

SPECTRAL EVIDENCE FOR LONG-LIVED RADICAL-ELECTRON PAIRS: PHOTOIONIZATION OF PHENOL IN ALCOHOLS

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Summary

The transient solvated electron generated by photoionization of phenol shows a 100 nm blue spectral shift in both ethanol and 1-propanol with respect to the known absorption spectra. No spectral change is observed in methanol. However, in all three solvents, the photoionized electron disappears by non-homogeneous kinetics. The spectral shift decreases during the electron decay in ethanol. These results and others are discussed in terms of the formation of long-lived radical-solvated electron pairs.

1. Introduction

Considerable attention has been paid to the photochemistry and particularly to the photoionization of small aromatic molecules such as phenols and indoles [1 - 12] because of their relevance in photobiology. However, less is known of the photoionization of these types of molecules in environments of lower dielectric constant than water [13]. In water, the unusual decay kinetics of the solvated electron, generated from the photoionization of phenol, suggest the formation of long-lived radical-solvated electron pairs as interpreted by Grossweiner and coworkers [9, 11, 12]. In a preliminary report, we present here the results of a laser flash photolysis study of the photoionization of phenol in various alcohols which may further lend support to this interpretation.

2. Experimental details

The excitation source was the fourth harmonic (266 nm, 6 ns) of a Quanta Ray Nd-YAG laser. The beam was scattered through ground quartz at right angles to the analyzing beam for uniform intensity distribution [14].

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A computer was used to control the flash photolysis system and analyze the data. The actinometry was performed with the naphthalene triplet absorption as the reference [15] using a monochromator slit width of less than 2 nm at the observation wavelength (414 nm). The pulse radiolysis equipment has been described elsewhere [16].

Phenol was purchased from Aldrich (Gold Label) and used as received. Phenolate was prepared by adding NaOH to a solution of phenol until the absorption spectrum of phenolate was obtained. The solute concentrations were typically between 10^{-4} and 10^{-3} M. The alcohols were spectra analyzed from Fisher Scientific Co. All the solutions were deaerated by purging with nitrogen.

3. Results

Immediately after the laser pulse, the characteristic spectrum of the solvated electron (e_s^-) and that of the corresponding phenol radical were observed in all alcohols. For example, in methanol, the transient spectrum has the characteristic peaks of the phenoxy radical ($\lambda_{\max} = 380$ nm and $\lambda_{\max} = 395$ nm) [17] and the broad absorption of e_s^- with a maximum around 630 nm [18].

While the absorption spectrum of the solvated electron generated from the photoionization of phenol ($e_s^-(PI)$) in methanol was as expected, in ethanol and 1-propanol it was very different from those known for the isolated e_s^- generated by pulse radiolysis [19]. Figure 1 shows how the maximum of the initial $e_s^-(PI)$ spectrum is shifted by nearly 100 nm in both ethanol ($\lambda_{\max} = 625$ nm) and 1-propanol ($\lambda_{\max} = 640$ nm) compared with the isolated e_s^- spectrum. The known spectral maxima of e_s^- are given by the vertical broken lines. Furthermore, the $e_s^-(PI)$ spectrum in ethanol, for example, evolved with time towards the red: in other words closer to what is expected of an isolated e_s^- (Fig. 1).

The apparent photoionization quantum yield was found to be sensitive to the laser intensity in all solvents, indicating the presence of a consecutive biphotonic contribution. When the e_s^- yield over the laser intensity I was plotted *versus* I a linear curve was obtained. The product of the monophotonic photoionization quantum yield Φ and the extinction coefficient ϵ of the solvated electron was extrapolated at $I = 0$ using the naphthalene triplet absorbance as a reference. The product $\Phi\epsilon$ was found to be $360 \text{ M}^{-1} \text{ cm}^{-1}$ at 630 nm in methanol. If we assume that ϵ at 630 nm is the same as that determined for the isolated e_s^- by pulse radiolysis ($16\,000 \text{ M}^{-1} \text{ cm}^{-1}$ [18]), $\Phi = 0.02 \pm 0.01$ in methanol. This value is an order of magnitude larger than that determined by continuous photolysis at 254 nm (0.0018 [13]). This literature value was obtained using 2-chloroethanol as a scavenger followed by quantitative measurement of Cl^- . Similar discrepancies in the photoionization quantum yields obtained by laser flash photolysis and continuous irradiation have been observed before for phenol in water [8]. In

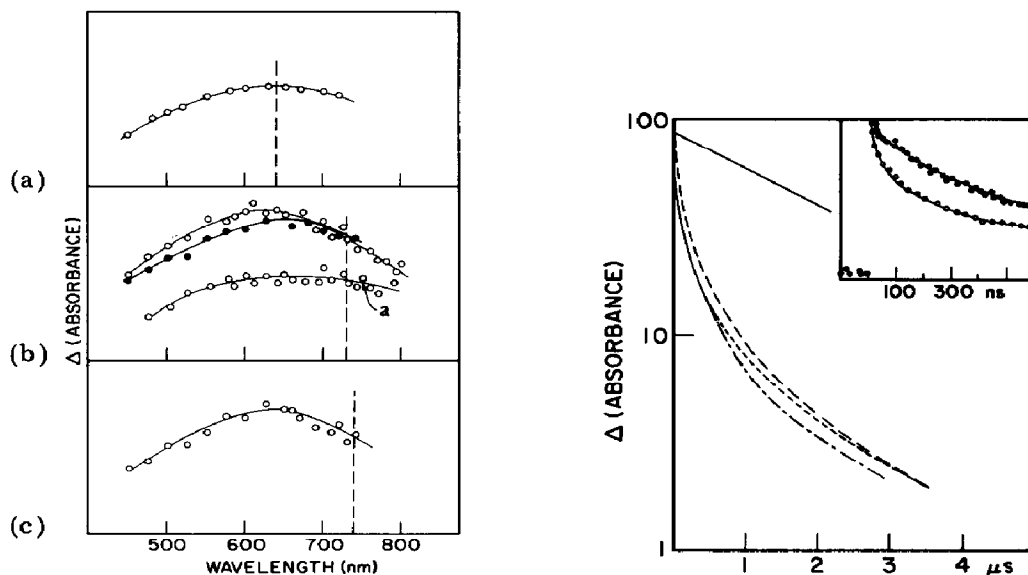


Fig. 1. Spectra of the solvated electron generated by photoionization of phenol (\circ) and phenolate (\bullet) immediately after the laser pulse except where otherwise indicated: (a) in methanol; (b) in ethanol (curve a, $t = 500$ ns); (c) in 1-propanol. The vertical broken lines indicate the expected absorbance maxima [19].

Fig. 2. Decay kinetics of the solvated electron generated by pulse radiolysis in methanol (—), by photoionization of phenol in methanol (---), in ethanol (- · -) and in 1-propanol (----). Inset, oscilloscope trace of the initial decay of the solvated electron generated in ethanol by photoionization of phenol (\circ) and phenolate (\bullet).

this case, however, since both values represent only the monophotonic contribution, the difference may be due to the experimental error: for example, in our calculations potential sources of error are the extinction coefficients of the solvated electron and the reference.

In all three alcohols, the decay kinetics of the e_s^- (PI) were not simple. For example, in methanol, Fig. 2 shows the difference in the decay kinetics of the isolated e_s^- generated by pulse radiolysis and that of e_s^- (PI). In both cases, the initial solvated electron concentration was less than 10^{-5} M although it was slightly smaller in the pulse radiolysis compared with the laser flash photolysis. The isolated e_s^- is much more stable and disappears by first-order kinetics, as a result of reaction with the solvent and/or impurities, with a half-life of about $2 \mu\text{s}$. The much faster decay of e_s^- (PI) cannot be explained by the presence of the solute, since the rate constant for the reaction between e_s^- and phenol is only $7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in methanol [20] and the phenol concentration was less than 10^{-3} M. From the plot of the logarithm of the absorbance *versus* time in Fig. 2, it is also evident that the decay of e_s^- (PI) does not fit first-order kinetics. Neither does it fit second-order kinetics: it decays much faster than would be expected from the homogeneous recombination reaction between e_s^- and the phenoxy radical. The observed initial half-life is only about 125 ns. If a recombination rate

constant of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ is assumed; the first half-life would be longer than $10 \mu\text{s}$, with the initial concentration of e_s^- and the phenoxy radical being less than 10^{-5} M . Similarly, the reaction $e_s^- + e_s^-$ does not contribute to any extent since the rate constant for that reaction is about $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [21]. Therefore the $e_s^-(\text{PI})$ appears to be disappearing by complex kinetics which approach the expected first-order decay only at the very end. Figure 2 also shows that similar decays were observed in ethanol and 1-propanol although the dielectric constant of the solvent decreased from 32 in methanol to 20 in 1-propanol.

Finally, for comparison, Fig. 1 includes the spectrum of $e_s^-(\text{PI})$ in ethanol resulting from the photoionization of phenolate which also shows a strong shift with a maximum around 650 nm. The $e_s^-(\text{PI})$ decay kinetics are very similar to those of phenol although initially, on the nanosecond time scale, they are significantly slower as shown by Fig. 2, inset.

4. Discussion

The decay kinetics of the $e_s^-(\text{PI})$ reported above indicate that the $e_s^-(\text{PI})$ is mostly subject to non-homogeneous kinetics. The significant spectral changes of $e_s^-(\text{PI})$ in ethanol and 1-propanol suggest that it is not isolated but rather is in close proximity to its radical partner. Similar spectral blue shifts for the solvated electron have been observed in pulse radiolysis experiments in the presence of cations such as Mg^{2+} and Ca^{2+} as a result of the association between these cations and the solvated electron [22]. Therefore both the kinetic behavior and the spectral changes support the idea that the $e_s^-(\text{PI})$ and its radical partner undergo geminate-type recombination although this is much slower than expected in polar solvents.

Only the unusual decay kinetics of the $e_s^-(\text{PI})$ have been observed before by Grossweiner and coworkers [9 - 11] for similar solutes in aqueous solutions. More recently, Hirata and Mataga [23] have shown through photoconductivity measurements the slow dissociation of the radical-solvated electron pairs in alcohols when *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) is photoionized. However, the rise time of the photocurrent showed no correlation with the dielectric constant of the solvent. Similarly, the $e_s^-(\text{PI})$ decay kinetics did not appear to change significantly when this parameter was varied in our study. These observations seem to be in disagreement with the various theoretical models used to explain the unusual decay kinetics of the $e_s^-(\text{PI})$ which predict a dependence on the dielectric constant of the solvent [11, 12].

Our results also indicate that the long-lived radical-solvated electron pairs originating from the photoionization of either phenol or phenolate behave in very much the same way, although definite differences are observed in the initial decay kinetics. Therefore, it is most likely that the presence of a positively charged species (either the radical cation or the proton resulting from its dissociation [8]) plays a role in the behavior of these geminate-type pairs.

Many questions arise from our results and the previous studies reported above. Variation of physical parameters such as temperature, viscosity and magnetic field is necessary in order to gain further insight into these types of long-lived radical-solvated electron pairs. Our efforts are continuing in this direction.

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