Laser Flash Photolysis of trans-1,2-Bis(4-pyridyl)ethylene in Aqueous Solution

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Reactions of trans-1,2-bis(4-pyridyl)ethylene (neutral form: M) and its conjugate acids, HM⁺ and H₂M²⁺, following excitation by laser pulses, were studied in aqueous solution. The initial photoreaction of M (at pH > 7, $\lambda_{exc} = 248$ nm) is photoionization in a one quantum process, thereby forming the radical cation ($\lambda_{max} = 325$ nm, lifetime 80 ns) and the hydrated electron (e_{aq}^{-}) in low quantum yield (0.01). The H adduct radical (HM[•], $\lambda_{max} = 455$ nm) is formed by addition of e_{aq}^{-} to M followed by protonation with water, as in pulse radiolysis. HM[•] and its conjugate acid (H₂M^{•+}, $\lambda_{max} = 500$ nm) are in equilibrium with $pK_a = 9.8$ in buffered solution. H_2M^{*+} is also formed (in low yield) via biphotonic photoionization of HM⁺ at pH 4-5 and of H_2M^{2+} at pH <3.6. For H_2M^{2+} the photohydroxide (H_2M^+OH , $\lambda_{max} = 400$ nm) was observed. H_2M^+OH is the only transient in neat aqueous solution, when photoionization does not occur ($\lambda_{exc} = 308$ nm) and decays by protonation (rate constant 7×10^7 dm³ mol⁻¹ s⁻¹) to give the photohydrate, as is supported by time-resolved conductivity measurements. In 2-propanol/water (1:9 and 1:1, $\lambda_{exc} = 248$ or 308 nm) HM[•] or H₂M^{•+}, depending on pH, are mainly formed by H-atom abstraction from the alcohol involving the ¹(n, π^*) states of M and HM⁺. Excited H₂M²⁺, however, yields H₂M⁺OH, as it does in the absence of 2-propanol.

Introduction

The photochemistry of trans-1,2-bis(n-pyridyl)ethylenes (n. n'-DPE, n, n' = 2-4) has been the subject of several studies.³⁻¹⁰ In organic solvents photoreduction of 4,4'-DPE competes with fluorescence and trans \rightarrow cis photoisomerization.³⁻⁵ For the three trans-DPEs intersystem crossing is too small to play a significant role in fluid solution, and only the triplet of trans-2,2'-DPE could be detected by our means.^{9,10} Long-term irradiation has been reported to lead predominantly to trans \rightarrow cis isomerization for 3,3'-DPE and to reduction products (the ethane derivative and solvent C-H adducts) for the 2,2' and 4,4' isomers.⁵ The major transient of the n,n'-DPE's, observed by laser flash photolysis in organic solvents in the absence of water, is an H adduct radical, the yield of which is significant only for 4,4'-DPE.¹⁰ The radical HM[•] (M denotes the neutral form of trans-4,4'-DPE) is formed by H-atom abstraction from the solvent involving the (n,π^*) state and decays by disproportionation and combination with solvent radicals.5,10

The photochemical properties of DPEs in aqueous solution are influenced by the ground-state equilibria 1a and 1b. The pK_a

$$M + H_3O^+ \rightleftharpoons HM^+ + H_2O \tag{1a}$$

$$HM^+ + H_3O^+ \rightleftharpoons H_2M^{2+} + H_2O$$
 (1b)

values of HM⁺ and H_2M^{2+} in ethanol/water (1:9) are 5.6 and 3.65.¹¹ In the preceding pulse radiolysis study we have shown

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that the radical HM[•] and its conjugate acid H_2M^{*+} are in equilibrium (eq 2) at pH 9.8.¹² The photochemistry of H_2M^{2+}

$$HM^{\bullet} + H_2O \rightleftharpoons H_2M^{\bullet+} + OH^{-}$$
(2)

and 1,2-bis(N-methyl-4-pyridylium)ethylene (Me₂M²⁺, bisquaternary salt), a methylated analogue of 4.4'-DPE, is characterized by the nucleophilic addition of water or alcohols to yield photohydrates and ethers, respectively.6.7

This work contains new results from photolysis measurements of 4,4'-DPE in the presence of water and extends the information^{10,12} concerning the properties of the two radicals HM[•] and H_2M^{*+} . Three types of photoreactions were observed by transient conductivity and optical detection: photoreduction, hydroxide formation, and electron ejection. Photoionization upon 248-nm laser excitation has been reported for various aromatic molecules in aqueous solution.^{10,13-17} Generation of the hydrated electron (e_{aa}) from M, HM⁺, and H₂M²⁺ opens a photochemical pathway for the formation of radicals or radical ions, this being a dominant process in the absence of H-donating solvents. Excitation at 308 nm of H_2M^{2+} , thereby avoiding photoionization, yields the photohydroxide (H₂M⁺OH); its decay by protonation could be directly measured for the first time.

Experimental Section

The laser flash photolysis apparatus, using 20-ns pulses at 248 or 308 nm, was the same as in previous work.^{9,10,15,16} The transient optical and conductivity signals were fed into transient digitizers (Tektronix, types 390 AD and R7912 AD, for low or higher time resolution, respectively) and analyzed by using an Archimedes 440 computer. The time-resolved conductivity increase ($\Delta \kappa$) was measured in a quartz cell (path length 5 mm) containing three glassy carbon electrodes (distance 10 mm) and using either a 1-MHz ac bridge operating at 40 V (peak-to-peak) for signals longer than 10 μ s or a dc bridge (200 V) with a time resolution of 50 ns.¹⁵ For the conductivity measurements generally smaller concentrations ($\approx 1 \times 10^{-4} \text{ mol dm}^{-3}$) were used, and the volume

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Figure 1. Transient absorption spectra of *trans*-4,4'-DPE (a) in argonsaturated and (b) in N₂O-saturated aqueous solution, both at pH 12, and (c) in argon-saturated acetonitrile; $\lambda_{exc} = 248$ nm (-, --, and --- refer to 20, 100, and 2000 ns after the pulse, respectively).

was exchanged after each pulse. For the optical signals a flowthrough cell (1-cm path length) was used where necessary, e.g., because of significant chromophore loss.

The DPE samples (trans isomers throughout) were the same as in refs 10 and 12, and the concentrations were about 2×10^{-4} mol dm⁻³ unless otherwise indicated. Water was purified by using a Millipore Milli-Q system. The other solvents and KI were from Merck. For measurements of the pH dependence of the respective yields the concentrations of one series of samples were adjusted for the same A_{248} (or A_{308}) value ($\pm 10\%$) or ΔA was corrected for the changes in A_{248} (or A_{308}). In some cases Titrisol buffers (Merck, Darmstadt, pH 1–12; $\lambda_{exc} = 308$ nm) or phosphate buffers (pH 4.5–9, for the more acidic or alkaline ranges HClO₄ or NaOH was added, respectively; $\lambda_{exc} = 248$ nm) were used. Where the intensity dependence was studied, the laser beam was not focused, corresponding to a value of $I_{L}^{max} = 5 \times 10^{6}$ W cm^{-2.16} All measurements were carried out at 23–25 °C.

Results and Discussion

Transients in Neutral and Alkaline Aqueous Solution from 248-nm Excitation. Three transients were observed for trans-4,4'-DPE ((1-3) × 10⁻⁴ mol dm⁻³) in argon-saturated aqueous solution at pH 12 using $\lambda_{exc} = 248$ nm: the longer lived transient T_{455} , which is assigned to the radical HM[•] (see below), and two shorter lived species. One of these (denoted as T_{325}) exhibits two maxima; the major is $\lambda_{max} = 325$ nm and the second around 460 nm. The third transient ($\lambda_{max} \approx 710$ nm, Figure 1a) is assigned to e_{aq}^- since it is scavenged by N₂O, 2-chloroethanol, or oxygen. Formation of e_{aq}^- is explained by photoionization (electron ejection) of the neutral substrate (eq 3).

$$M \xrightarrow{h\nu} e_{aq}^{-} + M^{\bullet+}$$
(3)

 T_{325} , formed within the pulse width, is assigned to the radical cation (M^{•+}). A successor radical of M^{•+}, e.g., produced by reaction with water, is unlikely since T_{325} was also observed as the major transient in acetonitrile (Figure 1c), where the solvated electron is rapidly converted into a dimer adduct (CH₃CN)₂^{•-}, the latter being shorter lived than 100 ns.¹⁸ The decay of T_{325} follows first-order kinetics. The lifetime of M^{•+} is about 1 μ s in acetonitrile and \approx 80 ns in aqueous solution at pH 12. The latter corresponds to a rate constant of 2.2 × 10⁵ dm³ mol⁻¹ s⁻¹ for the reaction with water. The products arising from M^{•+} are suggested

SCHEME I: Formation and Decay of Transients from *trans*-4,4'-DPE in Aqueous Solution at pH 10-12 Involving Photoionization



TABLE I: Transients of trans-DPEs in Aqueous Solution^a

compd	added solvt ^b	pН	λ _{max} , nm	$t_{1/2}, \mu s$	species
4,4'-DPE	none	14.5	465	>100	НМ•
	none	12	325, 465	0.08	M•+ °
		12	450, 650	>100	HM•4
	methanol	12	455, >660	≈200	HM•ª
	2-propanol	12	455, 640	≈200	HM•ª
	none	8	455, 650	е	HM• <i>ª</i>
	none	6	325		M•+
		6	455,650	е	HM•4
		6	500, >680	>100	H ₂ M•+
	2-propanol	6	455, 660	е	нм∙₄
	•••	6	500, >680	>100	H ₂ M•+
	2-propanol	4	≈450	е	нм∙₄
		4	500, >700	≈200	H2M•+
	none ^f	3	400	20	H ₂ M+OH
	none ^f	2	400	2	Н₂м⁺он
	none	2	400		н₅м+он
		2	500, >700		H-M•+
	none ^f	1	400	0.2	н,м⁺он
	2-propanol	1	≈400	≈0.2	н,м⁺он
	• •	1	500, >700	>100	н , м. +
3,3'-DPE	none	8	≈430	>10	d
2,2'-DPE	none	8	440	>50	d

^aIn argon-saturated solution at 24 °C (concentrations of (1-5) × 10⁻⁴ mol dm⁻³); $\lambda_{exc} = 248$ nm unless otherwise indicated. ^bThe added volume is 10%. ^cMajor species in N₂O-saturated aqueous solution. ^dObservation of e_{aq}⁻ in the 600-800-nm range. ^eDecay of HM[•] and formation of H₂M^{•+} coincide, see text. $f_{\lambda_{exc}} = 308$ nm (concentrations of $\approx 2 \times 10^{-4}$ mol dm⁻³).



Figure 2. Formation and decay of ΔA at 325 nm (mainly M⁺⁺), at 455 nm (partly HM⁺), and at 700 nm (essentially e_{aq}^{-}), using *trans*-4,4'-DPE (a) in argon-saturated aqueous solution at pH 7; (b) corresponding signals in the presence of ~10% N₂O; λ_{exc} = 248 nm.

to be OH adduct radicals (M°OH) and a proton (Scheme I). Calibration against e_{aq} as internal standard gives $\epsilon_{325} \approx 3.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. T_{325} was also detected in neutral aqueous

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Figure 3. ΔA_{700} (full symbols, pulse end), ΔA_{455} (×, 0.1 μ s), and/or ΔA_{500} (open symbols, 10 μ s after the pulse) as a function of the incident laser intensity for *trans*-4,4'-DPE in argon-saturated aqueous solution at (a) pH 11, (b) pH 4.4, and (c) pH 2.5; $\lambda_{exc} = 248$ nm.

solution (Table I), whereas a 325-nm transient is not accessible at pH < 5 due to a red shift of the (ground-state) absorption spectrum.

The assignment to M^{*+} is supported by the result that saturation with N₂O does not markedly affect ΔA_{325} , the transient absorbance at 325 nm (Figure 1b), and the decay (Figure 2b). A radical cation is generally not affected by N₂O. In N₂O-saturated aqueous solution the lifetime of e_{aq}^{-} is reduced to ≈ 4 ns due to reaction 4. The spectra in Figure 1b, c indicate that M^{*+} exhibits a second

$$e_{aq}^{-} + N_2 O + H_2 O \rightarrow OH + OH^{-} + N_2$$
(4)

band around 460 nm that is overlapped by the absorption of T_{455} in water under argon. On the basis of pulse radiolysis measurements one may assume that a part of the remaining spectrum in Figure 1b is due to OH adduct radicals ($\lambda_{max} = 390$ nm); the extinction coefficient ($\epsilon_{390} \le 1 \times 10^4$ dm³ mol⁻¹ cm⁻¹) of M°OH is smaller than that of HM° ($\epsilon_{455} = 4.0 \times 10^4$ dm³ mol⁻¹ cm⁻¹).¹² This is probably the reason that formation of M°OH in the absence of N₂O concomitant with the decay of M°⁺ (Figure 1a) could not be observed.

The decay of e_{aq}^{-} , detected at 700 nm, is accompanied by the growing of ΔA_{455} (essentially owing to the absorption of T_{455} , HM[•]), as shown in Figure 2a for M in argon-saturated aqueous solution at pH 7. From the time dependences it follows that the decay of e_{aq}^{-} parallels the formation of HM[•] in the pH range 7–12, i.e., for neutral M. We therefore propose that HM[•] is formed by one-electron addition followed by reaction with water (eq 5).

$$\mathbf{e}_{aq}^{-} + \mathbf{M} \to [\mathbf{M}^{\bullet-}] \xrightarrow{+\mathbf{H}_2\mathbf{O}, -\mathbf{OH}^{-}} \mathbf{H}\mathbf{M}^{\bullet}$$
(5)

The radical anion $(M^{\bullet-})$ was not detected by our means, even not at pH 14.5. In nonprotic solvents however, $M^{\bullet-}$ has been observed by ESR measurements upon reaction of M with sodium.¹⁹

The rate constant for the reaction of e_{aq} with M is approximately 1.6×10^{10} dm³ mol⁻¹ s⁻¹, a value similar to that found by pulse radiolysis.¹² When N₂O is added in increasing amounts (Figure 2b), the lifetime of e_{aq} is reduced from about 200 to <10 ns and $\Delta A_{455}(1 \ \mu s)$ becomes smaller (by more than a factor of 10), i.e., reactions 4 and 5 are competing processes. The results in Figures 1 and 2 clearly show that T_{455} is formed by electron addition to the substrate, keeping in mind that the absorption spectrum of M^{*+} also has a peak around 460 nm.

Figure 3a shows that formation of e_{aq}^{-} in aqueous solution (pH 6-12) depends linearly on the incident laser intensity (I_L). The quantum yield is estimated to be $\Phi_{e^-} = 0.01$ using a value of $\Phi_{e^-} = 0.29$ for KI as reference.¹⁷ From the linear intensity dependence we suggest that the photoionization of neutral M occurs monophotonically (eq 3). This is different for the singly and doubly protonated substrate (see below). The postulated and observed



Figure 4. Transient absorption spectra in argon-saturated aqueous solution of *trans*-4,4'-DPE ($2 \times 10^{-4} \text{ mol dm}^{-3}$) at pH 7 in the presence of phosphate buffer at 20 ns (—), 100 ns (---), and 2 μ s (---) after the pulse. Inset: pH dependences of ΔA_{455} at 0.1 (\bullet) and 2 μ s (O) and ΔA_{500} at 2 μ s (\Box); $\lambda_{exc} = 248 \text{ nm}$.

intermediates of *trans*-4,4'-DPE in "neat" water at pH 10–12, produced by laser pulse excitation at 248 nm, and the pathways involved are depicted in Scheme I. The intermediacy of a higher excited singlet state ($^{1}M^{*'}$) is assumed because electron ejection does not occur when λ_{exc} is changed to 308 nm (see below).

In buffered aqueous solution at pH 7 the spectra (Figure 4) reveal, apart from e_{aq}^{-} and M^{*+}, two transients: T_{455} (HM^{*}, see above) as precursor and subsequently T_{500} , which was already assigned to the conjugate acid radical H₂M^{*+,12} The decay of HM^{*} parallels the formation of H₂M^{*+} due to equilibrium 2. From the pH dependencies of ΔA_{455} and ΔA_{500} at appropriate time intervals and using buffers in the pH range 5–12, in order to rapidly establish equilibrium 2, two ranges can be distinguished (inset of Figure 4). Above and below pH 9.8 HM^{*} (ΔA_{455} at 2 μ s) and H₂M^{*+} (ΔA_{500} at 2 μ s) are the main transients, respectively. In the absence of buffers establishment of the acid-base equilibrium is not fast enough compared to the bimolecular decay of HM^{*}.

Transients in Acidic Aqueous Solution from 248-nm Excitation. At pH 4-5, where the substrate is singly protonated, one of the initial transients is again e_{aq} . Its intensity dependence is nonlinear (Figure 3b), indicating that the main portion of e_{aq} is formed by a biphotonic absorption step (eq 6). The radical cation

$$HM^{+} \xrightarrow{2h\nu} e_{aq}^{-} + [HM^{\cdot 2+}]$$
 (6)

could not be observed, but T_{500} was major long-lived transient. H₂M^{•+} is suggested to be formed by reaction 7.¹² The intensity

$$e_{aq}^{-} + HM^{+} \rightarrow HM^{\bullet} \xrightarrow{H^{+}} H_{2}M^{\bullet+}$$
(7)

dependence of T_{500} , if generated via reaction 7, also is not linear (Figure 3b), and ΔA_{500} is proportional to $I_{\rm L}^2$ rather than to $I_{\rm L}$.

In the acidic pH range reaction 7 competes with neutralization

$$e_{aq}^{-} + H^{+} \rightarrow H^{\bullet}$$
 (8)

Formation of H_2M^{*+} via e_{aq}^- as precursor was ascertained by saturation with N₂O at pH 3-5; here, the lifetime of e_{aq}^- which is already reduced in the absence of N₂O by reaction with H⁺ (eq 8), is further reduced (\leq pulse width). As consequence ΔA_{500} is about 10 times smaller than under argon.

 H_2M^{*+} was also detected in argon-saturated solution at pH 2-3, where the substrate is doubly protonated (Table I). Involvement of e_{aq^-} in the formation of H_2M^{*+} is indicated by a smaller ΔA_{500} value in the presence than in the absence of N₂O. Formation of H_2M^{*+} from the doubly protonated form is described by electron ejection followed by eqs 8 and 9. At pH <3 e_{aq}^- is not observable

$$H^{\bullet} + H_2 M^{2+} \rightarrow H_2 M^{\bullet+} + H^+$$
 (9)

because reaction 8 is faster than 10 ns. Formation of H_2M^{++} from



Figure 5. Transient absorption spectra in argon-saturated aqueous solution of *trans*-4,4'-DPE at pH 2, 0.2 (O, T_{400}) and 3 μ s (\bullet) after the pulse, and ground-state absorption prior to ($A_{308} = 1.5$) and after 1, 3, and 10 pulses. Insets: kinetics at 300 and 400 nm; $\lambda_{exc} = 308$.



Figure 6. Semilogarithmic plots of the rate constants for decay from optical detection (O) and conductivity (Δ) as a function of pH for *trans*-4,4'-DPE in argon-saturated aqueous solution; $\lambda_{exc} = 308$ nm. Insets: transient absorption (a, b) and conductivity (c, d) at pH 1.8 (a, c) and pH 3.2 (b, d).

 H_2M^{2+} is in agreement with a biphotonic absorption step since the intensity dependence (Figure 3c) is analogous to the case of HM⁺ but different from the monophotonic ionization of M (Figure 3a).

Apart from the photochemical formation of the radical cations, laser flash photolysis (using $\lambda_{exc} = 248$ nm) and pulse radiolysis (in the absence of OH radicals) should give the same transients. In fact, the same absorption spectra were recorded by both methods, either at pH >8 (compare Figure 1a of this with Figure 1a of the preceding paper¹²) or at pH 4–6. Formation of the two radicals HM[•] and H₂M^{•+}, when initiated by e_{aq}^- is illustrated in Scheme I of ref 12.

Transients in Aqueous Solution from 308-nm Excitation. Virtually no transient was recorded for trans-4,4'-DPE ((1-3) × 10⁻⁴ mol dm⁻³) in aqueous solution at pH 5-10 when λ_{exc} was changed to 308 nm. In particular e_{aq}^{-} could not be detected. This is further support for the above-discussed involvement of e_{aq}^{-} in the formation of radical HM[•] and its conjugate acid. At pH ≤ 4 however, a new transient (denoted T_{400}) appears. Its absorption spectrum shows $\lambda_{max} \approx 400$ nm and extends to about 500 nm, whereas in the 270-340-nm range a bleaching of the ground-state absorption dominates (Figure 5). The kinetics at 300 and 400 nm are identical (inset of Figure 5).

 T_{400} is formed within the laser pulse width, and its yield depends linearly on $I_{\rm L}$. It is the only transient in aqueous solution at pH <4 when ionization is avoided (Table I). The rate constant for decay of T_{400} (k_{400}) depends strongly on the pH but not on the



Figure 7. Plots of ΔA_{400} (O), the amplitude of $\Delta \kappa$ (Δ) (both at <0.1 μ s after the pulse), and the relative quantum yield for chromophore loss at 300 nm (\Box) as a function of pH for *trans*-4,4'-DPE in argon-saturated (neat) aqueous solution; $\lambda_{exc} = 308$ nm. Inset: transient absorption spectra in 2-propanol/water (1:9) at pH 1 at 50 ns (-) and 0.1 ms (---) after the pulse; $\lambda_{exc} = 248$ nm (note: T_{400} is not the precursor of T_{500}).

oxygen concentration. This inertness against oxygen (e.g., at pH 3-4) indicates that T_{400} is not a radical. The dependence of log k_{400} on pH and examples for the first-order decay kinetics at pH 1.8 and 3.2 are shown in Figure 6. From the linear plot of log k_{400} vs log [H⁺], the rate constant for protonation of T_{400} was determined, $k_{10b} = 7 \times 10^7$ dm³ mol⁻¹ s⁻¹.

Under these conditions, a search for laser-induced conductivity was successful. The buildup and decay of the conductivity signal are very similar to those of T_{400} in the following: First, a substantial conductivity increase at the pulse end was found only at pH <4. The amplitude of $\Delta \kappa$ increases with decreasing pH, the inflection point is at 3.6 (Figure 7). Second, the increase is faster than 50 ns, as shown in Figure 6. Third, the decay of $\Delta \kappa$ follows first-order kinetics. Finally, the rate constant exhibits the same pH dependence as does k_{400} (Figure 6). This is strong evidence for the proton being responsible for the $\Delta \kappa$ changes. H⁺ is suggested to be formed within the laser pulse width and to disappear by reaction with T_{400} . Formation of a proton necessitates the assumption of T_{400} being a monocation. We assign T_{400} to the photohydroxide with the structure



To account for the findings, the two-step reaction 10 is proposed. Since for the doubly protonated molecule n,π^* states are not

$${}^{1*}(H_2M^{2+})_{\pi,\pi} + H_2O \rightarrow H_2M^+OH + H^+$$
 (10a)

$$H_2M^+OH + H^+ \rightarrow H_3M^{2+}OH$$
(10b)

present, reaction with water should involve the $l(\pi,\pi^*)$ state. The stable photoproduct is the photohydrate with the structure



An analogous intermediate with $\lambda_{max} = 440$ nm has apparently been observed by Whitten et al. upon flash photolysis of Me₂M²⁺ in aqueous solution.⁶ The early assignment to a photohydroxide (Me₂M⁺OH) was based on the structure of the photohydrate as the only photoproduct, and protonation of the photohydroxide had to be assumed.

Our results lend experimental evidence to the nonradical and monocationic nature of H_2M^+OH . In particular we have directly demonstrated the protonation of the photohydroxide at carbon

SCHEME II: Formation and Decay of Transients from trans-4,4'-DPE in 2-Propanol/Water Mixtures Excluding Photoionization



and measured the rate constant, which is less than diffusion controlled, as usually found for this type of process.²⁰ As to the structure of the photohydroxide we refer to photolysis experiments with D_2M^{2+} in acidic D_2O solution and NMR analysis.²¹ These measurements led to $D^+(4-Py)CDHCHOD(4-Py)D^+$, thereby excluding other alternatives for the structure of H_2M^+OH .

 T_{400} and the proton are the initial products (eq 10a), which both disappear afterward (eq 10b). Steady-state irradiation at 313 nm (results not shown) or pulsed laser excitation at 308 nm (Figure 5) both lead to chromophore loss around 300 nm mainly in the acid range. The relative quantum yield for this process, being in competition with trans \rightarrow cis photoisomerization, increases with decreasing pH and shows an inflection point at 3.6 (Figure 7). These findings are in agreement with eqs 10a and 10b. These reactions are further supported by results obtained in mixtures of water with 2-propanol (see below) since proton formation is paralleled by the decrease in the yield of H_2M^{*+} due to a change in the mechanism from H-atom abstraction to electrophilic behavior (reaction 10).

Radicals and Radical Ions Obtained from M in 2-Propanol-/Water Mixtures. On addition of 2-propanol to aqueous solution of M at pH >10, ΔA_{455} increases significantly when excited at 248 nm. The spectrum of the transient is the same in mixtures of water with 2-propanol or methanol (Table I). The increase in the yield of HM[•] on addition of 10 and 50% (v/v) 2-propanol to (neutral) water is about 3- and 5-fold, respectively. This suggests that in the presence of these alcohols (>1%) an additional photochemical pathway leads to HM[•]. The photochemical formation of HM[•] occurs also when $\lambda_{exc} = 308$ nm is used (see below); under these conditions e_{aq}^- is not formed in a measurable yield. The main difference between the two excitation wavelengths is the mixed pathway for generation of HM[•] and H₂M^{•2+} with $\lambda_{exc} = 248$ nm and the nonoccurrence of the route via e_{aq}^- with $\lambda_{exc} = 308$ nm.

 $\lambda_{exc}^{cnc} = 308$ nm. The reactions of excited M, HM⁺, and H₂M²⁺ in 2propanol/water, not involving the solvated electron, are summarized in Scheme II. Apart from H₂M⁺OH, the transients under these conditions are HM[•] and H₂M^{•+}. Their relative yields with $\lambda_{exc} = 308$ nm in 2-propanol/water mixtures (1:9 and 1:1) in the presence of buffers are shown in parts a and b of Figure 8, respectively. The rate of formation of H₂M⁺⁺ from HM[•] is significantly enhanced by buffers. While $\Delta A_{455}(20 \text{ ns})$ shows no pH dependence in the range 6–12, $\Delta A_{500}(1 \ \mu s)$ increases on going from pH 12 to 8 and remains constant for a wide range. $\Delta A_{455}(1 \ \mu s)$ decreases correspondingly; one has to take into account that T_{500}



Figure 8. Dependencies of ΔA_{455} at 20 ns (\bullet) and 1 μ s (O) after the pulse and ΔA_{500} (\Box , 1 μ s) in the presence of Titrisol buffers and conductivity amplitude (Δ , 10 μ s, no buffers) as a function of the pH for *trans*-4,4'-DPE (3 × 10⁻⁵ mol dm⁻³) in argon-saturated 2-propanol/water mixtures (a) 1:9 and (b) 1:1; $\lambda_{exc} = 308$ nm.

absorbs also at 455 nm ($\approx 20\%$ of ΔA_{500}^{max}). Equilibrium 2 accounts for the pH dependences of ΔA_{455} and ΔA_{500} at the appropriate time intervals after the laser pulse. We concur with previous conclusions for the case of neat 2-propanol (H₂R)¹⁰ that HM[•] is formed via eq 11 also in mixtures with neutral or basic aqueous solution.

$$M \xrightarrow{h\nu} {}^{1*}M_{\pi,\pi} \xrightarrow{} {}^{1*}M_{n,\pi} \xrightarrow{+H_2R, -HR^*} HM^*$$
(11)

The conjugate acid H_2M^{*+} (T_{500}) was recorded as a second, longer lived transient after the decay of HM^{*}. The rate constant for quenching of H_2M^{*+} by oxygen was determined to be 8×10^7 dm³ mol⁻¹ s⁻¹ in the 1:1 mixture, i.e., well below the diffusioncontrolled limit. The corresponding value for HM^{*} in 2-propanol is 3×10^8 dm³ mol⁻¹ s⁻¹.¹⁰ The rate constant for reaction 2, obtained from both the decay of HM^{*} and formation of H_2M^{*+} , is $k_2 \approx 1 \times 10^6$ s⁻¹ in 2-propanol/water (1:9) at pH 6. With this and $pK_a = 9.8$ it follows that the deprotonation is diffusion controlled ($k_{-2} \approx 1.8 \times 10^{10}$ dm³ mol⁻¹ s⁻¹), in accord with the general expectation. The pK_a value is shifted from about 9.8 (Figure 8a and ref 12) to about 9.1 in the 1:1 mixture (Figure 8b). It should be mentioned that the two pK_a values of the *trans*-4,4'-DPE ground state in the 1:1 mixture also shifted to lower pH values, 4.7 and 3.0, respectively.

The effect of pH on ΔA_{455} and ΔA_{500} (\approx maximum formation) in the 1:1 mixture using $\lambda_{exc} = 248$ nm is shown in Figure 9. In the pH range above 6 ΔA_{455} remains constant for few 100 ns, and

⁽²⁰⁾ Perrin, D. D.; Dempsey, B.; Serjeant, E. P. In pK, Prediction for Organic Acids and Bases; Chapman and Hall: London, 1981.

⁽²¹⁾ Koltzenburg, G. Private communication.



Figure 9. Dependencies of ΔA_{455} (\bullet , at 20 ns) and ΔA_{500} (\blacksquare , +, and \square at 20 ns, 2 μ s, and 20 μ s after the pulse, respectively) as a function of the pH for *trans*-4,4'-DPE (8×10^{-5} mol dm⁻³) in argon-saturated 2-propanol/water mixtures (1:1) (a) in the absence of buffers and (b) in presence of phosphate buffers; $\lambda_{exc} = 248$ nm.

at longer times (1-50 μ s after the pulse) HM[•] equilibrates only partially with H₂M^{•+}. From the optical detection in the absence of buffers (Figure 9a) it follows that formation of H₂M^{•+} is incomplete in the pH range 5-9 because it probably competes with other deactivation processes of HM[•] (e.g., bimolecular decay). From pulse radiolysis it follows that HR[•] does not react with neutral M.¹² When the pH is decreased from 10 to 7, ΔA_{500} (20 μ s after the pulse) increases steadily, steeply around 5, and passes through a maximum (Figure 9a). Here further reactions of HM⁺ and H₂M²⁺ have to be considered.

Radicals and Radical Ions in Mixtures of 2-Propanol with Acidic Water. Around pH 4, where the substrate is mainly present as HM⁺, both HM[•] and H₂M^{•+} are formed within less than 0.1 μ s; the absorption of HM[•] at 455 nm is overlapped by that of H₂M^{•+} (Table I), which also absorbs at this wavelength ($\approx 20\%$ of ΔA_{500}).¹² Photochemical formation of H₂M^{•+} from HM⁺ is partly described by eq 12 (for an additional pathway see below).

$$HM^+ \xrightarrow{h\nu} {}^{1^{\bullet}}(HM^+)_{\pi,\pi} \rightarrow {}^{1^{\bullet}}(HM^+)_{n,\pi} \xrightarrow{+H_2R, -HR^*} H_2M^{*+} (12)$$

The H-atom transfer reaction via eq 12 involves the ${}^{1}(n,\pi^{*})$ state of HM⁺, in analogy to the ${}^{1}(n,\pi^{*})$ state of the neutral substrate.¹⁰ Photoreactions 11 and 12 are monophotonic using either 248 or 308 nm. Formation of radicals involving photoionization, e.g., via reaction 7, using $\lambda_{exc} = 248$ nm is probably negligible. This is concluded from the result that $\Delta A_{455}(20 \text{ ns})$ is not discernibly reduced by N₂O saturation. However, there is the possibility of a photochemical route from HM⁺ to HM^{*}, e.g., via ${}^{1^{\circ}}(HM^+)$ and deprotonation. This is not excluded since the yield of $\Delta A_{455}(20 \text{ ns})$ is not zero at pH 4 (Figure 9a).

The markedly larger increase in ΔA_{500} after maximum formation ($\approx 20 \ \mu s$) at pH 3.5-4.5, compared to the initial ΔA_{455} values in the neutral and basic range (Figure 9a), is ascribed to reaction 13 of the 2-hydroxy-2-propyl radical (HR[•]) with HM⁺.

$$HR^{\bullet} + HM^{+} \longrightarrow R + H_{2}M^{\bullet+}$$
(13)

Reaction 13 with R = acetone was already used to account for the pulse radiolysis results in the presence of 2-propanol (in small amount) under N₂O.¹² The larger increase of ΔA_{500} between 20 ns and 20 μ s compared to the initial value indicates that the quantum yield for eq 12 is probably smaller than that for reaction 11. Photolytic formation of HM[•] and H₂M^{•+} is confirmed by preliminary ESR measurements; a radical was detected in neat 2-propanol and a different radical in 2-propanol/water mixtures (1:9 and 1:1) at pH 2-4.²² Coupling constants have already been reported in the literature.⁷

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For H_2M^{2+} there is no n,π^* state available. In fact, H_2M^{*+} could not be detected in the strongly acidic range by using λ_{exc} = 308 nm. The inflection points of its yield are about 3.6 and 3.0 in 1:9 and 1:1 mixtures, respectively (Figure 8). The main transient is H_2M^+OH as in the absence of 2-propanol (see Figure 7). This is confirmed by conductivity measurements in 2-propanol/water in the absence of buffers (Figure 8). At pH 5-10 only a small Δx value was observed after the laser pulse. However, on decreasing the pH below 4, the amplitude, measured 10 μ s after the pulse, increases by more than a factor of 10. At pH 2 not only the amplitude of the conductivity signal but also the half-life of decay is affected: $t_{1/2}$ is reduced on increasing [H⁺], and below pH 2 $t_{1/2}$ becomes 5-10 μ s (limit of resolution of the ac bridge). Formation of the photoalkoxide (H_2M^+OR with $R = OCH-(CH_3)_2$), as in the case of Me2 M^{2+} , 6 is also conceivable.

A small contribution of e_{aq} via reaction 8 even in the 1:1 mixture is indicated by the formation of H₂M^{*+} below pH 3 (Figure 9). The absorption spectrum at pH 1 reveals the short-lived T_{400} transient (H₂M⁺OH) and the longer lived H₂M⁺⁺ radical (inset of Figure 7 and Table I). T_{400} is not the precursor of T_{500} since the rate constants for the decay at 400 nm and formation at 500 nm are not coupled. An alternative to account for the formation of H_2M^{*+} at pH <3.6 could be that ${}^{1*}(H_2M^{2+})$ reacts with 2-propanol by an overall electron-transfer reaction in which course a proton is released. Indeed, proton formation is envisaged by results from the transient conductivity measurements (the pH dependence is similar to that shown in Figure 8b). A second possibility could be that the excited singlet state first deprotonates and that H₂M^{*+} is then generated from ^{1*}(HM⁺) by H-atom abstraction from the alcohol (eq 12). However, $H_2M^{\bullet+}$ could not be detected when photoionization was avoided (λ_{exc} = 308 nm, see above). This strongly suggests the involvement of e_{ao} in a minor biphotonic route also in the presence of 2-propanol and excludes the above two possibilities, which should be independent of the excitation wavelength. Formation of H_2M^{++} at pH <3 in the presence of alcohols using $\lambda_{exc} = 248$ nm is therefore explained by electron ejection as the initial step followed by eqs 8 and 9 rather than H-atom abstraction from the alcohol.

2,2'- and 3,3'-DPE. Concerning trans-2,2'-DPE and trans-3,3'-DPE, it has recently been shown that the yield of formation of the radical in neat 2-propanol is smaller than 10% of that for 4,4'-DPE.¹⁰ Also the yield of electron ejection and formation of HM^{*} type radicals in aqueous solution (Table I) is significantly smaller. Thus, both isomers could not be subjected to a detailed study.

Conclusion

Monophotonic photoionization of trans-4,4'-DPE in "neat" aqueous solution at pH > 7 yields the radical cation and the hydrated electron. M^{•+} reacts with water to give M[•]OH and a proton, and e_{aq} eventually reacts with a second neutral molecule M, thereby forming the H adduct radical HM[•] (Scheme I). H_2M^{*+} , the conjugate acid of HM^{*}, is produced (i) by one-electron reduction of M, followed by double protonation via reaction with water and a proton (eqs 5 and 2), (ii) by one-electron reduction of HM⁺ followed by protonation (eq 7), and (iii) by reaction of H_2M^{2+} with hydrogen (eq 9). In 2-propanol/water mixtures at pH >3 HM[•] and H_2M^{++} are produced mainly via H-atom abstraction from the alcohol involving excited n,π singlet states (Scheme II). H_2M^{++} is also formed by reaction 13 of the 2hydroxy-2-propyl radical with HM⁺. In the acidic pH regime the photohydroxide is formed as major intermediate by a reaction of ${}^{16}(H_2M^{2+})$ with water (eq 10a); protonation leads to the stable photohydrate (eq 10b).

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