Organic and Biological Chemistry

Optical Generation of Hydrated Electrons from Aromatic Compounds. II[1]

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Abstract: A flash-photolysis survey of aromatic compounds in aqueous solution has shown that optical e_{aq}^- generation is likely for the following types: benzene derivatives with only electron-donating substituents; the aryl acids $C_6H_5(CH_2)_nCOO^-$ for $n = 0$–4; heterocycles with five-membered rings and one heteroatom. For molecules of phenol structure (phenol, cresols, dihydroxybenzenes, methoxyphenols, aniline, thiophenol) e_{aq}^- formation was accompanied by phenoxyl-type radicals ($O\cdot$). However, the predominant radicals produced from anisoles (anisole, phenoxyacetic acid, dimethoxybenzenes, thioanisole) were of the phenoxymethyl type ($OCH_2\cdot$). The formation of phenyl from benzoic acid and benzyl from phenylacetic acid suggests that the longer chain aryl acids of this group photoionize at the terminal COO^- group with the release of CO_2. Transient spectra were obtained from many aromatics which did not yield a detectable e_{aq}^- absorption. In some cases this was probably due to rapid electron scavenging by the parent molecules (*e.g.*, heterocycles with doubly bonded nitrogen) while in others it was due to alternative photochemical paths, particularly bond splitting (*e.g.*, phenoxyphenols, benzyl derivatives, halogenated benzenes). Filter experiments in typical cases showed that photoionization is induced by irradiation in the longest wavelength aromatic band. It is suggested that electron release takes place from a charge-transfer intermediate populated *via* the excited singlet state of the ring system. The relationship of this mechanism to the photolysis of aromatics in rigid media at low temperature is discussed.

It has been known for many years that the ultraviolet irradiation of easily oxidized aromatics in rigid media leads to electron ejection and the stabilization of the resulting free-radical products.[2,3] More recent work has shown that photolysis of aromatics in aqueous solution produces radical products and the same hydrated electron species that is generated by the action of ionizing radiation on water.[4–6] Grossweiner and Joschek[7] surveyed a number of aromatic compounds and found that the ones for which the e_{aq}^- absorption could be detected at 5 μsec after an ultraviolet light flash fall into these classes: (a) benzene derivatives with electron-donating substituents, (b) arylcarboxylic acids, (c) some heterocycles with five-membered rings. It was shown that e_{aq}^- optical generation correlates with low gas-phase photoionization potential (PIP), negative Hammett σ_p constants, and low reactivity of the parent molecules with e_{aq}^-. This paper reports spectral data for the compounds studied in part I,[7] the results of wavelength filter experiments, and flash photolysis data for some additional compounds.

Experimental Procedures and Results

The spectra were taken with a Hilger E498 quartz prism spectrograph on Kodak I-N plates using a 15-μsec (over-all) spectroflash from a xenon lamp. The samples were contained in a 25 cm long Vycor cell (optical transmission: 3% at 210 mμ; 50% at 237 mμ; >85% above 300 mμ) with fused silica windows. The photoflash was of 40 μsec (over-all) duration obtained by discharging 700 joules (at 9 kv) through two fused silica lamps containing 5 cm of xenon. The minimum peak-to-peak time delay was 5 μsec. A more detailed description of the apparatus has been given elsewhere.[8,9]

The solute concentrations were selected to give OD/cm ≈ 1 at the maxima of the longest wavelength absorption bands. The weighed samples were completely dissolved to minimize the effects of impurities in compounds of low solubility. The solutions were evacuated to 5×10^{-6} mm for 2 hr by vigorous shaking under pumping. For oxygen-sensitive solutions the solvent was first evacuated and the solute was added under nitrogen, after which the solution was evacuated again. A similar procedure was used for volatile solutes and the optical absorption was measured *in situ* to ensure that the final concentration was suitable. The best available grades of chemicals were used. Purification by distillation or recrystallization was done when considered necessary. The following compounds were prepared according to the literature:

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Table I. Summary of Flash Spectra Taken at 5-μsec Delay

	Parent molecule[a]	Solvent[b]	Transient absorption maxima, mμ			Radical assignment	e_{aq}^- [c]	Oxygen quenching[d]
O-1	Phenol (0.5)	H_2O	398 (n,s)	383 (n,s)	362 (n,w)	Phenoxyl	+	−
O-2	*o*-Cresol (0.5)	H_2O	395 (n,s)	380 (n,s)	363 (n,w)	*o*-Methylphenoxyl	+	−
	m-Cresol (0.5)	H_2O	412 (n,s)	387 (n,s)	373 (n,w)	*m*-Methylphenoxyl	+	−
	p-Cresol (0.5)	H_2O	405 (n,s)	388 (n,s)	358 (n,w)	*p*-Methylphenoxyl	+	−
O-3	Catechol (0.6)	H_2O	≈350 (vb,s)	306 (n,s)		*o*-Hydroxyphenoxyl	+	−
	Resorcinol (0.6)	H_2O	430 (n,s)	408 (n,w)	<400 (vb,s)	*m*-Hydroxyphenoxyl	+	−
	Hydroquinone (0.3)	H_2O	428 (n,vs) <390 (vb,s)	406 (n,s)	402 (n,s)	*p*-Hydroxyphenoxyl	f	−
O-4	Benzoquinone (0.06)	H_2O	428 (n,vs) <390 (vb,s)	406 (n,s)	402 (n,s)	*p*-Hydroxyphenoxyl	−	−
O-5	4,4′-Dihydroxybiphenyl (0.3)	H_2O	≈630 (vb, vs)	450 (n,s)	400 (b,vs)	*p*-(4-Hydroxyphenyl)-phenoxyl	Δ	−
	3,3′-Dihydroxybiphenyl (1.3)	H_2O	≈550(b,s)	<400 (vb,vs)			+	+
	2,2′-Dihydroxybiphenyl (0.4)	H_2O	≈630 (vb,s)	453 (n,w)	<450 (bv,s)		Δ	+
	2,4′-Dihydroxybiphenyl (0.4)	H_2O	≈430 (vb,s)				+	
O-6	Diphenoquinone (0.1)	H_2O	≈630 (vb,s)	450 (n,s)	400 (b,vs)	*p*-(4-Hydroxyphenyl)-phenoxyl	Δ	
O-7	Anisole (0.7)	H_2O	400 (n,vw)	340 (b,vw)		Phenoxymethyl	++	+
		EtOH	400 (n,s)	342 (n,s)		Phenoxymethyl		+
		Cyclohexane	400 (n,s)	343 (b,s)		Phenoxymethyl		+
O-8	Phenoxymethyl chloride	Cyclohexane	400 (n,s)	≈340 (b,w)		Phenoxymethyl		+
O-9	Phenoxyacetic acid (0.1)	H_2O (pH 9.0)	400 (n,s)	384 (n,s)	<340 (b,w)	Phenoxymethyl	f	+
O-10	*o*-Dimethoxybenzene (0.4)	H_2O		None			++	
	m-Dimethoxybenzene (0.7)	H_2O	425 (n,vw)	≈335 (b,vw)		*m*-Methoxyphenoxymethyl	++	+
		EtOH	425 (n,w)	≈335 (b,w)		*m*-Methoxyphenoxymethyl		+
		Cyclohexane	425 (n,vs)	≈335 (b,s)		*m*-Methoxyphenoxymethyl		+
	p-Dimethoxybenzene (0.5)	H_2O	455 (n,vs)	427 (n,vs)	≈340 (b,vw)	*p*-Methoxyphenoxymethyl	+	+
		EtOH	410 (b,vs)	≈350 (b,w)		*p*-Methoxyphenoxymethyl		+
		Cyclohexane	400 (b,vs)	345 (n,vs)		*p*-Methoxyphenoxymethyl		+
O-11	*o*-Methoxyphenol (0.6)	H_2O	380 (n,s)			*o*-Methoxyphenoxyl	+	−
	m-Methoxyphenol (0.6)	H_2O	432 (b,s)	412 (n,w)	<400 (vb,w)	*m*-Methoxyphenoxyl	+	−
	p-Methoxyphenol (0.5)	H_2O	420 (n,vs)	<400 (vb,s)		*p*-Methoxyphenoxyl	+	−
O-12	*o*-Phenoxyphenol (0.5)	H_2O	<380 (vb,s)			*o*-Hydroxyphenoxyl	−	−
	m-Phenoxyphenol (0.9)	H_2O	430 (n,vw)	408 (n,vw)	<400 (vb,vw)	*p*-Methoxyphenoxyl	−	−
	p-Phenoxyphenol (0.5)	H_2O	428 (n,w) <390 (vb,w)	406 (n,w)	402 (n,w)	*p*-Hydroxyphenoxyl	−	−
O-13	Diphenyl ether (4.7)	H_2O–EtOH (1:1)	≈330 (vb,w)				−	
O-14	Benzyl alcohol (9.0)	H_2O	316 (n,w)			Benzyl	−	
O-15	β-Phenylethyl alcohol (7.7)	H_2O	<340 (b,w)				−	
O-16	Benzyl methyl ether (4.7)	H_2O	≈315 (b,s)				f	
O-17	β-Phenylethyl methyl ether (6.7)	H_2O	315 (n,w)			Benzyl	f	
O-18	Styrene oxide (2.5)	H_2O	315 (n,s)				−	+
O-19	Benzoic acid (0.1)	H_2O (pH 9.2)	≈440 (b,w)	<340 (vb,s)		Phenyl; triplet	+	+
O-20	Phenylacetic acid (10.0)	H_2O (pH 8.4)	315 (n,s)			Benzyl	+	
O-21	β-Phenylpropionic acid (9.8)	H_2O (pH 8.4)		None			+	
O-22	γ-Phenylbutyric acid (4.6)	H_2O (pH 8.6)	<400 (vb,w)				+	

Table I (*Continued*)

	Parent molecule^a	Solvent^b	—— Transient absorption maxima, mμ ——			Radical assignment	e_{aq}^{-} ^{c}	Oxygen quenching^d
O-23	δ-Phenylvaleric acid (2.9)	H_2O (pH 8.7)		None			+	
O-24	Methyl benzoate (0.9)	H_2O	<330 (vb, w)				−	
O-25	*o*-Hydroxyphenylacetic acid (0.6)	H_2O (pH 8.6)	398 (n, vw)	≈380 (n,vw)		$\cdot OC_6H_4CH_2COO^-$	++	−
O-26	3-(*p*-Hydroxy)-phenylpropionic acid (0.6)	H_2O (pH 11.7)	408 (n,s)	389 (n,s)		$\cdot OC_6H_4(CH_2)_2COO^-$	+	
O-27	*p*-Methoxyphenoxyacetic acid (0.2)	H_2O (pH 8.9)	≈460 (b,s)^e	416 (n,s)	<410 (b,s)	$\cdot CH_2OC_6H_4OCH_2COO^-$	+	+
O-28	Benzaldehyde (0.2)	H_2O–EtOH (1:1)		None			−	
O-29	Acetophenone (0.1)	H_2O	<400 (vb, vs)				−	+
N-1	Aniline (2.3)	H_2O	425 (n,s)	402 (n,vw)		Anilino	++	−
N-2	*p*-Phenylenediamine (0.2)	H_2O	475 (b,s)			$H_2NC_6H_4NH_2^+$	+	−
N-3	Benzylamine (8.0)	H_2O	315 (n, vw)			Benzyl	−	
N-4	β-Phenylethylamine (2.6)	H_2O		None			−	
N-5	γ-Phenylpropylamine (6.1)	H_2O		None			−	
N-6	N-Dimethylaniline (0.2)	H_2O	460 (b,vs)			$C_6H_5N(CH_3)_2^+$	+	−
N-7	Diphenylamine (1.5)	H_2O (pH 8.6)	≈600 (vb,s)				Δ	
N-8	Triphenylamine (0.4)	H_2O–EtOH	≈610 (vb,bs)				Δ	+
N-9	Benzonitrile (1.3)	H_2O	<360 (vb,vw)				−	
S-1	Thiophenol (0.1)	H_2O	≈500 (b,vs)	<360 (vb,vs)		Thiophenoxyl	++	−
		EtOH, cyclohexane	≈500 (b,vs)	<360 (vb,vs)		Thiophenoxyl		
S-2	Thioanisole (0.2)	H_2O (pH 8.9)	≈500 (b,vs)	<310 (vb,vs)		Thiophenoxymethyl	+	+
S-3	Diphenyl disulfide (2.6)	H_2O–EtOH (8:2)	≈500 (b,w)	<350 (vb, w)		Thiophenoxyl	−	−
		EtOH, cyclohexane	≈500 (b,s)	<350 (vb,s)		Thiophenoxyl		
S-4	Benzyl mercaptan (4.7)	H_2O–EtOH (1:1)	315 (n,vw)			Benzyl	−	
S-5	β-Phenylethyl mercaptan	H_2O–EtOH (1:1)	<330 (vb,w)				−	
S-6	Sodium phenoxymethysulfonate	H_2O	400 (n,s)	≈342 (b,w)		Phenoxymethyl	+	+
B-1	*p*-Xylene (7.8)	H_2O–EtOH (7:3)	320 (n,s)				++	+
B-2	Biphenyl (0.08)	H_2O–EtOH (6:4)	≈360 (b,vs)	≈650 (vb,vs)		Triplet; molecular anion	Δ	+
B-3	Naphthalene (0.3)	H_2O–EtOH (9:1)	≈415 (b,s)	<320 (vb,s)		Triplet; molecular anion	Δ	+
B-4	Tolane (0.03)	H_2O–EtOH (9:1)	≈390 (vb,s)				+	+
C-1	*o*-Bromophenol (0.5)	H_2O	<320 (vb,s)				−	
C-2	*p*-Bromophenol (0.1)	H_2O	380 (n,s) weak, narrow bands 390 to 460	367 (n,w)			−	
M-1	Phenylphosphine	H_2O–EtOH (7:3)	<400 (vb,w)				−	
M-2	Triphenylphosphine	H_2O–EtOH (1:1)	330 (n,s)	320 (n,s)			−	+
M-3	Phenylalanine (3.0)	H_2O (pH 11.7)	315 (n,s)	305 (n,w)		Benzyl	+	
M-4	Tryosine (1.1)	H_2O (pH 11.7)	408 (n,s)	390 (n,vw)		$\cdot OC_6H_4$-Ala	+	
H-1	Pyrrole (1.4)	H_2O		None			+	
H-2	Benzofuran (0.2)	H_2O (pH 8.2)	≈380 (b,vs)				+	+
H-3	Thiophene (0.2)	H_2O–EtOH (0.95:0.05)		None			f	

Table I (*Continued*)

	Parent molecule[a]	Solvent[b]	Transient absorption maxima, mμ			Radical assignment	e_{aq}^- [c]	Oxygen quenching[d]
H-4	Benzothiophene (0.2)	H_2O	412 (n,vs)	≈340 (b,s)			+	+
H-5	Indole (0.2)	H_2O (pH 8.6)	≈450 (vb,s)	<330 (vb,w)			++	+
H-6	2-Methylindole (0.2)	H_2O	≈480 (vb,s)	<330 (vb,s)			+	+
H-7	3-Methylindole (0.3)	H_2O	≈480 (vb,s)	<330 (vb,s)			+	+
H-8	3-Indolecarboxylic acid (0.3)	H_2O (pH 9.0)	≈480 (vb,s)	<330 (vb,s)			+	+
H-9	3-Indoleacetic acid (0.05)	H_2O (pH 8.6)	≈480 (vb,s)	<330 (vb,s)			++	
H-10	3-Indolepropionic acid (0.3)	H_2O (pH 9.0)	≈480 (vb.s)	<330 (vb,s)			++	
H-11	Tryptophan (0.2) (0.2)	H_2O	≈480 (vb,s)	<330 (vb,s)			+	
H-12	Pyridine	H_2O–EtOH (0.95:0.05)		None			−	
H-13	Quinoline (0.3)	H_2O (pH 8.7)	475 (n,s)	450 (n,s) <330 (vb,s)	≈410 (b,vs)		f	+
H-14	Acridine (0.02)	H_2O (pH 8.9)	≈450 (b,vs)	≈340 (vb,s)			+	+
H-15	Pyrimidine (0.5)	H_2O		None			f	
H-16	Benzimidazole (0.3)	H_2O	≈370 (vb,vw)				−	
H-17	Benzoxazole (0.4)	H_2O		None			−	
H-18	Benzothiazole (0.3)	H_2O		None			−	
H-19	Purine (0.2)	H_2O		None			−	
H-20	Benzotriazole (1.0)	H_2O	≈440 (vb,vs)				−	

[a] The number following each compound is the solute concentration in millimoles per liter. [b] The runs indicated as H_2O were made with triply distilled water, those indicated as pH 8.4 to 9.2 were made with $Na_2B_4O_7$ buffer solutions, and those indicated as pH 11.7 were made with 0.04 M Na_3PO_4 in which case the incident light was filtered with concentrated buffer to suppress photolysis of the solvent. [c] The observed initial yield of e_{aq}^- is given as: (++) photographic density (PD) > 1; (+) 0.2 < PD < 1; (f) 0.05 < PD < 0.2; (−) PD < 0.05; (Δ) indeterminate case because of an overlapping band. [d] + indicates that transient was strongly quenched when air-saturated solutions were irradiated. [e] This band was shorter lived (<25 μsec) than the others (≈100 μsec).

2,4′-dihydroxybiphenyl,[10] diphenoquinone,[11] 2-hydroxybiphenyl ether,[12] 4-hydroxybiphenyl ether,[13] phenylphosphine,[14] sodium phenoxymethylsulfonate, and sodium phenoxymethyl chloride;[15] 3,3′-dihydroxybiphenyl was prepared by demethylating the purchased methylated compound. The solvents used were triply distilled water, Fisher Spectroanalyzed methanol, Commercial Solvents ethanol, and Fisher Spectroanalyzed cyclohexane.

Table I summarizes the transient spectra obtained at 5-μsec time delay. The band widths and intensities are indicated as: n (narrow band, <25 mμ), b (broad band, 25 to 100 mμ), vb (very broad band, >100 mμ); vs (very strong), s (strong), w (weak), and vw (very weak). The last two columns indicate the strength of the e_{aq}^- absorption as ++, +, f, −, and Δ (defined in I[7] and footnote *c* to Table I) and in some cases whether the other transient bands were detected in air-saturated solutions. Table I does not include many of the compounds reported in I[7] which gave no detectable transients or only the e_{aq}^- absorption. The wavelength effect was investigated for selected cases by irradiating in a fused silica cell with a 1-cm coaxial outer jacket for solution filters. Parallel measurements were taken in which the incident light was passed through distilled water (λ >200 mμ) and an $NaNO_3$ filter solution whose concentration was adjusted to absorb below the longest wavelength aromatic band; (Table II, upper). In some cases the Vycor cell restricted light absorption in the same way and these data are summarized in Table II also (lower).

Discussion

The purpose of this investigation was to survey a number of aromatics for optical generation of the hydrated electron. The first part of the discussion considers the identification of the transient spectra. Assignments based on limited data are indicated as tentative (T). The absence of the e_{aq}^- absorption does not prove that photoionization was negligible unless the extent of scavenging by the parent molecule can be evaluated from measured rate constants. On the other hand, an e_{aq}^- yield of + indicates that the scavenging rate constant is lower than $\approx 2 \times 10^5/[S]$ where [S] is the actual solute concentration.

Comments on Table I. The production of e_{aq}^- and neutral phenoxyl radicals from phenol (O-1) cresols (O-2), 3-(*p*-hydroxyl)phenylpropionic acid (O-26), and tryosine (M-4) has been reported.[4,6] The phenoxyl radicals had an observed lifetime >100 μsec and did not react rapidly with dissolved oxygen. The transients obtained from the dihydroxybenzenes (O-3)

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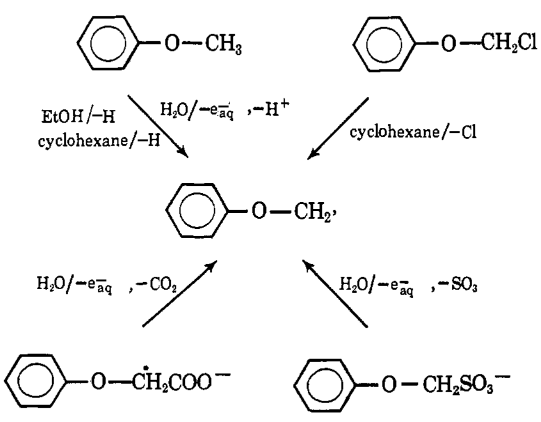
Table II. The Effect of Wavelength on e_{aq}^- Optical Generation[a]

1	2	3	4		5	6
			PD(rad)/PD(e_{aq}^-)			
Parent molecule[b]	$NaNO_3$, mole/l.	Radical band, mμ	H_2O filter	$NaNO_3$ filter	PD(rad) in H_2O/PD (rad) in $NaNO_3$	PD (e_{aq}^-) in $NaNO_3$
Phenol (1.1)	0.02	399	1.05	1.29	1.3	1.5
p-Dimethoxybenzene (0.6)	0.02	440	2.65	2.72	1.05	1.08
Aniline (0.8)	0.1	425	1.26	1.23	1.07	1.10
2-Methylindole (0.3)	0.02	450	1.34	1.50	1.00	1.18

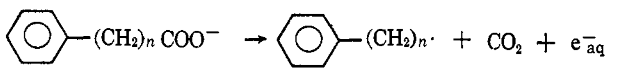
Parent molecule	Radical band, mμ	PD(rad)/ PD(e_{aq}^-), Vycor cell
Benzoic acid (0.1, pH 9.2)	435	1.94
p-Phenylenediamine (0.2)	475	1.96
Biphenyl (0.1)	385	1.73
Benzofuran (pH 8.8)[c]	385	2.23

[a] The upper data gives the photographic densities (PD) of the radicals and the e_{aq}^- absorption (700 mμ) when the incident light on the fused silica cell was filtered by distilled water and $NaNO_3$ (aqueous). The lower data gives the PD ratios for irradiation in the Vycor cell. [b] The number following each compound is the solute concentration in millimoles per liter. [c] OD/cm at 242 mμ was 1.2.

are assigned to phenoxyl radicals also, athough the spectrum from hydroquinone in water is significantly altered from results obtained previously in ethanol[16] and liquid paraffin.[17] However, the production of identical transients from hydroquinone and benzoquinone (O-4) supports the identification. Only the 4,4′-derivative of the dihydroxybiphenyls (O-5) gave a transient with definite phenoxyl properties, which was identical with the transient from diphenoquinone (O-6). In earlier work the spectra obtained by photolyzing anisole (O-7) in ethanol[16] and methylpentane (MP) glass[18] were identified with phenoxyl based on the narrow bands near 400 mμ, although bands at shorter wavelengths were noted also.[18] Pulse radiolysis studies of pure anisole gave transient bands both near 340 mμ and in the phenoxyl absorption region.[19,20] This work has shown that the anisole transient is shorter lived (≈50 μsec) and strongly quenched by oxygen. Therefore it cannot be predominantly phenoxyl, although a small contribution of the latter to the absorption near 400 mμ would account for a lifetime variation at different wavelengths[20] which has been observed in this work also. The same transient was obtained by photolyzing phenoxymethyl chloride (O-8), phenoxyacetic acid (O-9), and phenoxymethylsulfonate (S-6). We propose that the responsible species is phenoxymethyl, formed in each case as shown. The spectrum from *m*-dimethoxybenzene (O-10) was similar to the anisole transient and is assigned to the corresponding phenoxymethyl radical. The absorption obtained from the *para* derivative was quite different in water and the organic solvents (as was noted with hydroquinone) and is assigned to *p*-methoxyphenoxymethyl (T) based on the short lifetime (≈50 μsec) and oxygen quenching. The *ortho* derivative gave a strong e_{aq}^- absorption and no other transients. The methoxy-substituted phenols (O-11) gave phenoxyl radicals as did the phenoxyphenols (O-12). Diphenyl ether (O-13) cleaves in the same way as the phenoxyphenols[21] but we did not detect phenoxyl and the yield must be low.



The benzyl absorption was obtained from benzyl alcohol (O-14)[22,16] and β-phenylethyl methyl ether (O-17), indicating a split at the side-chain α bond. The transient from styrene oxide (O-18) was almost identical with benzyl and may be due to the biradical $C_6H_5\dot{C}HCH_2O\cdot$ (T). Although the insulating methylene groups in benzyl alcohol and β-phenylethyl alcohol (O-15) suppress e_{aq}^- production, this is not the case for the aryl acids $C_6H_5(CH_2)_nCOO^-$ with n = 0, 1, 2, 3, and 4. The longer wavelength band obtained with benzoic acid (O-19) corresponds to the phenyl absorption in the gas phase[23] with a blue shift consistent with the n–π* assignment. The band below 340 mμ may be the triplet (λ_{max} 310 mμ in liquid paraffin[24]) or possibly is the phenyl π–π* absorption. The production of benzyl from phenylacetic acid (O-20) and phenoxymethyl from phenoxyacetic acid (O-9), and the absence of detectable transients for the molecules with n = 2, 3, and 4 all indicate that splitting takes place at the terminal carbon.



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[16] L. I. Grossweiner and W. A. Mulac, *Radiation Res.*, **10**, 515 (1959).

[17] E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016 (1963).

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[19] A. MacLachlan and R. L. McCarthy, *J. Am. Chem. Soc.*, **84**, 2519 (1962).

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[21] F. L. Bach and J. C. Barclay, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 98.

[22] G. Porter and M. W. Windsor, *Nature*, **180**, 187 (1957).

[23] G. Porter and B. Ward, *Proc. Chem. Soc.*, 288 (1964); *Proc. Roy. Soc.* (London), **A287**, 457 (1965).

[24] G. Porter and M. W. Windsor, *ibid.* **A245**, 238 (1958).

The above mechanism requires intramolecular excitation transfer between nonconjugated chromophores for which there are examples in the literature.[25] The transients obtained from the aryl acids with an additional "active" group appear to be typical of the latter. The transients from the hydroxyl-substituted acids O-25 and O-26 had typical phenoxyl bands and did not react with oxygen. On the other hand, O-27 gave a spectrum with long-lived bands ($\approx$100 μsec) and short-lived (<25 μsec) bands both of which were partially quenched by oxygen. This case is typical of anisole derivatives and indicates that a phenoxymethyl radical (T) is a major product.

The production of e_{aq}^- and anilino radicals[26] from aniline (N-1), *p*-phenylenediamine (N-2), and N-dimethylaniline (N-6) fits the phenoxyl scheme, where the radicals are relatively long lived and do not react rapidly with oxygen. The e_{aq}^- optical generation was suppressed by the methylene groups in N-3 and N-5. The production of benzyl from benzylamine (N-3) is known.[16] The transients from diphenylamine (N-7) and triphenylamine (N-8) were identified with the radical cations in EPA glass at 90°K by Lewis and Lipkin,[2a] but in more recent studies by Linschitz and co-workers[27,28] the 610-mμ band from diphenylamine was attributed to an intermediate with closed-ring polar structure populated *via* the triplet. The sulfur derivatives parallel the phenols: thiophenol (S-1) and diphenyl disulfide (S-3) gave identical transients which we assign to thiophenoxyl; the transient from thioanisole (S-2) was shorter lived and reacted rapidly with oxygen and is identified with thiophenoxymethyl (T) by analogy with anisole; the methylene groups in S-4 and S-5 suppress e_{aq}^- production; benzyl mercaptan (S-4) gave benzyl in correspondence with O-14.

Benzene gave negative results (a change from I) while toluene gave a faint e_{aq}^- absorption in water–ethanol solutions. The high e_{aq}^- yield from *p*-xylene (B-1) demonstrates the strong influence of ring electron density on photoionization probability. The long-lived ($\approx$200 μsec) band at 320 mμ is typical of benzyl radicals, although it should be noted that similar bands produced by pulse radiolysis of xylene (and other liquid hydrocarbons) were attributed by MacLachlan and McCarthy[19] to conjugated radicals formed by the addition of the initial reactive radicals to the parent molecules. The 360-mμ band from diphenyl (B-2) corresponds to the triplet spectrum, obtained both by flash photolysis in liquid paraffin[24] and pulse radiolysis in 3-methylpentane (3-MP).[29] The 650-mμ band corresponds to the diphenyl anion, as obtained by γ-irradiation in hydrocarbon glass at 77°K[30] and by pulse radiolysis in tetrahydrofuran[31] and cyclohexane.[32] The transient from naphthalene (B-3) is predominantly the triplet;[24] the weak absorption above 600 mμ may be the molecular anion.[30] Although neither the e_{aq}^- absorption nor radical spectra were detected with fluoro-, chloro-, and bromobenzene, a pH decrease for the last two cases indicates that splitting of the carbon–halogen bonds takes place, in agreement with recent photochemical studies.[33] Fluorobenzene has been found to be quite resistant to photolysis.[34] A pH decrease was observed also with *o*-bromophenol (C-1) and *p*-bromophenol (C-2). The transient obtained from the latter includes well-resolved, narrow bands in the visible and near-ultraviolet regions which may be due to *p*-hydroxyphenyl (T). The aromatic phosphorous derivatives studied were phenylphosphine (M-1), triphenylphosphine (M-2), and triphenylphosphine oxide, none of which gave a detectable e_{aq}^- absorption. The transient from M-2 was long lived ($\approx$400 μsec) and reacted rapidly with oxygen, which suggests the triphenylphosphine radical cation (T).

The e_{aq}^- absorption was obtained from five-membered ring heterocycles with one heteroatom: H-1 to H-11. In such molecules the heteroatom contributes approximately two π electrons to the ring system and carries a net positive charge. It is expected that the e_{aq}^- scavenging reactions are slow for these structures, which has been shown for pyrrole and thiophene.[35] On the other hand, the e_{aq}^- absorption was faint or absent for structures with doubly bonded nitrogen: H-12, H-15 to H-19. In these cases the nitrogen atom contributes approximately one π electron and carries a net negative charge. However, the replacement of a carbon atom by tertiary nitrogen increases the electron scavenging rate constants by two orders of magnitude in pyrrole and thiophene[35] and it is known that pyrimidines and purines react very rapidly.[36] Thus, the observed dependence of e_{aq}^- yield on structure may reflect only changes in the scavenging reactivity. The relationship between ring electron density and e_{aq}^- yield is also shown by the sequence: pyridine (H-12)/quinoline (H-14)/acridine (H-15), where the addition of fused benzene rings enhances the observed yield. Again, the substitutions also should decrease the reactivity with e_{aq}^-. Another example of this effect is the higher e_{aq}^- yield from benzothiophene (H-4) compared to thiophene (H-3). The transients from the heterocycles were moderately short lived ($\approx$50 μsec) and reacted rapidly with oxygen. Little can be concluded about their identifications from the flash spectra. The quinoline and acridine triplets absorb between 400 and 500 mμ[37] and undoubtedly account for part of their transient spectra. It is presumed that radical cation products must be present in cases where e_{aq}^- was observed.

Filter Experiments

In one set of experiments parallel runs were made with water and $NaNO_3$ in the outer jacket of the fused silica cell (Table II, upper). Within experimental error, the radical-to-electron absorption ratio was not

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(25) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 2322 (1965).

(26) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).

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(29) F. S. Dainton, T. J. Kemp, G. A. Salmon, and J. P. Keene, *Nature*, **203**, 1050 (1964).

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(32) J. P. Keene, E. F. Land, and A. J. Swallow, *J. Am. Chem. Soc.*, **87**, 5284 (1965).

(33) H. I. Joschek and S. I. Miller, *ibid.*, **88**, 3269 (1966).

(34) I. Loeff, L. M. Revetti, and G. Stein, *Nature*, **204**, 1300 (1964).

(35) A. Szutka, J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, **69**, 289 (1965).

(36) E. J. Hart, S. Gordon, and J. K. Thomas, *ibid.*, **68**, 1271 (1964).

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increased by the addition of the short-wavelength irradiation (column 4). The radical and e_{aq}^- yields for the two cases (columns 5 and 6) are approximately the same, which suggests that the shorter wavelength light was not effective in producing either radicals or e_{aq}^-. The compounds listed in the lower part of Table II were irradiated in a Vycor cell which cut off light below the longest wavelength aromatic bands. The electron-to-radical yields (uncorrected for molar absorbance) were lower but appreciable. The data were taken at 5-μsec time delay where diffusion-limited, radical–radical reactions could not have progressed to a significant extent. On the other hand, the results would have been influenced by fast solute–radical reactions and must be considered as qualitative. The essential conclusion to be drawn is that the photon energy of the longest wavelength aromatic band is adequate to induce photoionization in aqueous solution for the molecules studied.

General Discussion

The above results show that photoionization is a likely primary photochemical process for many aromatics in aqueous solution. As discussed in I, e_{aq}^- optical generation was observed for benzene substituents with negative σ_p: OH, OR, NH_2, SH, SR, COO^-, and was not observed for those with positive σ_p: NR_3^+, NO_2, CN, CF_3, $COCH_3$, halogen, CH_2OH. Electron release was correlated also with low gas-phase PIP for a broader class of aromatics. In the disubstituted benzenes which have been studied the substituents with $\sigma_p > 0$ suppress e_{aq}^- generation even when combined with those with $\sigma_p < 0$ (Table III). It is interesting to note which radicals were present when several types are possible (Table IV): phenoxyl (O·) was observed when it could be formed and phenoxymethyl (OCH_2·) was more readily produced from OCH_3 than from OCH_2COO^-.

Table III. Hydrated Electron Yield from Disubstituted Benzenes

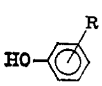
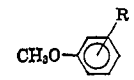
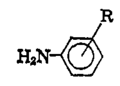
Parent molecule	e_{aq}^- yield +	e_{aq}^- yield −
	CH_3 OH OCH_3 C_6H_4OH	OC_6H_5 Br NO_2
	OCH_3 OH	Br NO_2
	NH_2	

Table IV. Radicals from Disubstituted Benzenes

Substituents		Radical products
OH	OCH_3	O·
OH	CH_2COO^-	O·
OH	$CH_2CH_2COO^-$	O·
O*CH_3	OCH_2COO^-	O*CH_2·
OH	Br	C–Br bond splitting
OH	NO_2	None obsd
OCH_3	Br	C–Br bond splitting
OCH_3	Br	None obsd

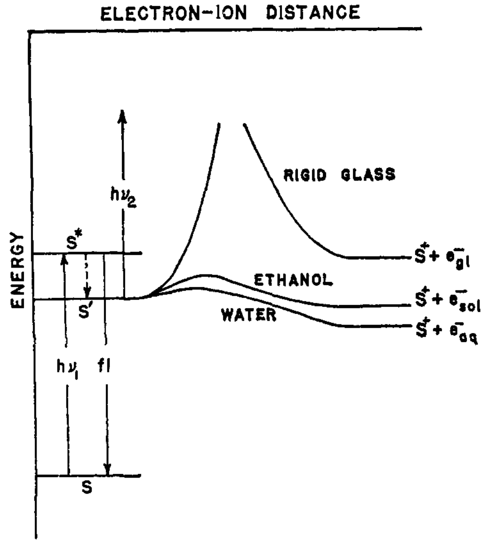


Figure 1. Possible energy levels involved in photoionization of aromatic molecules in different media. The levels indicated are for the ground state (S), the first excited singlet state (S*), the complex formed with the solvent (S'), and the radical ion (S^+). The diagram indicates that thermally assisted, single-photon ionization is possible in fluid polar solvents while two-photon ionization is required in low dielectric constant rigid media.

The filter experiments show that photoionization is induced by excitation of the ring system to the lowest π–π* excited singlet state. It is unlikely that the electron is released from this level because the electron yields were much lower (or zero) in organic solvents compared to water, while the radical yields were comparable in many cases. (In contrast, the electron and radical–ion yields from the halide ions were of the same order in water and ethanol solutions.[38,39] In this case, it is probable that the electron is released directly from the "charge-transfer-to-solvent" (CTTS) state, in which the excited electron occupies a discrete quantum level established by the coulombic field of the oriented hydration sheath.) It was suggested in I[7] that photoionization of aromatics in aqueous solution takes place *via* a charge-transfer complex populated from the π–π* excited singlet state and that the high dielectric constant of the aqueous medium lowers the coulomb valence force potential well and permits the electron to escape. Recent studies of the photolysis of aromatics in rigid hydrocarbon glass at 77°K have indicated that photoionization is a two-photon process. Gibbons, *et al.*,[40] measured the thermoluminescence of toluene, phenol, aniline, naphthalene, phenanthrene, fluorene, diphenylmethane, perylene, and diphenyl in 3-MP and found that the emission was proportional to the square of the photolyzing light intensity. It was proposed that the first photon populates the triplet which is ionized by the second photon, and that light emission results from electron–ion recombination. Thermoluminescence was not detected with benzene, pyridine, fluorobenzene, and nitrobenzene, which gave low or negative e_{aq}^- yields in this work. Two-photon ionization with a triplet intermediary has been proposed also by Cadogan and Albrecht[41] for N,N,N',N'-

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(38) L. I. Grossweiner, E. F. Zwicker, and G. W. Swenson, *Science*, **141**, 1180 (1963).

(39) G. Dobson and L. I. Grossweiner, *Radiation Res.*, **23**, 290 (1964).

(40) W. A. Gibbons, G. Porter, and M. I. Savadatti, *Nature*, **206**, 1356 (1965).

tetramethyl-*p*-phenylenediamine in 3-MP. The minimum total energy required for photoionization was found to be 2.8 ev ($T \leftarrow S_0$) + 3.1 ev ($T \rightarrow R^+ + e^-$) compared to the gas-phase PIP of 6.6 ev. Thus, the medium provides only 0.7 ev of solvation energy, which agrees with an estimate made by Gibbons, *et al.*[40] In closely related work, Hélène, *et al.*,[42] measured epr signals obtained by irradiating nucleic acid derivatives with ultraviolet light in frozen aqueous solutions. It was concluded in this case also that the initial act is photoionization *via* a two-photon mechanism with a triplet state intermediary.

Although the new evidence for two-photon photoionization of aromatics in low temperature rigid systems is convincing, it cannot be concluded that this mechanism applies to aqueous solutions at room temperature. As shown in I[7] the solvation energies of the electron and radical ions can supply the energy deficit for one-photon ionization in typical cases. Furthermore, Dobson and Grossweiner[6] found no evidence for a nonlinear dependence of the e_{aq}^- yield on flash intensity for aqueous *p*-cresol, although the experimental scatter was considerable because of the short e_{aq}^- lifetime.[43] Possible energy levels for compounds of the type C_6H_5XR (*e.g.*, phenol, anisole, aniline, thiophenol) are shown in Figure 1. In high dielectric constant solvents, such as water or ethanol, the coulomb valence force barrier is low and thermal excitation permits electron release from a short-lived intermediate state. However, in rigid, low dielectric constant environments the intermediate state is stabilized by the matrix and the absorption of a second photon is required to induce ionization. The intermediate may be the triplet or possibly is a charge-transfer complex between the aromatic molecule and the solvent that is populated *via* the triplet.

Any adequate mechanism of e_{aq}^- optical generation must explain why the electron-to-radical yields are much lower for neutral phenol and the cresols compared to their anions.[6] As was pointed out in ref 6, the acidity constants of the excited states are lower than the ground states by five orders of magnitude and it is probable that the excited phenolic molecule transfers a proton to the solvent prior to electron release. (The effects of substituents on pK_a^* of phenols have been measured in a recent paper.)[44] Nevertheless, this factor alone does not explain the diminished electron-to-radical yields unless there is a high probability for recapture of the electron by the released proton prior to solvation. Alternatively, there may be a competition between splitting of the OH bond and formation of the state which ultimately releases the electron. The latter might also explain why the electron yields were much lower in polar organic solvents compared to water, because steric effects should reduce the probability of forming the charge-transfer complex and permit bond rupture to occur.

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(41) K. D. Cadogan and A. C. Albrecht, *J. Chem. Phys.*, 43, 2550 (1965).

(42) C. Hélène, R. Santus, and P. Douzou, *Photochem. Photobiol.*, **5**, 127 (1966).

(43) It should be noted that a direct two-photon process is not inconsistent with the available flash photolysis light intensities. For example, a 500-joule lamp discharging in 20 μsec can provide ≈20 einsteins/sec in a typical first aromatic absorption band and a comparable intensity in the triplet absorption. Taking 3×10^{-7} *M* for the minimum detectable e_{aq}^- yield in a 25 cm long cell, 10^3 for the average triplet molar absorbance, 1 cm for the cell diameter, and 0.1 for the triplet photoionization quantum yield gives $\approx 3 \times 10^{-6}$ *M* for the minium required initial triplet concentration. For a triplet lifetime of 10^{-5} sec and triplet population quantum yield of 0.1, the same flash intensity can provide an approximate triplet concentration during the flash of $\approx 2 \times 10^{-5}$ *M*, which is well within the requirements for two-stage photoionization.

(44) W. Bartock and P. J. Lucchesi, *Photochem. Photobiol.*, **4**, 499 (1965).