17.3)
cyclohexanol	9.6	6890 (15.1)	6450 (16.1)	6630 (15.7)
ethylene glycol	17.9	7410 (7.5)	6210 (9.0)	5680 (9.8)
methanol	24.7	3890 (10.4)	2840 (14.3)	3260 (12.4)
1,4-dioxane	11.7	3210 (26.7)	3252 (26.3)	3370 (25.4)
diethyl ether	9.6	3430 (30.4)	2730 (38.2)	4210 (24.7)
tert-butyl methyl ether	8.4	3420 (34.8)	2200 (54.1)	5050 (23.6)
isooctane	6.1	4360 (37.6)	3650 (44.9)	7580 (21.6)
3-methylpentane	7.7	4010 (32.4)	3370 (38.5)	5890 (22.1)
cyclohexane	9.3	4690 (23.0)	4880 (22.0)	5050 (21.3)
methylene chloride	15.6	780 (82.9)	810 (79.1)	840 (76.3)
1,2-dichloroethane	12.5	1270 (63.2)	1630 (49.1)	1680 (47.6)
acetone	13.6	1460 (50.5)	1200 (61.3)	2530 (29.1)
acetonitrile	19.2	890 (58.3)	620 (84.0)	1260 (41.3)
H_2O	55.5	4300 (4.2)	4580 (3.9)	4000 (4.5)

[a] Units are M^{-1} s^{-1} (μs). [b] This work. [c] Obtained by using the additivity data of Hurst and Schuster.[20]

extracted by Hurst and Schuster.[20]

(iv) Water is very closely approximated by both methods whereas methanol is not well-fitted by either.

(v) Δ_{C-Cl} appears to be negligible in comparison to Δ_{CH_2}, etc. Similarly, the ether linkage C–O–C has been assigned zero strength. This works well for 1,4-dioxane, but the acyclic ethers fall away from a good fit. Since calculated k_Δ values for diethyl ether and *tert*-butyl methyl ether are different from the experimental values by widely different amounts, it is thought unlikely that misassignment of Δ_{C-O-C} is the cause.

Conclusion

To a fair degree of approximation the solvent dependence of k_Δ is apparently capable of being broken down into component parts that may be identified with specific atomic groupings within the solvent molecule. This additive nature of k_Δ supports the contention that nonradiative decay results from collisional interactions between $O_2(^1\Delta_g)$ molecules and solvent molecules. The present work, taken together with recent $O_2(^1\Delta_g)$ lifetimes,[14–17,20] indicates that a simple relationship[11] between k_d and the solvent absorbances at 7880 and 1590 nm^{-1} is not tenable. Hurst and Schuster,[20] while retaining the basic concept of intermolecular electronic-to-vibrational energy transfer, prefer a mechanism based on exchange energy transfer rather than the dipole–dipole mechanism proposed earlier.[11] They invoke a relationship between the frequency of the solvent fundamental vibrational mode and the additivity factor. This removes attention from the overtone and combination bands. Hurst and Schuster maintain[20] that the higher the solvent vibrational frequency, the further down the $O_2(^3\Sigma_g^-)$ vibrational ladder will a single quantum transfer take the system, thereby making available the larger Franck–Condon factors between the lower oxygen vibrations. This zeroth order approximation is fine-tuned by incorporating an "off-resonance factor" that is related to the energy difference between the vibronic transition of O_2 and the solvent vibrational level. The data presented here are supportive of this concept. They do indicate, however, that different arrangements of the carbon skeleton cause significant differences in the oxygen–solvent interactions. Concomitant differences in the vibrational frequencies attributable to C–H modes are not evident in the infrared region around 2200 cm^{-1}. It may be that the reason for the progression $\Delta_{CH_2} > \Delta_{CH_3} > \Delta_{CH}$ is concerned with subtle changes in the individual off-resonance parameters.

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Photoprocesses in Diphenylpolyenes. 2. Excited-State Interactions with Stable Free Radicals[1]

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Abstract: Singlet and triplet quenching by two stable free radicals, viz., di-*tert*-butylnitroxy (DTBN) and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTMP), have been studied with three all-trans α,ω-diphenylpolyenes, Ph(t-C=C)$_n$Ph, n = 2–4, as excited-state substrates in different solvents. Data are presented for fluorescence quenching rate constants (0.8–2.1 × 10^{10} M^{-1} s^{-1} in cyclohexane/methanol), the fraction of singlet quenching events that result in triplet generation (0.06–0.60), and rate constants for triplet quenching (0.18–4.8 × 10^8 M^{-1} s^{-1} in solvents ranging from dimethyl sulfoxide to cyclohexane). As with aromatic hydrocarbons, the dependence of triplet quenching rate constants for polyenes on triplet energy (E_T) is found to be parabolic; that is, they first decrease systematically on going from *trans*-stilbene (n = 1) to *trans*-1,6-diphenyl-1,3,5-hexatriene (n = 3) and then increase on going from the latter to *trans*-1,8-diphenyl-1,3,5,7-octatetraene (n = 4). Possible interactions in terms of charge transfer, energy transfer, and electron exchange as well as roles of torsional motions and twisted configurations of polyenes in the quenching processes are discussed.

Molecular oxygen in its triplet ground state is by far the most commonly encountered paramagnetic species that has been studied extensively for its involvement in photoprocesses, particularly in enhancing spin-forbidden transitions through bimolecular or other types of interactions. Analogous paramagnetic effects[2] are expected from free radical doublets, although complications and differences may arise from potential contributions of energy transfer and charge transfer. In fact, stable free radicals such as nitric oxide, di-*tert*-butylnitroxy (DTBN), and piperidinyl-1-oxy derivatives have been shown to be efficient quenchers of photoexcited species such as triplets,[3–7] singlets,[8–10] and excimers.[12]

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