Rate Constants and Relative Yields of Solvated Electrons in Concentrated Solutions

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Summary Pulse radiolytic investigations provide evidence against the 'dry electron' interpretation of previous results in ethanolic benzene and in aqueous phenol.

RECENTLY Wolff *et al.*[1] provided experimental support for the hypothesis[2,3] that electrons formed by radiolysis of aqueous solutions may react with solutes prior to hydration, *i.e.* while they are still 'dry electrons' (e^-). According to their interpretation, e^- reacts with all efficient scavengers of e^-_{aq} studied so far with one notable exception, namely $H_3O^+_{aq}$. The relative rate constants measured[1] for e^- are generally not identical with those for e^-_{aq}.

In view of this, the recent experiments of Khorana and Hamill[4] are of great interest, indicating that benzene and phenol are efficient scavengers of e^-. Since these solutes react only moderately quickly with e^-_{aq} (k *ca.* 10^7 l mol^{-1} s^{-1}), their results seem to rule out an interpretation of the previous data in terms of time-dependent rate constants.[5,6] We have found it worthwhile to investigate the electron scavenging by benzene and phenol by a more direct method. We have measured the reaction rate constants and relative yields of e^-_{eth} and e^-_{aq} in the presence of high solute concentrations by means of a conventional pulse radiolysis technique.

The decay of the absorbance at 600 nm was recorded following the 30 ns electron pulse of either a 4 MeV Vickers Linac or a 8 MeV Varian Linac (operated at 5 MeV). Owing to noise produced by the electron pulse the absorbance could not be properly recorded until *ca.* 200 ns after the pulse. In order to determine $G(e^-_{aq})$ or $G(e^-_{eth})$ the absorbance decay curve must be extrapolated to zero time. However, zero time was difficult to fix accurately because of the finite length of the electron pulse. Therefore, in order to avoid a possible systematic error caused by an erroneous fixing of zero time the decay curves obtained with benzene and phenol were always compared with those obtained for solutions of H_2SO_4 or HCl the concentrations of which were adjusted to give a similar decay time. The concentrations of H^+ needed for this are too small to cause any scavenging of e^-.

TABLE 1[a]

Solvent	Solute	Solute concentration/M	Number of exp.	Optical density	Relative dose[c]	k/l mol^{-1} s^{-1}
H_2O	None		4	0·054	A	
	H_2SO_4	1·8 × 10^{-4}	4	0·054	A	3·0 × 10^{10}
	PhOH	0·20	9	0·057	A	1·6 × 10^{7}
	PhONa + 0·2M-NaOH	0·19	3	0·030	B	3·7 × 10^{5}
	PhONa + 0·2M-NaOH	2·13	6	0·024	C	4·0 × 10^{5}
	NaOH	0·2	3	0·029	C	
	$MeCO_2Na$	1·8	3	0·034	C	4·3 × 10^{4}
Ethanol	HCl	0·4 × 10^{-4}	8	0·024	D	1·2 × 10^{10}
	C_6H_6	0·10	7	0·022	D	4·2 × 10^{6}
	HCl	1·45 × 10^{-4}	5	0·018	E	1·0 × 10^{10}
	C_6H_6	0·25	3	0·016	E	4·1 × 10^{6}
	PhOH	0·025	4	0·024	F	4·5 × 10^{7}
	C_5H_9Br	1 × 10^{-4}	2	0·018	G	2·3 × 10^{9}
	H_2SO_4	1·07 × 10^{-4}	3	0·022	H	1·4 × 10^{10} [b]

[a] Relative yields of e^-_{aq} and e^-_{eth} measured by the extrapolated optical density at 600 nm and the corresponding rate constants. The error of the yields is ±5% while that of the rate constants does not exceed ±15%. The light path is 20 mm. [b] Rate constant calculated by assuming that only the first hydrogen is fully ionized. [c] Experiments in which the relative doses are indicated by the same letters were all carried out at exactly the same dose.

In order to check if the relatively high concentrations of benzene and phenol affected the absorption spectrum of e^-_{eth}, some of the solutions were studied at wavelengths between 400 and 620 nm.

The decay of absorbance from *ca.* 200 ns onwards was found to be exponential at all wavelengths and for all solutions studied. The pseudo-first order plots of log optical density *vs.* time were linear over at least a sixfold concentration change. From such plots an extrapolated optical density could be obtained with a reasonable reproducibility (±5%). The mean values of the extrapolated optical density at 600 nm found for the various solutions are in Table 1. It can be seen that 0·2M-phenol in water did not reduce the initial optical density compared with an aqueous solution of H_2SO_4 with approximately the same decay time. Similar results were obtained for concentrations up to 0·25M-benzene in ethanol. According to the data in Table 2 the absorption spectra of e^-_{aq} and e^-_{eth} are only slightly if at all affected by the presence of phenol and benzene. We therefore conclude that for the concentrations studied, no scavenging of e^- by these solutes is detectable within the limits of experimental accuracy (<10%). Hence, an interpretation of the existing data in terms of time-dependent rate constants cannot be ruled out. It must be emphasized, however, that our results by no means exclude the possible importance of reactions with e^- in polar solutions.

TABLE 2[a]

Relative absorbances

λ/nm	Ethanol	Benzene in ethanol	Water	Phenol in water
620	1·00	1·00		
600			1·00	1·00
550			0·71	0·77
500	0·68	0·67	0·44	0·47
450	0·54	0·55	0·27	0·30
400	0·42	0·43		

[a] Relative values of the absorbance at different wavelengths in 0·12M-benzene in ethanol and 0·2M-phenol in water compared with the pure solvents. Each number gives the average of six experiments. Errors do not exceed ±5%. The light path through the test solutions was 120 mm.

The present results contradict those of Khorana and Hamill[4] who predict that 0·2—0·25M-phenol and -benzene solutions should scavenge *ca.* 40% of e^-. If e^- is the major precursor of e^-_{eth} and e^-_{aq}, $G(e^-_{eth})$ as well as $G(e^-_{aq})$ should also be reduced by approximately the same fraction. We feel, therefore, that there must be some effect in the system which they did not take into account. We note that their competition studies lead to a value of $k(e^-_{eth} + H^+)/k(e^-_{eth} + C_5H_9Br)$ of 2·0, whereas according to other measurements this ratio is *ca.* 5·5.

The rate constants (Table 1) do not support the assumption that the reactivities of e^-_{aq} and e^-_{eth} are equal. Thus, the rate constants of e^-_{aq} and e^-_{eth} with benzene are 1·46 and 0·42 × 10^7 l mol^{-1} s^{-1} respectively, while in the case of phenol, e^-_{eth} has a reactivity which is nearly three times that of e^-_{aq}, *i.e.* the difference is in the opposite direction. Finally we note that our results for phenolate and acetate ions yield rate constants which are definitely lower than the upper limits published previously.

(*Received, July 2nd,* 1971; *Com.* 1118.)

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