# Formation and Photodissociation of Hydrated Electron Dimers

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Summary   Hydrated electrons produced by the u.v. flash photolysis of OH^-_{aq} undergo a bimolecular combination reaction to form a species—postulated to be a hydrated dielectron—which, on subsequent i.r. flash photolysis, regenerates monomeric hydrated electrons.

By the use of a novel double-flash photolysis technique, evidence has been obtained for the following processes:

$$2\, e^-_{aq} \rightarrow (e^{2-}_2)_{aq} \qquad (1)$$

$$(e^{2-}_2)_{aq} + h\nu(\lambda > 700 \text{ nm.}) \rightarrow 2\, e^-_{aq} \qquad (2)$$
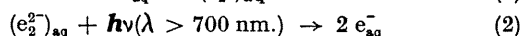
Hydrated electrons (e^-_{aq}) were formed in the first flash by u.v. photolysis of OH^-_{aq} in a deoxygenated aqueous solution containing 10^{-3}M-NaOH and 7×10^{-4}M-H_2.

$$OH^-_{aq} + h\nu(\lambda < 220 \text{ nm.}) \rightarrow e^-_{aq} + OH\left(\xrightarrow[OH^-]{H_2} e^-_{aq}\right)$$
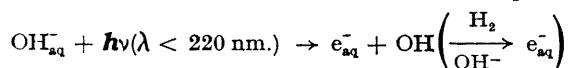
In this mixture the OH radicals produced by photolysis were converted into e^-_{aq} by reaction with H_2 and OH^-, thus doubling the quantum efficiency of e^-_{aq} production and ensuring that reaction (1) was the main decay process of e^-_{aq}. Concentrations of e^-_{aq} of ca. 10^{-6}M were produced. The dielectron is presumed to be an activated complex in the reaction leading to the formation of H_2 by the combination of hydrated electrons and is written $(e^{2-}_2)_{aq}$ on the assumption that it is best represented as two electrons in one cavity-solvation sheath and unspecified spin state. Our data indicates it has a lifetime at pH 11 of about 0·1 sec. but the kinetics of its decay are neither simple first nor second order. When the product of the reaction (1) was photolysed by a second flash containing only wavelengths >700 nm. monomeric hydrated electrons were again formed, a process represented by step (2).

Although stable dielectron entities are known to occur as trapped species in polar solids[1,2] and in metal–ammonia or –ether solutions,[3] to our knowledge this is the first demonstration of short-lived solvated dielectrons in water, or any protic liquid solvent.

The double flash photolysis equipment consisted of two photolysis lamps (one on each side of the reaction vessel and separated from it by spaces capable of containing colour glass filters) which could be fired successively with any preselected time delay.[4] A conventional spectroflash lamp could be triggered from either of these photolysis flashes and a spectrum taken in the usual manner at any delay time. Alternatively for kinetic studies the 632·8 nm. light from a 5 mw He–Ne c.w. laser was directed down the reaction vessel and the time dependence of the absorbance of this light by e^-_{aq} ($\epsilon_{633} = 12,000$M^{-1}cm.$^{-1}$)[5] was followed with a photomultiplier–oscilloscope arrangement.

A typical kinetic study at 633 nm. is shown in the Figure as curve (a), in which the first lamp gave all wavelengths
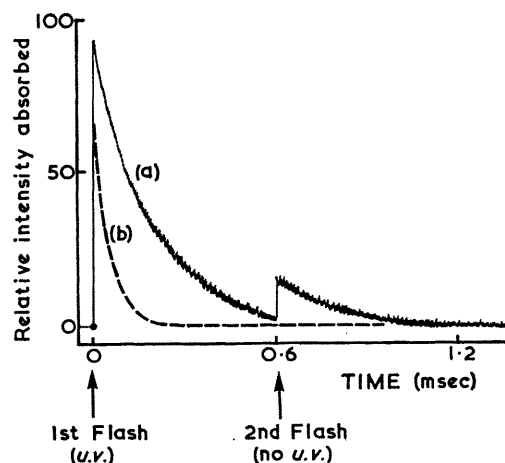

FIGURE. Drawings of oscilloscope display showing the time dependence of the absorption of 633 nm. light during a double-flash photolysis experiment in which the first flash contained all wavelengths >190 nm. but the second flash had light λ >270 nm. completely removed by Pyrex filters.

Curve (a) refers to 10^{-3}M-NaOH and 7×10^{-4}M-H_2 in deoxygenated water. Curve (b) was the same solution but containing ca. 5×10^{-5}M-O_2.

(though absorption occured only at $\lambda < 220$ nm.) and the second incorporating a Pyrex filter gave only $\lambda > 270$ nm. By the use of various colour filters it was shown that only $\lambda > 700$ nm. were effective in producing the second peak. The size of the second peak decreased with increasing delay time and indicated a half-life for the photolysed species of about 0.1 sec. A spectrum taken during the first peak corresponded to the known spectrum of e_{aq}^-[5] and kinetic and scavenger studies confirmed this. The decay after both flashes was predominantly second-order and with a rate constant of *ca.* $0.5 \times 10^{10} \mathrm{M}^{-1}\mathrm{sec.}^{-1}$, in close agreement with the known value for the bimolecular reaction of e_{aq}^-. It has not yet been possible to obtain a spectrum of either the intermediate (which may only absorb where it is photodissociated at $\lambda > 700$ nm.) or the species responsible for the second peak, though all the kinetic evidence indicated the latter was e_{aq}^-. Similar results were obtained using other chemical systems [for instance $\mathrm{Ba(OH)_2}$–alcohol] and served to confirm these conclusions.

Curve (b) of the Figure shows that when *ca.* $5 \times 10^{-5}\mathrm{M}$-$O_2$ was added to the same solution the e_{aq}^- decay was much more rapid (first order) thus eliminating reaction (1) and preventing the formation of e_2. Now the second flash produced no detectable e_{aq}^- absorption. For this and other reasons the production of the second peak can be attributed to process (2).

If these conclusions are correct and $(e_2^{2-})_{aq}$ is formed and possesses very much greater stability than e_{aq}^-—towards water, itself and the inevitable impurities—then it probably plays an important role in certain pulse radiolysis systems and in the formation of H_2 by the cathodic decomposition of alkaline water and in the chemical reduction of water.[6]

[1] J. J. Markham, "F-centers in Alkali Halides," Academic Press, 1966.
[2] L. Kevan, D. R. Renneke and R. J. Friauf, *Solid State Comm.*, 1968, **6**, 469.
[3] J. Eloranta and H. Linschitz, *J. Chem. Phys.*, 1963, **38**, 2214.
[4] N. Basco, to be published.
[5] J. P. Keene, *Radiation Res.*, 1964, **22**, 1.
[6] D. C. Walker, *Adv. Chem. Series*, 1968, **81**, 49.