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The Formation of Solvated Electrons in the Photochemistry of the Phenolate Ion in Aqueous Solutions

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Evidence for the photochemical formation of solvated electrons in aqueous solutions of the phenolate ion is obtained. N_2O and acetone are employed as specific scavengers for the solvated electrons produced from the thermal dissociation of the excited state. The dependence of the quantum yield of N_2 on $[N_2O]$ is found to agree with cage scavenging kinetics. The solvated electron–phenoxy radical pair in the solvent cage is formed in a secondary process from the spectroscopic excited state of the ion. Spectroscopic data indicate that this excited state arises from an internal $\pi-\pi^*$ excitation and does not involve a c.t.t.s. (charge transfer to the solvent) state as in the case of solvated electron formation in the photochemistry of the halide ions in solution.

Introduction

The occurrence of photoionization processes of aromatic molecules in rigid solvents was first established by the pioneering work of Lewis and his school.^{1,2} Later investigators^{3,4} considered the nature of the photoejected electron, trapped by solvation in the rigid glass, and followed the kinetics of the electron–radical ion recombination luminescence. Land, Porter, and Strachan⁵ were able to prove that such photoionization processes are not restricted to condensed glassy media and may also occur in liquid solutions. This was accomplished by comparing the spectra of the short-lived intermediates formed in the flash photolysis of a large number of phenols and naphthols in water⁵ with the photolysis products obtained from the same molecules in rigid solution.⁶ It was thus suggested^{5,7} that the primary photochemical act in the case of aqueous phenolate ion involves an electron ejection process. These conclusions were recently confirmed by an investigation⁸ of the photochemistry of the phenolate ion in aqueous and alcoholic NaOH–KOH glasses at 77°K. where the spectrum of the trapped, photoejected, electron was identified.

The purpose of the present work was to provide direct chemical evidence for the photoionization of the phenolate ion in aqueous solutions, to get a closer insight into the electron ejection process, and to investigate the fate of the ejected electron in this system. In previous work^{9–11} we investigated the photochemical consequences of light absorption in the charge transfer to the solvent (c.t.t.s.) bands of the monoatomic negative halide ions in solution. By using specific scavengers, chemical evidence was obtained here for the transient formation of solvated electrons by thermal ionization of the c.t.t.s. excited state. These chemical kinetic methods, in which specific scavengers for solvated electrons are employed, were now applied to the investigation of the photochemistry of the phenolate ion, providing us with new tools in the study of photoionization processes of molecules in solution.

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Experimental

Light Sources and Actinometry.—The light source at 229 $m\mu$ was an Osram Cd/1 cadmium lamp operated at 12 v. and 1.5 amp. The spectral distribution of the lamp was determined by an Optica CFU spectrophotometer. The only lines absorbed by our solutions were the 2288 Å. line and the very weak 2144 Å. line. The light output at 2288 Å. was determined by a differential actinometric method using the uranyl oxalate actinometer. In a first experiment the actinometric solution in the reaction vessel was irradiated directly. In a second experiment a 1-cm. path length 4 *N* acetic acid solution filter, absorbing all the light below 2400 Å., was inserted between the reaction vessel and the lamp. The chemical change on illumination was determined in both cases by titration with 0.01 *N* $KMnO_4$ solution. From the difference between the two values the light intensity at 2288 Å. was determined as $J = 3.4 \times 10^{-7}$ einstein $l^{-1} sec^{-1}$.

The light source at 2537 Å. was a Thermal Syndicate low pressure mercury arc operated at 1000 v. and 50 amp. A I_2/I^- filter⁹ was employed to cut off other lines. The light intensity at this wave length was $J = 8.1 \times 10^{-7}$ einstein $l^{-1} sec^{-1}$.

Procedure.—A 1-cm. quartz spectrophotometer cell was adapted for vacuum-photochemical experiments.

The procedure in experiments involving N_2O was previously described.¹⁰ The pressure of the gas evolved after irradiation was determined by means of a McLeod gage and its composition ascertained by combustion in the presence of hydrogen or oxygen. The pH was adjusted by means of NaOH.

In all cases total light absorption by the phenolate ion in the reaction cell could be assumed (see Fig. 4 for the values of the extinction coefficients). Absorption of light by the OH^- ion could be neglected even at 2288 Å. as here $\epsilon_{OH^-} = 0.5$ $l. mole^{-1} cm^{-1}$, $\epsilon_{C_6H_5O^-} = 7500$ $l. mole^{-1} cm^{-1}$, and $[C_6H_5O^-]/[OH^-]$ was never below 0.1. The same refers to absorption of the 2144 Å. cadmium line, which is approximately one-thirtieth that of the 2288 Å. line (here $\epsilon_{OH^-} = 15$ $l. mole^{-1} cm^{-1}$ and $\epsilon_{C_6H_5O^-} = 4000$ $l. mole^{-1} cm^{-1}$).

Results and Discussion

The Phenolate– N_2O System.—Experiments were carried out with aqueous solutions of 10^{-3} *M* phenol, 10^{-2} *M* NaOH, 1 *M* ethanol, and varying concentrations of dissolved N_2O . At pH 12 almost all the phenol ($pK_a = 10$) exists in its ionized form. Ethanol was added in order to scavenge OH (or O^-) radicals, thus preventing the formation of H_2O_2 which may cause, by further reactions with OH radicals, the evolution of O_2 as a second gaseous product. The gas evolved on irradiating the solutions was found to be pure N_2 . From the slopes of the linear plots of $[N_2]$ vs. the irradiation time, we calculate the quantum yields for N_2 evolution, $\gamma(N_2)$, which depend markedly on the N_2O concentration. These results are presented in Table I.

An examination of Table I shows that the ratio $\gamma(N_2)_{2288 \text{ Å.}}/\gamma(N_2)_{2537 \text{ Å.}}$ is constant at constant N_2O concentration. At high $[N_2O]$ values a limiting constant quantum yield independent of $[N_2O]$ is obtained.

TABLE I

THE DEPENDENCE OF $\gamma(N_2)$ ON $[N_2O]$ IN AQUEOUS SOLUTIONS OF $10^{-3} M$ PHENOL, $10^{-2} M$ NaOH, AND $1 M$ EtOH AT 28°
 $J = 3.4 \times 10^{-7}$ einstein l.⁻¹ sec.⁻¹ at 2288 Å.; $J = 8.1 \times 10^{-7}$ einstein l.⁻¹ sec.⁻¹ at 2537 Å.

$[NO_2]$, mole l. ⁻¹	$\gamma(N_2)$ at 2288 Å.	$\gamma(N_2)$ at 2537 Å.
...	<0.02 ^a	<0.02
1.22×10^{-4}	0.192	...
2.64×10^{-4}	.204	.160
8.5×10^{-4}	.225	...
1.96×10^{-3}	.245	.180
4.3×10^{-3}	.280	...
7.7×10^{-3}	.292	.224
1.2×10^{-2}	.300	.230
1.9×10^{-2}	.300	.228

^a Values referring to quantum yields of all gaseous products.

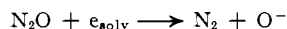
The values of $\gamma(N_2)$ reported in Table I were found to be independent of both OH^- and phenolate ion concentrations. This is demonstrated in Table II.

TABLE II

N_2 QUANTUM YIELDS AT VARIOUS NaOH AND PHENOL CONCENTRATIONS

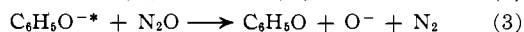
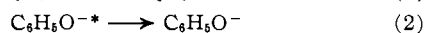
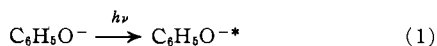
$[N_2O]$, M	Wave length, Å.	$[NaOH]$, M	$[Phenol]$, M	$\gamma(N_2)$
1.2×10^{-2}	2537	10^{-1}	10^{-2}	0.302
1.2×10^{-2}	2537	10^{-2}	10^{-2}	0.298
1.96×10^{-3}	2537	10^{-2}	10^{-2}	1.178
1.96×10^{-3}	2537	10^{-2}	10^{-3}	0.180
1.2×10^{-3}	2288	10^{-1}	10^{-2}	.228
2.64×10^{-4}	2288	10^{-2}	10^{-2}	.160
2.64×10^{-4}	2288	10^{-2}	10^{-3}	.160

Previous photochemical¹⁰ and radiation-chemical¹² studies indicate that N_2O may act as a specific scavenger for solvated electrons in aqueous and nonaqueous¹³ solutions. The scavenging process leads to dissociation of the N_2O molecule, yielding molecular nitrogen



These conclusions are supported by mass-spectrometric studies involving electron capture by N_2O in the gas phase.^{14,15} We thus conclude that the photochemical evolution of nitrogen in the phenolate- N_2O system may be due to electron capture by N_2O . Two possible mechanisms for such a process should be considered.

(a) A mechanism involving direct charge transfer from the excited state of the phenolate ion, $C_6H_5O^{*-}$, to a N_2O molecule. This process competes with deactivation of the excited state according to the kinetic scheme



According to this scheme the nitrogen quantum yield should be represented by

$$\gamma(N_2) = \frac{k_3[N_2O]}{k_3[N_2O] + k_2} \quad (4)$$

and a plot of $1/\gamma(N_2)$ vs. $1/[N_2O]$ should be linear. Figure 1 represents the plot of the experimental results at 2288 Å. (see Table I) according to eq. 4, clearly demonstrating their inconsistency with the mechanism presented by eq. 1-3.

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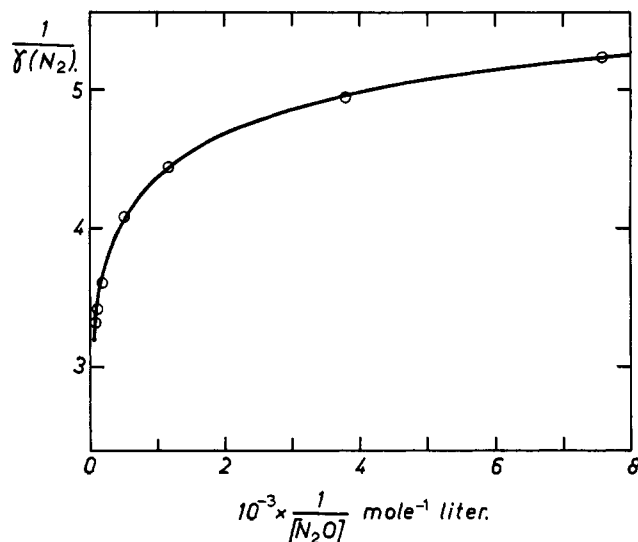
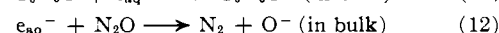
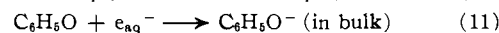
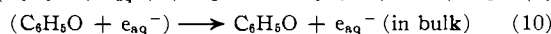
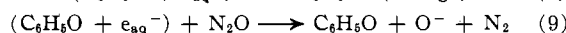
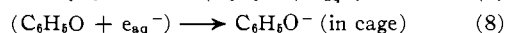
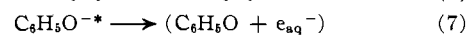
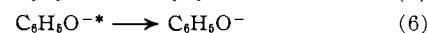
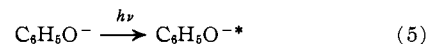


Fig. 1.—Test of the dependence of $\gamma(N_2)$ on $[N_2O]$ according to eq. 4.

(b) The alternative mechanism proposed is formally similar to the one previously described by us in the photochemistry of the halide ions in solution.^{9,10} It may be represented by the kinetic scheme



The excitation step (5) is followed by a "dissociation" of the excited state (7) which leads to the formation of the radical pair C_6H_5O and e_{aq}^- (the solvated electron) in the solvent cage; $(C_6H_5O + e_{aq}^-)$ denotes this photochemical cage in which the solvated electron and the phenoxyl radical may undergo a secondary diffusive recombination (eq. 8). Reaction 9 represents the cage-scavenging process, competing with reaction 8. The limiting quantum yield at high N_2O concentrations (denoted by Γ) means complete scavenging of e_{aq}^- by N_2O and should thus be identified with the yield of formation of the radical pair $C_6H_5O + e_{aq}^-$ in the photochemical cage. The numerical value of Γ is determined by the relative efficiency of processes 6 and 7. Reaction 10 stands for the "residual yield," γ_r , of radicals escaping cage recombination in the absence of a radical scavenger ($[N_2O] = 0$). The value of γ_r is determined by the competition between reaction 8 and reaction 10 representing diffusion of C_6H_5O and e_{aq}^- from the cage to the bulk.

The quantum yield in such a photochemical system, where scavenging competes with cage recombination, is given according to Noyes^{16a} by the expression

$$\gamma(N_2) = \gamma_r + \Gamma 2a \sqrt{\pi k_{N_2O + e_{aq}^-} [N_2O]} \quad (13)$$

where a is a parameter depending on the solvent and on the nature of the cage radicals.^{16b} Equation 13 is an approximation valid only at relatively low N_2O concentrations but is not applicable at extremely low $[N_2O]$ values when N_2O competes with radical recombination in the bulk (eq. 11 and 12).

(16) (a) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955); (b) **78**, 5486 (1956).

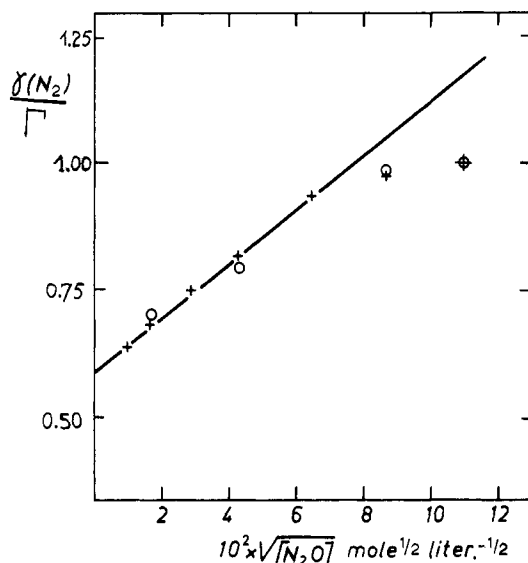
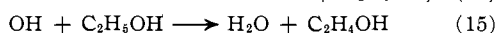
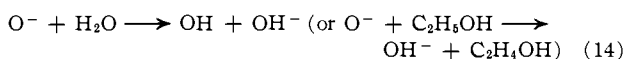


Fig. 2.—Cage scavenging of solvated electrons by N_2O . The dependence of $\gamma(N_2)$ on $\sqrt{[N_2O]}$ (eq. 13): +, photochemistry at 2288 Å. ($\Gamma = 0.3$); O, photochemistry at 2537 Å. ($\Gamma = 0.23$).

The plot of our experimental results according to eq. 13 is presented in Fig. 2. Good agreement exists between theory and experiment at low scavenger concentrations. The deviations at higher $[N_2O]$ values are typical in such systems^{9,10} and should be assigned to the inadequacy of eq. 13 at high scavenger concentrations when $\gamma \rightarrow \Gamma$.

It should be noted that O^- radicals are scavenged according to the scheme¹⁰



and do not contribute to the quantum yield of gas evolution.

From the intercept in Fig. 2 and the values (see Table I) $\Gamma_{2288 \text{ Å.}} = 0.3$ and $\Gamma_{2537 \text{ Å.}} = 0.23$, we get $\gamma_r = 0.176$ for the photochemistry at 2288 Å. and $\gamma_r = 0.142$ at 2537 Å. However, in the complete absence of N_2O the quantum yield for gas evolution is very low (see Table I), indicating an efficient bulk recombination (probably $C_6H_5O + e_{aq}^- \rightarrow C_6H_5O^-$), totally preventing dissociative electron capture by the solvent, which could ultimately lead to hydrogen evolution.⁹ The slope in Fig. 2 yields the value $2a\sqrt{\pi k_{N_2O} + e_{aq}^-} = 51.1^{1/2} \text{ mole}^{-1/2}$ which is wave length independent. We may therefore conclude that the only effect of changing the photon energy from 2288 to 2537 Å. is a decrease in Γ , while the cage parameter $2a\sqrt{\pi k_{N_2O} + e_{aq}^-}$ appears to be unaffected by changes in wave length of the absorbed quantum.

The N_2O -Phenolate-Acetone System.—The experimental results and the kinetic treatment presented in the preceding section yield evidence supporting two main conclusions. First, that the principal photochemical step does not involve a direct interaction between N_2O and the excited state of the phenolate ion, but it consists in scavenging of radicals formed in a photochemical cage by a secondary process. Second, that the scavenged species is a solvated electron. The alternative possibility, namely, that we are dealing with hydrogen atoms scavenged from a photochemical cage by N_2O according to the process⁹ $H + N_2O \rightarrow N_2 + OH$, should be rejected as no hydrogen is formed in the absence of N_2O although an efficient hydrogen atom scavenger, such as ethanol, is present (see Table I).

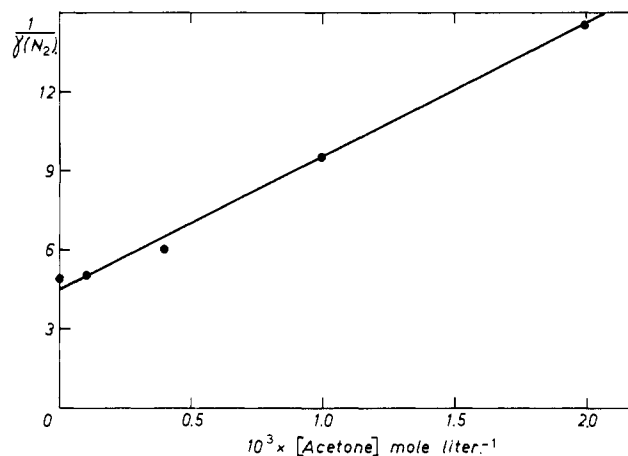


Fig. 3.—The competition between N_2O and acetone for solvated electrons, treated according to eq. 20.

In order to confirm these conclusions, a few experiments in acetone-containing solutions were carried out. Radiation chemical data¹⁷ indicate that acetone acts as a specific scavenger for solvated electrons in a process which is not followed by gas evolution. Thus, the addition of acetone to the N_2O -phenolate system should cause a decrease in the N_2 yield. The results in Table III entirely confirm this assumption.

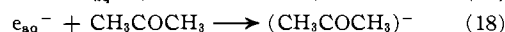
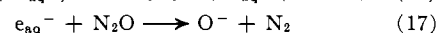
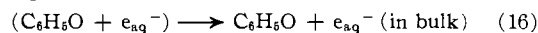
TABLE III

THE DEPENDENCE OF $\gamma(N_2)$ ON ACETONE CONCENTRATION AT CONSTANT $[N_2O] = 2.64 \times 10^{-4} M$ IN SOLUTIONS IRRADIATED AT 2288 Å.

Concentrations of phenol, NaOH, and EtOH, light intensity, and temperature as in Table I

[acetone], M	10^{-4}	3×10^{-4}	10^{-3}	2×10^{-3}
$\gamma(N_2)$	0.204	0.200	0.167	0.105

The value $\gamma_r = 0.175$ obtained at 2288 Å. from eq. 13 and Fig. 1 indicates that the competition experiments presented in Table III were carried out in a region where only 10% of the scavenging occurs from the photochemical cage. The main competition between N_2O and acetone for the solvated electrons is therefore due to bulk reactions where ordinary steady-state kinetics applies. The following scheme will thus account for the experimental data of Table III



(reaction 18 does not lead to the formation of gaseous products¹⁷).

The quantum yield for N_2 evolution in the presence of acetone will therefore be

$$\gamma(N_2) = \gamma_0 \left(\frac{k_{17}[N_2O]}{k_{17}[N_2O] + k_{18}[CH_3COCH_3]} \right) \quad (19)$$

where γ_0 is the quantum yield in the absence of acetone and approximately equals γ_r .

Equation 19 can be rearranged to the form

$$\frac{1}{\gamma(N_2)} = \frac{1}{\gamma_0} + \frac{1}{\gamma_0} \left[\frac{k_{18}}{k_{17}[N_2O]} \right] [CH_3COCH_3] \quad (20)$$

the plot of $1/\gamma(N_2)$ vs. $[Ac]$ is presented in Fig. 3. A straight line is obtained where

$$\frac{k_{18}}{k_{17}} = \frac{(\text{slope})}{(\text{intercept})} [N_2O] \cong 0.3$$

This value may be compared with that obtained in other independent systems. The rate-constant ratio $k_{Ac + e_{aq}^-}/k_{H_2O + e_{aq}^-}$ has been evaluated from radiation

(17) J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962).

chemical data¹⁷ where the value 0.2 to 0.3 was obtained. The ratio $(k_{N_2O} + e_{aq}^-)/(k_{H_2O} + e_{aq}^-)$ as calculated from radiation chemical¹² and photochemical¹⁰ data is approximately 0.5. One therefore gets $k_{Ac} + e_{aq}^-/k_{N_2O} + e_{aq}^- = 0.4$ to 0.6, in fair agreement with the value obtained in our treatment.

These results yield a further independent support to the identification of the species formed from the excited state of the phenolate ion and scavenged by N_2O as being the solvated electron.

The Photochemistry of Phenol in Aqueous Solutions.—It should be added at this point that solvated electrons are not formed, or at most are formed with very low quantum yields, on irradiation of neutral or acid aqueous solutions of phenol at 2288 Å. This was confirmed by two experiments in which 0.178 *M* or 1.78 *M* H_2SO_4 was employed as the solvated electron scavenger, in the presence of 1 *M* ethanol serving as scavenger for hydrogen atoms formed by the reaction between e_{aq}^- and H_3O^+ .⁹ In both cases the quantum yields for H_2 evolution were approximately 0.025, independent of the concentration of H_2SO_4 , and almost equal to the value ($\gamma = 0.02$) obtained in neutral solutions of phenol. Similar values were obtained for $\gamma(N_2)$ when 1.2×10^{-2} *M* N_2O , instead of H_3O^+ , was used as the electron scavenger. These results indicate that the minor gas evolution in these solutions is not due to solvated electrons scavenged by H^+ from a photochemical cage, thus excluding an efficient electron ejection process in this system. A possible mechanism for gas evolution in this system may involve the dissociation $C_6H_5OH^* \rightarrow C_6H_5O + H$. However, the small values of γ_{gas} in neutral and acid solutions led to experimental difficulties which prevented an exact elucidation of the photochemistry of the neutral phenol molecule.

Environmental Effects on the Spectrum of the Phenolate Ion.—The present work yields evidence for the formation of solvated electrons from an excited state of the aqueous phenolate ion. Regarding the nature of the excited state responsible for solvated electron formation two possibilities may be advanced. (a) A $\pi \rightarrow \pi^*$ excitation leads to an excited state which is an "internal" state of the aromatic system. This state is capable of an electron transfer to the adjacent solvent molecules where, after a suitable polarization process, the solvated electron is formed. (b) Excitation involves charge transfer to the solvent. The excited state consists of a symmetric electronic orbital where the electron is bound in the field of the organized medium due to the polarization of the negative phenolate ion. This will involve a physical picture similar to that previously derived for the c.t.t.s. bands^{18,19} of the solvated halide ions. Photochemical investigations^{9,10} showed that these excited states are thermally ionized, leading to the formation of a halogen atom and a solvated electron in the same solvent cage.

In order to discriminate between the two possibilities, a brief spectroscopic investigation of aqueous phenolate solutions was carried out. It is well known that the charge-transfer bands of the halide ions in solution are sensitive to environmental changes and exhibit typical shifts on changing the temperature²⁰ or the solvent^{21,22} and on adding salts and organic solutes.²³ Burak and

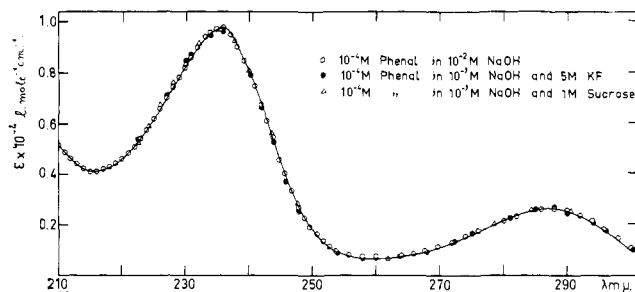


Fig. 4.—Environmental effects on the absorption spectrum of the phenolate ion in aqueous solutions

Treinin²⁴ recently investigated the effects of such environmental changes on the absorption spectrum of the N_3^- ion and have been able to detect a charge-transfer band, superposed on a second band due to an internal transition of the ion.

Marked blue shifts in the absorption bands of the iodide ion are caused by the addition of ionic salts, such as KF, or nonpolar solutes such as sucrose.²⁵ In the presence of 2 *M* KF the 226 $m\mu$ I_{aq}^- band is shifted symmetrically by approximately 4 $m\mu$, while the addition of 0.5 *M* sucrose causes a shift of about 2 $m\mu$. We therefore investigated the effect of adding 5 *M* KF and 1 *M* sucrose on the absorption spectrum of the aqueous phenolate ion, between 210 and 300 $m\mu$, in order to establish whether a charge-transfer transition may contribute to the absorption in the region where our photochemical experiments were carried out. The results are presented in Fig. 4, clearly indicating the absence of any environmental effect due to the high concentrations of added solutes. Thus any substantial contribution of a charge-transfer state in this region may be ruled out. Such a transition may of course be difficult to detect if it occurs with a very small extinction coefficient compared to that of the internal $\pi \rightarrow \pi^*$ transition. This assumption is unreasonable considering the relatively high oscillator strengths of c.t.t.s. transitions.²⁵ Besides, in such a case, the c.t.t.s. contribution to the photochemical electron ejection process, which occurs with a relatively high quantum yield, will also be negligible.

The excited state which ultimately leads to the formation of solvated electrons in the case of the phenolate ion is, therefore, an "internal" state of the aromatic molecule arising from a $\pi \rightarrow \pi^*$ excitation. By contrast, it is the expanded electronic orbital, on the hydration layers of the ion,¹⁸ which is responsible for solvated electron formation in the case of the halide ions in solution.⁹⁻¹¹ Another argument which supports this conclusion is that quantum yields of the same order of magnitude are observed at 2288 and 2537 Å. This probably would not be the case if a charge transfer band would be hidden below the $\pi \rightarrow \pi^*$ band. There is only a slight wave length dependence of Γ . At both wave lengths the same electronic excited state is involved. The slight increase of Γ with increasing the photon energy may perhaps be due to the effects of higher excited vibrational levels on the competition between deactivation and photoionization of the excited state. Similar effects on the quantum yields for photoionization of aromatic molecules in rigid solvents were recently observed.^{26,27}

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