# Laser Flash Photolysis Study of the Effects of Substituents, Solvents, and Quenchers on the Triplet State of Benzaldehydes. H/D Exchange Following Quenching by $D_2O$

Helmut Görner\* and Hans Jochen Kuhn

Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a. d. Ruhr, West Germany (Received: February 18, 1986)

The deactivation pathways of the lowest triplet state of benzaldehyde (BA), a series of substituted derivatives (OCH<sub>3</sub>, CH<sub>3</sub>, F, Cl, Br, CHO, and CN), and some related aromatic aldehydes were examined at room temperature by laser flash photolysis in several solvents including water. The triplet state ( $\lambda_{max} = 325$  nm for BA in acetonitrile) was identified by energy-transfer measurements. All benzaldehydes studied exhibit phosphorescence in glassy media, but only some of them in fluid acetonitrile. Triplet deactivation in the presence of alcohols (rate constant for triplet BA in acetonitrile with 2-propanol:  $3.6 \times 10^7 \, \text{M}^{-1}$  $s^{-1}$ ) includes H-atom abstraction and formation of the  $\alpha$ -hydroxybenzyl radical and/or the corresponding radical anion, depending on the pH. The rate constant for self-quenching is below the diffusion-controlled limit (BA:  $<1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). Triplet quenching by (heavy) water was observed for the benzaldehydes whose lowest triplet has  $n,\pi^*$  character. This quenching reaction does not lead to  $\alpha$ -hydroxybenzyl free radicals. On increasing the [H<sub>2</sub>O]/[CH<sub>3</sub>CN] ratio the triplet lifetime (BA: 1.5 µs in acetonitrile, 60 ns in water) passes through a minimum. This indicates a relative stabilization of the triplet toward quenching by (heavy) water (>10 M) and is in accord with the assumption of an enhanced  $\pi,\pi^*$  character of the lowest triplet in water. The apparent quenching constant ( $k_{obsd}/[H_2O]$ ), which remains unchanged only between about 1 and 20% water content (BA:  $3.0 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>), shows an increasing trend for benzaldehydes with electron-withdrawing substituents and a decreasing trend with electron-donating substituents. Triplet quenching of benzaldehydes by  $D_2O$  leads to H/D exchange at the formyl group. A new pathway for the photodeuteriation is considered which by passes the classical benzoyl- $\alpha$ -hydroxybenzyl radical pair.

## Introduction

The photochemical reduction of aromatic ketones in solution is well documented.<sup>1-4</sup> A key reaction is hydrogen abstraction of the ketone in the  $n,\pi^*$  triplet state from another ketone molecule, the solvent, an additive, or intramolecularly. For benzophenone, acetophenone, and valerophenone as well as for benzaldehyde (BA) corresponding H-abstraction reactions have been studied by using flash photolysis,<sup>4-10</sup> pulse radiolysis,<sup>11,12</sup> ESR,<sup>13</sup> CIDNP,<sup>13,14</sup> and steady-state techniques.<sup>15</sup> As a consequence of the high reactivity of the  ${}^{3}(n,\pi^{*})$  state of ketones, the triplet lifetime is rather short at ambient temperature and the quantum yield of phosphorescence is small. In water, classified as "relatively inert" solvent,6 the triplet reactivity is generally lower than in many organic solvents.<sup>6,9</sup> Porter et al. have discussed the formation of the diphenylhydroxymethyl radical as a result of H abstraction from water by the benzophenone triplet.<sup>6</sup>

For BA in the presence of  $D_2O$  a mechanism has recently been

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suggested in which the  $\alpha$ -hydroxybenzyl radical [we prefer to use the term  $\alpha$ -hydroxybenzyl radical rather than ketyl radical, in agreement with the IUPAC nomenclature], formed by reaction of <sup>3</sup>BA\* with ground-state BA (self-quenching), undergoes H/D exchange at the hydroxyl group; subsequent disproportionation with the benzoyl radical leads to formyl-deuteriated BA ( $BA_D$ ).<sup>16,17</sup> Photodeuteriation of BA occurs in  $D_2O$  or in mixtures of  $D_2O$ with acetone or acetonitrile. In turn, D/H exchange occurs with  $BA_D$  in solutions containing  $H_2O^{17}$  The quantum yields ( $\phi_D$  and  $\phi_{\rm H}$ ) range from 0.4 to 0.9 ( $\lambda_{\rm irr}$  = 313-366 nm). From a study of a series of substituted BA's and analogues in acetone/ $D_2O(3:1)$ it has been inferred that  $\phi_D$  is substantial when the lowest triplet has mainly  $n, \pi^*$  character.<sup>17</sup> From phosphorescence studies with BA's in condensed phase it is known that the nature of the emitting triplet state may be changed from a  ${}^{3}(n,\pi^{*})$  to a  ${}^{3}(\pi,\pi^{*})$  state by introduction of a suitable substituent and/or by variation of the solvent properties (e.g., polarity).18-26

The present work is an attempt to understand more clearly the reactions the lowest triplet state of BA's can undergo and, in particular, the mechanism of photodeuteriation. So far, the phosphorescence of BA's, mainly in glassy media,<sup>19-26</sup> and some properties of BA<sup>5,12-14,27,28</sup> and its derivatives<sup>29-34</sup> have been studied

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### Triplet State of Benzaldehydes

but little is known about the photophysical features and photochemical reactions of substituted BA's.<sup>17</sup> We have studied some spectroscopic and kinetic properties of the initially formed triplet and the subsequently formed transients by laser flash photolysis in several solvents. As a measure for the reactivity of this triplet, the rate constant for quenching by 2-propanol was determined for BA's in acetonitrile solution.

Since the rate constant for self-quenching of the BA's was found to be relatively low, we have to postulate a new pathway for photodeuteriation of BA's involving triplet quenching by  $D_2O_1$ in addition to the known radical pair mechanism.<sup>17</sup> An analogous quenching reaction of aromatic ketone triplets by H<sub>2</sub>O or D<sub>2</sub>O has not been reported so far. In addition to the series of 2-, 3-, and 4-substituted BA's some other aromatic aldehydes (e.g., pyridine-, naphth-, fluorene-, and anthraldehydes) were also studied.

#### **Experimental Section**

The laser flash photolysis apparatus has been described elsewhere.<sup>35,36</sup> It was also used to measure the phosphorescence decay. Unless otherwise indicated an excimer laser (Lambda Physik, EMG 200; energy 30-500 mJ, pulse width 20 ns) was used for excitation at 248 nm. The energy was reduced either by quartz plates or by wire-mesh filters to values typically below 10 mJ (up to 50 mJ for photoionization measurements). Phosphorescence decay was observed after laser excitation using a glass fiber between the cell and the monochromator and cutoff filters. Due to the extremely weak phosphorescence signal and the relatively large scattering signal during the pulse, distortion of the phosphorescence decay even after a few hundred nanoseconds could not be completely avoided. Therefore,  $\tau_p$  in Table II should be regarded as a lower limiting value.

For a few studies (e.g., in acetone or for sensitized excitation) the third harmonic (353 nm) of a Nd laser (J.K. Lasers) was used.<sup>35</sup> Data acquisition and analysis were carried out on a transient digitizer (Tektronix 7912 AD) attached to a computer (PDP 11/34). The conductivity cell (Suprasil, flow system) in which two platinum electrodes were placed with a 6-mm separation (area  $5 \times 5 \text{ mm}^2$ ) was shielded by a metal housing to reduce electromagnetic noise from the laser discharge. The conductivity change, applying a dc voltage of up to 200 V, was monitored with the transient digitizer (time resolution of 20 ns). The samples were freshly prepared and purged with argon for at least 10 min (water: 30 min) before flashing and also during the measurements unless otherwise indicated. Typical concentrations for excitation at 248 nm were  $(1-5) \times 10^{-4}$  M. Unless otherwise indicated (e.g., phosphorescence and T-T absorption at -196 °C) the measurements were carried out at  $24 \pm 2$  °C. The experimental error is  $\pm 2$  ( $\pm 5$ ) nm for phosphorescence (absorption) maxima,  $\pm 40\%$ for Stern-Volmer constants from phosphorescence quenching,  $\pm 20\%$  for lifetimes (absorption), and  $\pm 30\%$  for quenching rate constants unless specified otherwise.

The steady-state emission spectra were recorded on two spectrofluorimeters (Perkin-Elmer LS 5 for quenching measurements and Spex-Fluorolog for corrected spectra) and the absorption spectra on a Perkin-Elmer 554.<sup>35</sup> For BA in acetonitrile the phosphorescence excitation spectrum (uncorrected) was found to be in agreement with the absorption spectrum. The absorbance was adjusted to 0.1–0.4 at  $\lambda_{exc}$  (1 cm cell length), corresponding to [BA] of typically  $(1-6) \times 10^{-5}$  M. The Stern-Volmer dependence was obtained from the phosphorescence spectra (quenching up to about 80%) in argon-saturated acetonitrile solutions.

For continuous irradiation at wavelengths longer than 300 nm or at 254 nm an electronically integrating actinometer with a



Figure 1. Absorption and emission spectra of BA in acetonitrile (full lines) and water at 24 °C (dashed lines), and in ethanol at -196 °C (dotted line).

1000-W Hg-Xe high-pressure lamp<sup>17</sup> or a low-pressure mercury lamp (Gräntzel, 250 mA, Vycor filter), respectively, were used. BA/BA<sub>D</sub> analysis was carried out by GC either after extraction by dichloromethane (continuous irradiations)<sup>17</sup> or directly (flashed solutions).

The benzaldehydes and the polycyclic aromatic analogues were the same as in previous work.<sup>17</sup> Additionally, 4-carboxybenzaldehyde (EGA) and 9-phenanthraldehyde (EGA) were used. Mono- and dideuteriation of terephthal- and isophthalaldehyde were established by GC/MS analysis. Xanthone (EGA) and 1,3-cyclohexadiene (EGA) were used as received, naphthalene (Merck) was zone-refined, and 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich) was purified by sublimation. The quality of solvents (Merck) was z.A. (ethylene glycol, 2-propanol, ethanol, dichloromethane, cyclohexane) or Uvasol (acetone, acetonitrile, deuterium oxide, 99.9%); methanol and butyronitrile were purified by distillation; water was tridest (continuous irradiations) or from a Milli-Q reagent water system (Millipore). Solvent mixtures are given as volume ratios (before mixing).

#### Results

Absorption and Phosphorescence. The absorption spectra of BA in acetonitrile and aqueous solutions exhibit significant differences (Figure 1). The maxima, 243, 280, and 323 nm in acetonitrile, are less pronounced in water (pH  $\approx$  6) and red-shifted for the first (248 nm) and blue-shifted for the third maximum (cf. the case of benzophenone).<sup>6</sup> Analogous shifts were observed for  $4-R = CH_3$ , F, Cl, and Br.

No emission could be detected (at wavelengths longer than 400 nm) for BA in water and in 2-propanol at 24 °C ( $\lambda_{exc} = 230-330$ nm). However, in glassy ethanol at -196 °C BA (3 × 10<sup>-5</sup> M,  $\lambda_{\text{exc}} = 250 \text{ nm}$ ) exhibits the well-known phosphorescence spectrum<sup>19-22</sup> (Figure 1 and Table I). Very similar emission spectra appear in 2,2-dimethylbutane/n-pentane (8:3), butyronitrile, and ethylene glycol/water (2:1) at -196 °C as well as in argon-saturated acetonitrile solution at 25 °C. The spectrum influid solution is less structured and shows emission also in the range  $\lambda < 390$ nm. This emission may be due to fluorescence (either of BA or of traces of impurities) since the quantum yield of phosphorescence at 24 °C is very small (<3  $\times$  10<sup>-4</sup> for the BA's throughout). Similar spectra, in some cases (e.g., 4-CN-BA) with a small red shift, were recorded for several substituted BA's (Table I). No phosphorescence could be recorded for some BA's (e.g., the three Br-BA's, 4-OCH<sub>3</sub>-BA) at 24 °C and for 4-NO<sub>2</sub>-BA at either temperature, -196 and 24 °C.

Addition of water to acetonitrile solution at 24 °C reduces the phosphorescence intensity  $(I_p)$  of BA at 430 nm significantly; 5%  $H_2O$  is sufficient to suppress  $I_p$  below the tail of the shortwavelength emission. From a plot of  $I_p^0/I_p$  vs. [H<sub>2</sub>O] (Figure 2) a Stern–Volmer constant  $(K_{\rm H_{2}O})$  of about 2 M<sup>-1</sup> was estimated. This corresponds to  $k_{\rm H_{2}O} = 1.7 \times 10^6 \,\mathrm{M^{-1} \, s^{-1}}$  (in the range [H<sub>2</sub>O] < 2 M) with a phosphorescence lifetime ( $\tau_p$ ) of 1.2  $\mu$ s, as observed around 430 nm on laser excitation (Table II). Within experi-

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**Figure 2.** Stern–Volmer plots of phosphorescence quenching of BA by H<sub>2</sub>O (open symbols) and 2-propanol (full symbols) in acetonitrile:  $\tau_T$  (O,  $\bullet$ ),  $\tau_p$  ( $\Box$ ), and  $I_p$  ( $\Delta$ ). Inset: time dependence of triplet-triplet absorption and phosphorescence in the absence of additives.



Figure 3. Transient absorption spectra in acetonitrile solution (a) for BA 50 ns (O) and 5  $\mu$ s ( $\bullet$ ) after the pulse; (b) for 4-R = CN (O), CH<sub>3</sub> ( $\blacksquare$ ), and OCH<sub>3</sub> ( $\Delta$ ) 50 ns after the pulse.

mental error the same value was estimated from the reduction of  $\tau_p$  by water. Where phosphorescence at ambient temperature was detected, the Stern-Volmer constants for quenching by 2propanol are larger (by a factor of >10) than those for quenching by water; the latter values show an increasing trend when the substituent becomes a stronger electron acceptor (Table I). In oxygen-saturated acetonitrile solution both,  $\tau_p$  and  $I_p$  are reduced by a factor of more than 5.

Transients from BA and Related Compounds in Acetonitrile. On excitation ( $\lambda_{exc} = 248$  nm) of BA ([1-5] × 10<sup>-4</sup> M) in argon-saturated acetonitrile solution at room temperature two transients were observed, a major (short-lived) one (T), and a minor (longer-lived) one  $(T_r)$  which remains after the decay of T (Figure 3a). After subtraction of the transient absorbance ( $\Delta A$ ) of T<sub>r</sub>, the decay of T obeys essentially a first-order law (rate constant:  $k_{obsd}$ ). The lifetime ( $\tau_T = k_{obsd}^{-1}$ ) is approximately 1.5  $\mu$ s and is reduced by oxygen; from (interpolated) linear plots of  $k_{obsd}$  vs. [O<sub>2</sub>] (argon-, air-, and oxygen-saturated solutions) a quenching rate constant of  $k_{ox} = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was obtained. A similar pattern was found for a series of substituted BA's (with the exception of  $4-NO_2-BA$ ). Absorption spectra of the main transient (T) are shown for 4-CN-, 4-CH<sub>3</sub>-, and 4-OCH<sub>3</sub>-BA (Figure 3b). The absorption maximum  $(\lambda_{max})$  is increasingly red-shifted in the order 4-R = CN, H, Cl, CH<sub>3</sub>, Br, and OCH<sub>3</sub> (Table III), and  $\tau_{T}$  is longer than approximately 1  $\mu$ s (Table II). A markedly shorter lifetime for the Br-BA's and the nonoccurrence of phosphorescence may be due to the heavy atom effect. For 2- and 3-substituted BA's  $\tau_{\rm T}$  is significantly shorter and a second maximum was recorded around 280 nm (Figure 4). Quenching by oxygen, with  $k_{ox} = (1-7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , was observed throughout (Table IV). Both T and T<sub>r</sub> were observed for



**Figure 4.** Transient absorption spectra: (a) For 3-Cl-BA and (b) 2-Cl-BA in acetonitrile  $(\bullet)$  and aqueous  $(\Box)$  solution (end of pulse); ground-state absorption spectra, dotted and dashed lines.



**Figure 5.** Transient absorption spectra: (a) for 4-CH<sub>3</sub>-BA in acetonitrile in the presence of 4% 2-propanol 100 ns (O) and 2  $\mu$ s ( $\oplus$ ) after the pulse; inset: oscillograph traces monitored at 280 and 350 nm. (b) For BA (O), 4-R = Cl ( $\oplus$ ), CN ( $\square$ ), and NO<sub>2</sub> ( $\blacktriangle$ ) in 2-propanol solution 50 ns after the pulse.



**Figure 6.** Plots of  $k_{obsd}$  vs. [H<sub>2</sub>O] (in vol %) in acetonitrile solution for BA (O), 4-R = CH<sub>3</sub> ( $\nabla$ , ×10), F ( $\blacksquare$ ), Br ( $\Delta$ ), and CN ( $\bullet$ ).

several BA's; in most cases  $\Delta A(T_r)/\Delta A(T)$  is smaller than 0.05.

The lifetime of T is also reduced on addition of 2-propanol, water, or deuterium oxide (Figure 2). The time-resolved absorption spectrum of 4-CH<sub>3</sub>-BA in acetonitrile/2-propanol (24:1) clearly shows two transients (Figure 5a), namely T and a new (longer-lived) one (K). From a linear plot of  $k_{obsd}$  vs. [2-propanol] (up to values of  $k_{obsd}$  of about  $3 \times 10^7 \text{ s}^{-1}$ ) a slope of  $k_{2.P} = (36 \pm 4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  was obtained for BA. For H<sub>2</sub>O and D<sub>2</sub>O, deviations from linearity were found at below 1% (Figure 2) and above about 20-40% H<sub>2</sub>O or D<sub>2</sub>O (Figures 6 and 7); therefore,

TABLE I: Phosphorescence Maxima of Benzaldehyde and Stern-Volmer Constants for Phosphorescence Quenching by Water<sup>a</sup>

		temp,		
substituent	solvent	°C	$\lambda$ , nm	$K_{\rm H_{2}O},^{b} \rm M^{-1}$
4-0CH <sub>3</sub>	butyronitrile	-196	407, 430, 461 sh	
4-CH3	butyronitrile	-196	403, 430, 456, 484	
5	acetonitrile	25	402, 429, 455	0.4
no (BA)	2,2-dimethylbutane/n-pentane (8:3)	-196	402, 431, 463, 500	
	ethanol	-196	400, 427, 460, 495, 530 sh	
	ethylene glycol/water (2:1)	-196	399, 426, 456, 487	
	butyronitrile	-196	397, 425, 457, 490, 530	
	acetonitrile	25	405, 431, 462, 502 sh	≥2 <sup>c</sup>
4-F	butyronitrile	-196	392, 418, 448, 483, 520	
	acetonitrile	25	402, 427, 456, 495	≥2.6
3-F	ethanol	-196	405, 434, 465, 503	
	acetonitrile	25	410, 430, 470, 508	≥5
2-F	acetonitrile	25	416, 435, 472, 510 sh	≥4
4-C1	butyronitrile	-196	405, 432, 460, 493 sh	
	acetonitrile	25	408, 437, 465, 504	≥3
3-C1	ethanol	-196	405, 434, 465, 503	
	acetonitrile	25	416, 442, 469	≥6
2-C1	butyronitrile	-196	407, 438, 468, 504	
	acetonitrile	25	424, 448 480, 515 sh	≥6 <sup>c</sup>
4-Br	butyronitrile	-196	408, 436, 462, 500 sh	
3-Br	ethanol	-196	406, 432, 465, 503	
2-Br	butyronitrile	-196	408, 436, 467, 503	
4-CHO <sup>d</sup>	butyronitrile	-196	401, 431, 460, 495 sh	
	acetonitrile	25	407, 435, 465	
4-CO <sub>2</sub> H	ethanol	-196	414, 444, 478, 515	
4-CN	butyronitrile	-196	422, 453, 485, 516	
	acetonitrile	25	424, 450, 483, 520	
3-CN	ethanol	-196	406, 435, 466, 504	
	acetonitrile	25	416, 441, 467, 508 sh	≥10

<sup>*a*</sup> In argon- and air-saturated solutions at 24 and -196 °C, respectively.  $\lambda_{exc} = 240-280$  nm, [BA] = (1-8) × 10<sup>-5</sup> M. <sup>*b*</sup> K<sub>H<sub>2</sub>O</sub> obtained for  $I_p^0/I_p$  = 2. <sup>*c*</sup> Smaller K<sub>H<sub>2</sub>O</sub> values with  $\lambda_{exc} = 320-350$  nm are in agreement with contribution of self-quenching. <sup>*d*</sup> E<sub>T</sub> seems to be higher than reported in ref 21 and 25.

TABLE II: Lifetime of the Triplet State (T and  $T_{H_2O}$ ) of Benzaldehydes in Several Solvents<sup>a</sup>

TABLE III:	Absorption	Maxima	of the	Triplet	State (T	' and	T <sub>H2O</sub> )	of
Benzaldehvde	s in Several	Solvents	a				-	

		$ au_{\mathrm{T}}^{,b}$	μs		
substituent	CH <sub>3</sub> CN	CH <sub>3</sub> COCH <sub>3</sub> <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O	D <sub>2</sub> O
4-OCH <sub>3</sub>	3		>1	3	1.6
4-CH <sub>3</sub>	3 (≥0.8)	0.4	0.6	2	1.2
no (BA)	1.5 (≥1.2)		0.5	0.06	0.10
no (BA <sub>D</sub> )	0.9	0.2		0.09	0.2
4-F	2 (≥1.3)	0.1	0.3	0.12	0.2
3-F	0.8			0.04	0.06
2-F	0.8			0.03	
4-Cl	3 (≥1)	0.6	1.3	0.4	0.7
3-Cl	0.7			0.06	
2-Cl	0.7			0.02	
4-Br	0.09	0.05	0.1	0.2	0.3
3-Br	0.2			0.03	
2-Br	0.08			0.03	
4-CHO	2 (≥0.5)		1	0.04	
3-CHO	2			0.03	
4-CO <sub>2</sub> H	1			0.04	
4-CN	1	0.05	2	d	
3-CN	≤2 (≥0.3)			d	

<sup>a</sup> In argon-saturated solutions at 24 °C, water: pH 5-8, [BA] =  $(1-5) \times 10^{-4}$  M, obtained from triplet-triplet absorption unless indicated otherwise. <sup>b</sup> Values in parentheses ( $\tau_p$ ) were obtained from phosphorescence decay at 430-470 nm. <sup>c</sup> $\lambda_{exc}$  = 353 nm, [BA] =  $((0.3-3) \times 10^{-2}$  M. <sup>d</sup>No triplet observable.

the quenching rate constants were calculated from the linear parts  $[k_{\rm H_2O} = (3.0 \pm 0.3) \times 10^6$  and  $k_{\rm D_2O} = (2.6 \pm 0.3) \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> for BA]. For most BA's the  $k_{2.P}$  values are larger than those for  $k_{\rm H_2O}$  or  $k_{\rm D_2O}$  (Table V). The three rate constants for triplet quenching show a decreasing trend in the order 4-R = CN, CHO, H, CH<sub>3</sub>, and OCH<sub>3</sub>. Taking into account that the plots of  $k_{\rm obsd}$  vs. [H<sub>2</sub>O] are initially upward curved, we believe that the  $k_{\rm H_2O}$  values are in agreement with those estimated from the Stern-Volmer constants (Table I). For BA it was found that  $\Delta A(T_r)$  is reduced on addition of water. After complete quenching of T by H<sub>2</sub>O or D<sub>2</sub>O practically no further transient could be observed

		$\lambda_{\max}$ , 1	nm	
substituent	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	EtOH <sup>d</sup>	H <sub>2</sub> O
4-OCH <sub>3</sub>	385	400	395	395
4-CH3	350	355	345	360
no (BA)	325	320	340	335
no (BA <sub>D</sub> )	325			335
4-F	330	340		348
3-F	<280, 310			330
2-F	270, 315			350
4-Cl	345	355	350	365
3-Cl	275, 320			340
2-Cl	275, 320			325, 355 sh
4-Br	370	370	365	380
3-Br	280, 325			325, 385 sh
2-Br	280, 325			325, 365 sh
4-CHO	338	340		320-350
3-CHO	280, 340			350
4-CO <sub>2</sub> H	325			345
4-CN	320	320	327	ь
3-CN	275, 310 sh	<285, 325		Ь
4-NO <sub>2</sub>	Ь		с	Ь

<sup>a</sup>In argon-saturated solution at 24 °C unless indicated otherwise. <sup>b</sup> $\Delta A$  too low in the 300-400-nm range. <sup>c</sup>A transient ( $\tau \le 1 \mu s$ ) in the 350-700-nm range. <sup>d</sup>At -196 °C.

for most BA's (see below; a remaining longer-lived transient with discernible  $\Delta A$  in the UV range was found for 4-CHO-BA).

The rate constant for self-quenching  $(k_{BA})$  was estimated from plots of  $k_{obsd}$  (for decay of T) vs. [BA] in acetonitrile solution on exciting at 353 nm. The  $k_{BA}$  values are well below the diffusion-controlled range (Table IV); for BA<sub>D</sub> 10% and 90% D<sub>2</sub>O have practically no effect on  $k_{BA}$ .

Some properties of the triplet state of polycyclic aromatic aldehydes and related ketones (benzophenone, acetophenone) are given in Table VI. For anthraldehyde and naphthaldehydes  $\lambda_{max}$ is red-shifted and  $\tau_T$  is prolonged as compared to BA. The rate constants for triplet quenching by water and 2-propanol are of

TABLE IV: Rate Constants for Self-Quenching and Triplet Quenching of Benzaldehyde (in Units of  $M^{-1} s^{-1} \times 10^9$ ) by Oxygen, 1,3-Cyclohexadiene, and Maleic Acid in Acetonitrile and Water<sup>a</sup>

		СН	3CN		$k_{\rm BA}({ m H_2O}/{ m CH_2CN})$
substituent	k <sub>ox</sub>	$k_q^{b}$	k <sub>BA</sub> <sup>c</sup>	$k_q^b$ (H <sub>2</sub> O)	(1:1))
4-OCH <sub>3</sub>	7	3	0.02	3	
4-CH <sub>3</sub>	4	4 [7]	0.015	5	0.01
no (BA)	4	5 [6]	0.08 (0.04)		<0.3
no (BA <sub>D</sub> )	4			6 <sup>d</sup>	$e^d$
4-F	5	5	0.06 (0.05)		
4-Cl	2	4 [8]		5	
4-Br	>1	[10]			
4-CHO	1.5	[8]			
4-CN	1	4 [8]	<0.1 (<0.1)		

<sup>*a*</sup>In argon-saturated solution at 24 °C. <sup>*b*</sup>Quencher: maleic acid; values in brackets: 1,3-cyclohexadiene. <sup>c</sup>Values in parentheses refer to acetone as solvent,  $\lambda_{exc} = 353$  nm. <sup>*d*</sup>H<sub>2</sub>O is replaced by D<sub>2</sub>O. <sup>*e*</sup>Values <1 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> for 0, 10, and 90% D<sub>2</sub>O.

TABLE V: Rate Constants for Quenching of the Triplet State (T) of Benzaldehydes by 2-Propanol and (Heavy) Water in Acetonitrile and Acetone<sup>a</sup>

	1	$0^{-6} k, M^{-1} s^{-1}$		
substituent	2-P	H <sub>2</sub> O	D <sub>2</sub> O	
4-OCH <sub>3</sub>	<0.05	<0.02	<0.01	
4-CH <sub>3</sub>	3 (4)	0.1 (0.6)	0.06	
no (BA)	36	3.0	2.6	
no (BA <sub>D</sub> )	34 (40)	3.1 (4)	2.5	
4-F	40 (>20)	3.4 (4)	2.9	
3-F	50	15	11	
2-F	40	9	7	
4-Cl	9 (15)	3.0 (6)	2.4	
3-Cl	≥60	16	13	
2-Cl	55	11	9	
4-Br	6 (10)	3.2 (>4)	2.6	
3-Br	20	14	10	
2-Br	≥20	>4	>3	
4-CHO	40	50	40	
3-CHO	45	30	26	
4-CN	60 (60)	35 (50)	30	
3-CN	40	40	35	

<sup>a</sup>In argon-saturated acetonitrile solution at 24 °C: values in parentheses refer to acetone,  $\lambda_{exc} = 353$  nm.



Figure 7. Plot of  $k_{obsd}$  vs. [D<sub>2</sub>O] (in vol %) for BA in acetonitrile solution.

the order of  $10^6 \text{ M}^{-1} \text{ s}^{-1}$  only for 2-pyridinealdehyde but much smaller for 2-fluorenealdehyde, the two naphthaldehydes, 9-phenanthraldehyde, and 9-anthraldehyde.

Transients from Benzaldehydes in Other Organic Solvents. In neat 2-propanol solution the long-lived transient K of all BA's could be observed. T does not appear in most cases (e.g., for BA, 4-F-, 4-CHO-, 4-CN-, 3-CHO-, and 3-CN-BA) since  $\tau_{\rm T}$  is reduced to lifetimes shorter than the pulse width (20 ns). For 4-CH<sub>3</sub>-BA and 4-OCH<sub>3</sub>-BA T could be detected ( $\tau_{\rm T}$  = 0.03 and 1.5 µs, respectively) in addition to K since the  $k_{2,\rm P}$  values are much smaller (Table V). Transient K (Figure 5 and Table VII) decays

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TABLE VI: Properties of the Triplet State of Related Compounds<sup>a</sup>

			10 <sup>-9</sup> k	10 <sup>-6</sup> k, 1	M <sup>-1</sup> s <sup>-1</sup>
compound	$\lambda_{max}$ , nm	$\tau_{\rm T}, \ \mu { m s}$	$M^{-1} s^{-1}$	2-P	H <sub>2</sub> O
benzophenone acetophenone 4-pyridine- aldehyde	≤330, 530 ≤330, <450 sh d	>1 >1		$\substack{(1.3)^b\\(\approx 1)^b}$	<0.01 <sup>c</sup> <0.01
2-pyridine- aldehyde	290, 425	>5	2	4.3	0.6
1-naphth- aldehyde	480	>3	1.5	<0.01	<0.01
2-naphth- aldehyde	430	>4	1.5	<0.03	<0.01
2-fluorene- aldehyde	435	>5	1	<0.03	<0.01
9-phenanthr- aldehyde	390	2	3		<0.01
9-anthr- aldehyde	330, 430	>5	2.5	<0.02	<0.01

<sup>*a*</sup> In argon-saturated acetonitrile solution at 24 °C. <sup>*b*</sup> Values in parentheses refer to benzene solution.<sup>1,3</sup> <sup>*c*</sup> A value of <10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> has been reported for a water-soluble benzophenone.<sup>96</sup> <sup>*d*</sup> No triplet observable, main transient ( $\lambda_{max} = 350, 450$  nm) not identified.

essentially by second-order kinetics. Half-lives  $(t_{1/2})$  longer than 10  $\mu$ s were observed throughout; these should be taken as minimum values since the half-life of K is possibly reduced (e.g., by traces of oxygen). T is suggested to be the precursor of K since for 4-CH<sub>3</sub>-BA in a mixture of 2-propanol and acetonitrile K increases with the same rate constant as T decays (inset of Figure 5a). Similar results were found for several BA's, with two exceptions: 4-OCH<sub>3</sub>-BA and 4-NO<sub>2</sub>-BA. For the former  $\Delta A(K)$  is too small and for the latter T could not be observed. For BA in acetonitrile, rate constants of 1.6 × 10<sup>6</sup>, 15 × 10<sup>6</sup>, and 40 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>, for quenching by *tert*-butyl alcohol, methanol, and ethanol, respectively, were obtained.

Further information about the properties of T and/or K was gained in several other solvents. In dichloromethane the main transient is T, as suggested by  $\lambda_{max}$  (Table III), the shape of the spectrum, the first-order decay kinetics ( $\tau_{T}$  is somewhat smaller than in acetonitrile, Table II), and the fact that it is guenched by oxygen (rate constant:  $(1-2) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for BA, 4-CN-, 4-Br-, and 4-CH<sub>3</sub>-BA). In cyclohexane K either was found to be the main transient (Table VII) or was observed together with T (4-CH<sub>3</sub>-BA). In ethanol solution at 24 °C K appears during the laser pulse. At -196 °C, where most BA's exhibit phosphorescence in large yield, the main transient attributed to the lowest triplet state decays in the millisecond range. Values for  $\lambda_{max}$  obtained in glassy ethanol are very similar to those in dichloromethane and acetonitrile solutions at ambient temperature (Table III). For BA in butyronitrile at -196 °C T is the main transient while at ambient temperatures both T and K were observed.

The assignment of T for the BA's  $([0.3-3] \times 10^{-2} \text{ M}, \lambda_{exc} = 353 \text{ nm})$  in acetone is based on the similarity of the data with those in acetonitrile under the same conditions (Table II). In both solvents the lifetime is reduced by self-quenching. In acetone the rate constants for quenching of T by 2-propanol and H<sub>2</sub>O are comparable to those in acetonitrile (Table V).

Transients in Aqueous Solution. In argon-saturated aqueous solution of BA ([1-5]  $\times 10^{-4}$  M at pH around 6) K was not observed, in contrast to the case in alcohols. The main transient of several BA's (first-order decay kinetics), denoted as  $T_{H_2O}$ , shows absorption spectra closely similar to those of T in acetonitrile (compare Figures 8a and 3). A general trend is a red shift of  $\lambda_{max}$  (Figure 4 and Table III). However, the lifetime of  $T_{H_2O}$  is significantly shorter than that of T (for BA, 4-F-, 4-Cl-, and 4-CHO-BA, see Table II). Addition of acetonitrile to water reduces the lifetime even further (Figure 6). A corresponding dependence was found for BA in CH<sub>3</sub>CN/D<sub>2</sub>O mixtures (Figure 7). Exceptions from this general trend are 4-NO<sub>2</sub>-BA (no transient under our conditions), 4-CHO-BA (long-lived, unidentified additional transient), 3- and 4-CN-BA's (virtually no transient in neat

TABLE VII: Properties of the  $\alpha$ -Hydroxybenzyl Radical (K) and the Radical Anion (A) of Benzaldehydes<sup>a</sup>

	K <sup>*</sup>				
	$10^{-9}k_{}$		10 <sup>-9</sup> k	A, $\lambda_{max}$	, nm
substituent	$\lambda_{max}$ , nm	$t_{1/2},  \mu s$	M <sup>-1</sup> s <sup>-1</sup>	method I <sup>c</sup>	method II <sup>d</sup>
 4-OCH <sub>1</sub>	<315	>10			
4-CH3	278	>30	1.5	310, 460	320, 490
no (BA)	275 (275) <sup>e</sup>	>25		310, 440	320, 465
4-F	283	>20		300, 450	315, 475
4-C1	290	>30	3	315, 460	330, 440
4-Br	295 (280) <sup>e</sup>	>30	>1	320, 470	330, 475
3-Br	280, 320	>20	1	·	
4-CHO	310	>100	3	315, 380, 600	380, 590
3-CHO	270	>80	2.5		
4-CO <sub>2</sub> H	320	>50			
4-CN	310 (300)*	>20	3	360, 510	365, 520
3-CN	265, 290	>90	4	·	
4-NO2	330	>100		375, 600	380, 660
		Ē Ē			

<sup>*a*</sup> In argon-saturated solutions at 24 °C; [BA] =  $(1-5) \times 10^{-4}$  M; for R = NO<sub>2</sub> and CN see ref 42. <sup>*b*</sup> In 2-propanol solution (100%). <sup>*c*</sup> In acetonitrile/2-propanol/water(pH 12) (2:1:2),  $t_{1/2} \ge 100 \ \mu s$  throughout. <sup>*d*</sup> In acetonitrile solution containing (1-5) × 10<sup>-3</sup> M DABCO,  $t_{1/2}$  ranges between 1 and 10  $\mu s$ . <sup>*c*</sup> Values in parentheses refer to cyclohexane.



Figure 8. Transient absorptions spectra: (a) In aqueous solution at pH 5 for 4-R = H (O), Cl ( $\blacksquare$ ), and OCH<sub>3</sub> ( $\triangle$ ), and (b) in acetonitrile/2-propanol/water (pH 12) (95:5:5) for BA at 10 ns (O), 100 ns ( $\blacksquare$ ), 2 µs ( $\triangle$ ) after the pulse.

water), and 4-OCH<sub>3</sub>-BA. For the latter and for the polycyclic aromatic aldehydes (Table VI)  $k_{H_2O}$  is too small.

**Photoionization.** A further minor transient in water shows (1)  $\lambda_{max}$  around 700 nm ( $\lambda_{exc} = 248$  nm),  $\Delta A$  being largest for 4-OCH<sub>3</sub>-BA, (2) first-order decay kinetics (lifetime < 1  $\mu$ s), and (3) quenching by oxygen and N<sub>2</sub>O (which at saturation reduce lifetimes to <100 or <20 ns, respectively). This transient is identified as the hydrated electron ( $e_{aq}^{-}$ ).<sup>37,38</sup> For BA in 2-propanol/water (1:1) scavenging of  $e_{aq}^{-}$  by either H<sub>2</sub>O<sub>2</sub> or N<sub>2</sub>O did not markedly reduce the half-life of K (observed as a long-lived transient). This indicates that K cannot be quenched by the OH radical under these conditions.

Conductivity measurements with several BA's in aqueous solution reveal a fast increase of the signal (<20 ns) concomitant with the laser pulse, and a decay in the  $0.1-1-\mu$ s range (a fast first-order and a subsequent smaller, longer lived component); the half-life of the fast component ranges from 0.1 to 1.0  $\mu$ s for R = 4-OCH<sub>3</sub>, 4-CH<sub>3</sub>, H, and 4-F, but differs from the decay half-lives of e<sub>aq</sub><sup>-</sup> and T<sub>H20</sub>. In N<sub>2</sub>O-saturated solution the decay of the conductivity signal is prolonged as expected from the behavior of the OH<sup>-</sup> ion which arises from scavenging of e<sub>aq</sub><sup>-</sup>. For BA and 4-OCH<sub>3</sub>-BA it was shown that  $\Delta A(T_{H_{20}})$  depends linearly on the incident laser intensity, whereas both  $\Delta A(e_{aq}^{-})$  and the amplitude of the conductivity signal show a quadratic intensity dependence. At high laser intensities the absorption of e<sub>aq</sub><sup>-</sup> was observed throughout with only a few exceptions (e.g., 4-NO<sub>2</sub>-BA).

On excitation of BA ([0.3–3] × 10<sup>-2</sup> M) at 353 nm only  $T_{H_{20}}$  but neither  $e_{aq}^- (\Delta A_{360} / \Delta A_{700} > 20)$  nor a conductivity signal could



Figure 9. Transient absorption spectra in acetonitrile solution in the presence of DABCO  $(2 \times 10^{-3} \text{ M})$ : (a) For 4-CH<sub>3</sub>-BA at 20 ns (O) and 200 ns ( $\bullet$ ) after the pulse; inset. Oscillograph traces monitored at 350 and 480 nm. (b) For 4-R = H (O), CN ( $\blacksquare$ ), and NO<sub>2</sub> ( $\Delta$ ), 20 ns after the pulse.

be observed. The assignment of  $T_{H_2O}$  is supported by the result that the absorption spectrum at wavelengths longer than 330 nm is similar to that obtained by  $\lambda_{exc} = 248$  nm and by comparable lifetimes, taking self-quenching into account.

Effects of pH and DABCO. pH variation in aqueous solution has only a small effect on the relative yield (measured by  $\Delta A$ ) and lifetime of T<sub>H<sub>2</sub>O</sub> (e.g.,  $\tau_{\rm T} = 40$ , 60, and 40 ns for BA at pH 2, 6, and 12, respectively). For 4-Cl-BA, which has a markedly longer lifetime than BA,  $\tau_{\rm T}$  is about 0.2, 0.4, and 0.3  $\mu$ s at pH 2, 6, and 12, respectively. This places the rate constants for quenching of T<sub>H<sub>2</sub>O</sub> by H<sup>+</sup> (HClO<sub>4</sub>) or OH<sup>-</sup> (NaOH) to less than  $2 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>.

A new transient (A) with two maxima (a major one in the UV and a minor one in the 450–550-nm range) and  $\Delta A$  values much smaller than those of  $T_{H_{2O}}$  appears for BA's in 2-propanol/water mixtures on increasing the pH value above 11. Since  $\Delta A$  values are larger in the presence of acetonitrile, acetonitrile/2propanol/water mixtures (40:20:40) were used (referred to as *method I* for production of A). For BA at pH 5–8 the time-resolved absorption spectra reveal two transients, the initial one being  $T_{H_{2O}}$  and the second, longer lived one K. In alkaline solutions the initial transient is again  $T_{H_{2O}}$ , but the longer lived is identified as A (mainly second-order decay,  $t_{1/2} > 100 \ \mu$ s,  $\lambda_{max} = 310$  and 440 nm; Figure 8b). Similar results with half-lives longer than 100  $\mu$ s and a significant dependence of  $\lambda_{max}$  on the substituent were found for several BA's (Table VII).

Excitation of BA in acetonitrile in the presence of DABCO (>1  $\times$  10<sup>-3</sup> M) is referred to as *method II*. For a given BA the

<sup>(37)</sup> Grossweiner, L. I.; Baugher, J. F. J. Phys. Chem. 1977, 81, 93.
(38) Schrank, R. Ph.D. Thesis, Ruhr-Universität Bochum, 1980.

transient absorption spectrum after 200 ns (Figure 9) is very similar to that of A obtained by method I (Table VII). Control measurements with DABCO alone show that  $\Delta A$  around 460 nm (radical cation absorption) is small under our conditions.<sup>39</sup> Also the  $\Delta A_{700}$  value of the hydrated electron is as small as found in aqueous DABCO solution in the presence of BA  $(\Delta A(e_{aa})/\Delta A(e_{aa}))$  $\Delta A(A) < 0.05$ ) and in its absence. With method II the decay of A (mainly second-order kinetics, lifetime in the  $1-10-\mu s$  range) is much faster than with method I. T is the precursor of A since  $k_{obsd}$  depends linearly on [DABCO] (slope for BA:  $k_{DABCO} = 3$  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>) and the rate constant for decay of T and the increase of  $\Delta A(A)$  are very similar for a given [DABCO]. An example is shown for 4-CH<sub>3</sub>-BA (inset of Figure 9a). It is remarkable that A (and K) could clearly be detected even for 4-NO<sub>2</sub>-BA although T could not be observed, presumably because of its short lifetime.

Energy-Transfer Measurements. In order to test for the triplet nature of T and  $T_{H_2O}$  energy-transfer measurements were carried out either with a sensitizer or with triplet quenchers (Q). For several BA's in acetonitrile and mixtures with water the lifetimes of T and  $T_{H_2O}$ , respectively, were reduced by naphthalene, 1,3cyclohexadiene, and maleic acid. From linear plots of  $k_{obsd}$  vs. [Q] quenching rate constants in the range  $k_q = (3-10) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  were determined for the last two quenchers (Table IV). From  $\Delta A$  values at  $\lambda_{max}$  and under normalized conditions (same absorbance at 248 nm and same laser intensity) values of  $\epsilon_{325}(T) \ge 1 \times 10^4$ ,  $\epsilon_{335}(T_{H_2O}) \ge 1 \times 10^4$ , and  $\epsilon_{310}(A$  with method II) =  $2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  were estimated for BA by using naphthalene in ethanol ( $\epsilon_{TT} = 4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\phi_{isc} = 0.75)^{40}$  as a reference. For BA ( $\approx 5 \times 10^{-3}$  M,  $\lambda_{exc} = 353$  nm) in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1

or 1:9) in the presence of naphthalene  $(1 \times 10^{-2} \text{ M})$  the lifetime of  $T_{H,O}$  is reduced and the triplet-triplet absorption spectrum of naphthalene ( $\lambda_{max} = 415$  nm) appears. Similar results for 4-F-BA and 4-Cl-BA clearly show that the naphthalene triplet is generated by energy transfer from  $T_{H_2O}$  (control experiment: no triplettriplet absorption of naphthalene in the absence of BA). In addition, xanthone  $(1 \times 10^{-2} \text{ M})$  as a high-energy triplet sensitizer was excited at 353 nm in acetonitrile solution. On increasing [BA] the rate for decay of the xanthone triplet ( $\lambda_{max} = 620 \text{ nm}$ ) increases linearly (up to  $5 \times 10^7 \text{ s}^{-1}$ ). The rate constant depends somewhat on the substituent, e.g.,  $1 \times 10^9$ ,  $4 \times 10^9$ , and  $0.3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for BA, and 2-Br- and 3-Br-BA, respectively. This is in agreement with energy transfer from the xanthone triplet to ground-state **BA**. The remaining transient absorption spectrum (at  $\lambda > 360$ nm) is very similar to that of T (e.g., for BA, 4-Cl-BA, and 4-OCH<sub>3</sub>-BA). Xanthone triplet quenching by 4-NO<sub>2</sub>-BA together with the lack of a transient in the 360-800-nm range again indicate a short lifetime of the 4-NO<sub>2</sub>-BA triplet

Photodeuteriation. Continuous irradiations of BA ( $\lambda_{irr} = 254$ or 313-365 nm) in acetonitrile/ $D_2O$  mixtures yield  $BA_D$ .<sup>17</sup> Conversely, irradiation of BA<sub>D</sub> in acetonitrile/H<sub>2</sub>O mixtures yields BA. Quantum yields first increase linearly with (heavy) water content (see Table VIII), then go through a maximum, and decrease slightly thereafter.<sup>17</sup> Analogous results were found on repeated flashing at  $\lambda_{exc} = 248$  nm. This shows that both methods of triplet population lead to H/D exchange. An almost constant ratio of  $\phi_D(\text{in } D_2 O)/\phi_H(\text{in } H_2 O) = 1.37 \pm 0.1$  was measured ( $\lambda_{\text{irr}}$ = 313 nm) in the range 5–50% (heavy) water. In acetonitrile/ $D_2O$ (3:1) it was found that  $\phi_D$  ( $\lambda_{irr} = 254$  nm) decreases on decreasing [BA] but remains substantial even in dilute solution:  $\phi_D^{re}$ (concentration in M) 1.0 (0.1), 1.0 (0.06), 0.72 (0.01), and 0.61 (0.006). For BA (0.05 M,  $\lambda_{irr}$  = 313 nm) it was found that  $\phi_D$ in  $CH_3CN/D_2O$  (3:1) is not decreased by saturation with air and that the amount of decomposition of BA is the same ( $\approx 5\%$ ) as with argon.

Inertness of the organic solvents with respect to the H/D exchange was established by the following results: In neat  $CD_3CN$ 

TABLE VIII: Quantum Yield of Photodeuteriation of Benzaldehydes<sup>a</sup>

		φ <sub>D</sub> f	or vol %		
substituent	concn, M	5	10	25	slope <sup>b</sup>
4-CH <sub>3</sub>	0.05	<0.01	<0.01	<0.01	
	0.005	0.028	0.072	0.12	0.06 (0.02)
	0.05	0.11	0.29	0.43	0.3
no (BA)	0.05	0.33	0.60	0.70	0.55
	0.005	0.51	0.68	0.74	1.0 (1.0)
no (BA <sub>D</sub> )	0.05	0.26 <sup>d</sup>	$0.44^{d}$	0.52 <sup>d</sup>	0.43
	0.005	0.51 <sup>d</sup>	0.64 <sup>d</sup>	0.69 <sup>d</sup>	0.86 (0.96)
4-F	0.05	0.52	0.76	0.92	1.1 (1.1)
4-Cl	0.05	0.59	0.86	0.92	1.2 (0.9)
4-Br	0.05	0.10	0.25	0.38	0.24 (1.0)
4-CHO <sup>e</sup>	0.05	0.25	0.14	0.06	5.0 (15)
3-CHO <sup>e</sup>	0.05	0.43	0.38	0.27	1.5 (10)
4-CN	0.05	0.64	0.80	0.85	2.4 (12)
	0.005	0.95	0.95	0.98	2.6

<sup>*a*</sup>In acetonitrile solution at 24 °C,  $\lambda_{irr} = 313$  nm; not corrected for decomposition.<sup>17</sup> <sup>*b*</sup>Slope of the initial linear plot of  $\phi_D$  vs. [D<sub>2</sub>O] (<3 M) (normalized for BA, 0.005 M); relative  $k_{D_2O}$  values (from Table V) are given in parentheses. <sup>c</sup>In acetone,  $\lambda_{irr} = 334$  nm. <sup>*d*</sup> $\phi_H$  for H<sub>2</sub>O. <sup>*e*</sup> $\phi_D$  values obtained from the sum of mono- and dideuteriated products.

 $\phi_{\rm D}$  is below 0.02 for BA (1 × 10<sup>-3</sup> M,  $\lambda_{\rm exc}$  = 248 nm). No deuteriation of BA (0.05 M) in CD<sub>3</sub>CN and CD<sub>3</sub>COCD<sub>3</sub> even on prolonged irradiation ( $\lambda_{irr} = 365$  nm) was detected; the recovery of BA was 97% and 90%, respectively. No BA<sub>D</sub> was found in 2-propanol (2-D or O-D) but mainly reduction products instead, while in CH<sub>3</sub>OD ( $\phi_D = 0.015$ ) and in 2-propanol- $d_8$  ( $\phi_D = 0.001$ ) some BA<sub>D</sub> was detected besides the reduction products. For BA  $(5 \times 10^{-2} \text{ M}, \lambda_{irr} = 365 \text{ nm})$  in D<sub>2</sub>O at pH 1, 7, and 13  $\phi_D$  changed by less than  $\pm 10\%$ ; i.e., variation of the pH has no discernible effect on  $\phi_{\rm D}$ . For pulsed excitation  $\phi_{\rm D}^{\rm rel}$  was estimated from the initial slope of  $[BA_D]/([BA] + [BA_D])$  as a function of the number of laser pulses, using the  $\phi_D$  value obtained by continuous irradiation. Under these conditions H/D exchange was found to be not significantly impaired in air-saturated  $D_2O$  solutions containing 0-90% acetonitrile. For substituted BA's in  $CH_3CN/D_2O$  mixtures  $\phi_D$  values and slopes from the (initial linear) dependences of  $\phi_D$  on  $[D_2O]$  (at low  $[D_2O]$ ) are listed in Table VIII.

#### Discussion

Identification of T and  $T_{H,O}$  as Triplet States. The triplet nature of transient T in organic solvents is deduced from the following results: (1) For a given substituent the spectra of T in several solvents are similar (Table III and Figures 3-5a). (2) Virtually the same transient absorption spectra are found in acetonitrile at 24 °C and in glassy butyronitrile and ethanol solutions at -196 °C (Table III) in which cases also phosphorescence (Figure 1) appears in large yield, cf. ref 19-23. (3) In acetonitrile solution at 24 °C the lifetime of T is comparable to the phosphorescence lifetime (Figure 2 and Table II). (4) T is formed on xanthone-sensitized excitation (triplet energy:  $E_{T}$ = 74 kcal/mol); a rate constant for energy transfer in the order of  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  is in agreement with an energy gap of approximately 2 kcal/mol. (5) 1,3-Cyclohexadiene ( $E_T = 53 \text{ kcal/mol}$ ) and maleic acid quench T efficiently (Table IV). (6) The naphthalene triplet ( $E_{\rm T}$  = 61 kcal/mol) is generated on BA-sensitized excitation (see Results, Energy-Transfer Measurements). (7) Oxygen quenches T at a rate constant close to the diffusion-controlled limit (Table IV). The phosphorescence spectra (Table I) and points 4-7 are in agreement with  $E_{\rm T}$  = 71.6 kcal/mol for BA, and with slightly smaller values for several substituted BA's, cf. ref 17. In analogy to related ketones<sup>1-3</sup> the quantum yield for intersystem crossing should be close to unity for the BA's examined.

It may be questioned whether or not  $T_{H_2O}$ , the main transient in water (Figures 4 and 8a),<sup>27</sup> is necessarily also a triplet because it is so short-lived.  $T_{H_2O}$  was also observed (with  $\Delta A$  comparable to that of T) under conditions where the yield of photoionization is low and cannot be assigned to the radical cation which escapes our observation probably because of its short lifetime. We assign  $T_{H_2O}$  to a triplet since (1) its absorption spectrum is very similar

<sup>(39)</sup> A low absorption of the DABCO ground state at 248 nm and a small AA value of the excited species is the reason for choosing this particular amine.
(40) Dempster, D. N.; Morrow, T.; Quinn, M. F. J. Photochem. 1973/74, 2, 329.

to that of T for a given BA (Table III), (2)  $T_{H_{2}O}$  is quenched by maleic acid with a rate constant similar to that for T (Table IV), and (3) the naphthalene triplet is formed by energy transfer also in acetonitrile/water mixtures [with  $\Delta A_{415}$  of the same order of magnitude as  $\Delta A(T_{H,O})$ ]. It is not surprising that no phosphorescence could be observed in water at ambient temperature (in contrast to the ethylene glycol/water mixture at -196 °C) in view of the short lifetime of  $T_{H_2O}$  (Table II). It should be noted that in glassy EPA<sup>22</sup> and in the gas phase<sup>28</sup> the detection of two BA triplet states has been reported.

Identification of Other Transients. Transient K (Table VII) is assigned to the  $\alpha$ -hydroxybenzyl (ketyl) radical for the following reasons. (1) For BA in ethanol/water (1:1) the absorption spectrum of K has already been observed by Porter et al. using conventional flash photolysis,<sup>5</sup> (2) the  $\Delta A$  value (at 275-300 nm) increases on addition of small amounts of 2-propanol in acetonitrile solution, and (3) the rate constants for the growing-in of K and for the decay of T are practically identical (inset of Figure 5a). We conclude that T is the precursor of K. The  $\alpha$ -hydroxybenzyl radical decays in a bimolecular reaction.<sup>5</sup> For aromatic ketones it is well-known that H-adduct radicals are generated by H abstraction from the solvent, an additive (e.g., 2-propanol), or intramolecularly (valerophenone).<sup>1,2,10,15</sup> K from BA's was also observed in other alcohols (tert-butyl alcohol, methanol, ethanol), in cyclohexane, and with low  $\Delta A$  even in acetonitrile (in the latter cases denoted as  $T_r$ , see Results and Figure 3a).

Transient A which was generated either in the presence of water (pH > 11, method I) or in acetonitrile in the presence of DABCO (method II) is assigned to the radical anion of the BA's on the following basis: With method II the radical anion should be generated by electron transfer according to eq 1. It is known

$$\overset{O}{\overset{}}_{\overset{}}^{\phantom{}}^{\phantom{}}^{\phantom{}}^{\phantom{}}}^{3*}Ph \overset{O}{\overset{}}^{\phantom{}}^{\phantom{}}^{\phantom{}}}_{\phantom{}}^{\phantom{}}^{\phantom{}}^{\phantom{}}} H + DABCO \overset{O}{\overset{}}^{\phantom{}}^{\phantom{}}^{\phantom{}}} Ph \overset{O}{\overset{}}^{\phantom{}}^{\phantom{}}_{\phantom{}}^{\phantom{}}^{\phantom{}}^{\phantom{}}}_{\phantom{}}^{\phantom{}}^{\phantom{}}^{\phantom{}}}^{\phantom{}}^{\phantom{}}}$$

that triplet quenching of ketones by amines involves electron transfer (and/or hydrogen transfer which is less likely in the case of DABCO).<sup>1-3</sup> The absorption spectrum of A (Figure 9; estimated value for BA:  $\epsilon_{310} = 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) is clearly different from that of K and the radical cation of DABCO ( $\epsilon_{465} = 2 \times 10^3$ M<sup>-1</sup> cm<sup>-1</sup>).<sup>41</sup> For BA the rate constant for electron transfer is below but close to the diffusion-controlled limit. The short lifetime of the radical anion can be explained by electron back-transfer. For unsubstituted BA the spectrum of A, obtained with method I (Figure 8b), is in agreement with the one reported by Porter et al. ( $\lambda_{max}$  < 330 and 445 nm in ethanol/water (1:1) at pH =  $(13)^5$  and that obtained with pulse radiolysis.<sup>12</sup> The radical anion also of other BA's<sup>42</sup> was observed in alkaline solution (Table VII). The pH dependence of the spectra is explained by assumption of an equilibrium between K and A (eq 2)<sup>12</sup> ( $pK_a = 10.5$  for BA in

$$\begin{array}{c} OH \\ | \\ Ph-C-H+OH \end{array} \xrightarrow{O} Ph-C-H+H_2O \quad (2) \\ transient K \\ transient A \end{array}$$

alcohol/water, 1:1).<sup>5</sup> We should emphasize that  $\Delta A$  values of K and A, if obtained in the presence of water, are lower limits since triplet quenching by water is still efficient with most BA's not affording R-PhCHOH (Table V).

Decay of the Triplet State in Organic Solvents. Figure 10 shows the reactions proposed for the lowest triplet state of BA in nonaqueous solutions. In glassy media <sup>3</sup>BA\* decays mainly by phosphorescence<sup>19-23</sup> (Figure 1 and Table I) while at room temperature in an "inert" solvent even at sufficiently low [BA] the quantum yield of phosphorescence and  $\tau_p$  are small. This indicates that quenching reactions are efficient;  $k_q$  includes all



Figure 10. Deactivation pathways of triplet BA in nonaqueous solution.

quenching processes not involving H abstraction or electron transfer (Table IV). It is also possible that a nonradiative step is involved  $(k_0)$ . At high laser intensities triplet-triplet annihilation, as indicated by a second-order component for triplet decay, may contribute. This reaction was observed for the longer lived triplet state of the polycyclic aromatic aldehydes (Table VI) but plays only a minor role for the BA's.

<sup>3</sup>BA\* can also react with ground-state BA (reaction 3) leading in part to the radical pair [PhCO + PhCHOH] and finally to benzoin and/or to the ground state of BA.<sup>14,17</sup> For several BA's

$$^{3*}Ph-C-H + Ph-C-H \xrightarrow{^{*}BA} [Ph-C+Ph-C+H] (3)$$

in acetonitrile and acetone the rate constant for self-quenching is in the range  $(1-10) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (Table IV) while in hexane<sup>1</sup>  $k_{BA} = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Values for benzophenone<sup>8</sup> are smaller (e.g.,  $1.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  in water).<sup>9</sup> For the measurements of transient absorption (and phosphorescence) with typical BA concentrations of  $(1-5) \times 10^{-4}$  M self-quenching plays only a minor role. This may be different in CIDNP studies<sup>13,14</sup> and continuous irradiation measurements at high BA concentrations (see below).<sup>17</sup>

An important reaction is triplet quenching by H abstraction from an additive or from the solvent. This reaction is not very fast for the BA's with 2-propanol since  $k_{2-P}$  is smaller than  $1 \times$  $10^8\ M^{-1}\ s^{-1},$  i.e., less than 0.5% of the encounters lead to the  $\alpha$ -hydroxybenzyl radical (Table V). Values of  $k_{2,P}$  are largest for 4-CN-BA and tend to decrease as the 4-substituent becomes a stronger electron donor. The  $k_{2,P}$  value for BA is significantly larger than those for benzophenone and acetophenone.<sup>1-3</sup> An electron-donating group increases the  ${}^{3}(\pi,\pi^{*})$  character of the lowest triplet and hence reduces the rate constant of H abstraction. The similar trend observed for quenching by water and deuterium oxide might indicate that the rate-determining step of the quenching reaction is similar and that only the subsequent product-forming steps are different.

The Nature of the Lowest Triplet State. The energy of the  $\pi,\pi^*$  states of aromatic ketones is lowered by increasing the solvent polarity while that of the  $n,\pi^*$  states is increased.<sup>1,6,7,15</sup> For the excited singlet state of benzophenone this effect is most pronounced in water.<sup>6</sup> The change in the absorption spectrum of BA on going from acetonitrile to water fits into this general picture (Figure 1). It is also generally accepted that a change in the orbital character of the lowest triplet state of ketones from  $^{3}(n,\pi^{*})$  to  $^{3}(\pi,\pi^{*})$  is accompanied by a lower chemical reactivity.<sup>1,10,15</sup> Ledger and Porter<sup>6</sup> have argued that quenching of triplet benzophenone by the proton and H abstraction from water may be possible because in water the  ${}^3(\pi,\pi^*)$  state is slightly higher in energy than the reactive  ${}^{3}(n,\pi^{*})$  state. Lindqvist et al.<sup>7</sup> have shown that for acetophenone in solvents of low polarity the lowest triplet is the  ${}^{3}(n,\pi^{*})$  state while in polar solvents it is the  ${}^{3}(\pi,\pi^{*})$  state; a similar change toward  $\pi, \pi^*$  triplet character can be achieved

<sup>(41)</sup> Ernstbrunner, E. E.; Girling, R. B.; Grossman, W. E. L.; Hester, R.
E. J. Chem. Soc., Faraday Trans. 2 1978, 74, 501.
(42) A (and K), generated from 4-NO<sub>2</sub>-BA, are probably not benzyl-type radicals but radicals which carry the negative charge (H atom) on the oxygen of the nitro group, cf.: Jagannadham, V.; Steenken, S. J. Am. Chem. Soc. 1984, 106, 6542. An analogous situation may prevail with the CN-BA's.

by introduction of an electron-donating substituent in the 4-position.

For the BA's and polycyclic aromatic aldehydes examined in this work the triplet states have been classified as follows. For BA and 4-CH<sub>3</sub>-BA in nonpolar solvents<sup>19-21</sup> and for 4-NO<sub>2</sub>-BA<sup>29</sup> the lowest triplet is <sup>3</sup>(n, $\pi^*$ ). By analogy with NO<sub>2</sub>-BA's we expect this also for 3- and 4-CN-BA. The observation of dual phosphorescence for BA in glassy EPA<sup>22</sup> points to a small energy gap between the <sup>3</sup>( $\pi$ , $\pi^*$ ) and <sup>3</sup>(n, $\pi^*$ ) states. A certain contribution of <sup>3</sup>( $\pi$ , $\pi^*$ ) character has been reported for 4-Cl-BA and 4-Br-BA while for 4-OCH<sub>3</sub>-BA the lowest triplet is the <sup>3</sup>( $\pi$ , $\pi^*$ ) state.<sup>19,20</sup> While for the two pyridinealdehydes some <sup>3</sup>(n, $\pi^*$ ) content of the lowest triplet has been reported,<sup>26</sup> the triplet of the other aldehydes listed in Table VI has most likely <sup>3</sup>( $\pi$ , $\pi^*$ ) character, cf. ref 17 and 32.

As with benzophenones and acetophenones, increasing solvent polarity presumably increases also the  $\pi,\pi^*$  character of the excited states of the BA's; the gap between the  ${}^3(n,\pi^*)$  and  ${}^3(\pi,\pi^*)$  states is reduced with increasing water content which may even lead to a levels crossing. This effect explains the reduced reactivity of  $T_{H_2O}$  in water compared to T in acetonitrile and the maximum in the plot of  $k_{obsd}$  vs. [H<sub>2</sub>O] (or [D<sub>2</sub>O]) in mixtures of acetonitrile and (heavy) water (Figures 6 and 7). A similar behavior was found for triplets of 4-F-, 4-Cl-, 4-Br-, and 4-CHO-BA and, less pronounced, for 4-CH<sub>3</sub>-BA but not for 4-OCH<sub>3</sub>-BA (no maximum).

Fate of the Triplet in Aqueous Solution. Two deactivation steps of the excited singlet state ( ${}^{1}BA^{*}$ ) are indicated by laser flash photolysis experiments in water ( $\lambda_{exc} = 248$  nm). The major deactivation step involves the triplet  $T_{H_2O}$  and the minor one leads to photoionization, as concluded from the observation of the hydrated electron. This is not surprising since various aromatic compounds, including benzene and its methoxy derivatives can be ionized by pulsed laser excitation at 248 nm.<sup>37,38</sup> Photoionization occurs via a biphotonic step rather than monophotonically, as judged from transient absorption and conductivity measurements as a function of the laser intensity (see Results).

The observation that BA is deuteriated (1) on continuous irradiation<sup>16,17</sup> and on laser excitation, (2) with substantial yield even in the presence of oxygen, i.e., when PhCHOH is not formed, and (3) under conditions where self-quenching is unimportant (see below) led us to search for a mechanism of H/D exchange involving triplet quenching by  $D_2O$ . Such a mechanism may involve (I) free radicals, (II) radicals in a solvent cage, (III) free ions, or (IV) other intermediates.

While a H/D exchange at the formyl group of BA as a consequence of self-quenching may involve free-radical intermediates (see Introduction), this is excluded on the basis of present and earlier results<sup>17</sup> for H/D exchange involving quenching by  $D_2O$ :

Ia. A free-radical pathway might follow  $\alpha$ -cleavage of the formyl H to give the benzoyl radical (eq 4). A fast D abstraction

$$\overset{O}{\overset{}_{||}}^{3*}Ph - C - H \longrightarrow Ph - C + H \cdot \xrightarrow{D_2O} BA_D + HOD (4)$$

by the benzoyl radical from  $D_2O$  is not possible under our conditions in view of the large difference in C-D and D-OD bond energies. H/D exchange of atomic H with  $D_2O$  through reaction with D<sup>+</sup> or OD<sup>-</sup> is possible and the subsequent addition of atomic D to the benzoyl radical would give  $BA_D$ . However, this bimolecular termination reaction is probably much slower than atomic D addition to the BA aromatic ring to give a cyclohexadienyl-type radical. Subsequent disproportionation with the benzoyl radical would lead to both H- and D-abstraction, the former leading to deuteriation of the aromatic ring. Since deuteriation was only observed at the formyl group<sup>17</sup> this possibility of H/D exchange involving free radicals is discarded. Furthermore, addition of atomic D to the carbonyl group is excluded because the resulting PhCHOD radical was not observed.

Ib. D abstraction by triplet BA from  $D_2O$  should yield  $\alpha$ deuterioxybenzyl (PhCHOD) and OD<sup>•</sup> radicals (eq 5). Such a possibility has been discussed by Porter et al.<sup>6</sup> for a reaction of triplet benzophenone with H<sub>2</sub>O. However, we did not observe

\*Ph-C-H 
$$\xrightarrow{D_2O}$$
 Ph-C-H + OD.  $\xrightarrow{-HOD}$   
OD  
Ph-C = BA<sub>D</sub> (5)

з

PhĊHOD on decay of triplet BA in  $D_2O$  although we readily observed PhĊHOH in the presence of alcohols.

II. To explain the difference one may assume ad hoc a 100% in-cage reaction of the OD<sup>•</sup> radical with PhCHOD to give the  $\alpha$ -deuterioxyphenylcarbene (Ph-<u>C</u>-OD) and HOD. The carbene may isomerize to BA<sub>D</sub> or react with D<sub>2</sub>O to give the heavy hydrate which dissociates into ground-state BA<sub>D</sub> (eq 4). Such an in-cage reaction cannot presently be excluded.

III. H/D exchange involving free ions according to eq 6 is also unlikely because hardly any ions were detected by conductivity measurements upon excitation with the 353-nm pulse and weak conductivity changes observed with the 248-nm pulse cannot be correlated to triplet decay.

$${}^{3*}Ph = C = H \xrightarrow{D_2O} Ph = C(-) + D_2HO^+ \longrightarrow BA_D + HOD$$
(6)

We are then left with molecular mechanisms of H/D exchange. IVa. Addition of  $D_2O$  to BA in the reactive  ${}^3(n,\pi^*)$  state to form a hydrate and subsequent elimination of HOD (eq 7) are excluded. There is only a small percentage of hydrate in equi-

$$\overset{O}{\overset{}}_{\overset{}}{\overset{}}_{\overset{}}^{\text{OD}} \xrightarrow{} \overset{OD}{\overset{}}_{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}_{\overset{}}^{\text{OD}} \xrightarrow{}_{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}_{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}_{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}_{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}_{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}^{\text{OD}} \xrightarrow{} \overset{O}{\overset{}}^{\text{OD}} \overset{O}{\overset{}} \overset{O}{\overset{O}} \overset{O}{\overset{}} \overset{O}{\overset{O}} \overset{O}{\overset{O$$

librium with ground-state BA (equilibrium constant: 0.01, 0.016, and 0.2 for BA, 4-Cl-BA, and 4-NO<sub>2</sub>-BA, respectively).<sup>33</sup> However, the ground-state hydrate does not lead to H/D exchange.<sup>17</sup> A reaction involving an excited hydrate seems to be unlikely since the triplet energy of this species must be much higher than that of <sup>3</sup>BA\*.

Two possibilities (involving an intermediate X) are left to be considered:

IVb. A reaction of triplet BA with  $D_2O$  in a concerted reaction to form a zwitterionic intermediate (Ph- $\underline{C}$ - $\underline{OD}$ ) or the  $\alpha$ deuterioxyphenylcarbene and HOD; Ph- $\underline{C}$ -OD then turns into BA<sub>D</sub>.

IVc. Isomerization of triplet BA by a 1,2-H shift into a carbene (Ph- $\underline{C}$ -OH) which either isomerizes to BA, or exchanges H for D, or adds D<sub>2</sub>O to give PhCD(OH)OH which then loses HOD to form BA<sub>D</sub>.

The chemical analogy of the reaction of phenyl ketone triplets with that of structurally related oxyl radicals (RCH<sub>2</sub>-O<sup>•</sup>) has been discussed in the past.<sup>2</sup> An isomerization of alkoxyl radicals possessing  $\alpha$ -H atoms, which seems to require water as solvent (eq 8), has recently been discovered.<sup>43</sup> The mechanism of this

$$\begin{array}{c} H \\ R \\ - C \\ H \end{array} \begin{array}{c} O \\ R \end{array} \begin{array}{c} H \\ R \end{array} \begin{array}{c} C \\ - O \\ R \end{array} \begin{array}{c} O \\ R \end{array} \begin{array}{c} O \\ R \end{array}$$

latter reaction is still unknown. The analogy with possibilities IVb and IVc is emphasized.

Deuteriation via Two Different Pathways. In our previous work it has been proposed that photodeuteriation of BA occurs via eq 3 followed by reaction  $9.1^7$  For [BA] = 0.05 M, as typically used

$$Ph = \overset{O}{c} + Ph = \overset{O}{c} - H \xrightarrow{D_2O} Ph = \overset{O}{c} + Ph = \overset{O}{c} - H \xrightarrow{Ph} BA_D + BA (9)$$

in continuous irradiations,<sup>17</sup> a triplet lifetime of 250 ns is expected

<sup>(43)</sup> Gilbert, B. C.; Holmes, R. G. G.; Norman, R. O. C. J. Chem. Res. (S) 1977, 1.





by using the value  $k_{BA} = 8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  in acetonitrile. However,  $k_{obsd}^{-1}$  is significantly smaller in the presence of a few percent H<sub>2</sub>O (Figure 6) and D<sub>2</sub>O (Figure 7). Therefore, reaction 3 followed by 9 could play a role mainly for [BA] > 0.1 M and/or [D<sub>2</sub>O] < 1 M. Triplet quenching not involving the radical pair should also be the dominant process for 4-R = F, Cl, Br, CHO, and CN when more than 1% of (heavy) water is present (Tables IV and V).

In view of the above considerations the mechanism of deuteriation should be supplemented by a second pathway. We propose that  ${}^{3}BA^{*}$ , when mainly surrounded by acetonitrile molecules ( $[D_2O] < [CH_3CN]$ ), forms an encounter complex with  $D_2O$  leading to a transition state or an intermediate (X, zwitterion or carbene, see II or IVb/c) which then decays into  $BA_D$  and BA(Scheme I).

While reactions 3 and 9 describe a radical pair mechanism of H/D exchange involving two BA molecules, the new mechanism involves only triplet BA but no free radicals. Scheme I is in accordance with the linear dependence of  $k_{obsd}$  on  $[D_2O]$  (between approximately 0.5 and 5 M). It accommodates also the similar dependences on the 4-substituent of the slope of the initial linear plot of  $\phi_D$  vs. [D<sub>2</sub>O] and  $k_{D_2O}$  (Table VIII). The influence of the  $[D_2O]/[CH_3CN]$  ratio on the branching ratio for decay of X into BA<sub>D</sub> and BA will be discussed in a forthcoming paper.<sup>44</sup> Generally, the relative contribution of the two pathways is determined by the ratio  $k_{D_2O}[D_2O]/k_{BA}[BA]$ . While  $k_{D_2O}$  is strongly influenced by medium and substituents and varies over a large range (Table V),  $k_{BA}$  does not (Table IV);  $\phi_D$  depends on the relative effectiveness of the forward (to BA<sub>D</sub>) and reverse (or side) reactions, for example, on the ratio  $[X]/[{}^{3}BA*]$  and the branching ratio from X into BA and BA<sub>D</sub>.

Substituent Effects on Photodeuteriation. For a series of substituted BA's and some related aldehydes in  $acetone/D_2O$  (3:1) it has been shown<sup>17</sup> that the rate of deuteriation is comparable to that of BA when the lowest triplet has  ${}^3(n,\pi^*)$  nature, but that it is virtually zero when the lowest triplet is a  ${}^3(\pi,\pi^*)$  state. This is in line with the present results in acetonitrile and aqueous solutions, i.e., quenching by D<sub>2</sub>O involving H/D exchange can readily compete with other decay steps in the case of  ${}^3(n,\pi^*)$  states, but not in the case of  ${}^3(\pi,\pi^*)$  states.

An exception from this general pattern is 4-nitrobenzaldehyde. The absence of deuteriation<sup>17</sup> can be attributed to fast photoreactions in accordance with the suspected short triplet lifetime. Wubbels et al.<sup>29</sup> have suggested that formation of 4-nitrosobenzoic acid in aqueous solution involves another isomer (a ketene) of the aldehyde. This is formed probably much faster than triplet decay via H/D exchange. Despite the fast rate of the ketene formation

(44) Görner, H.; Kuhn, H. J.; Koltzenburg, G., to be published.

H abstraction is possible under certain conditions since the Hadduct radical and a radical anion could be observed (Table VII).

The other extreme case of the BA's is 4-methoxybenzaldehyde the triplet state of which is strongly reduced in reactivity because of its  $\pi,\pi^*$  nature. Here, (1) the triplet lifetime in water is larger and rate constants of quenching by 2-propanol and (heavy) water are markedly smaller than for other substituted BA's, (2) the yield of  $\alpha$ -hydroxybenzyl radical formation is low, and (3)  $\phi_D$  is practically zero.<sup>17</sup> Similar results were obtained for several polycyclic aromatic aldehydes (Table VI). Among the BA's studied 4-methylbenzaldehyde deserves special mention since  $\phi_D$  differs significantly on going from acetonitrile to acetone (Table VIII), cf. ref 44. Quenching by H<sub>2</sub>O or D<sub>2</sub>O has not been reported so far with triplets of polycyclic aromatic aldehydes and ketones (Table VI). Preliminary results indicate that the photodecarboxylation of phenylglyoxylic acid is a second case where triplet quenching by water is involved.<sup>45</sup>

One may expect a correlation between the triplet reactivity and Hammett  $\sigma$ -parameters. However, there is no linear correlation between log  $k_{D_2O}$  (as well as log  $k_{2,P}$ ) and  $\sigma$  values. A similar situation was encountered with triplet valerophenones, where the plot of the log of the rate constant for  $\gamma$ -hydrogen abstraction vs.  $\sigma$  is not linear.<sup>15</sup> Wagner and Siebert have suggested that Hammett constants do not adequately describe substituent effects on energies of  $\pi,\pi^*$  states and that different Boltzmann factors come to bearing once the  $\pi,\pi^*$  triplet becomes the lowest.<sup>15</sup> In BA's there may be also interaction between the close-lying  ${}^3(\pi,\pi^*)$ and  ${}^3(n,\pi^*)$  states but the dependence of the energy gap on substitution and the effect of solvent polarity in fluid media are not yet known.

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Registry No. 4-OCH3-BA, 123-11-5; 4-CH3-BA, 104-87-0; 4-F-BA, 459-57-4; 3-F-BA, 456-48-4; 2-F-BA, 446-52-6; 4-Cl-BA, 104-88-1; 3-Cl-BA, 587-04-2; 2-Cl-BA, 89-98-5; 4-Br-BA, 1122-91-4; 3-Br-BA, 3132-99-8; 2-Br-BA, 6630-33-7; 4-CHO-BA, 623-27-8; 4-CO<sub>2</sub>H-BA, 619-66-9; 4-CN-BA, 105-07-7; 3-CN-BA, 24964-64-5; 3-CHO-BA, 626-19-7; 4-NO2-BA, 555-16-8; CH3CN, 75-05-8; CH3COCH3, 67-64-1; CH2Cl2, 75-09-2; H2O, 7732-18-5; D2O, 7789-20-0; O2, 7782-44-7; 4-OCH<sub>3</sub>-K, 103776-42-7; 4-CH<sub>3</sub>-K, 103776-43-8; K, 2406-15-7; 4-F-K, 103776-44-9; 4-Cl-K, 103776-45-0; 4-Br-K, 103776-46-1; 3-Br-K, 103776-47-2; 4-CHO-K, 103776-48-3; 3-CHO-K, 103776-49-4; 4-CO<sub>2</sub>H-K, 103776-50-7; 4-CN-K, 103776-51-8; 3-CN-K, 103776-52-9; 4-NO<sub>2</sub>-K, 103776-53-0; 4-OCH<sub>3</sub>-A, 99393-40-5; 4-CH<sub>3</sub>-A, 99438-22-9; A, 34473-57-9; 4-F-A, 34473-59-1; 4-Cl-A, 103776-54-1; 4-Br-A, 77510-40-8; 3-Br-A, 103776-55-2; 4-CHO-A, 51978-27-9; 3-CHO-A, 51978-29-1; 4-CO<sub>2</sub>H-A, 103776-56-3; 4-CN-A, 34512-34-0; 3-CN-A, 103776-57-4; 4-NO<sub>2</sub>-A, 34512-33-9; BA, 100-52-7; benzophenone, 119-61-9; acetophenone, 98-86-2; 4-pyridinealdehyde, 872-85-5; 2-pyridinealdehyde, 1121-60-4; 1-naphthaldehyde, 66-77-3; 2-naphthaldehyde, 66-99-9; 2-fluorenealdehyde, 343-43-1; 9-phenanthraldehyde, 4707-71-5; 9-anthraldehyde, 642-31-9; 1,3-cyclohexadiene, 592-57-4; maleic acid, 110-16-7; 2-propanol, 67-63-0.

<sup>(45)</sup> Defoin, A.; Defoin-Straatmann, R.; Hildenbrand, K. Bittersmann, E.; Kreft, D.; Kuhn, H. J. J. Photochem. 1986, 33, 237.