

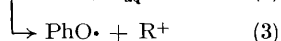
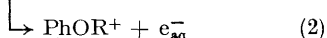
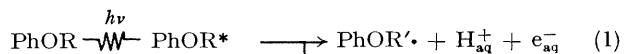
Photogeneration of Radical Cations from Aqueous Methoxylated Benzenes

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Summary Formation of radical cations resulting from photoinduced electron ejection from methoxylated benzenes in aqueous solutions has been observed.

THE electron ejection process from excited phenols and methoxylated benzenes in aqueous solutions¹⁻⁵ can be represented by equations (1), (2), and (3).



For the e_{aq}^- formation from anisole (R = Me) reaction (1) was proposed.⁶ However, reaction (2) is also conceivable, which would result in the appearance of the corresponding radical cation. In the case of phenol (R = H) the subsequent reaction (3) can be assumed, leading to the observable phenoxyl radical.^{3,7}

In order to examine whether reaction (1) or (2) is essential in the photogeneration of e_{aq}^- from methoxylated benzenes, anisole (AN), and 1,4-dimethoxybenzene (DMB) (10^{-4} – 10^{-3} mol dm⁻³) were used as model compounds in aqueous solutions. The quantum yields of solvated electrons, $Q(e_{\text{aq}}^-)$, for the 1. and 2. singlets, were obtained by steady-state experiments at 25 °C, using C₂H₄ClOH as a specific electron scavenger at low light intensities ($I_0 = 10^{16}$ – 8×10^{17} hν ml⁻¹ min⁻¹). They are represented by $Q(\text{Cl}^-)$ in the Table, together with the data of phenol. Irradiation and actinometry techniques have been previously described.^{5,8}

TABLE. Initial $Q(e_{\text{aq}}^-)$ -values for the 1 and 2 singlets of phenol, anisole, and 1,4-dimethoxybenzene in neutral aqueous solutions.

Compounds	S_1 $Q(\text{Cl}^-)$	S_2 $Q(\text{Cl}^-)$
Phenol	0.021	0.033
AN	0.008	0.120
DMB	0.017	0.30

The transient spectrum (A) obtained by flashing 2×10^{-4} mol dm $^{-3}$ AN at pH = 1.45 ($\lambda_{\text{max}} < 300, 330, \text{ and } 430 \text{ nm}$) and spectrum (B) measured in 5×10^{-4} mol dm $^{-3}$ DMB at pH = 0.36 ($\lambda_{\text{max}} = 315, 430, \text{ and } 455 \text{ nm}$) are shown in the Figure.

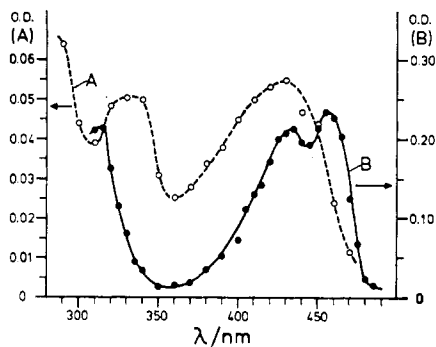


FIGURE. Absorption spectra of transients produced by flash photolysis (half-peak flash duration $7 \mu\text{s}$) of anisole (AN) and 1,4-dimethoxybenzene (DMB) in aqueous solution, saturated with argon. Spectrum (A) (○): 4×10^{-4} mol dm $^{-3}$ AN, pH = 1.45; $200 \mu\text{s}$ after triggering of flash. Spectrum (B) (●): 5×10^{-4} mol dm $^{-3}$ DMB, pH = 0.36; 4.5 ms after triggering of flash.

The absorption bands with $\lambda > 400 \text{ nm}$ are assigned to the corresponding radical cations, AN $^+$ and DMB $^+$. This is based on the following observations. (i) The spectral and kinetic data are in good agreement with those already

observed as a result of one-electron oxidation by pulse radiolysis of aqueous methoxylated benzenes.^{9,10} In agreement with other authors¹⁰ we found a mixed order decay for AN $^+$, arising from the reaction: $\text{AN}^+ + \text{AN} \rightarrow (\text{AN})_2^+$ ($k = 6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and the bimolecular reaction of the radical cation ($2k = 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at pH = 4.5). At pH = 1 DMB $^+$ is found to decay by a very slow second order reaction ($2k = 7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). (ii) Identical spectra, as in the Figure, have been additionally obtained by an one-electron oxidation of AN and DMB by light-induced electron transfer from AN and DMB, respectively, to excited anthraquinone-2,6-disulphonate; electron transfer to $\text{SO}_4^{\cdot-}$ radical anions formed by photolysis of $\text{S}_2\text{O}_8^{2-}$, and reduction of excited Fe^{3+} -ions. (iii) The absorptions of both AN $^+$ and DMB $^+$ show a characteristic pH dependence. In alkaline solution their spectrum disappears because of reaction with OH^- . This reaction has been confirmed by its ionic strength behaviour.

These results strongly support the formation of radical cations as a result of electron ejection from methoxylated benzenes. The radical cation of phenol, however, seems to have a very short life-time and is therefore difficult to observe.

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