

SUBSTITUENT EFFECTS IN THE PHOTOCHEMICAL GENERATION OF HYDRATED ELECTRONS FROM AQUEOUS SOLUTIONS OF PHENOLATES

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Summary

Aqueous solutions of various phenolates at pH 12 and containing N_2O were photolyzed with light of wavelength 253.7 nm. The quantum yields of N_2 , the only gaseous product, were determined and serve as a measure of Φ_{e^-} at this wavelength. The effect of a "transparent" substituent on the quantum yield was found to depend significantly on the position as well as the electronic nature and there was a good correlation to the Hammett substituent constant. It is shown that these results, together with the appreciable positive temperature coefficient of Φ_{e^-} , support the postulate that the immediate precursor of the solvated electron from phenolate is a CTTS type state, involving the oriented solvent molecules around the O atom.

Introduction

Several investigations have been made of the photochemical generation of solvated electrons from aqueous phenolate anions, either from product yields in steady illumination experiments [1] or by measuring, semi-quantitatively or quantitatively, transient absorption intensities of the solvated electron (720 nm) and/or of the corresponding phenoxyl radical (410 nm) by flash photolysis [2 - 4]. In the former type of experiment, where monochromatic light may be used, it has been shown [1] that N_2O concentrations electron scavenger in the presence of ethanol and that at N_2 concentrations $> 10^{-2} M$, a constant quantum yield of N_2 is obtained.

The extensive surveys of Grossweiner and Joschek [3] of the effect of ring substituents on photoionization were mostly performed at natural pH where phenols are undissociated. Since recent work by Feitelson *et al.* [5] indicates that the generation of electrons from the neutral phenol molecule is essentially biphotonic whereas from the anion it is monophotonic, the same influences need not be presumed to be operative.

Many influences on the photoionization process may be conceived for a substituent, but if "transparent" in the sense that it causes only slight change

to the spectrum of the phenolate and does not affect the character of the absorption at the excitation wavelength, then the major effect may be expected to be electronic interaction of the substituted group within the photoexcited phenolate anion. The aims of the present study are thus to obtain a range of data, by the product yield method, for the effect of substituent on the photoionization quantum yield from phenolate anions. All chromophores are avoided and as far as possible all three isomers are used, in order to distinguish the position of substitution from the nature of the substituent.

The temperature dependence of the photoionization of halide ions [6, 7] is considered significant evidence regarding the mechanism. For phenolate, little work has been reported on the temperature coefficient, perhaps because a slight effect was anticipated since the 236 nm band of aqueous phenolate exhibits [1] no environmental effects of the type associated with a CTTS absorption and is entirely assigned to a $\pi \rightarrow \pi^*$ absorption. Some data are presented here on the temperature effects on the solvated electron quantum yields from phenolate itself and from *para*-substituted phenols with both electron-withdrawing and electron-donating substituents.

Experimental

Materials

Nitrous oxide (B.O.C. anaesthetic grade) was purified by repeated trap-to-trap distillation, retaining the middle fraction and was degassed at -196°C immediately before use. Other chemicals used were B.D.H. Analar grade where available and in almost all cases these were used without further purification. The fluorophenols were Koch-Light "pure" grade and were used without further purification. The three cresols, the two chlorophenols and the 3-hydroxyphenol were B.D.H. reagent grade and the 4-*t*-butylphenol was Hopkin and Williams reagent grade. All were purified by the appropriate standard methods (recrystallization, or distillation and recrystallization, or steam distillation, extraction and recrystallization) and gave satisfactory crystalline samples except in the case of 3-chlorophenol, which is strongly deliquescent. Water was first de-ionized and then doubly distilled from alkaline permanganate.

Apparatus

The photolysis cells were similar to those used by Dainton and Logan [7] except that they contained no magnetic stirrer. The cells and all apparatus used in preparing solutions were cleaned by the following procedure. After immersing in a fresh solution of Decon 75 at 55°C for 4 h, they were repeatedly rinsed with de-ionized water until foaming no longer occurred, treated overnight with a solution of 5 parts 100 vol. hydrogen peroxide, 3 parts concentrated nitric acid, 1 part concentrated perchloric acid and 1 part water. They were then rinsed 25 times with de-ionized water, 15 times with doubly distilled water and left to dry in an oven at 130°C until required.

Procedure

Phenolate solutions were made up freshly for each experiment from the phenol, sodium hydroxide, ethanol and doubly distilled water. They were briefly de-aerated by bubbling argon, degassed in the bulb of the photolysis vessel by 6 cycles of freeze-pump-thaw and equilibrated at 25 °C with N₂O at 570 Torr. The cell was thermostated during irradiation and subsequently the permanent gases in the cell were collected and measured by a conventional Toepler pump. Samples of the permanent gas were analyzed by mass spectrometry and it was found to contain only N₂.

The light source was an Engelhard Hanovia low-pressure mercury lamp, emitting predominantly at 253.7 nm. The 185 nm line was absorbed by a quartz filter cell containing distilled water. Actinometry was carried out, before and after each photolysis experiment, using the ferrioxalate system [8], with corrections for the actinic effect of the longer wavelengths (about 10% of the total) estimated by replacing the water filter by one containing de-aerated aqueous KI. Since the phenolate solutions were transparent to these longer wavelengths, the photolyzing light was effectively monochromatic.

Results

The yield of N₂ from 10⁻³ M phenolate at pH 12 with 10⁻¹ M ethanol and 1.8 × 10⁻² M N₂O was found to be directly proportional to the light dose and at 25 °C the quantum yield was calculated to be 0.247, which is in satisfactory agreement with the value of 0.23 under these conditions reported [1] earlier. (Since 2 cm of a 10⁻³ M solution of phenolate transmits about 5% of the incident 253.7 nm light, a correction for this was made in calculating the quantum yields. Low phenolate concentrations obviate the possibility in an unstirred cell of a "skin" effect at the front surface and an accurate correction can be made for incomplete absorption.)

For all the substituted phenolates employed, N₂ yield was likewise proportional to light dose, except in the case of 4-t-butylphenol. Here the first portion of the curve, up to 10⁻⁶ Einsteins, was concave downwards but a linear relationship applied at higher doses up to 5 × 10⁻⁶ Einsteins. The quantum yield reported below is calculated from the slope of this linear portion.

At 25 °C, the quantum yields were determined as follows: phenolate, 0.247 ± 0.01; 4-methylphenolate, 0.296 ± 0.01; 3-methylphenolate, 0.259 ± 0.01; 2-methylphenolate, 0.191 ± 0.02; 4-chlorophenolate, 0.134 ± 0.01; 3-chlorophenolate, 0.121 ± 0.015; 4-fluorophenolate, 0.237 ± 0.01; 3-fluorophenolate, 0.129 ± 0.005; 2-fluorophenolate, 0.125 ± 0.005; 4-t-butylphenolate, 0.392 ± 0.01; 3-hydroxyphenolate, 0.458 ± 0.02. The values for the cresolates show poor correspondence with the results of Dobson and Grossweiner [2]. It may be seen that the effect of a particular substituent depends on its ring position as well as its electron-donating or electron-withdrawing

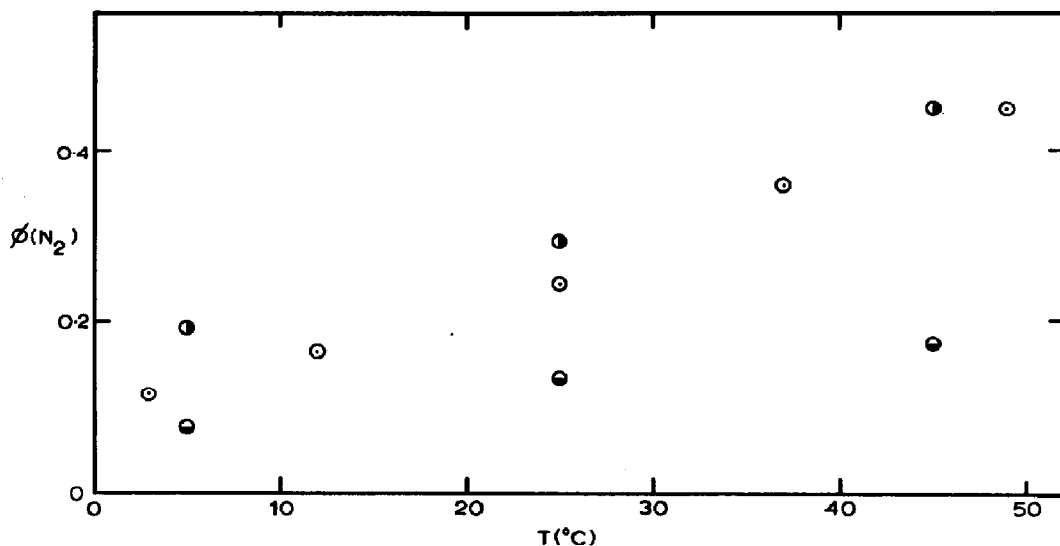


Fig. 1. Temperature dependence of $\Phi(N_2)$ from the 253.7 nm photolysis of 10^{-3} M aqueous solutions of phenolate (\circ), 4-chlorophenolate (\bullet) and 4-methylphenolate (\ominus) at pH 12 in 1.8×10^{-2} M N_2O and 10^{-1} M ethanol.

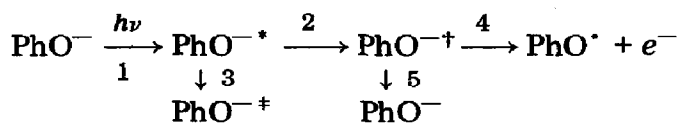
character and that high quantum yields occur with substituents that have a negative value of σ the Hammett substituent constant [10], whereas low yields occur with positive σ values.

The effect of temperature on the quantum yield was determined over the range 5 to 45 °C for phenolate, 4-chlorophenolate and 4-methylphenolate. For all three compounds, the quantum yield increases considerably with temperature, as shown in Fig. 1. This increase is in the same sense and of comparable magnitude to that found by Feitelson *et al.* [5], but is not in accord with the results referred to by Grossweiner [9].

Discussion

In considering the photochemistry of phenolate anion, it is clear that the initial excitation is $\pi \rightarrow \pi^*$ and that hydrated electrons and phenoxy radicals are produced. The photochemistry of inorganic anions, halides and oxyanions, shows clearly that whereas a CTTS state leads to photoionization, an internal excitation does not. While it is clear that there is no close parallel between phenolate and oxyanions such as NO_3^- , a reasonable assumption might be that the direct precursor of the solvated electron from phenolate is not the excited state produced initially. Grossweiner and Joschek [3] have suggested that it is a CTTS state which is populated from the $\pi \rightarrow \pi^*$ excited singlet. In considering the mechanisms of photoionization of aromatic compounds in general, Ottolenghi [11] proposes a semi-ionized CTTS state which may ionize by a diffusion mechanism.

Based on the above assumption, the mechanism would be tentatively written as follows:



where PhO^{-*} denotes the $\pi \rightarrow \pi^*$ singlet state, $\text{PhO}^{-\ddagger}$ the precursor of the solvated electron and steps 3 and 5 are the processes (or groups of processes) which are the respective alternatives to steps 2 and 4. Putting the quantum yield of PhO^{-*} equal to unity, we obtain:

$$\frac{1}{\Phi_{e^-}} = \left(1 + \frac{k_5}{k_4}\right) \left(1 + \frac{k_3}{k_2}\right) \quad (1)$$

In terms of our mechanism, the ring substituents will alter the quantum yields by affecting the relative rates of the photophysical processes of PhO^{-*} or of $\text{PhO}^{-\ddagger}$. If these influences are analogous to the substituent effects on chemical reactions or equilibria, then there should be a quantitative relationship between $\log(\Phi_{e^-}^{-1} - 1)$ and the Hammett substituent constant, σ (or, in the case of *ortho*-substituents, the analogous Taft σ^* constant). This is tested in Fig. 2 where, apart from one point, the correlation is seen to be as good as is frequently found for purely chemical examples.

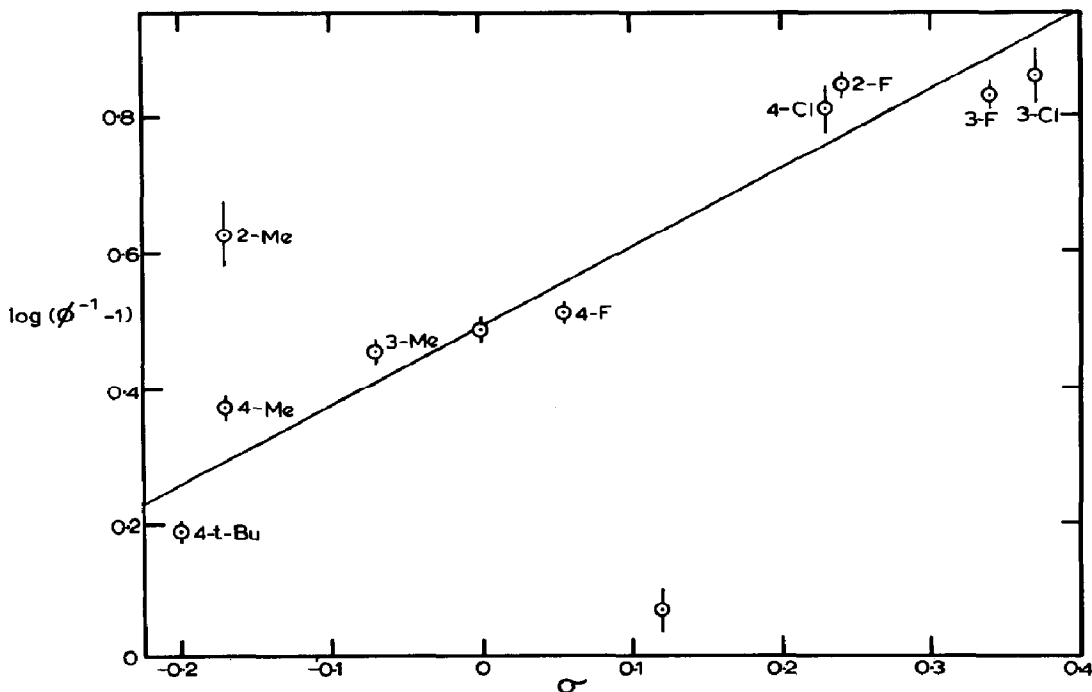


Fig. 2. Plot of $\log(\Phi_{e^-}^{-1} - 1)$ against the substituent constant, σ (or σ^*).

The major discrepancy arises with the 3-hydroxy substituent, but it is doubtful if this compound should be expected to conform since, although —OH is not a chromophore, the ultra-violet absorption spectrum of this anion differs considerably from that of phenolate. Consequently the effect of the substituent is not confined to its influence on steps 2 or 3/steps 4 or 5. In the further discussion, the results for this compound will be neglected.

Assuming that k_5/k_4 and k_3/k_2 both obey Hammett relationships, by differentiation of eqn. (1) we obtain:

$$\frac{d \log(\Phi^{-1} - 1)}{d\sigma} = \frac{(k_5/k_4) \rho_{5,4} + (k_3/k_2) \rho_{3,2} + (k_5 k_3/k_4 k_2) (\rho_{5,4} + \rho_{3,2})}{(k_5/k_4) + (k_3/k_2) + (k_5 k_3/k_4 k_2)} \quad (2)$$

where $\rho_{5,4}$ and $\rho_{3,2}$ denote the respective Hammett reaction constants for k_5/k_4 and k_3/k_2 . This equation indicates that there are three sets of conditions where formal linear relationships exist between $\log(\Phi^{-1} - 1)$ and σ .

$$\frac{k_5}{k_4} \gg \frac{k_3}{k_2} \ll 1, \text{ when the slope is } \rho_{5,4} \quad (I)$$

$$\frac{k_3}{k_2} \gg \frac{k_5}{k_4} \ll 1, \text{ when the slope is } \rho_{3,2} \quad (II)$$

$$\frac{k_5}{k_4} \gg 1 \text{ and } \frac{k_3}{k_2} \gg 1, \text{ when the slope is } (\rho_{5,4} + \rho_{3,2}) \quad (III)$$

The quality of the correlation in Fig. 2 suggests that one of these three situations is closely approached throughout the series of phenolates considered. Possibility (III) can be discounted, since it requires that Φ_{e^-} should be extremely small, whereas the experimental values range from 0.12 to 0.46. We suggest that it is situation (I) which is an acceptable approximation for the phenolates considered and, as it requires $k_2 \gg k_3$, this is tantamount to the virtual deletion of step 3 from the mechanism.

Thus it is proposed (a) that the observed variations in the solvated electron quantum yield arise principally from the effects of the substituents on the fate of $\text{PhO}^{-\dagger}$ and (b) that $\text{PhO}^{-\dagger}$ represents an electronic state in phenolates analogous to a CTTS state in compact ions, with the electron in a potential well formed by the oriented solvent molecules around the O atom. The following points may be cited in support of these postulates.

(1) The effect of substituents is clearly a function of the position as well as the electron withdrawing/donating nature. Figure 2 shows that the position of the substituent with respect to the O^- is important. (The anomalous behaviour of the 2-methyl compound may be readily rationalized on the basis of steric effects, which would be more important here than in the case of the other *ortho* substituent, since methyl is bulkier than fluorine.)

(2) The slope of the line in Fig. 2, ignoring the points from the 3-hydroxy and the 2-methyl compounds, gives a ρ value of +1.1. When situation (I) applies, this is identified as $(\rho_5 - \rho_4)$; since substituents are unlikely to have

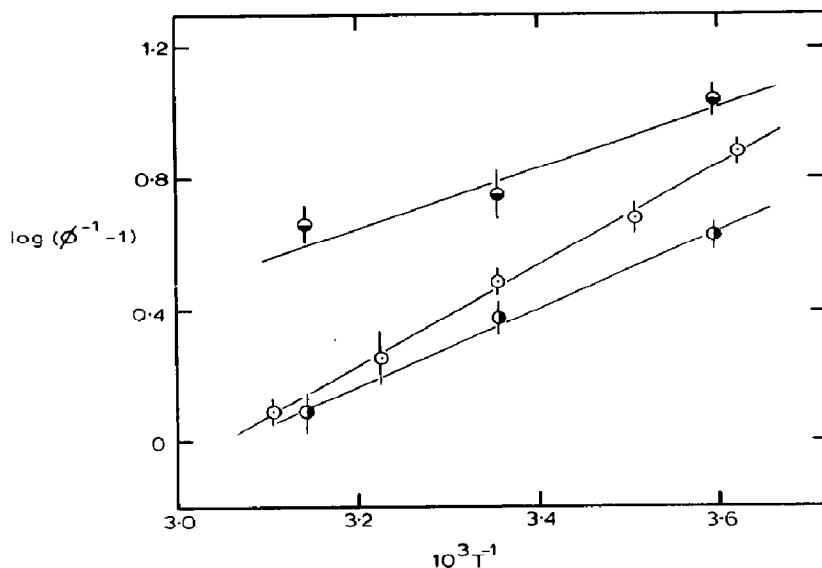


Fig. 3. Plots of $\log(\Phi_{e^-}^{-1} - 1)$ against T^{-1} for phenolate (○), 4-chlorophenolate (◐) and 4-methylphenolate (●) using the data presented in Fig. 1.

much effect on step 5, we conclude that $\rho_4 \approx -1.1$. For the reactions of hydrated electrons with *para*-substituted benzoic acids, Anbar and Hart [12] reported a ρ value of +0.74. Step 4 bears some analogy to the reverse of this reaction and our experimental estimate of ρ_4 does not appear an improbable value for it.

(3) The considerable effect of temperature on Φ_{e^-} is, by the revised model, considered a consequence of the temperature dependence of steps 4 and 5. The latter is expected to be slight whereas, in view of the CTTS nature attributed to $\text{PhO}^{-\dagger}$, the former should be appreciable. The general equation is as follows:

$$2.303 R \frac{d \log(\Phi^{-1} - 1)}{d(T^{-1})} = \frac{\frac{k_5}{k_4} (E_4 - E_5) + \frac{k_3}{k_2} (E_2 - E_3) + \frac{k_5}{k_4} \cdot \frac{k_3}{k_2} (E_4 - E_5 + E_2 - E_3)}{\frac{k_5}{k_4} + \frac{k_3}{k_2} + \frac{k_5}{k_4} \cdot \frac{k_3}{k_2}} \quad (3)$$

where E_2 , E_3 , E_4 and E_5 denote the Arrhenius activation energies of the respective steps, and for situation (I), the right hand side reduces to $(E_4 - E_5)$.

For the three compounds studied, Fig. 3 shows the plots of the temperature-dependence data. Better linearity is found in the case of phenolate itself than for the other compounds, but the deviations lie within the error limits. From the straight lines, the experimental activation energies are calculated as 29, 21 and 16 kJ/mol for phenolate, 4-methylphenolate and 4-chlorophenolate respectively.

The possible non-linearity of some of the plots in Fig. 3 and the variations in the values found for E_4 are adequately accounted for by the approximation involved in assuming that situation (I) applies. But the fact that all these values are of the same order of magnitude as the activation energy for self-diffusion in water over this temperature range [3] (19.6 kJ/mol) lends significant support to the claim that a CTTS-type state is the direct precursor of the solvated electron from photoexcited phenolate.

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