FLUORESCENCE QUENCHING OF METHOXYBENZYL ALCOHOLS BY THE HYDRONIUM ION IN AQUEOUS SOLUTION: ACID-CATALYZED FORMATION OF METHOXYBENZYL CATIONS FROM THE SINGLET EXCITED STATE

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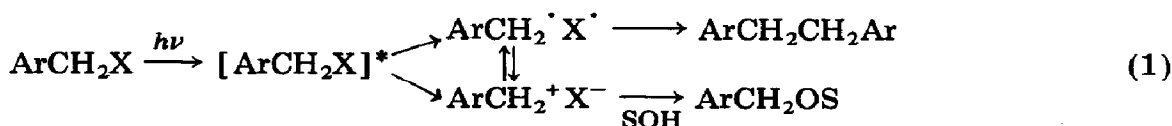*Department of Chemistry, Columbia University, New York, NY 10027 (U.S.A.)*

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Summary

The photochemical and photophysical behavior of a number of methoxy-substituted benzyl alcohols has been studied in aqueous solution as a function of pH. Evidence is presented which indicates that, on excitation to the singlet excited state, the ortho and meta methoxy-substituted benzyl alcohols undergo proton-assisted loss of hydroxide ion to give the corresponding benzyl cations. These results are discussed with reference to the photoselectivity observed by Zimmerman and Sandel in the photosolvolysis of methoxybenzyl acetates.

1. Introduction

The photochemistry of benzyl derivatives and related systems has been a topic of continued interest, and a recent thorough review of the subject is now available [1]. Numerous papers have been published concerning the efficiency of heterolysis (usually resulting in photosolvolysis) *versus* homolysis of the benzylic bond of these compounds [1]:

$$ArCH_2X \xrightarrow{h\nu} [ArCH_2X]^* \begin{array}{c} \nearrow ArCH_2^{\cdot} X^{\cdot} \longrightarrow ArCH_2CH_2Ar \\ \updownarrow \\ \searrow ArCH_2^+ X^- \xrightarrow[SOH]{} ArCH_2OS \end{array} \qquad (1)$$

A great deal of attention has also been drawn to the possibility of interconversion between the radical pair and the ion pair in eqn. (1) [1]. Because the majority of the compounds chosen for these studies do not exhibit ideal luminescence properties (*e.g.* they are generally only weakly fluorescent), none of these studies concerns the possible relationship between photochem-

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ical solvolysis and fluorescence and/or phosphorescence behavior. During the course of our investigation of the photochemistry of benzyl phenyl acetates [2], we had the opportunity to study the photophysical behavior of a number of benzyl alcohols and their corresponding acetates in aqueous solution. We report here a number of novel observations on the fluorescence behavior associated with the photochemistry of methoxybenzyl alcohols 1 - 4, which give new insights into the understanding of the photochemistry of these and related systems:

$$CH_2OH \quad OCH_3 \qquad CH_2OH \quad OCH_3 \qquad CH_2OH \quad CH_3O \quad OCH_3 \qquad CH_2OH \quad OCH_3$$

1   2   3   4
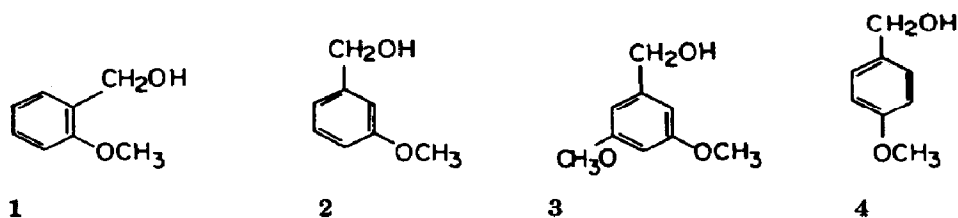
2. Results

2.1. Fluorescence behavior

Although the photochemical behavior of some benzyl alcohols has been studied previously in CH_2Cl_2 [3], and in the presence of electron donors [4], we are not aware of any studies of these systems in aqueous solution. Benzyl alcohols 1 - 4 were all strongly fluorescent in organic solvents and in neutral water ($\lambda_{max} \approx 290$ - 310 nm) with a fluorescence quantum yield of about 0.24, determined with anisole as reference. The corresponding acetates of 1 - 4 (i.e. $ArCH_2OCOCH_3$) exhibited only very weak fluorescence in organic solvents or in aqueous solution. The fluorescence of 1 - 4 is efficiently quenched on going to lower pH values, as shown in Fig. 1 for 3-methoxy-benzyl alcohol (2). As shown in Fig. 2, the quenching behavior is more efficient for 1, followed by 2 and 3, and finally by 4. At pH 1, the fluorescence of 1 - 3 is significantly or nearly completely quenched, while much higher acidities are required to effect a similar degree of fluorescence quenching for the para-substituted isomer 4.

2.2. Fluorescence lifetimes

To establish whether the observed fluorescence quenching phenomena are dynamic or static in origin, fluorescence lifetimes were measured for these compounds using an SLM 4800 spectrofluorimeter, via phase shift and relative modulation techniques. Lifetimes calculated via these two techniques are identical, within experimental error, indicating that the fluorescence decays are best described as single exponential. We found that fluorescence lifetimes for 1 - 4 decreased with increasing acidity; the proportionate decrease observed is essentially the same as the decrease in observed fluorescence intensity with increasing acidity. A plot of this observation is shown in Fig. 3 for 3-methoxybenzyl alcohol (3).
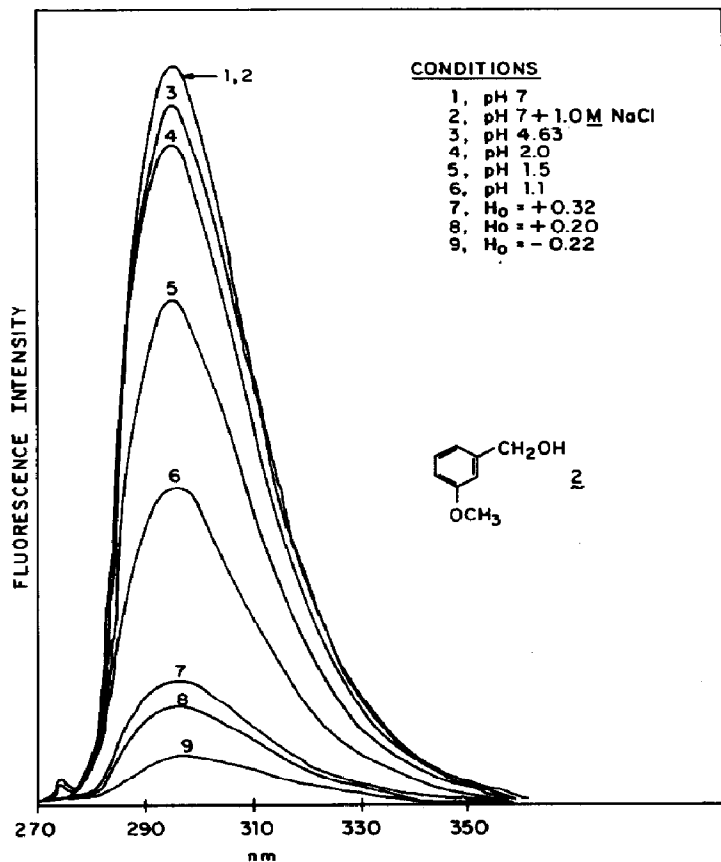
Fig. 1. Dependence of fluorescence intensity on medium acidity (aqueous HCl and H_2SO_4) for 3-methoxybenzyl alcohol (2) (excitation wavelength, 275 nm; substrate concentration, 10^{-4} M).

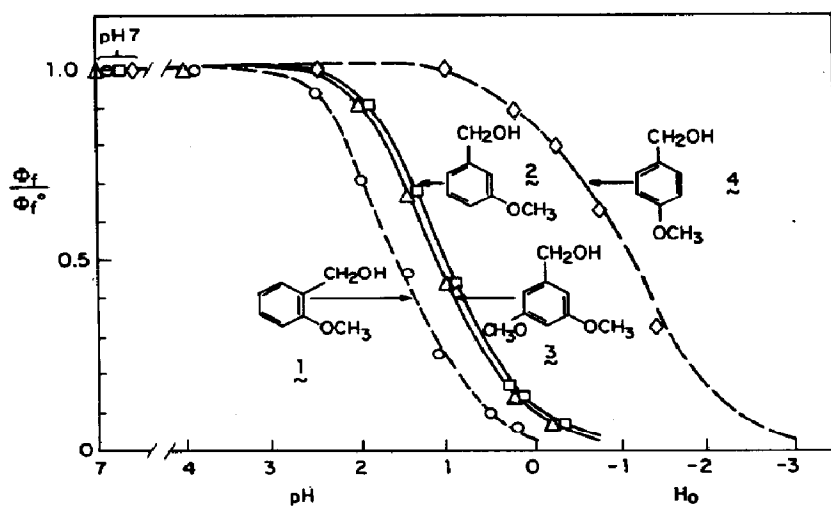Fig. 2. Fluorescence quenching as a function of medium acidity for benzyl alcohols 1 - 4. Φ_f° is defined as the fluorescence intensity at pH 7 (H_0 is the Hammett acidity function scale).
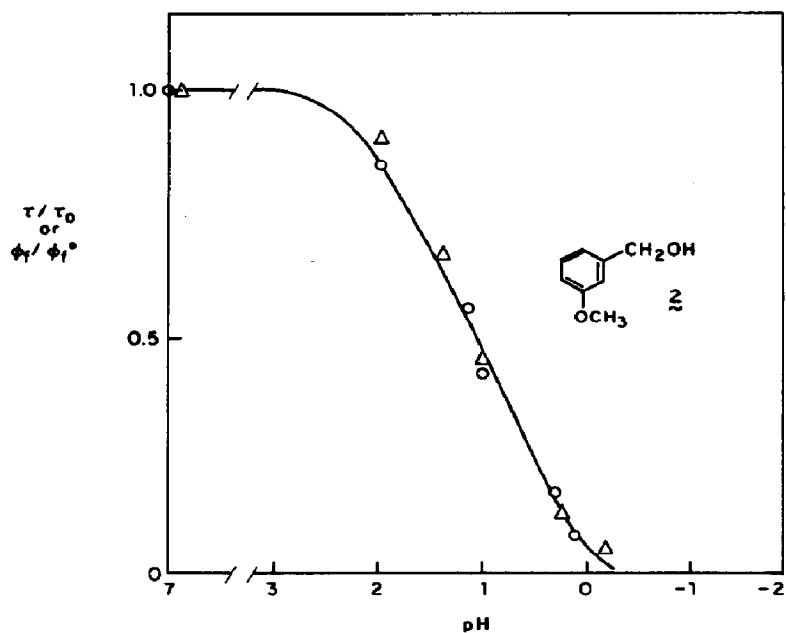
Fig. 3. Plot of τ/τ_0 (O) and ϕ_f/ϕ_f° ($\triangle$) for 3-methoxybenzyl alcohol (2) as a function of medium acidity. τ_0 and ϕ_f° are the lifetime and the fluorescence quantum yield in pH 7. The ratios are normalized to unity in pH 7.

The above results suggest that the observed fluorescence quenching by the hydronium ion is probably due to a dynamic phenomenon, the efficiency of which is strongly dependent on the position of the methoxy substitution. To test this hypothesis further, attempts were made to fit the observed fluorescence quenching results into the Stern–Volmer equation

$$\frac{\phi_f^\circ}{\phi_f} = 1 + k_q\tau_0[H_3O^+] \qquad (2)$$

where ϕ_f° is the fluorescence efficiency in pH 7 and τ_0 the corresponding fluorescence lifetime. For benzyl alcohols 1 - 3 the Stern–Volmer plots were linear (see Fig. 4 for 2-methoxybenzyl alcohol (1)); the Stern–Volmer constants and calculated k_q values are tabulated in Table 1. For 2 an additional Stern–Volmer plot of τ^{-1} *versus* $[H_3O^+]$ gave a straight line, with $k_q = (3.4 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, which is within experimental error of the value obtained via the steady state fluorescence quenching method for this compound (Table 1).

2.3. Product studies

Preparative photolysis of benzyl alcohols 1 - 4 in aqueous (pH 7 - 0) acetonitrile (10% - 20% CH_3CN-H_2O with added aqueous HCl; 254 nm) resulted in a complicated mixture of products, shown to be coupling products (*e.g.* 5 and 6) by gas chromatography–mass spectroscopy (GC–MS) analysis. Preparative photolysis in methanol–water or acetic acid–water solutions, however, resulted in much cleaner product mixtures. For 1 - 3 the
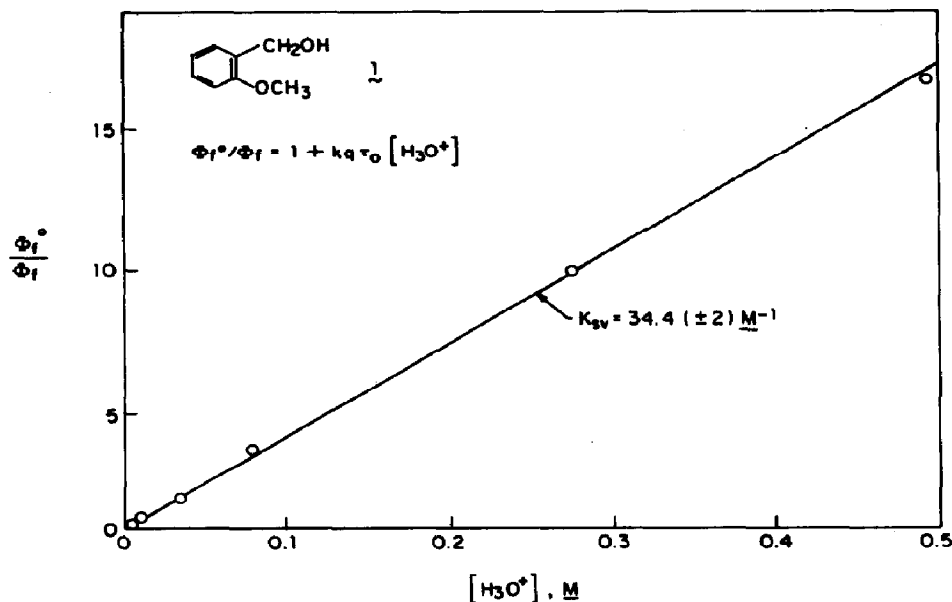
Fig. 4. Stern–Volmer plot of ϕ_f°/ϕ_f vs. $[H_3O^+]$ for 2-methoxybenzyl alcohol (1).
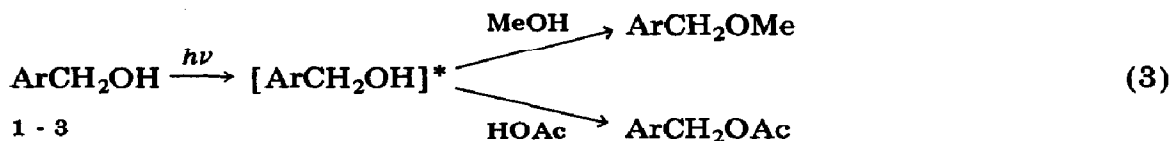
TABLE 1

Stern–Volmer quenching constants and fluorescence lifetimes for benzyl alcohols 1 - 4

Compound	K_{SV} (M^{-1})	τ_0 [a] (ns)	k_q (M^{-1} s^{-1})
1	34.4 (±2)	2.8 (±0.2)	$(1.2 \pm 0.1) \times 10^{10}$
2	16.2 (±1)	4.4 (±0.3)	$(3.7 \pm 0.2) \times 10^9$
3	14.0 (±0.7)	1.0 (±0.2)	$(1.4 \pm 0.3) \times 10^{10}$
4	—[b]	3.7 (±0.3)	—[b]

[a] Fluorescence lifetimes in neutral water (pH 7) as determined via phase shift and relative modulation techniques on an SLM 4800 spectrofluorimeter.
[b] Non-linear Stern–Volmer plot.

major product (more than 90% of the product mixture) was the corresponding methyl ether or acetate:

$$\text{ArCH}_2\text{OH} \xrightarrow{h\nu} [\text{ArCH}_2\text{OH}]^* \begin{array}{c} \xrightarrow{\text{MeOH}} \text{ArCH}_2\text{OMe} \\ \xrightarrow{\text{HOAc}} \text{ArCH}_2\text{OAc} \end{array} \qquad (3)$$

1 - 3

Only small amounts of dimeric products (less than or equal to 5%) were observed, as indicated by GC–MS analysis. These dimeric products were assigned to be either 5 or 6:

ArCH₂CH₂Ar   ArCH₂OCH₂Ar

5   6

Photolysis of 4 under similar conditions resulted in recovery of 90% or more of the starting material; methyl ethers or acetates were not observed.

The relative efficiencies for methyl ether or acetate formation (eqn. (3)) for 1 - 3 were dependent on pH; the relative quantum efficiencies increased with decreasing pH, as shown in Fig. 5 for benzyl alcohol (2). Moreover, the relative quantum yield for ether formation (Φ_p/Φ_p° where Φ_p° is yield with $H_0 = -1$ normalized to unity) increased in a manner that is complementary to the fluorescence quenching observed in Fig. 2 for this compound, indicating that the phenomenon of fluorescence quenching by hydronium ions is mechanistically related to the displacement of the hydroxyl group by methanol on photochemical excitation. Similar results were observed for 1 and 3 and a similar conclusion can be drawn. The behavior of 4-methoxybenzyl alcohol (4) in contrast, appears to be quite different from the rest of the benzyl alcohols studied in that this isomer failed to react under similar conditions.

The classic work of Zimmerman and Sandel [5] on the photosolvolysis of a number of methoxybenzyl acetates in aqueous dioxane has shown that 3-methoxybenzyl acetate or 3,5-dimethoxybenzyl acetate photosolvolyze efficiently to the corresponding benzyl alcohols via benzyl cation intermediates. 4-Methoxybenzyl acetate gave predominately benzyl-radical-derived products, and only a low yield of 4-methoxybenzyl alcohol was observed. To make the study complete, we have studied the photosolvolysis of 2-methoxybenzyl acetate in aqueous acetonitrile and have found that the major product (more than 95%) is 2-methoxybenzyl alcohol. Interestingly,
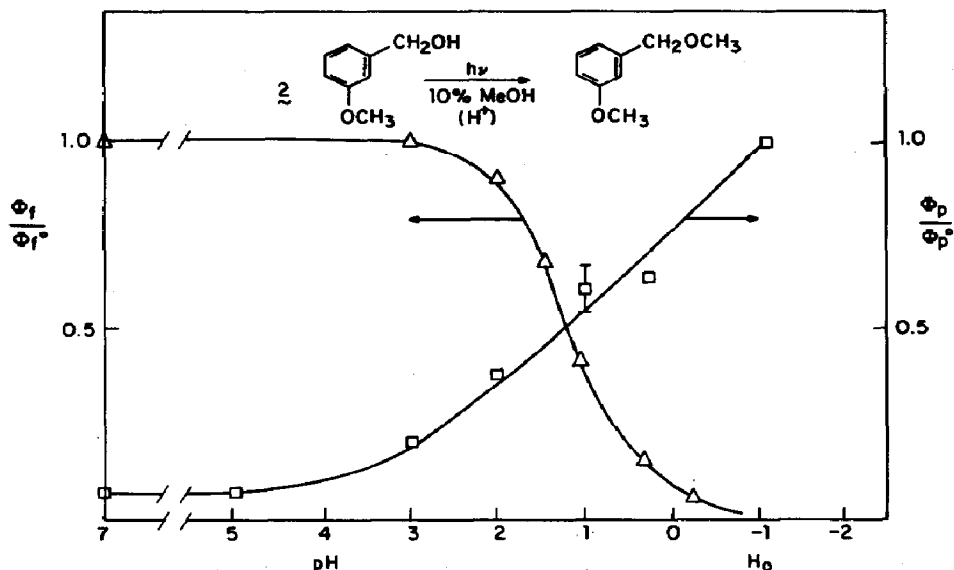

Fig. 5. Fluorescence quenching by acid and relative quantum efficiency for methyl ether formation for 3-methoxybenzyl alcohol (2). ϕ_p° is the yield of methyl ether at $H_0 = -1$, normalized to unity. Absolute quantum yields were not measured (fluorescence quenching experiments were performed in wholly aqueous solutions).

acid catalysis of photosolvolysis of these benzyl acetates is not observed over the pH (H_0) range from 7 to -1. However, there is a clear analogy between the efficiency of benzyl acetate photosolvolysis and the fluorescence quenching behavior of the corresponding benzyl alcohols.
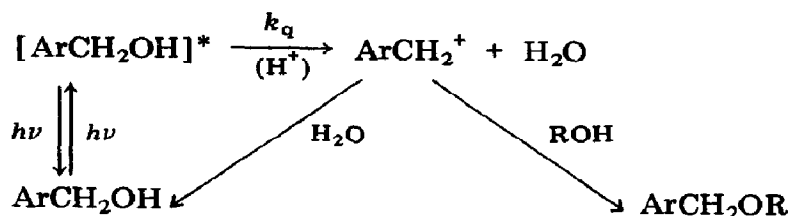
3. Discussion

The observation of fluorescence quenching by hydronium ion concurrent with methanolysis (or acetolysis) for benzyl alcohols 1 - 3 strongly indicates a mechanism involving benzyl cation formation as the primary photochemical step from the singlet excited state. Our proposed reaction mechanism for 1 - 3 is shown in the scheme in Fig. 6. The primary photochemical step involves proton-assisted cleavage of the benzylic—OH bond, to generate the corresponding benzyl cations $ArCH_2^+$. This intermediate may return to the substrate or else is trapped by external nucleophiles other than H_2O (e.g. MeOH or HOAc). For benzyl alcohol 4 the results suggest that simple acid-catalyzed benzyl cation formation is not an important deactivation pathway. Compound 4 was found[†] to undergo ground state ionization to form the corresponding benzyl cation at acidities above $H_0 \approx -1$. Therefore, it is likely that the fluorescence quenching observed for this compound (Fig. 2) is due to ground state ionization and not to an excited state dynamic phenomenon. Benzyl alcohols 1 - 3 do not undergo ground state ionization in the acidity region used for the fluorescence quenching experiments.

Photochemical dehydroxylation is not a new phenomenon. Irie [6] and others have reported such processes previously. However, these previous systems involve photogenerating exceptionally stable cations, thus explaining their photolability:

$$Ar_3C\underset{\frown}{OH} \xrightarrow{h\nu} [Ar_3COH]^* \to Ar_3C^+ + OH^- \qquad (4)$$
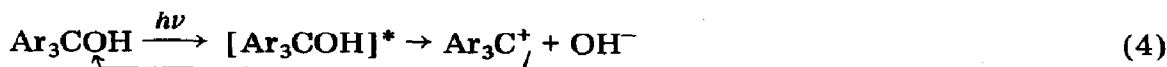
Additionally, no catalytic effects due to hydronium ion have been reported for these systems.

$$[ArCH_2OH]^* \xrightarrow[\text{(H}^+)]{k_q} ArCH_2^+ + H_2O$$

$$h\nu \updownarrow h\nu \qquad H_2O \qquad ROH$$

$$ArCH_2OH \qquad\qquad ArCH_2OR$$

1 - 3

Fig. 6. Proposed reaction mechanism for 1 - 3.

[†]Ground state ionization was detected by using MeOH as the benzyl-cation-trapping agent. The experiment involves stirring a mixture of benzyl alcohol (about 10^{-2} M) and 10 vol.% MeOH in the appropriate pH (or H_0) at room temperature and analyzing for methyl ethers after about 2 h via gas–liquid chromatography (GLC).

In the present study the ability to photogenerate benzyl cations from 1 - 3 is perhaps surprising, since Zimmerman and Sandel [5] have reported that compound 7 is not photolabile in aqueous dioxane:
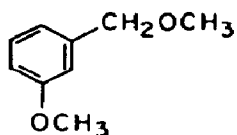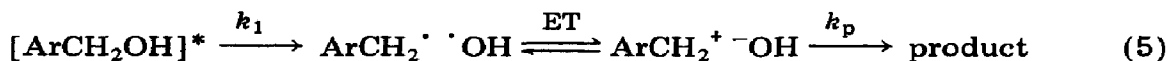

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However, they did not attempt any studies with added acid, which appears to be a required photocatalyst for photogeneration of benzyl cations from these simple benzylic systems with poor leaving groups (*e.g.* OH or OCH_3).

Some interesting quantitative information can now be extracted from the data presented in Table 1. The calculated k_q values for 1 - 3 can now be regarded as being the bimolecular proton-catalyzed rate constant for dehydroxylation, leading to benzyl cation formation. For alcohols 1 and 3 the process is essentially *diffusion controlled*. 3-Methoxybenzyl alcohol (2), in contrast, is much less reactive but nevertheless reacts much more efficiently than 4-methoxybenzyl alcohol (4), which does not display this behavior.

The possibility that the primary step involves homolytic cleavage followed by rapid electron transfer (ET) is now considered:

$$[ArCH_2OH]^* \xrightarrow{k_1} ArCH_2{}^{\cdot} \; {}^{\cdot}OH \xrightleftharpoons{ET} ArCH_2{}^+ \; {}^-OH \xrightarrow{k_p} product \qquad (5)$$

The observation of acid-catalyzed formation of methyl ether products (MeOH trapping of $ArCH_2{}^+$) can be explained by this alternative mechanism if the k_p step is assumed to be acid catalyzed. However, this scheme cannot account for hydronium ion quenching of fluorescence from these benzyl alcohols concurrent with acid-catalyzed methyl ether formation since the primary S_1 deactivation step (k_1 step) is unimolecular and, more importantly, does not require proton assistance. Since a small amount of radical-derived products are observed for 1 - 3, on photolysis in aqueous methanol or acetic acid, some molecules do apparently deactivate via eqn. (5). However, the predominant mode of deactivation is that shown in Fig. 6.

Although the photochemistry of numerous other benzyl-type systems has been studied in terms of the relative efficiencies of heterolytic *versus* homolytic pathways, the present system is the first of which we are aware which clearly demonstrates novel catalytic effects due to the hydronium ion for photosolvolysis. Additionally, it is also the first study which quantifies the long-postulated paradigm of different relative reactivities of isomeric methoxy-substituted benzenes [5, 7 - 10]. We anticipate that the results presented in this paper will be applicable to a number of other related systems.

4. Experimental details

4.1. Materials

Benzyl alcohols 1 - 4 were purchased from the Aldrich Chemical Company and were used without further treatment. GLC analysis indicated that these materials were more than 98% pure. Aqueous HCl and H_2SO_4 were purchased "pre-standardized" from Fisher or were diluted from standardized concentrated solutions. Methyl ethers and acetates of benzyl alcohols 1 - 4 were prepared via methylation using MeOH−NaOMe and acetylation using acetyl chloride respectively. The products were distilled prior to use and shown to be more than 98% pure by GLC. Acetonitrile and methanol were Fisher ACS grade reagents.

4.2. Fluorescence studies and lifetime measurements

Steady state fluorescence studies were performed on a Perkin−Elmer LS-5 spectrofluorimeter equipped with a microcomputer interface and are uncorrected. Solutions of the substrates (about 10^{-4} M) were prepared in 10 mm cuvettes and purged with a stream of nitrogen prior to measurement. The quantity of acetonitrile cosolvent employed is less than or equal to 1 vol.%.

Fluorescence lifetimes were measured using an SLM-4800 spectro-fluorimeter, via both phase shift and relative modulation techniques (SLM Instruments, U.S.A.). The data were fitted using programs available from SLM Instruments. All experiments were performed at room temperature (20 ± 2 °C).

4.3. Preparative photolysis studies

Preparative photolysis experiments were carried out in 10 ml quartz tubes with a Hanovia 450 W mercury lamp. Typically, 2 - 5 mg of substrate in 8 ml of aqueous H_2SO_4 and 2 ml of organic cosolvent were employed. Photolysis times were less than 30 min. Analyses were performed on a Varian Aerograph 3700 gas chromatograph (SE-30 capillary column) or a Finnigan 3300 GC−MS system. Methyl ethers and acetates produced in photosolvolysis of 1 - 3 were identified by comparison with reference samples.

Acknowledgments

References

1 S. J. Cristo and T. H. Bindel, *Org. Photochem.*, *6* (1983) 327.
2 N. J. Turro and C.-H. Tung, unpublished results.
   C.-H. Tung, *Ph.D. Dissertation*, Columbia University, 1983.

3 R. E. Balsells and A. R. Frasca, *Tetrahedron, 38* (1982) 2525.
4 C. Lin, P. Singh and E. F. Ullman, *J. Am. Chem. Soc., 98* (1976) 6711, 7848.
5 H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc., 85* (1963) 915.
6 M. Irie, *J. Am. Chem. Soc., 105* (1983) 2079, and references cited therein.
7 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin–Cummings, Menlo Park, CA, 1978, pp. 404 - 406.
8 E. Havinga and J. Cornelisse, *Pure Appl. Chem., 41* (1976) 1.
9 J. A. Barltrop and J. D. Coyle, *Excited States in Organic Chemistry*, Wiley, London, 1975, p. 288.
10 D. O. Cowan and R. L. Drisko, *Elements of Organic Photochemistry*, Plenum, New York, 1976, p. 534.