ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 109 (1997) 243–249

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Properties of singlet molecular oxygen $O_2(^1\Delta_g)$ in binary solvent mixtures of different polarity and proticity

Piotr Bilski *, Ralph N. Holt, Colin F. Chignell

Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences, P.O. Box 12233, Research Triangle Park, NC 27709, USA

Received 18 December 1996; revised 14 April 1997; accepted 28 April 1997

Abstract

We have measured $^1O_2$ lifetimes (τ) and radiative rate constants (k_r) for $^1O_2$ phosphorescence in a number of binary solvent mixtures with components of water, deuterium oxide, acetonitrile (AN), 1,4-dioxane (D), propylene carbonate (PC), or ethylene carbonate (EC). We have correlated k_r and τ with the mixtures' composition, polarizability, polarity and proticity. Our data show that $^1O_2$ properties are independent of both solvent polarity and solvent proticity, and confirm that the radiative rate constant k_r for $^1O_2$ phosphorescence best correlates with solvent polarizability. The prevailing trend is that k_r values increase with the increasing polarizability of solvent medium; in 1,4-dioxane mixtures, this increase is almost linear. However, for other solvents the correlation with polarizability is more solvent specific. For example, polarizability remains virtually unchanged over a wide composition range in AN–H_2O mixtures, but the k_r value increases by almost a factor of 5. In H_2O–D_2O mixtures, polarizability decreases with increasing D_2O concentration while the value of k_r increases twofold. This divergence suggests that, besides collision complexes, the interaction of $^1O_2$ with these solvents may involve a more specific interaction such as exciplex formation. Such specific interactions are probably responsible for considerable scattering that is usually observed in plots that relate k_r values measured in chemically different solvents to macroscopic polarizability. The best way to obtain accurate k_r and $k_d(\tau)$ values for $^1O_2$ in mixed solvents is still to measure them experimentally. We present here measured values of k_r and τ in a variety of mixed solvents; these values can be helpful in calculating $^1O_2$ yields from measurements of steady state phosphorescence. © 1997 Elsevier Science S.A.

Keywords: Singlet molecular oxygen; Phosphorescence; Radiative deactivation; Nonradiative deactivation; Polarity; Proticity; Solvent mixtures

1. Introduction

Singlet molecular oxygen, $O_2(^1\Delta_g)$, is much more reactive than O_2 in the ground triplet state, and readily oxidizes many compounds. In solution, the chemical reactions of $^1O_2$ compete with energy transfer to the solvent, which is even faster and generally determines $^1O_2$ lifetime in pure solvents. Another physical decay process is the radiative deactivation of $^1O_2$ via phosphorescence. While phosphorescence is relatively inefficient and does not greatly affect $^1O_2$ lifetime and reactivity, it is often exploited as the best diagnostic for the presence of $^1O_2$.

The phosphorescence that is used for $^1O_2$ identification originates from a forbidden transition ($^1\Delta_g \rightarrow {}^3\Sigma$, $0 \rightarrow 0$ oxygen vibration level), which is observed as a weak emission spectrum around 1270 nm. The spectral shape and position are little influenced by solvents [1–4]. However, solvents strongly affect the kinetics of both radiative and nonradiative deactivation processes, which together determine the phosphorescence intensity of $^1O_2$. A knowledge of both routes is essential for the proper interpretation of $^1O_2$ production in various media.

The influence of solvent on the nonradiative deactivation of $^1O_2$ has been known for a long time [5–9]. The nonradiative rate constant, k_d, depends on the solvent because deactivation occurs via a coupling of the $^1O_2$ electronic energy to the vibrational modes of solvent molecules [5–9]. Consequently, different functional groups in the solvent molecules contribute to this deactivation [6,7,9]. Overall, this process is often additive with regard to the group type and quantity, as has been shown for a series of alkane and alcohol homologs [7].

In contrast, an unexpectedly strong solvent dependence for the radiative rate constant, k_r, of $^1O_2$ was established in the last half decade [10–14]. A fair correlation of k_r with solvent polarizability (as expressed by refractive index) has been observed for a series of solvents [10,11]. The k_r value may increase about twenty fold in polarizable solvents as compared to non-polarizable solvents. Such a strong enhancement is much higher than that found for other molecular radiative

---

* Corresponding author.

PII S1010-6030(97)00147-0

transitions that are affected by the macroscopic polarizability of solvents. The enhancement is now believed to be mainly due to $^1O_2$ collisions with solvent molecules, and is called a collision-induced radiative transition [14b].

It is known that $^1O_2$ deactivation is little affected by the macroscopic polarity of solvents [10–14]. However, the potential influence of solvent proticity has not been separately investigated, to our knowledge. Furthermore, such a possibility cannot be ruled out without experimental evidence; carbonyl or ethereal oxygen atoms in many compounds function as proton or hydrogen acceptors to form hydrogen bonds. If dissolved oxygen molecules are similarly engaged, then solvent proticity might well affect the deactivation processes of singlet oxygen in solution.

Solvent mixtures are very often used in chemical practice because they possess desirable polarity or proticity, and they improve the solubility of many substrates. Solvent mixtures may be used to investigate processes where $^1O_2$ is involved. While $^1O_2$ lifetimes have been reported for numerous individual solvents [15], for solvent mixtures less information is available. Even fewer measurements are available for the radiative rate constants [10–14], which, to our knowledge, have not been systematically investigated in solvent mixtures. In addition, solvent mixtures offer an opportunity to correlate k_r with smoothly changing polarizability, so any subtle trends that would be otherwise difficult to notice may be revealed. Another property that may also be examined in solvent mixtures is the potential influence of solvent proticity on $^1O_2$ properties.

The main purpose of this paper was to correlate the properties of $^1O_2$ with those of solvent mixtures experimentally. We have studied radiative and nonradiative $^1O_2$ deactivation in binary solvent mixtures composed of water, deuterium oxide (D_2O), acetonitrile (AN), 1,4-dioxane (D), ethylene carbonate (EC) and propylene carbonate (PC). Some of these mixtures are frequently used as solvent media because their polarity and proticity may be varied over a wide range. We present here the measured $^1O_2$ lifetimes and radiative rate constants and their correlation with the mixtures' composition and properties.

2. Experimental section

Acetonitrile, 1,4-dioxane, (both spectrophotometric grade), propylene carbonate (1,2-propanediol cyclic carbonate), ethylene carbonate (1,3-dioxolan-2-one), deuterium oxide and perinaphthenone (phenalenone) were purchased from Aldrich Chemical Co. (Milwaukee, WI). We also used deuterium oxide from Cambridge Isotope Laboratories (Andover, MA). Aqueous solutions were prepared in deionized water. All experiments were performed in air saturated solutions that were freshly prepared and measured at room temperature, unless indicated otherwise.

Refractive indices were measured using a Bausch and Lomb refractometer at 25 °C, except for a few mixtures with a high concentration of ethylene carbonate that were solid at room temperature and required warming before measurements. In order to obtain a more accurate refraction reading and avoid blurring by the aberration inherent in polychromatic light, we used diffused light from a laser diode (Hitachi MI 1633) emitting at 633 nm to illuminate the sample in the refractometer. All refractive index values were measured at this wavelength.

Singlet oxygen phosphorescence was recorded on a steady-state $^1O_2$ spectrophotometer [16] whose optical system was optimized for higher sensitivity as in our pulse $^1O_2$ spectrophotometer [17]. The new optical configuration includes a parabolic mirror to collect all $^1O_2$ emission, which rendered the correction for different refractive indices of solvents unnecessary. In most cases samples containing a photosensitizer were excited from a 200 W mercury lamp through a 366 nm interference filter. The $^1O_2$ phosphorescence spectra were recorded over the range of 1200–1350 nm and were normalized to the same number of absorbed photons at the excitation wavelength. The integral or amplitude values were used to correlate phosphorescence intensity with the mole fraction of solvents in the mixtures. For easy comparison, all intensities for $^1O_2$ phosphorescence in solvent mixtures were obtained under strictly identical conditions.

Absorption spectra were measured using an HP Diode Array Spectrophotometer model 8451 or 8452A (Hewlett Packard Co., Palo Alto, CA). The relative number of absorbed photons at the excitation wavelength was calculated using the Beer–Lambert law.

Singlet oxygen lifetimes in solvent mixtures were measured using a laser pulse spectrometer described in detail elsewhere [17]. Briefly, the apparatus utilized a MY-33 Nd:YAG laser (Laser Photonics, Orlando, FL) and a germanium diode (Model 403 HS, Applied Detector Corporation, Fresno, California) in conjunction with an efficient optical system. For data acquisition we used an HP 54111D Digitizing Oscilloscope (Hewlett Packard Colorado Springs, CO) interfaced to a PC computer. Singlet oxygen was produced by single pulse excitation at 355 or 532 nm of a proper photosensitizer (vide infra) dissolved in the solvent mixture to give an absorbance ca. one at the excitation wavelength. The $^1O_2$ lifetime was calculated from a monoexponential decay of its phosphorescence.

For steady-state $^1O_2$ production in solvent mixtures, we have used perinaphthenone (phenalenone) as a photosensitizer [18]. This ketone has been shown to photosensitize $^1O_2$ with a quantum yield close to unity in many different solvents, including acetonitrile, ethers, and water–alcohol mixtures, with the $^1O_2$ production independent of solvent polarity. The solvents we used in our investigation are chemically similar to those that were previously characterized [18], therefore we have assumed that the quantum yield of $^1O_2$ photosensitization by perinaphthenone remains constant in all the solvents mixtures we studied. We have positively verified this assumption for a few mixtures by using Rose Bengal as an alternative $^1O_2$ photosensitizer (not shown).

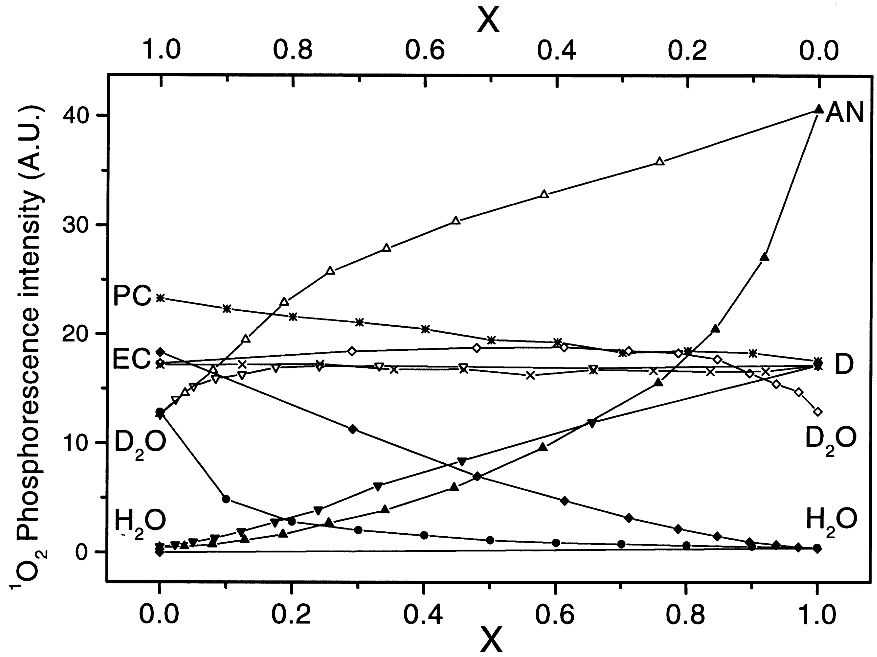

Fig. 1. Intensities of $^1O_2$ phosphorescence in the binary solvent mixtures as a function of the mole fraction of H_2O, D_2O, acetonitrile (AN), 1,4-dioxane (D), ethylene carbonate (EC), and propylene carbonate (PC). X = mole fraction.

Because perinaphthenone's rate for quenching singlet oxygen is extremely low [18], perinaphthenone was equally suitable as a photosensitizer for time-resolved measurements to determine $^1O_2$ lifetime in mixed solvents.

3. Results

We have correlated the properties of $^1O_2$ with the mole fraction (X) of solvents in binary mixtures composed of miscible solvents [1] such as water, deuterium oxide (D_2O), acetonitrile (AN), 1,4-dioxane (D), propylene carbonate (PC), and ethylene carbonate (EC). We wished to differentiate between solvent polarity and proticity, and some of these mixtures offer such a possibility. The same scale is used for all solvent combinations, and the positions of unmixed solvents are marked in the Figures for easy mixture identification.

In steady-state experiments, the intensity of $^1O_2$ phosphorescence (I_{so}) is described by Eq. (1), which is derived using a steady-state approximation:

$$I_{so} = A\phi k_r/(k_r + k_d) \qquad (1)$$

Because $k_r \ll k_d$, and $\tau = 1/k_d$, Eq. (1) can be simplified to Eq. (2):

$$I_{so} \approx A\phi k_r \tau \qquad (2)$$

where k_r and k_d are the radiative and the natural radiationless deactivation rate constants, respectively; ϕ is the quantum yield of $^1O_2$ production; τ is the $^1O_2$ lifetime; and A is an apparatus constant. If a series of experiments is performed under constant conditions, using a photosensitizer that produces $^1O_2$ with the same ϕ in all solvents, then k_r will be directly proportional to I_{so}/τ, where τ is measured directly from $^1O_2$ decay, and I_{so} is obtained from $^1O_2$ steady-state phosphorescence spectra. The values of k_r calculated in such a way are relative, and we have rescaled them assuming that $k_r = 0.3$ in acetonitrile [14]. Such a scale is relative to $k_r = 1$ in benzene, which has generally been used for comparison [10,11,14]. We believe that the accuracy of our relative k_r data is better then 15%, and our k_r values in pure acetonitrile, dioxane and D_2O are closely comparable to the relative values reported elsewhere for these solvents [14].

Fig. 1. shows that the steady-state intensities of $^1O_2$ phosphorescence in the solvent mixtures differ greatly. An equally broad range is observed for $^1O_2$ lifetime (Fig. 2). There is no discernible pattern of similarity between $^1O_2$ lifetime and phosphorescence intensity measured in the same mixture. If the radiative lifetime of $^1O_2$ phosphorescence was not so strongly affected by solvents, a relationship would be expected (vide infra).

In Fig. 3, the calculated k_r values are plotted as a function of the composition of the mixtures. For the mixtures of 1,4-dioxane with the carbonates, k_r is high and practically independent of the mixture composition (Fig. 3). However, for other mixed solvents, k_r values usually increase with the increasing concentration of the more polarizable component. A noticeable exception is the water–D_2O mixture, in which the opposite trend is observed (Fig. 3). The k_r values vary smoothly by a factor of up to eight in the solvents we used, but the variation differs in character in each case (Fig. 3).

---

[1] Propylene carbonate and water or D_2O are not completely miscible.

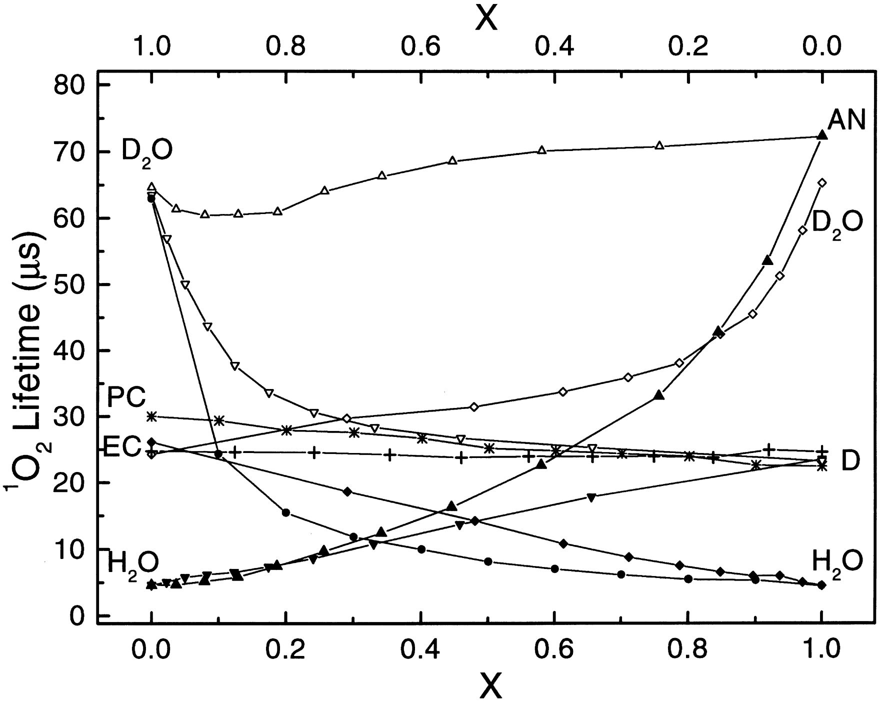

Fig. 2. Lifetimes of $^1O_2$ in the binary solvent mixtures as a function of the mole fraction of H_2O, D_2O, acetonitrile (AN), 1,4-dioxane (D), ethylene carbonate (EC), and propylene carbonate (PC). X = mole fraction.

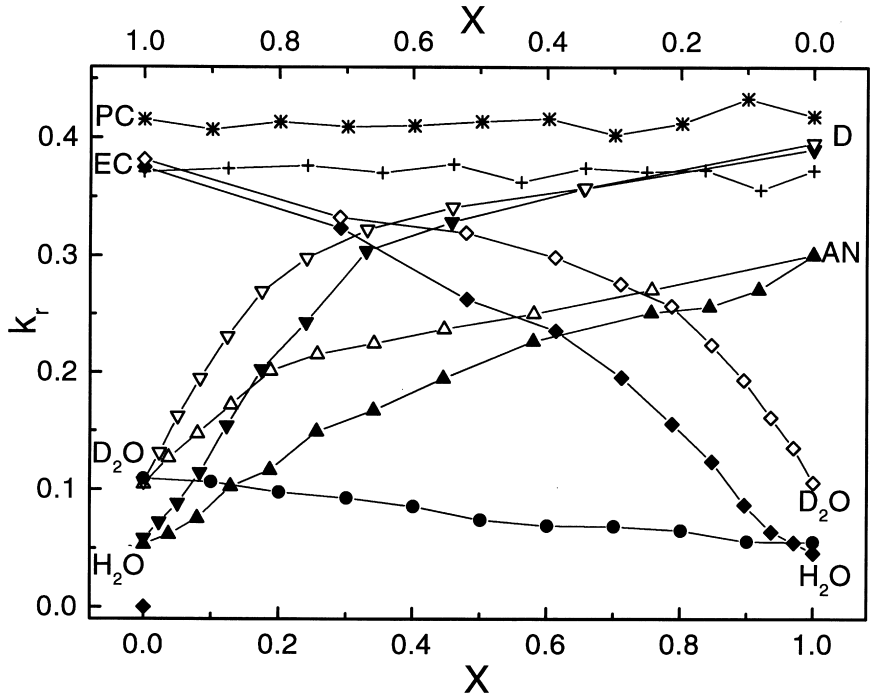

Fig. 3. Radiative rate constants for $^1O_2$ phosphorescence in the binary solvent mixtures as a function of the mole fraction of H_2O, D_2O, acetonitrile (AN), 1,4-dioxane (D), ethylene carbonate (EC), and propylene carbonate (PC). X = mole fraction.

The refractive indices of the mixed solvents are presented in Fig. 4. In Fig. 5, the calculated k_r values are plotted against the solvent polarizability $\alpha = (n^2 - 1)/(n^2 + 2)$, calculated from the respective refractive indices for the solvents mixtures we investigated.

4. Discussion

The correlation of k_r for $^1O_2$ phosphorescence with solvent polarizability has been previously reported by Scurlock and Ogilby [10] and by Schmidt and Afshari [11] for a number

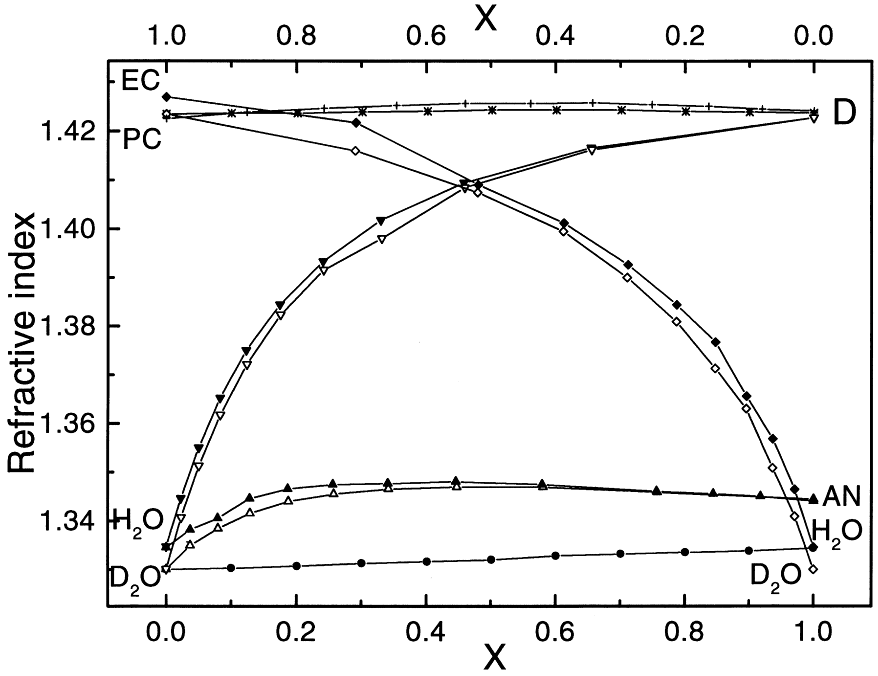

Fig. 4. Refractive indices of the binary solvent mixtures as a function of the mole fraction of H_2O, D_2O, acetonitrile (AN), 1,4-dioxane (D), ethylene carbonate (EC), and propylene carbonate (PC). X = mole fraction.

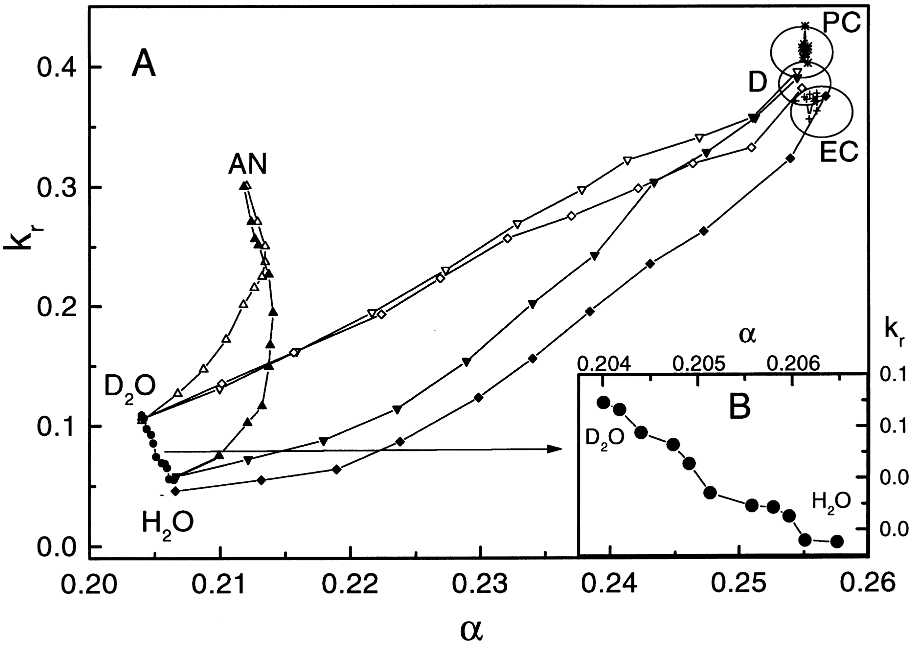

Fig. 5. (A) Radiative rate constant for $^1O_2$ phosphorescence in the binary solvent mixtures as a function of solvent polarizability $\alpha = (n^2 - 1)/(n^2 + 2)$; n, refractive index. (B) an expanded $k_r = f(\alpha)$ plot for H_2O–D_2O mixture.

of different solvents that covered a wide polarizability scale. The former workers concluded that, within the experimental error of their k_r values, there is a general relationship described by a line with a slight positive curvature. Schmidt and Afshari related k_r to the molar refraction, which resulted in a plot of scattered data that showed less correlation. Later, the k_r–polarizability relationship was refined by Scurlock et al. [14] using the averaged k_r values to better fit a line interpreted as a universal correlation. However, such a correlation may still be approximate because k_r may also depend somewhat on the individual properties of solvents.

In solvent mixtures, polarizability can be changed gradually to eliminate some of the uncertainty associated with using chemically different solvents to cover a range of polarizabilities. The prevailing trend is that k_r does indeed increase with increasing polarizability. However, the individual plots are very different in character, and there is at least one marked exception from this trend (vide infra). Thus, it is not surprising that k_r values for different solvents are scattered; the scatter must be due to a property of the emission process yielding k_r in solution, rather than to experimental error. If our k_r values in pure solvents were placed on a wider polarizability scale, they would fit a scattered pattern approximated by such a universal correlation line.

The water–D_2O mixture is an interesting exception from the trend that radiative rate constants increase with the increasing solvent polarizability. Based on the respective refractive indices (Fig. 4), the polarizability of H_2O is higher than D_2O (Fig. 5(B)). Nevertheless, in agreement with the previously published values [11], k_r for $^1O_2$ phosphorescence is twofold higher in D_2O than in H_2O. This increase in k_r contributes to the stronger $^1O_2$ phosphorescence in D_2O than in H_2O, which is very often attributed only to prolongation in $^1O_2$ lifetime. Thus, it is necessary to correct not only for τ but for different k_r values as well when the quantum yield of $^1O_2$ production is calculated from phosphorescence measurements performed in water (or in water–D_2O mixture) relative to a standard dissolved in D_2O, or vice versa.

The individual influences of polarity and proticity are often difficult to separate, especially in aqueous media which are both polar and protic. However, we can see the isolated effects in appropriate solvent mixtures. In the series of mixtures of propylene carbonate or ethylene carbonate and water or D_2O (Fig. 3) we can see the effect of varying proticity where polarity remains effectively constant. In these mixtures, proticity increases with increasing concentration of the aqueous phase. A wider range can be covered with EC, which is miscible with water, unlike propylene carbonate. The polarities of water and EC are high [19] ($\varepsilon_{\text{water}} = 78.30$, $\varepsilon_{\text{EC}} = 89.6$), with a polarizability component in the mixtures that decreases somewhat with decreasing water or D_2O concentration (Fig. 4). In these very polar mixtures the k_r values are an approximately linear function of polarizability (Fig. 5). A very similar relationship has been observed in aprotic solvents mixtures (Fig. 5) where polarizability is the same but polarity is varied (vide infra). Based on such similarity, we conclude that solvent proticity does not affect k_r for $^1O_2$ phosphorescence. As would be predicted, the $^1O_2$ lifetime is decreased by H_2O and increased by D_2O in the EC mixtures (Fig. 2). Interestingly, the changes in k_r and k_d in the EC–D_2O mixtures effectively compensate for each other, resulting in quite a uniform intensity of $^1O_2$ phosphorescence (Fig. 1), despite the wide variation in solvent proticity.

To observe the effects of varying polarity, we can look at the mixture of 1,4-dioxane with propylene (or ethylene) carbonate. Propylene carbonate and 1,4-dioxane are chemically similar aprotic solvents. Although polarizability is not greatly affected by composition (Fig. 4), these two solvents differ dramatically in polarity, as shown by their dielectric constants [19] ($\varepsilon_{\text{D}} = 2.21$, $\varepsilon_{\text{PC}} = 64.92$). We can see that k_r for $^1O_2$ phosphorescence remains virtually constant over the range of changing composition and polarity (Fig. 3), which unambiguously confirms that k_r is indeed independent of solvent polarity. Interestingly, the $^1O_2$ lifetime also changes only slightly (Fig. 2), thus the phosphorescence intensity is also relatively constant compared to mixtures of other solvents (Fig. 1). As a result, 1,4-dioxane and PC can be used to make mixtures in which the $^1O_2$ properties do not change much, but the polarity of the solvent may be varied over a wide range.

In water(D_2O)–acetonitrile or water(D_2O)–dioxane mixtures, proticity and polarity change concomitantly, yet these mixtures are often used in laboratory practice. Polarizability increases more with increasing concentration of 1,4-dioxane than with acetonitrile in their respective mixtures (Fig. 4). In fact, the polarizability of pure acetonitrile is even slightly lower than that measured in some of the aqueous mixtures. This results in an interesting dependence: while polarizability scarcely changes over a wide composition range in AN–H_2O mixes, the k_r value increases by almost a factor of five [2] (Fig. 5). In contrast, for dioxane–H_2O(D_2O) mixtures k_r increases almost linearly with increasing solvent polarizability (Fig. 5). Unlike k_r, the $^1O_2$ lifetime does not seem to be sensitive to any of the solvent parameters, but rather to the H_2O concentration in the mixtures [3]. A practical observation is that residual moisture in solvents will affect $^1O_2$ phosphorescence intensity via τ more strongly in acetonitrile than in 1,4-dioxane and both carbonates (Fig. 1).

While the observations that we have made for several solvent mixtures are of practical importance, they can also be used to further refine our understanding of $^1O_2$ interaction with solvents. Recently, Schmidt and Bodesheim have shown that the values of the radiative rate constants for $^1O_2$ are mostly determined by the collisions with solvent molecules [14b]. This conclusion was based on measurements in the gas phase and in CCl_4 where a quadratic correlation with solvent polarizability was found [14b]. These workers proposed that the transition responsible for $^1O_2$ phosphorescence is enhanced by ''borrowing'' from the collision-induced transition involving solvent molecule via charge transfer mechanism [14b]. Thus, this process strongly depends on the polarizability of collider (solvent), which is reflected in the

---

[2] The enhancement of k_r by CH_3CN in aqueous mixtures must be due to some factors other than solvent polarizablity. Complex formation between $^1O_2$ and the π bonds of the –CN moiety may be involved. The possible involvement of complexation processes in singlet oxygen formation and deactivation has been proposed by Gorman et al. [20] and Moore et al. [21], respectively. Our data from CH_3CN–H_2O mixtures suggest that the interaction of $^1O_2$ with π electrons in other solvents may also lead to a poor correlation of k_r with macroscopic solvent polarizability.

[3] In the mixtures we have studied, the observed rate constant, k_d, for natural deactivation of singlet oxygen shows good additivity as indicated by linear plots of k_d against mixture compositions expressed in volumes [7] (not shown) (All tabulated data can be made available via electronic mail.) Such additivity is well known and has been observed for a number of solvent mixtures [7], including H_2O–D_2O. A minor departure from perfect linearity seems to occur in acetonitrile mixtures with either water or D_2O for which S-shaped relationships were observed. This is consistent with an anomalous behavior of the radiative rate constant k_r, and may further support the hypothesis that there is specific interaction between $^1O_2$ and the –CN group. However, the possible influence of changing solvent structure on the deactivation processes cannot be totally excluded.

observed dependence of k_r on solvent macroscopic polarizability [14]. Most of our k_r values, particularly those measured in aqueous 1,4-dioxane and carbonates mixtures, may fall on the universal $k_r = f(\alpha)$ curve predicted by the collision theory.

It is of interest to know whether more subtle trends or interactions could be hidden under the universal k_r–polarizability relationship. A closer examination of the experimental k_r values in water–D_2O and in $H_2O(D_2O)$–acetonitrile mixtures (Fig. 5) reveals such trends suggesting that there may be contributions from additional interactions besides collisions such as exciplex formation. It is well known that O_2 forms ground-state complexes with many solvents, and a similar complexation of some solvents with excited molecular oxygen seems possible. Obviously, if $^1O_2$ phosphorescence can 'borrow' intensity in collision complexes, the same phenomenon may occur in other more specific complexes between solvents and $^1O_2$.

5. Conclusions

Some of the solvent mixtures we have examined offer the opportunity to independently regulate the proticity and polarity of solvent media. We have used these mixtures to show that the properties of singlet molecular oxygen are not correlated with either solvent polarity or proticity; these mixtures may also be useful for investigating the separate influence of proticity and polarity on other processes. Our results confirm that the radiative rate constant, k_r, values for $^1O_2$ phosphorescence are correlated with solvent polarizability. The relationship that is observed for all plots of k_r as a function of polarizability in different solvent mixtures confirms the existence of an approximate universal correlation due to $^1O_2$ collisions with solvent molecules. However, a consistent departure from the theoretical line in mixtures such as acetonitrile and D_2O suggest additional interaction(s) that are more solvent-specific than collision complexes. In one plausible hypothesis, $^1O_2$–solvent exciplexes may be formed in some cases. Prediction of k_r based solely on solvent polarizability is a useful but rough approximation, and experiment still remains the best way to obtain accurate k_r values for $^1O_2$. The values of k_r and τ that we report here can be helpful in the determination of accurate $^1O_2$ production from its phosphorescence measured in the mixed solvents that we have investigated.

References

[1] A. Bromberg, C.S. Foote, J. Phys. Chem. 93 (1989) 4587.
[2] I.M. Byteva, G.P. Gurinovich, A.P. Losev, V.A. Mudryi, Russ. Opt. Spectrosc. 68 (1990) 545.
[3] A.N. Macpherson, T.G. Truscott, P.H.J. Turner, J. Chem. Soc. Faraday Trans. 90 (1994) 1065.
[4] J.M. Wessel, M.A.J. Rodgers, J. Phys. Chem. 99 (1995) 17586.
[5] P.B. Merkel, D.R. Kearns, J. Am. Chem. Soc. 94 (1972) 7244.
[6] J.P. Hurst, G.B.J. Schuster, J. Am. Chem. Soc. 105 (1983) 5756.
[7] M.A.J. Rodgers, J. Am. Chem. Soc. 105 (1983) 6201.
[8] A.A. Krasnovsky, Jr., V.E. Kagan, FEBS Lett. 155 (1983) 233.
[9] R. Schmidt, H.-D. Brauer, J. Am. Chem. Soc. 109 (1987) 6976.
[10] R.D. Scurlock, P.R. Ogilby, J. Phys. Chem. 91 (1987) 4599.
[11] R. Schmidt, E.J. Afsari, J. Phys. Chem. 94 (1990) 4377.
[12] A.A. Gorman, A.A. Krasnovsky, M.A.J. Rodgers, J. Phys. Chem. 95 (1991) 598.
[13] A.P. Darmanyan, Chem. Phys. Lett. 215 (1993) 477.
[14] (a) R.D. Scurlock, S. Nonell, S.E. Braslavsky, P.R. Ogilby, J. Phys. Chem. 99 (1995) 3521; (b) R. Schmidt, M. Bodesheim, J. Phys. Chem. 99 (1995) 15919.
[15] F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 24 (1995) 663, and references cited therein.
[16] R.D. Hall, C.F. Chignell, Photochem. Photobiol. 45 (1987) 459.
[17] P. Bilski, C.F. Chignell, J. Biochem. Biophys. Methods 33 (1996) 73.
[18] R. Schmidt, C. Tanielian, R. Dunsbach, C.J. Wolff, Photochem. Photobiol., A: Chem. 79 (1994) 11.
[19] (a) J. Riddick, W.B. Bunger, Techniques of Chemistry, Organic Solvents, vol. II, 3rd edn., Wiley, Toronto 1970, p. 312; (b) C. Reichardt, Solvents and Solvents Effects in Organic Chemistry, 2nd edn., VCH, Weinheim 1988.
[20] A.A. Gorman, C. Hamblett, B. Lambert, B. Spencer, M.C. Standen, J. Am. Chem. Soc. 110 (1988) 8053.
[21] S.H. Lin, J. Lewis, T.A. Moore, Photochem. Photobiol., A: Chem. 56 (1991) 25.