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Solvent Effects on the Photochemistry of a Ketocyanine Dye and Its Functional Analogue, Michler's Ketone[†]

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Spectral properties of a photosensitizer, a ketocyanine dye, 2,5-bis{[4-(diethylamino)phenyl]methylene}cyclopentanone DEAW, were examined in seven different solvents. The absorption and emission spectra, transient absorption spectra, and conductivity data are reported. Extinction coefficient of the triplet–triplet absorption is calculated using the singlet depletion method. The quantum yield of the triplet state is calculated and is found to have a value from 0.01 to 0.60 in different solvents studied using both 308- and 480-nm pulsed laser excitations. The quantum yield of fluorescence is also reported. The dipole moment of the excited singlet state is calculated using the energy gap between the absorption and emission bands in different solvents of similar refractive indices. Comparison is made with Michler's ketone (MK) in the discussion of photochemical processes because of the similarity in the structures of DEAW and MK, the only difference being the extended conjugation introduced by the methylene groups along with the cyclopentanone in DEAW.

Introduction

The ketocyanine dye, 2,5-bis{[4-(diethylamino)phenyl]-methylene}cyclopentanone DEAW, is used in several industrial applications of photopolymer imaging systems.[1] The study of the spectral properties of this dye was carried out in different solvents in order to find out variations in the efficiency of this dye as a photosensitizer. The photosensitizing capability depends on the photophysical and photochemical properties, i.e., the electronic excitation energy, the fluorescence, the formation of triplets, and the formation of radicals by chemical processes. Another bis-4-aminoketone of interest is the triplet sensitizer Michler's ketone, (MK) bis-(4-[dimethylamino]phenyl)methanone. This has been studied widely in different solvents, and hence it is selected as a model compound for comparison. The characteristics of the solvent effect observed with MK show that the photophysical and photochemical properties are quite different in different solvents,[2] and one must be cautious not to extrapolate any property from one solvent to another.

Experimental Section

Steady-state optical measurements were made using a Perkin-Elmer Lambda 4B spectrophotometer and a SPEX Fluorolog 2 spectrofluorimeter.

Laser Flash Photolysis. For excitation, we used the 480-nm monochromatic light beam from a Lambda Physik FL 3002 dye laser pumped by a Questek 2440 excimer laser. Full width at half-maximum (fwhm) of the dye laser pulse is ~20 ns, and the maximum output energy is 20 mJ/pulse. The kinetic spectrophotometer was used to monitor the transient absorption or emission, which is composed of a pulsed 70-W Xe lamp, a SPEX minimate monochromater, and a Hamamatsu R 1913 photomultiplier. A Tekronix DSA 601 digitizing signal analyzer with the sample rate up to 10^9 sample/s was used to record transient signals. The bandwidth of the amplifier used in DSA was 400 MHz. The data acquisition was controlled by a National Instruments's LABVIEW program in a Macintosh IIx computer. Signal averaging of 4–40 laser shots was used to improve the signal-to-noise ratio.

The same system was used for dc conductivity measurements. A dc conductivity setup was used to follow the transient conductivity signal. Details have been discussed elsewhere.[3]

Actinometry. The relative intensity of the incident laser beam was monitored by a photodiode (FND 100, EG&G) which was connected to a pulse generator circuit. The photodiode was calibrated by a Joule meter[3] (Scientech Model 362 with a Model 360001 head) and a $Ru(bpy)_3^{2+}/MV^{2+}$ chemical actinometer.[4] The results obtained from the Joule meter and the chemical actinometer were in agreement within ±10%. The calibrations show that the concentration of incident photons used in our experiments was in the range $(1 - 5) \times 10^{-5}$ einsteins/pulse.

Materials. The dye DEAW was supplied by Du Pont and used as received. MK was purchased from Aldrich, purified, and recrytallized from benzene. All the solvents used were HPLC or spectrophotometric grade and were purchased from Aldrich and Baxter. The concentration of DEAW was 1×10^{-5} M in most the experiments, and a flow system was used in the flash photolysis when a transient spectrum was recorded. The experiments were carried out at room temperature. Argon and oxygen (both UHP grade) were purchased from Matheson Gas Products and Scott Specialty Gases.

Results and Discussion

Absorption and Emission Spectra. The absorption spectra for DEAW were recorded in the following seven solvents: cyclohexane, toluene, dichloromethane, acetonitrile, 2-propanol, ethanol, and methanol. They are shown in Figure 1. In nonpolar solvents, there was a structured intense absorption peak between 440 and 500 nm which disappeared in polar solvents due to the dipole-dipole interaction of this intramolecular charge-transfer (ICT) state. The ICT band shifted to the red with increase in polarity of the solvent, 50-nm shift from cyclohexane to methanol. This can be explained by the fact that the ground state is less stabilized than the excited state in polar solvents, which reduces the energy gap for the transition to occur.

The absorption maximum around 275 nm is attributed to the π–π^* transition characteristic of aromatic ketones. It was not shifted appreciably in different solvents. There was a small peak at 335 nm which appeared in all the solvents studied. A similar peak had been assigned for the n–π^* transition in the dyes of

(1) (a) Chambers, W. J.; Eaton, D. F. *J. Imaging Sci.* **1986**, *30*, 230. (b) M. Baum, C. P. Henry; U. S. Patent 3,652,275.

(2) Suppan, P. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 539.

(3) Schmidt, K. H.; Sauer, M. C., Jr.; Lu, Y.; Liu, A. *J. Phys. Chem.* **1990**, *94*, 244.

(4) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83.
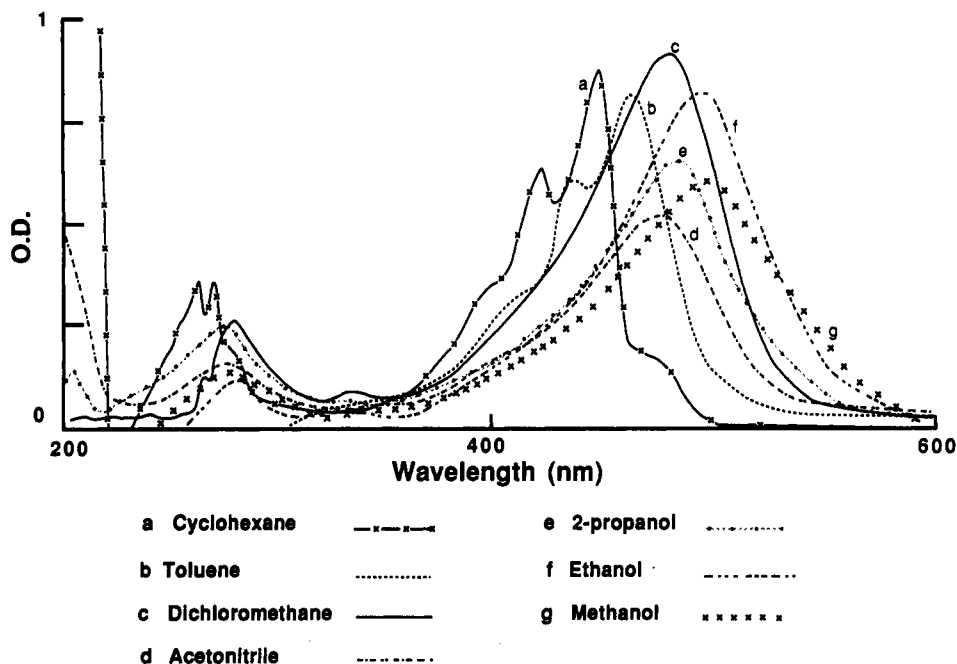
a Cyclohexane   — · — · —

b Toluene   ··············

c Dichloromethane   ———

d Acetonitrile   — ·· — ·· —

e 2-propanol   ··· — · ·······

f Ethanol   — ··· — ·· —

g Methanol   × × × × × ×

Figure 1. Absorption spectra of 1×10^{-5} M DEAW in different solvents.

TABLE I: Solvent Properties, Absorption and Fluorescence Maxima of DEAW (1×10^{-5} M), and Fluorescence Quantum Yields

solvent	E_T^N	ϵ^a	n_D	λ_{max}^{abs}/nm	λ_{max}^{flu}/nm	Φ_{flu}
cyclohexane	0.006	2.02	1.4262	445	453	0.005
toluene	0.099	2.38	1.4969	461	487	0.11
dichloromethane	0.309	8.93	1.4242	480	550	0.20
acetonitrile	0.460	35.94	1.3441	471	564	0.29
2-propanol	0.546	19.92	1.3772	485	586	0.50
ethanol	0.654	24.55	1.3614	492	618	0.25
methanol	0.762	32.66	1.3284	496	635	0.07

$^a \epsilon$ in this table is the dielectric constant.

similar structure (but not symmetrically substituted) studied by Wang.[5] One would expect a small blue shift of this peak with the increasing solvent polarity. However, it is possible that the n–π^* transition is buried in the ICT band as they both lie close to each other. So, it is assumed that the absorption due to this transition is around 410 nm in nonpolar solvents and at 400 nm in polar solvents, which is seen as a shoulder in the absorption spectra.

The absorption maxima and the fluorescence maxima are given in Table I along with some properties of the solvents used. Figure 2 shows the plot of the peak position versus the solvent polarity parameter, E_T^N.[6] The shifts in the fluorescence maximum (182 nm from cyclohexane to methanol) were greater than those of the absorption peaks. The ratio of the difference between the absorption and fluorescence shifts can be used to calculate the dipole moment of the first excited singlet state, assuming μ_g and μ_e are practically collinear and the direction of the charge transfer, $\Delta\mu$, to be in the plane of the π system. The simplified expression is

$$\mu_e = \mu_g \frac{\Delta E_f}{\Delta E_a}$$

where μ's are dipole moments and ΔE_a and ΔE_f are the solvatochromic shifts in the absorption and fluorescence spectra in different solvents of similar refractive indices.[7] μ_g's of DEAW and MK were calculated using the program PCMODEL. They are given in Figure 3. The μ_g value for MK was reported to be 5.3 D,[8] and the calculated was 4.7 D. On the basis of these, the value

(5) Wang, Y. *J. Phys. Chem.* **1985**, *89*, 3799.

(6) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH Publishers: New York, 1988.

(7) Suppan, P. *Chem. Phys. Lett.* **1983**, *94*, 272.

(8) Januszewski, J.; Stefaniak, L.; Urbanski, T.; Witanowski, M. *Rocz. Chem. Ann. Soc. Chem. Polonorum*, **1970**, *44*, 2361.
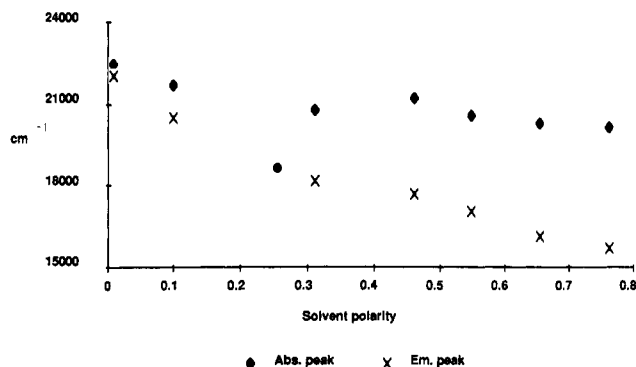
● Abs. peak   × Em. peak

Figure 2. Effect of solvent polarity (E_T^N) on the absorption and emission peak positions.
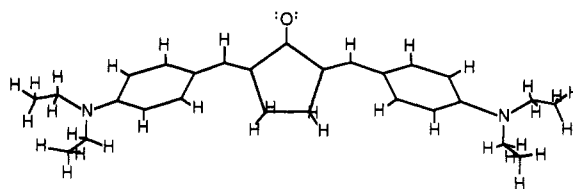

Figure 3. Structure of DEAW by PCMODEL. The dipole moment for this structure as calculated by PCMODEL is 4.4 D (for Michler's ketone it is 4.7 D).

for DEAW is taken to be 5.0 D from the calculated value of 4.4 D. The calculated μ_e for DEAW from the above equation is 14.0 D.

The fluorescence quantum yields, Φ_{flu}, calculated for DEAW in these solvents are also listed in Table I, the lowest being 0.005 in cyclohexane and the highest 0.29 in acetonitrile, while alcohols follow a different trend. These values have an experimental error of ~10% coming from the OD values, which are of low magnitude for the dilute solutions (1×10^{-5} M) used in the equation

$$\Phi_{flu} = S/N_{inc}(1 - 10^{-OD_{inc}})$$

where S is the area under the emission curve, N_{inc} is the number of incident photons, and OD_{inc} is the optical density at the excitation wavelength. The excitation wavelength was 400 nm for cyclohexane and toluene and 480 nm for the other solvents used. The Φ_{flu} value increased with increasing polarity (E_T^N) except for alcohols where the nature of the emitting state is different from that in other solvents. The Φ_{flu} values for this symmetrically

substituted dye in alcohols seem to be much greater than those reported for unsymmetrically substituted dyes 2-[(4-(dimethylamino)phenyl)methylene]-2,3-dihydro-1*H*-inden-1-one (DBI) and 9-[(2,3-dihydro-1-oxo-1*H*-inden-2-ylidene)methyl]-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine (JDI).[5] Another interesting observation was that this value is different when the excitation wavelength is 308 nm. This could be due to various photoprocesses that are possible at this higher photon energy, for example dissociation, self-quenching, etc.

Laser Flash Photolysis. The transient absorption spectra of 1×10^{-5} and 1×10^{-4} M DEAW (and MK) in different solvents were recorded using the 308- and/or 480-nm laser pulses. The region 300–850 nm was covered. The 480-nm laser flash photolysis of DEAW in cyclohexane did not give any observable transient absorption band, but upon the 308-nm laser excitation, a weak broad absorption band was observed in the region 300–750 nm. DEAW in the other solvents, i.e., toluene, dichloromethane, acetonitrile, 2-propanol, ethanol, and methanol, gave transient absorption peaks upon the 480-nm laser irradiation. It is interesting to note that for two other dyes (JDI and DBI) of similar structure, but not symmetrically substituted, the triplet state was not detected by nanosecond flash photolysis.[5] The reason for that is not clear, but no other detail was given in that work regarding the spectral region covered, the sensitivity of the detecting system, and the energy of the laser used, and hence it is inappropriate to conclude that only the triplet states of symmetrically substituted dyes are detectable.

The extinction coefficient for the triplet–triplet absorption was calculated using the singlet depletion method.[9] In this method, the observation of the change in OD due to the population of the triplet state was extended into the spectral region where the starting material absorbs (i.e., singlet, ground-state absorption). The main assumption involved in this method is that all the molecules which are pumped out of the ground state either return to S_0 or populate the lowest triplet state, T_1, within the time scale of the observations, and the change in OD can be expressed as

$$\Delta OD = (\epsilon_T - \epsilon_S)[^3M^*]l$$

where the $[^3M^*]$ is the concentration of the triplet state at the time of observation and l is the optical path length of the monitoring beam in the sample. The region of the ground-state absorption spectrum was selected for excitation (where the triplets formed on excitation are assumed not to absorb). When the change in OD_S due to this singlet depletion was measured at this wavelength, λ_1, we observed the change in absorbance, ΔOD, at some other higher wavelength, λ_2, where the ground state did not absorb. Using the following equations, ϵ_T is calculated.

$$\Delta OD_S(\lambda_1) = -\epsilon_S[^3M^*]l$$

$$\Delta OD_T(\lambda_2) = \epsilon^*_T[^3M^*]l$$

The upper limit to ϵ_T was derived by assuming the nascent triplet state does not absorb in the spectral region where the singlet depletion was monitored. (Note that this assumption is not valid for the transient spectra recorded for DEAW in cyclohexane and in toluene discussed later.) The extinction coefficient values were used for the calculation of triplet quantum yield. These values are given in Table II.

The extinction coefficients were calculated using only the data obtained with 1×10^{-5} M solution (for both the 308- and 480-nm laser flash photolyses) because of the high OD observed for the solutions of higher concentrations at the 480-nm photolysis (except cyclohexane and toluene) where the depletion occured. The ϵ_T values calculated in both cases (308- and 480-nm lasers) agreed within the experimental error. They are listed in Table II along with the calculated Φ_{T-T}.

Cyclohexane and Toluene. The transient absorption spectra obtained for DEAW in cyclohexane and toluene were different from those obtained in other solvents. These two solvents are nonpolar, and the dipolar solute interacts with these solvents

(9) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 13.

TABLE II: Extinction Coefficients of Ground-State and Triplet–Triplet Absorptions (ϵ_S and ϵ_T) and Quantum Yields of the Triplet

DEAW in	$\epsilon/$ M^{-1} cm^{-1}	$\epsilon_T/$ M^{-1} cm^{-1}	Φ_{T-T} (480)	Φ_{T-T} (308)
cyclohexane	57 000 (450)[a]		~0	0.4–1
toluene	84 500 (460)	3–7E4 (810)[b]	0.16–0.34	0.3–0.6
dichloromethane	94 000 (480)	1.5E5 (825)	0.15	0.12
acetonitrile	51 500 (470)	9.0E5 (820)	0.36	0.25
2-propanol	65 000 (480)	2.2E5 (800)	0.15	0.081
ethanol	83 000 (490)	2.0E5 (805)	0.10	0.10
methanol	59 400 (500)	1.0E5 (780)	0.031	0.095

[a] The numbers in parentheses are the wavelengths in nanometers at which the ϵ values are calculated. [b] Read as $(3–7) \times 10^4$.

differently. The intramolecular interaction between the chromophores is possible in nonpolar solvents and could result in the splitting of the absorption peak. In polar solvents, the chromophores individually interact with solvent molecules by a dipole–dipole interaction on either end of the DEAW molecule producing a single configuration (because of the symmetrical substitution) resulting in a single peak. It was reported previously, by Shvedova et al,[10] that because of the intramolecular interaction in symmetrical polyene bis(ω,ω'-dimethylamino) ketones (a ketocyanine dye, with an extended conjugation by methylene groups rather than benzene ring as in the case of DEAW) the singlet–singlet absorption peak as well as the triplet–triplet absorption peak were split into two with two maxima close to each other, in nonpolar solvents.

Figure 4 shows the transient absorption spectrum of 1×10^{-4} M DEAW in cyclohexane obtained using the 308-nm laser excitation. The spectrum obtained using the 480-nm laser did not give any observable transient absorption spectrum because of the low population in the first excited singlet state and hence the triplet state. A solution diluted 10 times gave a similar spectrum with less intensity but with the same first-order decay rate, i.e., 3×10^7 s^{-1}. The analysis of the spectrum showed that in the region 400–480 nm, where the singlet depletion occured, there was one or two more species absorbing because in the regions 320–380 nm and 500–580 nm (i.e., before and after the bleaching) the OD was not close to zero, and also the depletion spectrum was narrower than the ground-state absorption. Since the triplet–triplet absorption peak was very broad, there might be a contribution from that in the above-mentioned region also. The other possibility is that the ketyl radical formed by the reaction between the triplet state and the solvent absorbing at the same region. From the decay curve at 470 nm (insert in Figure 4), it is clear that the first few microseconds exhibit a recovery rate of 1×10^7 s^{-1}, the same as that of the decay rate of the triplet absorption (700 nm), and then there is a slow decaying species ($\sim 10^5$ s^{-1}) observed in the following 40 μs, characteristic of a ketyl radical. Because of these overlapping absorptions, the calculation of the extinction coefficient of the triplet state (by the singlet depletion method) is inaccurate. The quantum yield of the triplet in cyclohexane is almost 0 under the 480-nm laser irradiation, whereas it has an upper limit of 1 with the 308-nm laser. The upper limit was arrived at by using the lower limiting value of ϵ_T.

In toluene, the transient absorption spectra were similar when the 308- and 480-nm lasers were used, the former having more intensity than the latter. This absorption was not so broad as compared to that in cyclohexane; there were peaks clearly at 720 and 810 nm. They both gave the same first-order decay rate (1.5×10^7 s^{-1}). There was no concentration effect on this decay rate. Here the absorption of the ketyl radical formed did not show up as clearly as in the case of cyclohexane. Figure 5 shows the transient absorption spectrum for the 1×10^{-5} M solution (in

(10) (a) Shvedova, L. A.; Borisevich, Yu. E.; Tatikolov, A. S.; Kuz'min, V. A.; Krasnaya, Zh. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 819. (b) Shvedova, L. A.; Borisevich, Yu. E.; Tatikolov, A. S.; Kuz'min, V. A.; Krasnaya, Zh. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 1421.
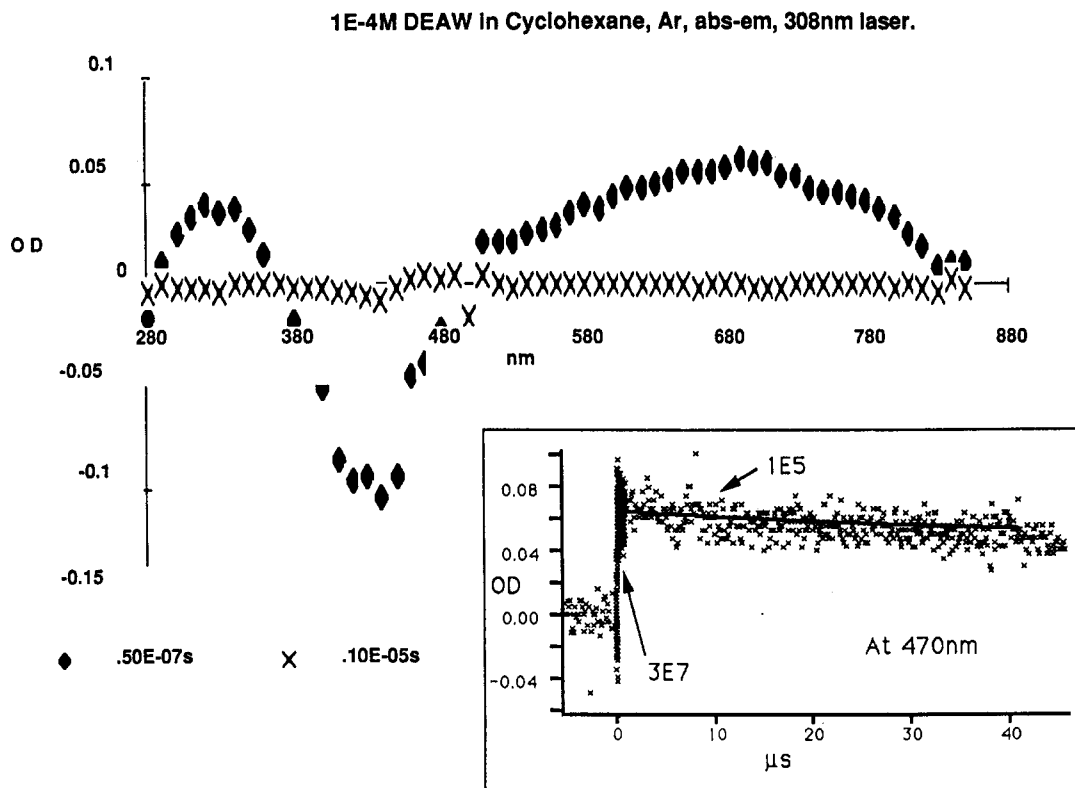
Figure 4. The transient absorption spectrum obtained for the solution 1×10^{-4} M DEAW in cyclohexane by the 308-nm laser flash photolysis.

TABLE III: Transient Absorption Maxima and the First-Order Rate Constants at the Depletion Wavelength and at λ_{max}^{T-T} [a]

DEAW in	λ_{dep}/nm	λ_{max}^{T-T}/nm	k_1/s^{-1} (Ar)	k_1/s^{-1} (O_2)
cyclohexane	450		$3.4E7$[b]	$8.5E7$
cyclohexane		620	$3.3E7$	
cyclohexane		690	$3.5E7$	
toluene	460		$1.5E7$	$4.0E7$
toluene		720	$1.5E7$	
toluene		810	$1.6E7$	$4.2E7$
dichloromethane	480		$2.2E6$	$1.6E7$
dichloromethane		825	$2.2E6$	$1.8E7$
acetonitrile	470		$2.8E6$	$5.1E7$
acetonitrile		820	$2.7E6$	$4.2E7$
2-propanol	490		$9.4E4$	$2.1E7$
2-propanol		800	$8.8E4$	$2.2E7$
ethanol	490		$3.1E4$	$1.8E7$
ethanol		805	$2.2E4$	$3.0E7$
methanol	500			
methanol		780	$2.2E4$	$2.0E7$

[a] The values for cyclohexane are from 308-nm laser flash, while the rest of them are using 480-nm laser. (The k_1 values are the same when 308- and 480-nm laser are used.) [b] Read as 3.4×10^7.

toluene) using the 480-nm laser light. Φ_{T-T} in toluene also shows that the 308-nm laser excitation gave a much larger value compared with that of 480-nm laser excitation.

Dichloromethane and Acetonitrile. Figure 6 gives the transient absorption spectrum of DEAW at 1×10^{-5} M in dichloromethane using the 480-nm laser flash. In acetonitrile it was similar. There was a sharp peak around 800 nm which had a shoulder at about 750 nm. Their equivalent kinetics showed that they are due to the same species. The rate of recovery from the singlet depletion (in the region 470–500 nm) is the same as the rate of decay of the species at 800 nm, both follow first-order kinetics, and the rate constants observed for the least-squares fit for these curves are given in Table III.

The triplet yields are smaller than expected. They are in contrast to the data of Shvedova et al.,[11] who found triplet yields
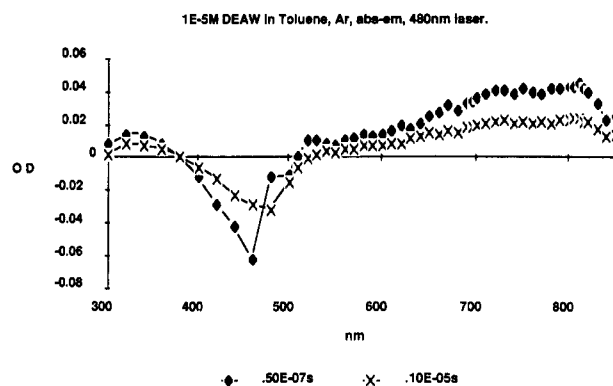
(11) Shvedova, L. A.; Tatikolov, A. S.; Darmanyan, A. P.; Kuz'min, V. A.; Krasnaya, Zh. A. *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1984**, *164*, 164.

Figure 5. The transient absorption spectrum obtained for the solution 1×10^{-5} M DEAW in toluene by the 480-nm laser flash photolysis.
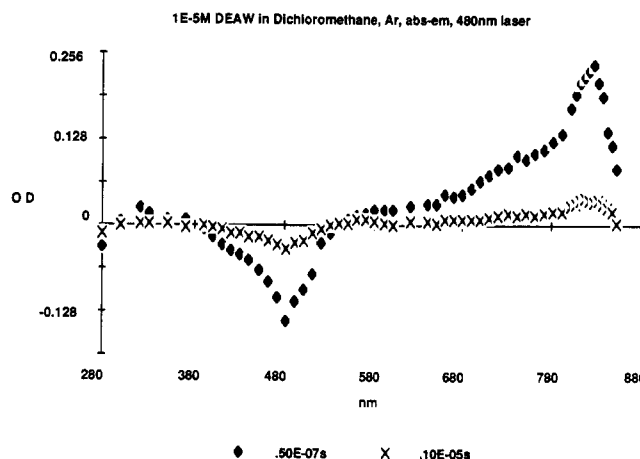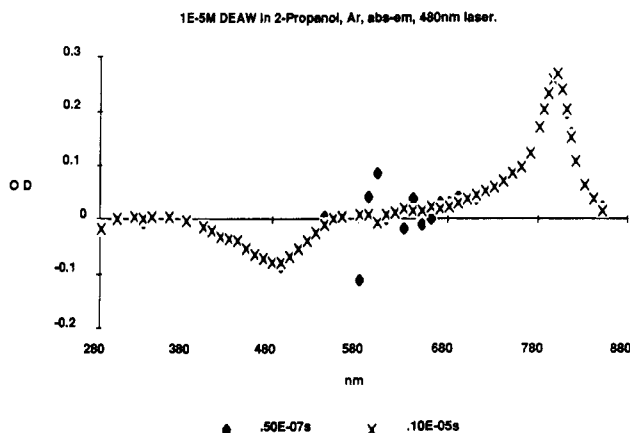

Figure 6. The transient absorption spectrum obtained for the solution 1×10^{-5} M DEAW in dichloromethane by the 480-nm laser flash photolysis.

of 0.3–0.5 for similar aminoketones. Also we did not observe the cation radical which was observed by them in the region 550–600 nm. The reason for this could be due to the much higher flash

1E-5M DEAW In 2-Propanol, Ar, abs-em, 480nm laser.

● .50E-07s   X .10E-05s

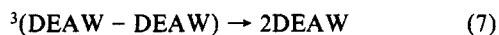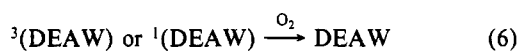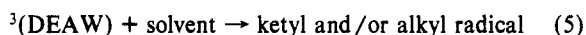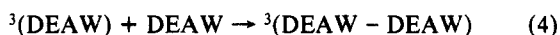**Figure 7.** The transient absorption spectrum obtained for the solution 1×10^{-5} M DEAW in 2-propanol by the 480-nm laser flash photolysis.

1E-4M MK In 2-Propanol, Ar, abs., 308nm laser.

● .10E-06s   ○ .10E-04s

Figure 8. The transient absorption spectrum obtained for 1×10^{-4} M MK in 2-propanol by the 308-nm laser flash photolysis.

energy used by them. The maximum value obtained for the 480-nm laser flash photolysis was for acetonitrile solution, which is 0.36. The 308-nm laser flash photolysis gave about two-thirds of that value.

2-Propanol, Ethanol, and Methanol. In alcohols, the transient spectra showed a single sharp peak. Figure 7 gives the transient absorption spectrum in 2-propanol; ethanol and methanol gave similar spectra with smaller intensities of absorption. The triplet lifetime was much longer in these alcohols compared with those of other solvents. This is not that surprising because of the charge-transfer character of the lowest triplet state, which can be easily and efficiently stabilized in alcoholic solvents through solvation and hydrogen bonding. Triplet yields decreased with the increasing polarity of the alcohols when the 480-nm laser was used. For an unsymmetrically substituted bis(ω,ω'-amino) ketone, it was reported[10b] that the triplet state did not give any yield directly. Here we see the triplet–triplet absorption in 2-propanol for DEAW with a low triplet yield with the 480-nm laser which is doubled with the 308-nm laser.

Mechanism

The different photochemical processes taking place during the flash photolysis of DEAW (and MK) can be written as follows:

$$DEAW + h\nu \rightarrow {}^1(DEAW) \qquad (1)$$

$${}^1(DEAW) \rightarrow {}^3(DEAW) \qquad (2)$$

$${}^3(DEAW) \rightarrow DEAW \qquad (3)$$

$${}^3(DEAW) + DEAW \rightarrow {}^3(DEAW - DEAW) \qquad (4)$$

$${}^3(DEAW) + solvent \rightarrow ketyl \text{ and/or alkyl radical} \qquad (5)$$

$${}^3(DEAW) \text{ or } {}^1(DEAW) \xrightarrow{O_2} DEAW \qquad (6)$$

$${}^3(DEAW - DEAW) \rightarrow 2DEAW \qquad (7)$$

$${}^3(DEAW - DEAW) \text{ or } {}^3(DEAW)_s \rightarrow$$
$$\qquad\qquad CIP, SSIP, \text{ or ion radicals} \qquad (8)$$

When the sensitizer absorbs a photon from the incident laser, it forms the excited singlet state which undergoes intersystem crossing (ISC) to give the triplet state, processes 1 and 2. The excited triplet state can go back to the ground state, process 3, or combine with another dye molecule to form a complex, process 4, or it can interact with the solvent to form a solvated excited state which can lead to the formation of a ketyl radical, process 5. It can be quenched by O_2, if O_2 is present in excess, process 6. The complex formed in process 4 can either go through some radiationless processes to give the ground-state molecules or form an ion pair and/or ion radical. The nature of the ion pair depends upon the polarity of the solvent. In nonpolar solvents, the ions are in contact and it is called a contact ion pair, CIP. In polar
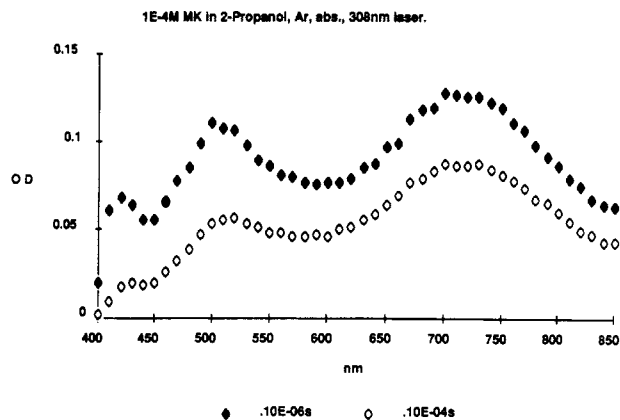
solvents, the ions are solvated and they are separated by solvent molecules and in this case SSIP, a solvent separated ion pair, is formed. When the ISC is not efficient, the singlet can also go through processes 3–8. Also the singlet (excited) can absorb a second photon to give a cation radical and an electron in the case of high-intensity laser beams, which can be tested by the excess of SF_6, in which case the electron is scavenged and slowed down the geminate recombination of the ion–electron pairs because of the less mobile species. These processes occur with various efficiencies with different sensitizers.

Comparison of DEAW with MK. In order to compare DEAW with MK, the 308-nm laser flash photolysis study of MK was carried out under the same experimental conditions. The transient spectrum observed for MK in cyclohexane and the triplet lifetime and yield calculated for MK in 2-propanol are in agreement with those reported previously.[12] The transient absorption spectrum obtained for MK in 2-propanol is shown in Figure 8. Previous studies concluded that there was no transient absorption in the region 425–600 nm when tried with microsecond flash photolysis.[12]

An important observation in this study is that the triplet yield of DEAW increases with an increasing E_T^N value of the solvent, except for alcohols where it decreases. The Φ_{T-T} from the 480-nm laser flash photolysis essentially includes only one kind of ISC because of the possibility that it can populate only the lowest excited singlet state, unlike the 308-nm laser excitation which can populate a higher energy level also. From the energy levels of the excited states of MK in cyclohexane and in ethanol[13] and also from the charge-transfer character of the intense ground-state absorption, the lowest excited singlet and triplet levels can be taken as the CT state.

The photochemistry of MK has been studied for a long time, and it is reported that in alcohols the ${}^3n\pi^*$ state lies above the ${}^1CT$, and hence the ISC from ${}^1CT$ to ${}^3n\pi^*$ is not possible. Since the ${}^1CT-{}^3CT$ involves an increase in energy, it is very inefficient. In cyclohexane, ${}^1CT-{}^3n\pi^*$ is possible because both ${}^3CT$ and ${}^3n\pi^*$ states lie below ${}^1CT$. So, even though the ordering of the energy levels are same in both polar and nonpolar solvents, the relative positions of different states vary and it is not always the lowest triplet state which is populated more by ISC. The various ISC efficiencies in different solvents and variation in the reactive state in different solvents can acccount for the trend in Φ_{T-T} observed in these solvents.

For DEAW, in this study, it is observed that the ${}^3CT$ and ${}^3n\pi^*$ are the states which lie below ${}^1CT$ in cyclohexane and in toluene, while in all the other solvents, only the ${}^3CT$ state lies below ${}^1CT$. This can account for the high reactivity of the triplet state in cyclohexane and toluene, i.e., process 5 is favorable in these solvents. The possibility of process 4 was checked with different

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concentrations, and it was found that in all the solvents the decay rate was not affected by higher concentrations. In the presence of an excess of O_2, the rate goes to the higher limit of 8×10^7 s^{-1}.

In nonpolar solvents, the charge-transfer state is not stabilized and contact ion pairs (CIP) are formed. In polar solvents like dichloromethane and in acetonitrile, the solvents stabilize the CT state by solvation and they form solvent separated ion pairs (SSIP). The decay curve for the dichloromethane solution at 470 nm shows that after bleaching not all of them are recovered back but a part of them are lost due to the interactions with solvent molecules.

In alcohols, the triplet is long lived. The interaction here is through solvation and H bonding which stabilizes the CT state. The triplet yield is very low in alcohols, as is the case with MK, which decreases with increasing polarity. The only competing reaction here seems to be quenching by O_2. In deoxygenated solutions, the observed decay rate is of the order 10^4 s^{-1}, whereas in the O_2 saturated solution, the decay rate is 10^9 M^{-1} s^{-1}. The ketyl radical formation is eliminated because of the reduced population in $^3n\pi^*$ state.

Conductivity Studies. The dc conductivity data were obtained using the 308-nm laser for MK and the 480-nm laser for DEAW. The signal observed for deoxygenated MK in cyclohexane showed that there was a fast geminate recombination (within a few nanoseconds after the pulse) of $MK^{+\bullet}$ and e^- after a biphotonic process, as shown by the square dependence of the signal amplitude with the laser intensity. This demonstrates the possibility of different photoprocesses with varying mechanisms as the intensity and energy of the laser increases. For this reason, we used a lower laser intensity and hence lower energy to avoid biphotonic processes. The sample saturated with SF_6 gave a similar signal with a reduction in signal amplitude and decay rate due to the sca-

venging of the electrons by SF_6. This was the case with toluene also.

Conclusions

The important finding in this study is the close resemblance of the photochemistries of DEAW and MK. The use of DEAW as an efficient sensitizer in the visible region in some solvents and its capability of being used as a laser dye in some other solvents are recognized.

The dipole moment of the first excited singlet state of DEAW is estimated to be 14.0 D from the solvatochromic shifts in the absorption and fluorescence spectra.

The quantum yield of fluorescence increases with increasing polarity of the solvent with the exception of alcohols, it varies with different excitation wavelengths.

The quantum yield for triplet–triplet absorption increases with decreasing E_T^N values. The first-order decay rate constant of the triplet state in alcohols is much smaller than that in nonpolar solvents, indicating the stabilization of the triplet state.

In nonpolar solvents, the energy of the lowest triplet state is estimated to be ~ 57 kcal mol^{-1}, and its fluorescence quantum yield is very low, with a high triplet yield which is essential for a molecule to act as a triplet sensitizer.

In alcohols, the energy of the lowest triplet state is very low (~ 35 kcal mol^{-1}), and low triplet yield with a relatively high fluorescence quantum yield makes it an efficient dye to be used in lasers. This dual role of DEAW makes it an excellent candidate for the use in both photoimaging and lasers.

State-to-State Vibration–Translation and Vibration–Vibration Rate Constants in H₂–H₂ and HD–HD Collisions

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A semiclassical collision model and a potential energy surface fitted to ab initio data has been used to calculate V–V and V–T/R rate constants for vibrational transitions in H₂–H₂ and HD–HD collisions. The theoretical values are compared with recent experimental data.

Introduction

Vibrational energy transfer in atom–diatom and diatom–diatom collisions plays an important role for the determination of nonthermal vibrational energy distributions in many physical important situations, as e.g., low-pressure plasmas[1] and chemical IR laser systems.[2]

Especially for H_2 the vibrational energy transfer in collisions with vibrationally excited H_2 molecules has within the last few years been of great interest, e.g., for the production of negative ions,[3] a field related to the nuclear fusion technology.[4] Also studies in the nonequilibrium vibrational kinetics in hydrogen[5] as well

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