Fluorescence of 2,3-Diazabicyclo[2.2.2]oct-2-ene Revisited: Solvent-Induced Quenching of the n,π*-Excited State by an Aborted Hydrogen Atom Transfer

Werner M. Nau,*,[‡] Gerhard Greiner,*,[§] Hermann Rau,[§] Julia Wall,[§] Massimo Olivucci,[¶] and J. C. Scaiano[†]

Institut für Physikalische Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland, Institut für Chemie, Universität Hohenheim, Garbenstr. 30, D-70599 Stuttgart, Germany, Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna, Via Selmi 2, 40126 Bologna, Italy, and the Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5, Canada

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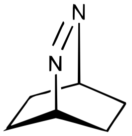
The fluorescence lifetimes of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) were determined in a large number of solvents and solvent mixtures, displaying variations from 825 ns in CD_3CN to 13 ns in $CHCl_3$. Large deuterium isotope effects (8−11) and significant activation energies (generally 2−15 kJ mol^{-1}) for fluorescence quenching of DBO are observed, which support a novel solvent-induced quenching mechanism via an aborted hydrogen atom transfer. In CCl_4 a photoinduced electron-transfer quenching mechanism may compete. The fluorescence quenching by solvent mixtures is not proportional to the mole fraction of the two components, indicating a preferential solvation of the excited state.

1. Introduction

The azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) and its derivatives possess the longest fluorescence lifetimes (up to 1 μs) among purely organic compounds. Although the exceptional photophysics of the parent DBO have already been examined 30 years ago,[1−5] the interest in this azoalkane has continued over the years[6−21] and remains the subject of ongoing investigations.[22−30]



Presently, we have examined the solvent-induced fluorescence quenching of DBO in experimental detail, which was first noted by Turro and co-workers for protic solvents.[8−10] Their originally assigned mechanism, which involved reversible proton transfer or hydrogen-bonding interactions as the quenching pathway, has been called into question, first by Engel and Nalepa[15] and more recently by our results.[27,29] Most importantly, in a preliminary work, we have demonstrated that nonprotic solvents such as chloroform are also potent quenchers of singlet-excited DBO[29] as well as other azoalkanes.[27] On the basis of the results from theoretical calculations,[29] the reaction coordinate for the quenching process can be presumed to involve hydrogen abstraction from a solvent molecule with the subsequent possibility for radiationless decay to the ground-state reactants at a conical intersection, as schematically depicted in Figure 1.

In the present experimental work we have studied the quenching by a large number of solvents, activation parameters of the quenching process, and the effect of solvent mixtures.

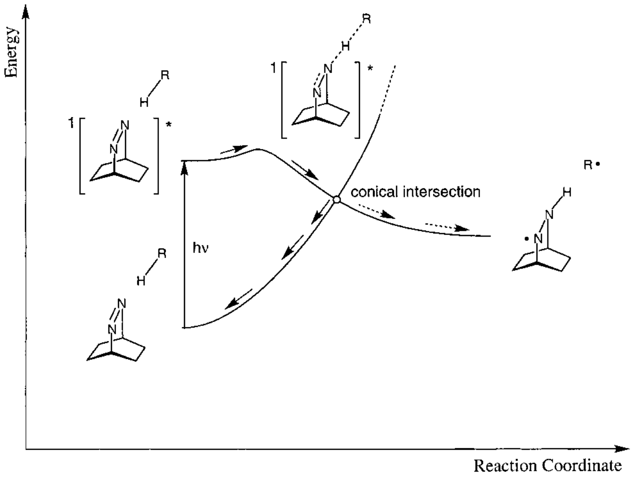


Figure 1. Schematic reaction coordinate for the hydrogen abstraction reaction between singlet-excited DBO and solvent molecules. The paper plane is an intersection through the hypersurfaces of the S_0 and S_1 states along the reaction coordinate for hydrogen displacement in the excited state.

2. Experimental Section

Materials. The azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) was synthesized according to literature procedures[31] and purified by sublimation and subsequent 2-fold recrystallization from *n*-hexane. Spectroscopic grade solvents (Aldrich, Fluka or Merck Uvasol) were used as received. Water was of bidistilled quality. Mixed solvents were prepared by weighing.

For the determination of the fluorescence lifetimes and quantum yields at variable temperatures from 4 to ca. 60 °C (temperature control ±0.2°) solutions of DBO in the particular solvents were placed in quartz cells with high-vacuum Teflon stopcocks and thoroughly deaerated by flushing them for 2 h with argon or nitrogen that was passed through an oxysorb cartridge to remove traces of oxygen. For the deter-

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[‡] Universität Basel.
[§] Universität Hohenheim.
[¶] Università di Bologna.
[†] University of Ottawa.

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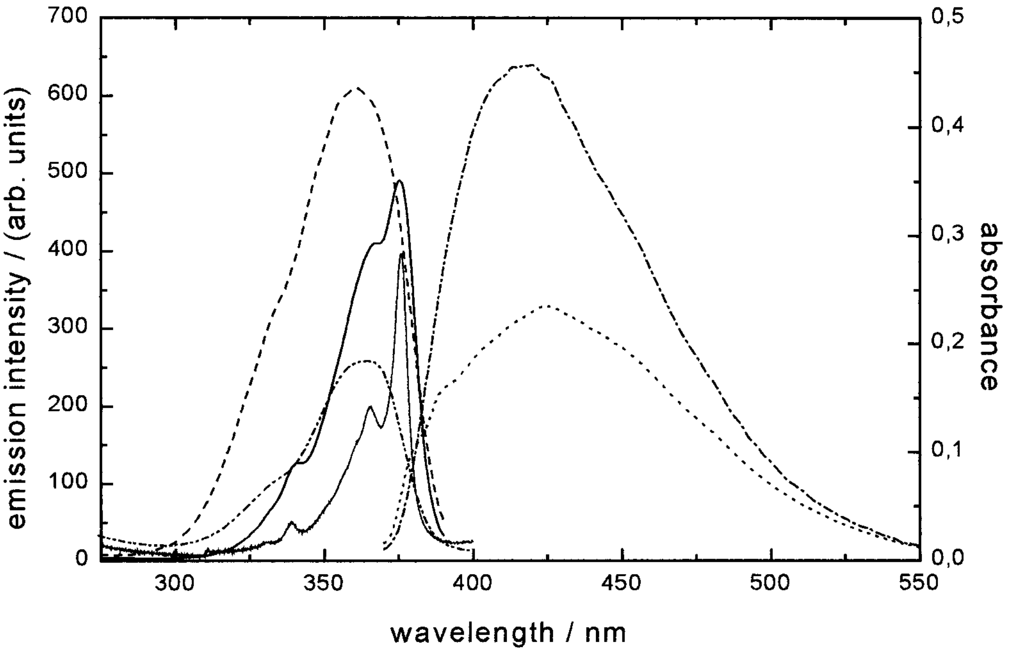

Figure 2. Absorption spectra of DBO in water (—••—) and in perfluoromethylcyclohexane (thick line), excitation spectra of DBO in water (- - -) and in perfluoromethylcyclohexane (thin line), and emission spectra of DBO in water (—•—) and in perfluoromethylcyclohexane (•••).

mination of the fluorescence lifetimes at low temperatures the solutions of DBO were degassed by at least five freeze—pump—thaw cycles in a special vessel, allowing the direct transfer of the solutions to fluorescence cells. The temperature of the sealed cells was kept constant in a CryoVac liquid nitrogen cryostat within ±1°.

Spectroscopic Measurements. Absorption spectra were recorded with a Hewlett-Packard 8452 diode array spectrophotometer (spectral resolution: 2 nm) or with a Cary 4E spectrophotometer (spectral resolution: 0.1 nm) from Varian (gas spectra). Due to the high vapor pressure of DBO at room temperature the absorption spectra could be registered in the gas phase after some crystals of DBO were put in a 10 cm quartz cell and subsequent evacuation of the cell.

The longer fluorescence lifetimes (τ > 100 ns) were determined by means of two different setups in two locations: (1) with a N_2-laser from Lambda Physics (K 600) as the excitation source at 337 nm (fwhm: 5 ns; 4.5 mJ) and the registration of emission of DBO at 430 nm by means of a digital storage oscilloscope (Philips PM 3392) or (2) with a XeF excimer laser (EMG 101 MSC) from Lambda physics (fwhm: 25 ns, 75 mJ) for excitation source at 351 nm. In the latter case the kinetic traces were registered by a transient digitizer and analyzed by nonlinear least-squares fitting of a monoexponential decay function. For the short lifetimes a time-correlated single photon counting (SPC) apparatus was used (5000U optical unit from IBH). A N_2-filled flashlamp (Edinburgh instruments) was employed for excitation at 337 nm. Fluorescence was detected at a right angle at 430 nm. Analysis of the data was performed with the deconvolution software of IBH, and the quality of the fit was checked by the χ^2 values. Some of the short lifetimes at room temperature were independently measured by the streak camera technique to afford consistent results.

Fluorescence spectra and fluorescence quantum yields were measured with a luminescence spectrometer of Perkin-Elmer (LS50B) with quinine sulfate as a standard ($\phi_f = 0.546$). The excitation wavelengths were chosen such that the DBO solutions and the standard solution of quinine sulfate in H_2SO_4 had the same absorption at the excitation wavelength. Care was taken that the absorbance (A) was low (<0.1) to allow the neglect of corrections for inner filter effects. The fluorescence spectra of DBO and quinine sulfate were multiplied by the LS50B instrument correction factors and the areas under the corrected spectra were evaluated between 370 and 550 nm by a program implemented in the LS50B software.

3. Results

The UV spectrum of gaseous DBO in the region of 26 000 cm^{-1} to 33 000 cm^{-1} is highly structured and reveals rotational features. This weak band is assigned to the n,π*-transition[9] (maximum at 26 593 cm^{-1}; ref 2, 26 610 cm^{-1}). In Figure 2 the absorption, excitation, and fluorescence spectra of DBO are shown in the highly nonpolar perfluoromethylcyclohexane (C_7F_{14}) and in water. The wavelength dependence of the absorption maxima (λ_{max} in water, 365.4 nm; λ_{max} in C_7F_{14}, 375.6 nm) corroborates the n,π* character of the transition. The fluorescence maxima occur at 417 nm in water and at 426 nm in C_7F_{14}. The shift may be due to different contributions of the vibrational bands. In the excitation spectrum, the maximum in water (360.5 nm) is clearly blue-shifted compared to C_7F_{14} (375.4 nm).

The emission spectrum of DBO in the gas phase, and similarly in solution, shows the unusual envelope already reported by Steel,[2] namely a structured short wavelength part (peaks at 26 610 cm^{-1} and 25 810 cm^{-1} in the gas phase) and a broad structureless band (maximum at 23 000 cm^{-1}) in the long wavelength region. Note that the broad band is absent in the emission spectrum of the next lower homologue, 2,3-diazabicyclo[2.2.1]hept-2-ene.[2]

It has been concluded that the occurrence of the broad emission band is not indicative of a dissociation because it is not seen in the absorption.[2] To examine an alternative hypothesis, namely that the emission of DBO may consist of two different transitions, i.e., one (at the short wavelength part of the emission spectrum) to a stationary electronic state and the other (within the broad emission band) to a dissociative level, we measured the fluorescence lifetime of DBO in cyclohexane within the structured short wavelength part of the emission band

TABLE 1: Fluorescence Lifetimes and Quenching Rate Constants of DBO in Different Solvents/Phases

solvent/phase	τ, ns[a]	k_q, 10^6 s^{-1} [b]
gas phase	930	≡0
CD_3CN[c]	825	0.14
D_2O[c]	730	0.29
CH_3CN	690	0.37
perfluorohexane	605	0.58
ethyl acetate	600	0.59
Freon-113	550	0.74
cyclohexane-d_{12}[c]	530	0.81
benzene-d_6[c]	500	0.92
benzene	455	1.1
H_2O	420	1.3
isooctane	360	1.7
CD_2Cl_2[c]	330	1.95
CD_3OD[c]	320	2.1
toluene-d_8[c]	310	2.2
methyl *tert*-butyl ether	310	2.2
2-methylpentane	290	2.4
n-heptane, *n*-hexane	255	2.8
toluene-methyl-d_3[c]	240	3.1
cyclohexane	230	3.3
toluene	200	3.9
acetic acid	190	4.2
CH_2Cl_2	185	4.3
1,2-dibromoethane	170	4.8
CH_3OD[c]	163	5.1
solid state	163	5.1
1,4-dioxane	155	5.4
$CDCl_3$[c]	110	8.0
dimethylformamide	85	10.7
formamide	74	12.4
CCl_4	72	12.8
tert-butyl alcohol	47	20.2
tetrachloroethylene	45	21.1
tetrahydrofuran	40	23.9
CD_3OH[c]	25	38.9
$(CF_3)_2CH(OH)$	24	40.6
CH_3OH	22	44.0
2-propanol	20	49.0
ethanol	19	52.0
2,2,2-trifluoroethanol	15	66.0
$CHCl_3$	13	76.0
trifluoroacetic acid	13	76.0
dimethyl sulfoxide	13	76.0

[a] Fluorescence lifetime measured by the laser-flash or SPC method at 430 nm. Maximum error in data is 5%. [b] Pseudounimolecular quenching rate constant from eq 1 with τ_0 = gas-phase lifetime. [c] Minimum isotopic purity was 99.5%, except for toluene-methyl-d_3 (98%) and CD_3OD and CD_3OH (both 99%).

TABLE 2: Fluorescence Quantum Yields and Natural Singlet Lifetimes of DBO in Different Solvents

solvent/phase	ϕ_f[a]	$\tau_{n,\ ns}$[b]
gas	0.56[c]	1660
$CDCl_3$	0.075	1465
$CHCl_3$	≈0.01	1300
toluene-d_8	0.22	1415
toluene	0.12	1665
benzene	0.21	1810
ethanol	≈0.01	1900
H_2O	0.20	2060

[a] Fluorescence quantum yield determined at room temperature relative to quinine sulfate, error ±10%. [b] Calculated as $\tau_n = \tau/\phi_f$, using the τ values from Table 1; error ±15%. [c] Reference 2; error as quoted ±18%.

at 25 °C, since two different transitions should display different lifetimes. However, between 370 and 390 nm the measured lifetime was independent (230 ± 5 ns) of the monitoring wavelength. Hence, a change of state appears also an unlikely explanation for the peculiar fluorescence spectrum of DBO.

To study the specific quenching effect of the solvent on the fluorescence of DBO, we measured the fluorescence lifetime (τ) of DBO in more than 40 deaerated solvents. Table 1, in which the solvents are arranged in increasing order of quenching efficiency, shows the enormous variation of τ and the pseudounimolecular quenching rate constant (k_q) of the various solvents: τ varies by nearly 2 and k_q over several orders of magnitude. k_q was calculated according to eq 1, where τ_0 is the

$$k_q = 1/\tau - 1/\tau_0 \qquad (1)$$

fluorescence lifetime of DBO in the gas phase (no solvent-induced fluorescence quenching) and τ is the measured fluorescence lifetime of DBO in the particular solvent.

To discriminate the influence of the solvent on the natural (τ_n) and measured (τ) fluorescence lifetime,[9] we determined the fluorescence quantum yields (ϕ_f) of DBO in a series of solvents (Table 2), including two deuterated ones. However, the natural fluorescence lifetime, calculated as $\tau_n = \tau/\phi_f$, did not vary dramatically and, in fact, may well be relatively constant within the rather large error of the quantum yield determination (±15%).

Since the proposed quenching pathway in Figure 1, which leads from the n,π* singlet-excited state to the conical intersection, is an activated one,[29] we have determined the activation parameters for fluorescence quenching in several solvents, assuming the Arrhenius relationship in eq 2.

$$k_q = 1/\tau - 1/\tau_0 = A \exp(-E_a/(RT)) \qquad (2)$$

The resulting Arrhenius parameters E_a and A and the Eyring parameters, the activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$), are shown in Table 3. The plots were linear over the accessible temperature range except for 2-methylpentane, where a deviation occurred at low temperatures (Figure 3). Here, the linear portion of the plot was used to approximate the activation parameters.

During our investigations in various laboratories the measurement of the fluorescence lifetimes of DBO in solvents with low k_q values (especially in acetonitrile) resulted in quite different τ values. It soon became evident that the purity of the solvents was responsible for these differences, not the purity of DBO or the different methods of measurement (SPC or flash photolysis). To characterize this effect, we chose two solvents (acetonitrile and water) in which DBO has relatively long fluorescence lifetimes (690 and 420 ns) and added ethanol as a quencher. In Figure 4 the relative changes in lifetime are plotted vs the solvent composition (mole fraction x_{EtOH}).

It is obvious that a small amount of ethanol added to acetonitrile or water changes the lifetime of DBO drastically whereas addition of acetonitrile or water to ethanol has little effect. An ideal behavior would result in the diagonal (- - -) of the plot. The observed deviations indicate selective or preferential solvation.

4. Discussion

Most azo compounds neither fluoresce nor show a fine structure in their spectra. This is either attributed to *cis*−*trans*

TABLE 3: Arrhenius and Eyring Parameters for Fluorescence Quenching of DBO by Solvents

solvent	E_A, kJ mol^{-1} [a]	A, s^{-1} [a]	$\Delta H^{\ddagger}$, kJ mol^{-1} [b]	$\Delta S^{\ddagger}$, J mol^{-1}
CH_3CN	18.2 ± 1.1	(6.7 ± 2.8) × 10^8	15.8	−85 ± 3.5
CD_3CN	21.7 ± 1.5	(1.2 ± 0.6) × 10^9	19.2	−80 ± 4.2
$CHCl_3$	8.5 ± 0.2	(2.2 ± 0.2) × 10^9	6.1	−74 ± 0.8
$CDCl_3$	13.1 ± 0.4	(1.6 ± 0.3) × 10^9	10.8	−77 ± 1.6
C_2H_5OH	9.5 ± 0.4	(2.2 ± 0.5) × 10^9	7.6	−73 ± 1.9
C_2D_5OD	14.5 ± 1.7	(2.4 ± 1.7) × 10^9	12.5	−75 ± 5.9
CH_3OH	8.9 ± 0.4	(1.5 ± 0.3) × 10^9	7.0	−76 ± 1.7
CH_3OD	14.5 ± 0.6	(1.9 ± 0.6) × 10^9	12.5	−74 ± 2.6
CD_3OD	13.3 ± 0.6	(0.49 ± 0.15) × 10^9	11.3	−86 ± 2.5
H_2O	1.7 ± 0.1	(2.6 ± 0.7) × 10^6	−0.85	−130 ± 2.2
D_2O	4.27 ± 1.2	(2.0 ± 0.9) × 10^6	1.85	−133 ± 3.7
2-methylpentane[c]	13.7	6.2 × 10^8	11.2	−85

[a] Errors calculated with $\Delta T = \pm 1$ K, $\Delta\tau = \pm 5$ ns. [b] Errors are the same as for E_A. [c] Evaluated from the linear part of the high-temperature region (Figure 3).

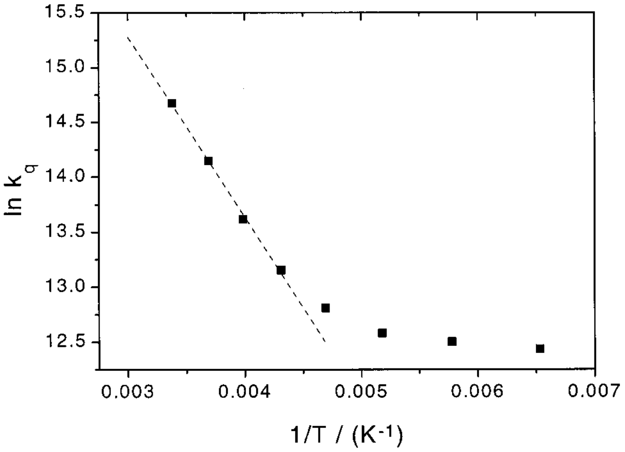

Figure 3. Arrhenius plot of DBO in 2-methylpentane with a linear regression line through the ln k_q values in the high-temperature region.

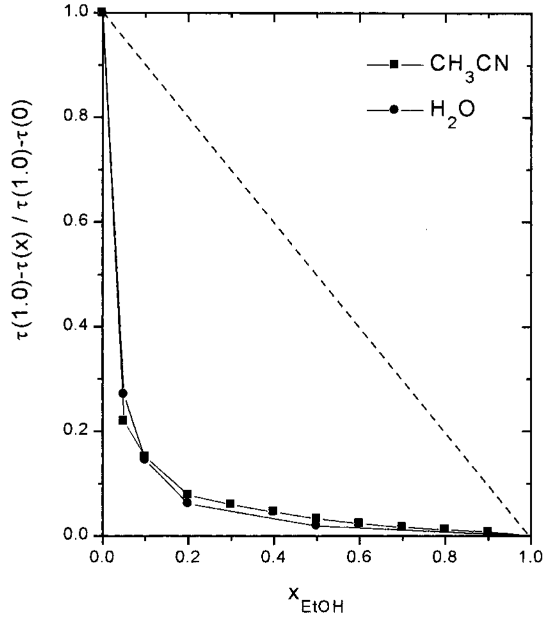

Figure 4. Relative fluorescence lifetimes of DBO vs the amount of ethanol in CH_3CN (■) and H_2O (●) mixtures with ethanol.

isomerization, to the photodissociation resulting in loss of nitrogen, or to some structure quenching effect (coupling to different states).[5] DBO as a member of the bicyclic *cis*-azo compounds shows fluorescence in the gas and solution phase and a highly structured absorption spectrum in the gas phase. The unusual envelope of the emission spectra (Figure 2) is still not fully understood (cf. Results).

Solvent Effects. The important result from the present work is that the fluorescence of DBO shows an unusual sensitivity to the solvent environment, which causes a lifetime variation by nearly 2 orders of magnitude (Table 1). Since the natural lifetime remains rather constant ($\tau_n = 1700 \pm 400$ ns, Table 2), the variations of τ in Table 1 must be ascribed to solvent-induced quenching.

While the spread of the quenching constants is very large, conventional guidelines such as polarity, acidity, or viscosity of the solvent fail to bring the data into a meaningful sequence. The quenching by the hydroxylic solvents is generally higher (with the exception of H_2O) than by most other solvents, but no ordering principle can be recognized within the groups of hydroxylic and non-hydroxylic solvents. In the group of chlorinated solvents the high quenching efficiency of $CHCl_3$ stands out.

Quenching Mechanism. The data in Table 1 hint to an unusual decay mechanism in which, however, H-atoms must play an important role, since the quenching efficiency decreases sharply upon deuteration of the solvent. For example, large deuterium isotope effects are observed for both the C−H bond of chloroform, $k_q(CHCl_3)/k_q(CDCl_3) = 8-11$, and for the O−H bond of methanol, $k_q(CH_3OH)/k_q(CH_3OD) = 8.5$.

The solvent-induced quenching process is thermally activated by ca. 2−15 kJ mol^{-1} (Table 3). Since this activation barrier is significantly smaller than that for photochemical decomposition of DBO (36 kJ mol^{-1}, independently quantified through the nitrogen quantum yield[18]) and since the photochemical decomposition of DBO at ambient temperature is of minor importance (ca. 2%) in solvents such as benzene and acetonitrile,[18] we relate the activation energies from fluorescence quenching (Table 3) to the solvent-induced quenching process.

The deuterium isotope effects, along with the observed sizable activation energies (Table 3) for the solvent-induced quenching process, suggest that a chemical reaction is involved. We propose that a partial H-transfer mechanism (“aborted hydrogen abstraction“) operates, where DBO partially abstracts a hydrogen atom from the C−H or O−H bonds of the solvent and undergoes subsequent deactivation to the ground state at a conical intersection (Figure 1). In support of such a mechanism, we have previously[29] shown for $CHCl_3$ and $CDCl_3$ as solvents, that the calculated activation energy for this H abstraction process agrees with experimental data within 4 kJ mol^{-1}. The difference in experimental activation energies of $CHCl_3$ and $CDCl_3$ (4.6 kJ mol^{-1}) can be attributed to zero-point vibrational energy (ZPE) differences, since a C−H bond is broken in the rate-determining (quenching) step.[29]

Exceptional Solvents. The proposed quenching mechanism should result in a complex dependence of the fluorescence lifetime on the molecular structure of the solvent, and this is indeed observed (Table 1). Hence, our detailed discussion of the solvent effects will be restricted to those solvents, which stand out, or which show distinct behavior: chloroform, methanol, acetonitrile, water, 2-methylpentane, CCl_4, and also solvent mixtures.

Chloroform ($k_q = 7.6 \times 10^7$ s^{-1}) and methanol ($k_q = 4.4 \times 10^7$ s^{-1}) are among the most potent quenchers, the reasons for which are not entirely understood. However, since methanol is a better quencher than acetic acid ($k_q = 4.2 \times 10^6$ s^{-1}) or water ($k_q = 1.3 \times 10^6$ s^{-1}), a correlation between acidity and quenching rate constant does not exist. Rather, the quenching efficiency is higher (methanol > acetic acid > water), when the O−H bond dissociation energy is lower ($435 < 443 < 498$ kJ mol^{-1}), although this energetic rationale fails to bring all data into agreement.[32]

Acetonitrile is a particularly poor quencher. This might not be too surprising since the chemical inertness of acetonitrile toward excited states, in particular in the reactions of n,π*-excited states such as ketones, has long promoted its extensive use as solvent in photochemical reactions. However, although the lifetime of singlet-excited DBO is quite long in acetonitrile, the observed deuterium isotope effect provides compelling evidence that some quenching of the singlet-excited DBO must occur even in acetonitrile and that the quenching must also involve hydrogen abstraction from the C−H bonds of acetonitrile. The low reactivity of DBO toward acetonitrile is also reflected in the activation energies derived from the temperature dependence of the fluorescence lifetimes. The latter are ca. 20 kJ mol^{-1} for acetonitrile and deuterioacetonitrile, significantly higher than the values for other solvents, which range from 2 to 15 kJ mol^{-1} (Table 3).

For 2-methylpentane, the experimental τ and k_q values at room temperature fit well into the sequence of the fluorescence parameters of Table 1, but interestingly, the temperature-dependent τ values deviate at low temperature from linear Arrhenius behavior (Figure 3). The latter was obeyed by all other examined solvents (Table 3). We tentatively attribute the deviation to tunneling at very low temperatures,[33] which could only be reached in the glassy solvent 2-methylpentane.

In the series of solvents, for which activation energies were measured (Table 3), D_2O and H_2O stand out. Here, the measured activation energies are very low, although DBO has a relatively long lifetime in the aqueous phase. In particular, the highly negative $\Delta S^\ddagger$ value (Table 3) leads to the suggestion that the solvent structure becomes more important and that the reaction is controlled by entropy. Alternatively, contributions of hydrogen tunneling may become important.

Electron Transfer. Although CCl_4 has no C−H bond it quenches the fluorescence of DBO. Engel et al.[19] suggested an electron-transfer mechanism for the fluorescence quenching of the cyclopropyl-substituted DBO by CCl_4 and supposed that this could also be assumed for DBO itself.[20] Indeed, if one calculates the standard Gibbs energy for the photoinduced electron transfer from DBO to CCl_4 according to Rehm and Weller,[34] one obtains a strongly negative value of $\Delta_r G° = -201$ kJ mol^{-1}, which suggests the possibility of an electron transfer for CCl_4. The same calculation for $CHCl_3$[34] indicates a less exergonic electron transfer with $\Delta_r G° = -69$ kJ mol^{-1}. But despite the less negative Gibbs energy of $CHCl_3$ compared to CCl_4 the former solvent is the better quencher ($k_q = 6.6$ vs 1.3×10^7 s^{-1}). Clearly, $CHCl_3$ quenches preferably by partial H-atom transfer, as evidenced by the large deuterium isotope effect (8−11).

Solvent Mixtures. The examination of solvent mixtures gave rise to an interesting effect. Namely, the large deviation of the relative changes in lifetime of DBO vs solvent composition from the diagonal in Figure 4 indicates that preferential solvation of excited DBO by ethanol in water or acetonitrile mixtures is involved.[37] For instance, from these data one can deduce that at $x_{EtOH} = 0.2$ the first solvation shell surrounding singlet-excited DBO is not composed of 20% EtOH and 80% H_2O (or CH_3CN) molecules as the bulk composition but of ca. 95% EtOH and 5% H_2O (or CH_3CN) molecules. These results demonstrate the importance of specific inner sphere effects.[38] From a practical point of view, extremely pure acetonitrile needs to be selected for quenching experiments.

5. Conclusions

The present examination of the fluorescence behavior of DBO, the organic molecule with the longest lifetime in its singlet-excited state, has revealed dramatic solvent effects. In the majority of the cases, the interaction with the solvent appears to involve a partial hydrogen atom transfer and radiationless decay at some point along the reaction coordinate, most likely at the recently computed conical intersection.[29] This novel fluorescence quenching mechanism constitutes a case of an aborted hydrogen abstraction reaction. Although this process involves an appreciable (8−15 kJ mol^{-1}) thermal activation for most solvents, the possibility of tunneling contributions, e.g., in water near ambient temperature and in 2-methylpentane at low temperatures, remains a real one.

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