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The Hydrated Electron

Properties and reactions of this most reactive and elementary of aqueous negative ions are discussed.

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Discovered and studied by radiation chemists, the hydrated electron, a unique ion, provides great potential for interpreting reaction mechanisms in chemistry and biology. Hydrated electrons, designated by the symbol e^-_{aq}, result from secondary electrons generated in water by ionizing radiations. Their negative charge polarizes surrounding water molecules, and e^-_{aq} is bound to these molecules with a half-life of greater than 300 microseconds. The interest to science of the hydrated electron rests not only in its importance in radiation chemistry, photochemistry, and electrochemistry and (in modified forms) possibly in thermal chemistry but also in the ease with which it can be detected and studied. The hydrated electron is an intensely colored ion. Consequently, rapid and reliable spectrophotometric techniques readily enable one to study its reactions and particularly to measure its reaction rate constants. In the brief time that has elapsed since its absorption spectrum was discovered, sufficient progress has been made to justify an optimistic prediction regarding its future role in science. Before discussing the properties and reactions of e^-_{aq}, I briefly review the radiolysis of water and the reasons why it was necessary for radiation chemists to postulate e^-_{aq} in the mechanisms they proposed (*1*).

Radiolysis of Water

Prior to 1960 most reactions taking place in irradiated water were explained by mechanisms involving hydrogen atoms and OH radicals only. But during the late 1950's several investigators found evidence for a second reducing species, more powerful than the H atom. This turned out to be e^-_{aq}, and the primary ionization reaction for irradiated water became:

$$2H_2O \rightarrow H_3O^+ + e^-_{aq} + OH. \quad (1)$$

Some direct dissociation may also occur as a result of excitation, giving H and OH radicals by way of the reaction

$$H_2O \rightarrow H + OH. \quad (2)$$

But because e^-_{aq} from reaction 1 is converted into H atoms by way of two very important reactions,

$$e^-_{aq} + H_2O \rightarrow H + OH^- \quad (3)$$

and

$$e^-_{aq} + H^+(\text{or } H_3O^+) \rightarrow H(\text{or } H + H_2O), \quad (4)$$

the overall process is simply reaction 2.

Indeed, because of the high rate constant for reaction 4, e^-_{aq} is converted to H atoms even in dilute acids. Therefore, unless solute concentrations greatly exceed hydrogen ion concentrations, reaction 4 minimizes the role of e^-_{aq}. But because of the slowness of reaction 3, in neutral and especially in alkaline solutions, e^-_{aq} proves to be the dominant reducing species. However, since H and e^-_{aq} reactions give identical products in many cases, it is impossible to prove the participation of e^-_{aq} rather than H in the majority of cases. The final products are identical in reactions such as

$$Cu^{++} + H \rightarrow Cu^+ + H^+ \quad (5)$$

and

$$Cu^{++} + e^-_{aq} \rightarrow Cu^+. \quad (6)$$

Also, the final products of the important pair of reactions

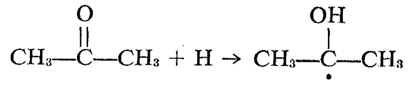
$$H + O_2 \rightarrow HO_2 \quad (7)$$

and

$$e^-_{aq} + O_2 \rightarrow O_2^- \quad (8)$$

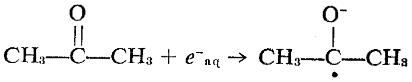
are identical, since protonization of O_2^- forms HO_2.

No distinction can be made between e^-_{aq} and H, even in organic reduction reactions like



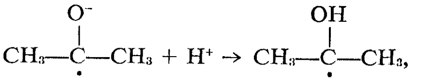
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H \rightarrow CH_3-\underset{\bullet}{\overset{\overset{OH}{|}}{C}}-CH_3$$

and



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + e^-_{aq} \rightarrow CH_3-\underset{\bullet}{\overset{\overset{O^-}{|}}{C}}-CH_3$$

since addition of a proton,



$$CH_3-\underset{\bullet}{\overset{\overset{O^-}{|}}{C}}-CH_3 + H^+ \rightarrow CH_3-\underset{\bullet}{\overset{\overset{OH}{|}}{C}}-CH_3,$$

produces the 2-hydroxyisopropanyl radical.

Need for Two Reducing Species

If the reaction products provide no clue to the identity of the reducing species, how is it possible to distinguish H from e^-_{aq}? The answer first became apparent because of a discrepancy in measurements of the rate-constant ratio for the H atoms formed in the reaction

$$OH + H_2 \rightarrow H + H_2O$$

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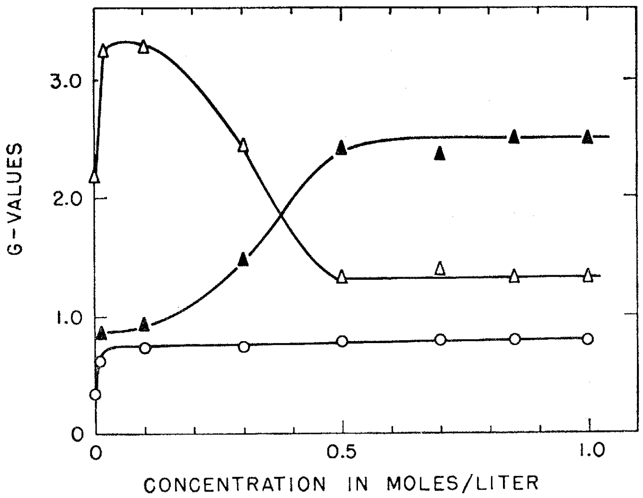


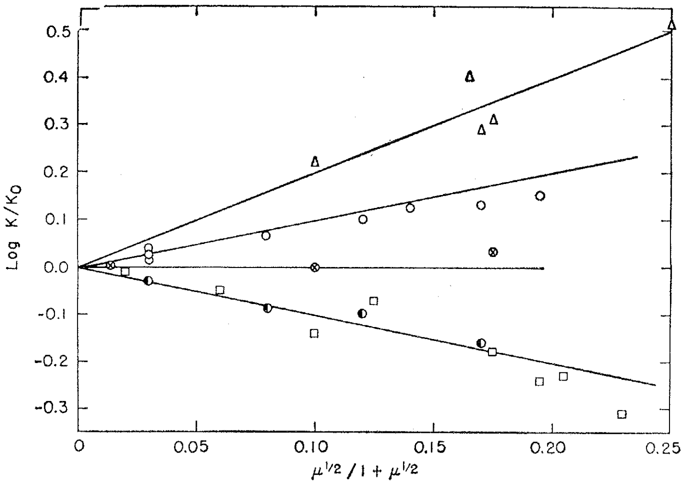


Fig. 1 (left). Dependence of initial yields upon concentration of monochloroacetic acid at *p*H 1.0 (*4*). Open triangles $G(H_2)$; solid triangles, $G(HCl)$; and circles, $G(H_2O_2)$. Fig. 2 (right). Effect of ionic strength on relative rate constants of e^-_{aq} reactions (*11*). Triangles, $KFe(CN)_6^{--}$ relative to N_2O; circles with cross, O_2 relative to H_2O_2; circles, half solid, H^+ relative to H_2O_2; open circles, NO_2^- relative to H_2O_2; and squares, Ag^+ relative to $CH_2{=}CH{-}CONH_2$.

and for the reducing species formed in reaction 1 in their reactions with hydrogen peroxide (*2*):

$$H + H_2O_2 \rightarrow H_2O + OH \qquad (9)$$

and

$$e^-_{aq} + H_2O_2 \rightarrow OH^- + OH \qquad (10)$$

The ratio for the rates of reactions 9 and 10,

$$k_{e^-_{aq}\ H_2O_2}/k_{H\ H_2O_2} = 500,$$

attests to the high reactivity of e^-_{aq} compared to H atoms in this reaction.

Among other reactions showing this difference in reactivity is the effect of metal ions such as Fe^{3+} and Cu^{++} on the hydrogen yield in irradiated solutions of methanol (*3*). Hydrogen formed by reaction

$$k_{e^-_{aq}+H_2O_2}/k_{H+H_2O_2} = 500,$$

is decreased by the addition of Fe^{3+} or Cu^{++} because the reaction

$$e^-_{aq} + Fe^{3+} \rightarrow Fe^{++} \qquad (12)$$

interferes with H-atom-producing reaction 4. Figure 1 gives a clear example of the lowering of the hydrogen yield $G(H_2)$ (in this case for monochloroacetic acid) which results from a difference in mechanism (*4*). Notice the reciprocal relationship between $G(HCl)$ and $G(H_2)$, the yields of HCl and H_2, respectively (*5*). As the concentration of monochloroacetic acid increases, $G(H_2)$ drops and $G(HCl)$ rises. As a result of the competition of H^+ and $ClCH_2COOH$ for e^-_{aq} in reactions 4 and 13, the H-atom yield decreases with increasing concentration of $ClCH_2COOH$. The amount of hydrogen formed by way of reaction 14 then diminishes.

$$e^-_{aq} + ClCH_2COOH \rightarrow Cl^- + \dot{C}H_2COOH \qquad (13)$$

$$H + ClCH_2COOH \rightarrow H_2 + Cl\dot{C}HCOOH \qquad (14)$$

Identification of Hydrated Electron

These experiments revealed the participation of two different reducing species in irradiated aqueous solutions. And while there was little doubt that the species dominant in neutral and alkaline solutions was e^-_{aq}, proof was still lacking.

Table 1. Determination of charge on e^-_{aq}.

Solute		Z_A	Slope*	$Z_{e^-_{aq}}$
A	B			
NO_2^-	H_2O_2	−1	+1.02	−1
O_2	H_2O_2	0	0.0	
H^+	H_2O_2	+1	−1.02	−1
$KFe(CN)_6^{--}$	N_2O	−2	+2.04	−1
Ag^+	$CH_2{=}CH\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2$	+1	−1.02	−1

* From Fig. 2, where log K/K_0 is plotted as a function of $\mu^{1/2}/1 + \mu^{1/2}$ K is the rate constant for solute A, and K_0 is the rate constant for the reference solute B.

On the theoretical side there were two schools of thought on the fate of the secondary electrons ejected from water. On the one hand it was reasoned that these electrons returned to their parent ion and that charge neutralization resulted, with formation of an excited water molecule (*6*).

$$H_2O^+ + e^- \rightarrow H_2O^* \qquad (15)$$

Dissociation then leads to the production of H and OH radicals by way of reaction 2.

On the other hand, hydration of the electron in lieu of return to the parent ion was also postulated (*7, 8*). On the basis of this picture the secondary electron (e^-_s) is thermalized (e^-_t) before hydration takes place, or even before reaction 15 takes place. The time scale of these processes leading to e^-_{aq} is:

$$H_2O + e^-_s \rightarrow H_2O^+ + e^-_s + e^-_s, \sim 10^{-16}\ \text{sec}$$

$$H_2O + e^-_s \rightarrow e^-_t + H_2O, \sim 10^{-13}\ \text{sec}$$

$$e^-_t + nH_2O \rightarrow e^-_{aq}, \sim 10^{-11}\ \text{sec.}$$

Thermalization occurs within 10^{-13} second and hydration within 10^{-11} second. And it is the hydrated electron rather than the thermalized electron that reacts with solutes. Since the thermalized electron is unattached to water molecules, it travels too rapidly to allow utilization of the energy available and required for hydration in reaction 3. Some predictions were that, (i) its hydration energy would be about 2.0 electron volts; (ii) the ion would absorb in the red part of the spectrum; and (iii) its mobility would correspond to an ef-

Table 2. Properties of e^-_{aq}.

Charge on ion, −1
Molar extinction coefficient:
  at 5780 Å, 9700 ± 1500 $M^{-1}cm^{-1}$
  at 7200 Å, 15000 ± 1500 $M^{-1}cm^{-1}$
λ_{max}, 7200 Å (1.72 ev)
E^0, 2.7 volts
Hydration energy, 1.75 ev
$k_{e^-_{aq}+H_2O} \leqq 4.4 \times 10^4$ sec^{-1}
$\tau_{1/2}$, $\geqq$ 300 μsec

fective electron mass of ⅕ an ionic mass (*7*). A question unanswerable in 1952 was the natural lifetime of e^-_{aq}. If the half-life $\tau_{1/2}$ is approximately 10^{-11} second, or even 10^{-9} second, as an early estimate indicated, it would be impossible to detect e^-_{aq} with spectroscopic means now available (*7*). Earlier attempts to locate a transient spectrum in x-ray-pulsed water (*9*) or to find the enhanced conductivity expected from the solvated electron in irradiated ammonia (*10*) failed because of low intensity.

Unit Negative Charge

While the result that e^-_{aq} possessed unit negative charge surprised no one, it provided the first acceptable proof that the second reducing species of exceptionally high reactivity is e^-_{aq}. For this proof, use was made of the Bronsted-Bjerrum theory of ionic reactions (*11*). This theory states that the rate constant K at ionic strength μ will vary with ionic strength of the solution according to the equation:

$$\log_{10}\frac{K}{K_0} = 1.02\,(Z_{e^-_{aq}})\,(Z_s)\,\{\mu^{1/2}/[1 + a(\mu^{1/2})]\}$$

where K_0 is the rate constant at zero ionic strength and $Z_{e^-_{aq}}$ and Z_s are the charges on e^-_{aq} and the solute, respectively. Since the expected value for $Z_{e^-_{aq}}$ is −1, K will increase if Z_s is negative, the rate will be unchanged if Z_s is 0, and the rate will decrease with increasing ionic strength if Z_s is positive. Because many e^-_{aq} reactions are very fast and means were not available in 1962 for measuring their absolute rate constants, reliance had to be placed on relative rate constants. Figure 2 and Table 1 show that a behavior consistent with $Z_{e^-_{aq}} = -1$ is obtained. In each of these curves the reaction rate of the indicated molecule or ion (*A*) is compared with that of a neutral molecule (*B*) whose rate is unaffected by ionic strength (that is, each curve represents the ratio of the rate constants of *A* and *B*). Relative rate constants are given as a function of ionic strength. The straight lines are drawn with slopes of + 1.02 for NO_2^-, + 2.04 for $KFe(CN)_6^{--}$, and −1.02 for H^+ and Ag^+. These data are summarized in Table 1. A dependence of relative rate constant on ionic strength consistent with the Bronsted-Bjerrum equation and unit negative charge on e^-_{aq} is obtained in the case of the charged reactants (Table 1, col. 5). No effect is expected, nor was any found for the neutral oxygen molecule.

Spectrum of Hydrated Electron

Because the solvated electron in ammonia solutions of alkali metals has high stability, its blue color persists for days. In contrast, the lifetime of e^-_{aq} is measurable in microseconds. For this reason the discovery of e^-_{aq} was delayed until the present era of high electron current, pulse accelerators, and fast reaction techniques (*12*). By synchronizing an electron pulse with light-flash absorption spectrophotometry, spectra of absorbing transient (or permanent) species generated in the water can be obtained. And it was in this way that the spectrum of e^-_{aq} was discovered, first in a sodium carbonate solution and then in pure water (*13–15*).

The quartz cell (see Fig. 3, insert) was irradiated from the side with a ribbon of 1.8-Mev electrons in a pulse of 2-microsecond duration. Simultaneously with irradiation by this pulse of electrons, a uranium-spark light source was triggered, and a pulse of continuous light of some 5 microseconds' duration was passed through the cell and into a spectrograph (*14, 16*). The resulting spectrum was recorded on a photographic plate. This spectrum and curves showing differences in optical density of irradiated 0.05*M* sodium carbonate solution and pure water are shown in Fig. 4. Spectrum *a* is from a flash that occurred before irradiation through 0.5*M* sodium carbonate solution, *b* is from a flash that occurred simultaneously with the electron pulse, and *c* is from a flash that occurred 30 seconds after the electron pulse. The darkened section (above 4500 Å) shows the intense absorption due to the transient e^-_{aq}. A well-defined maximum occurs near 7000 angstroms (*14*). Only a trace of the spectrum remained in a photograph taken 25 microseconds after the electron pulse. While the original assignment of this absorption band to e^-_{aq} was based on (i) its similarity to the absorption band of the solvated electron in ammonia solutions of alkali metals and (ii) to the fact that the band is obtained in pure water and in concentrated ammonia solutions and is suppressed by H^+, O_2, CO_2, H_2O_2, and other known e^-_{aq} scavengers, additional evidence in support of this assignment has since been obtained. Enhanced electrical conductivity with a decay period similar to that found in the spectral work gives gratifying verification through an entirely different means of detection (*16, 17*), and evidence that the transient species responsible for the

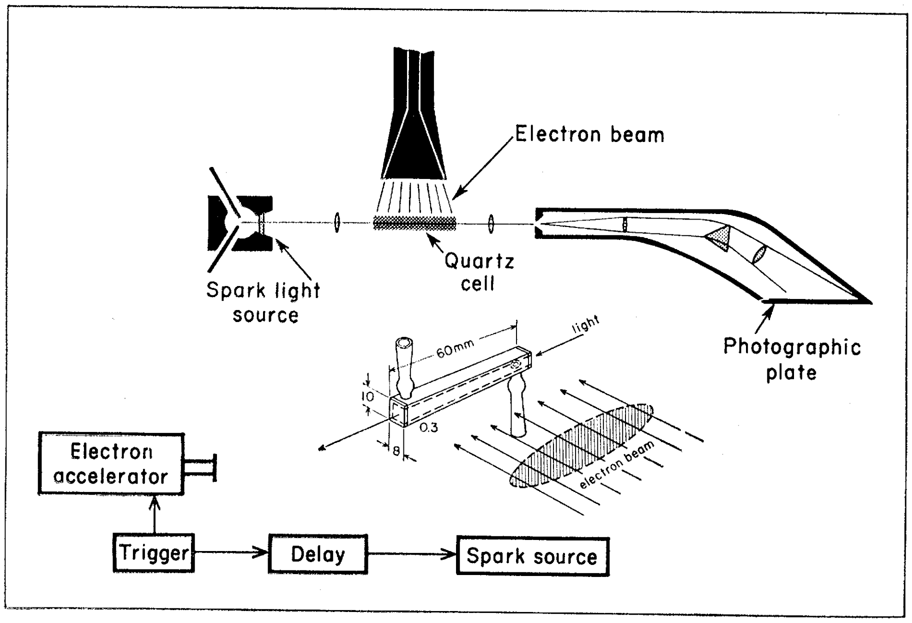


Fig. 3. Schematic diagram of apparatus used for kinetic absorption spectroscopy (*16*). Insert shows the construction of the absorption cell in greater detail.

Table 3. Reactions of e^-_{aq} with the species formed in irradiated water.

Reaction	$k(M^{-1}sec^{-1})$	Reference
$e^-_{aq} + H_2O \rightarrow H + OH^-$	$\leq 7.0 \times 10^2$* 4.9×10^2	(*28*) (*33*)
$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^-$	0.5×10^{10}	(*28*)
$e^-_{aq} + H \rightarrow H_2 + OH^-$	$\sim 3.0 \times 10^{10}$	(*29*)
$e^-_{aq} + OH \rightarrow OH^-$	$\sim 3.0 \times 10^{10}$	(*29*)
$e^-_{aq} + H_3O^+ \rightarrow H + H_2O$	2.3×10^{10}	(*28, 29*)
$e^-_{aq} + H_2O_2 \rightarrow OH^- + OH$	3.0×10^{10}	(*29*)
$e^-_{aq} + H_2 \rightarrow$ no reaction		

* First-order rate constant is 4.4×10^4 sec^{-1}; strongly basic aqueous ethanol solution (*28*); water (*33*). *Note added in proof*: Recent work indicates a rate constant lower by at least a factor of 10. Consequently $\tau_{\frac{1}{2}}$ of Table 2 is greater than 300 microseconds.

absorption spectrum carries unit negative charge was verified by measurements of the effect of ionic strength on the decay of the spectrum in $Fe(CN)_6^{3-}$ solutions (*18*).

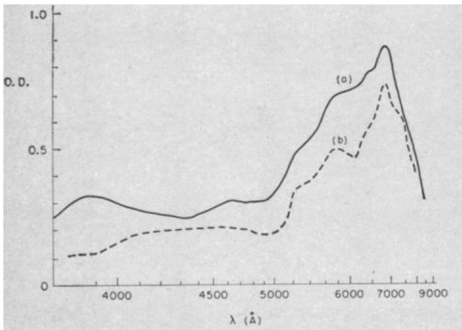
Not surprising is the result that hydrated electrons are produced in water irradiated by ionizing radiations such as electrons and gamma rays. But by means of its spectrum, proof has been provided that e^-_{aq} forms thermally from hydrogen atoms and photochemically from flash-irradiated ions and molecules as well.

In alkaline solutions, H atoms form e^-_{aq}. The reaction is:

$$H + OH^- = e^-_{aq} + H_2O \qquad (16)$$

This reaction was established by showing that relative rate constants of hydrogen atoms introduced in alkaline solutions paralleled those of e^-_{aq} rather than those of H atoms (*19*). Confirmation of this reaction was obtained by showing an increase in e^-_{aq} absorption as the *p*H was raised from 10 to 13 in solutions irradiated at a pressure of 100 atmospheres (hydrogen). Under those conditions hydroxyl radicals are converted first to H atoms and then to e^-_{aq} by way of reaction 16 (*20, 21*).

In Fig. 5, the lower decay curve was obtained at *p*H 10 under conditions where OH radicals react with H_2 and are replaced by H atoms. In the upper curve, at *p*H 13 the H atoms are converted to e^-_{aq} by way of reaction 16. The top horizontal line represents 100-percent absorption; the lower one, zero absorption. Note how the e^-_{aq} spectrum builds up during the 0.4-microsecond pulse and then decays. The increased concentration is apparent from the greater initial height of the decay curve. When the initial optical density is computed for these two curves, the increase in e^-_{aq} concentration is found to correspond closely to the yield of OH radicals of reactions 1 and 2.



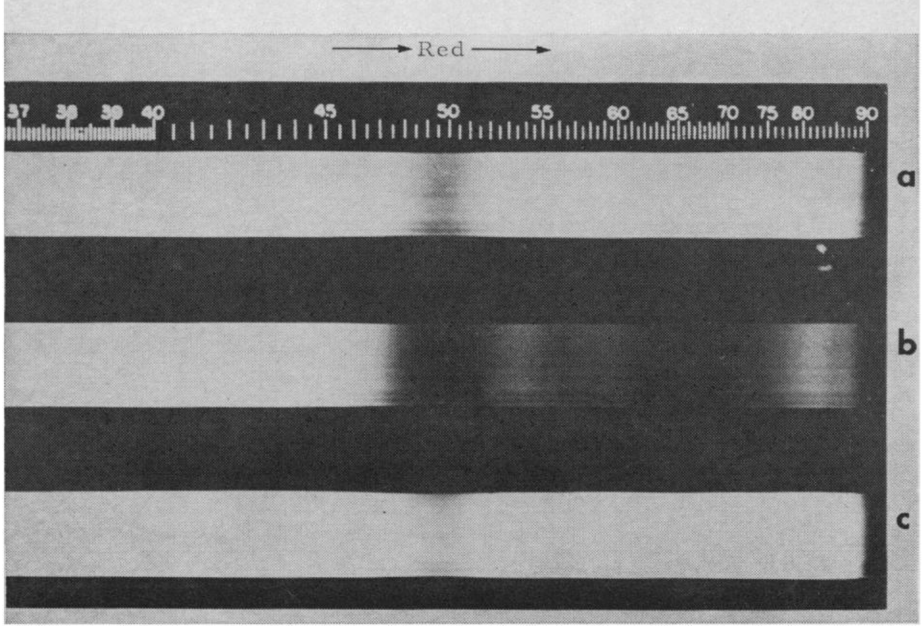


Fig. 4. (Left) Absorption band due to e^-_{aq} in irradiated solutions: (*a*) irradiated $0.05M$ Na_2CO_3 [mean dose, 7 krad (1 rad = 100 erg/g)]; (*b*) pure deaerated water. (Below) The red end of the spectrum: (*a*) flash before irradiation; (*b*) flash simultaneous with electron pulse, showing intense absorption due to e^-_{aq}; and (*c*) flash 30 seconds after electron pulse.

The conclusion that e^-_{aq} is liberated in the photolysis of dissolved ions (*22*) has also been confirmed by means of the e^-_{aq} spectrum (*23, 24*). In flash photolysis experiments with a number of inorganic ions—Cl^-, Br^-, I^-, OH^-, CNS^-, or $Fe(CN)_6^{4-}$—and with organic molecules such as phenol, *p*-cresol, alanine, tyrosine, and tryptophan, the spectrum of e^-_{aq} has been observed. A comparison of spectra *A* and *B* in Fig. 6 shows the similarity of the spectra from radiation-produced and light-produced e^-_{aq}. Besides, the extinction coefficient of 15,000 ± 4500 $M^{-1}cm^{-1}$ reported for photo-produced e^-_{aq} agrees with the value found for e^-_{aq} produced by radiolysis (*24*) (see Table 2).

Hydration of the electron appears to be a special case of a general phenomenon. Solvated electrons with a spectrum similar to that of e^-_{aq} have been discovered in irradiated ethanol (*25*). In Fig. 6, compare curve *A*, for e^-_{aq}, with curve *C*, for $e^-_{ethanol}$. Solvated electrons have also been observed by means of the optical photolysis of I^-, Br^-, and OH^- in ethanol (*26*). It is expected that solvated electrons will be found in all dipolar liquids nonreactive to such electrons. Because the e^-_{aq} and $e^-_{ethanol}$ rate constants are nearly identical for H^+ and O_2 (*25*), it will be interesting to find whether this correlation holds for a variety of solutes. For, if it does, e^-_{aq} rate constants may be estimated for compounds, such as the aromatic hydrocarbons, which are insoluble in water.

Redox Potential and Hydration Energy

Estimates of some thermodynamic properties of e^-_{aq} have already been made (*27*).

The redox potential (E^0) and the hydration energy may be derived from rate constants for the forward and reverse reactions in the equilibrium

$$e^-_{aq} + H_2O \rightleftarrows H + OH^-_{aq}.$$

On the basis of published values for these rate constants, K, the equilibrium constant, is taken to be $\leqslant 2.5 \times 10^{-5}$, giving $\triangle F \geqslant 6.3$ kcal. Then from the reactions

$$H \rightarrow \tfrac{1}{2}H_2$$

($\triangle F = -48.5$ kcal) and

$$H^+_{aq} + OH^-_{aq} \rightarrow H_2O$$

($\triangle F = -19.3$ kcal), we obtain $\triangle F = -61.5$ kcal and $E^0 \leqslant 2.7$ volts for the reaction.

$$e^-_{aq} + H^+_{aq} \rightarrow \tfrac{1}{2}H_2.$$

If a rate constant of 24.7 $M^{-1}sec^{-1}$ for $k_{e^-_{aq} + H_2O}$ is used, instead of 490 $M^{-1}sec^{-1}$, a lower and possibly more reliable value for E^0 of 2.5 volts is obtained. Since the redox potential of the H atom is 2.1 volts, e^-_{aq} is a stronger reducing agent than the H atom by 0.4 to 0.6 volt. A hydration energy of −40 kilocalories, corresponding to 1.75 electron volts, has also been calculated from these data, and it agrees well with the absorption maximum at 1.72 electron volts (7200 Å). This indicates that the free energy is made up almost entirely of hydration energy (*27*). A summary of some properties of e^-_{aq} is given in Table 2.

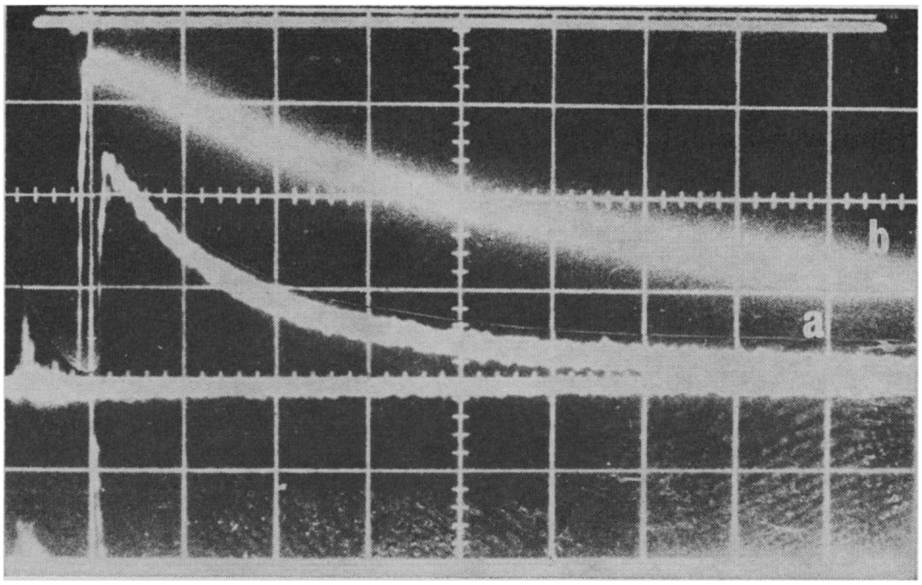


Fig. 5. Decay of e^-_{aq} absorption band at 5780 angstroms in alkaline solution under pressure of 100 atmospheres (hydrogen), (*a*) at *p*H 11, (*b*) at *p*H 13. The top horizontal trace is obtained with the shutter closed and represents 100-percent absorption; the middle curves show the buildup and decay of the e^-_{aq} absorption band; the lower horizontal trace was recorded 50 milliseconds after the electron pulse and represents 100-percent transmission. On the abscissa, the large divisions are 5 microseconds (*20, 21*).

Reactions of Hydrated Electrons

Within the past year extensive use has been made of the absorption spectrum of e^-_{aq} in the study of its reactions. Usually the hydrated electrons are introduced during an electron pulse of 0.2- to 2-microsecond duration, and the decay of the absorption spectrum is followed. Typical decay curves are given in Fig. 5. Since the molar extinction coefficient, ε, for e^-_{aq} is high [9700 M^{-1} cm^{-1} at 5770 to 5790 Å (*28*) and about 15,000 at the 7200-Å maximum], reactions may be followed when e^-_{aq} concentrations are in the range of 0.01 μM and higher (*15, 28, 29*). The spectral region is, conveniently, one where, for many ions and molecules, absorption is negligible or low. In much of the work discussed below, experimental conditions are arranged so that the decay of e^-_{aq} absorption follows first-order kinetics. The concentration of solute (C_s) is much greater than the concentration of e^-_{aq} and remains substantially unchanged during irradiation.

Reactions with species of irradiated water. Unfortunately, a pulse of electrons introduces several transient, reactive species besides e^-_{aq}. The radiolysis reaction is

$$H_2O \rightarrow H, OH, e^-_{aq}, H_3O^+, OH^-, H_2, H_2O_2.$$

Except for H_2 and OH^-, each of the species other than e^-_{aq} reacts with e^-_{aq}. These reactions and their rate constants are given in Table 3. The high rate of reaction (10^{10} $M^{-1}sec^{-1}$) of e^-_{aq} with these species indicates diffusion-controlled reactions. Because of inadequate data on the effective dielectric constant, the diffusion coefficient, and the interaction radius of e^-_{aq}, agreement of the rate constant obtained experimentally with the rate constant calculated from the Debye equation is unsatisfactory. Reasonably good agreement of the equation with some of the reactions is, however, found if a value of 2.7 angstroms for encounter distance and a diffusion coefficient of 10×10^{-5} cm^2sec^{-1} are used (*18, 20*). With the availability of rate constants for e^-_{aq} reactions with the radicals and ions formed in irradiated water, much refinement can be expected in the model used in diffusion kinetics. Heretofore it was necessary to assume values for many of the rate constants used in the diffusion equation.

The e^-_{aq} absorption spectrum decays by a first-order process at low concen-

Table 4. Hydrated electron rate constants for inorganic ions and molecules.

Reactant	Product	*p*H	Rate constant ($M^{-1}sec^{-1}$)	Reference
O_2	O_2^-	7	$1.88 \pm 0.2 \times 10^{10}$	(*29, 33, 34*)
NO	NO^-	7	$3.14 \pm 0.2 \times 10^{10}$	(*29*)
N_2O	$N_2 + O^-$	7	$8.7 \pm 0.6 \times 10^9$	(*29*)
CO_2	CO_2^-	7	$7.7 \pm 1.1 \times 10^9$	(*29*)
$Fe(CN)_6^{3-}$	$Fe(CN)_6^{4-}$	7, 10.3	$3.0 \pm 0.4 \times 10^9$	(*29*)
Cu^{++}	Cu^+	7	$3.3 \pm 0.3 \times 10^{10}$	(*29, 33*)
Ag^+	Ag	7	$3.6 \pm 0.4 \times 10^{10}$	(*29, 33*)
Zn^{++}	Zn^+	7	1.7×10^9	(*33, 35*)
Co^{++}	Co^+	7	1.35×10^{10}	(*33, 35*)
Ni^{++}	Ni^+	7	2.3×10^{10}	(*33, 35*)
Cd^{++}	Cd^+	7	5.5×10^{10}	(*33, 35*)
$Co(NH_3)_6^{3+}$	$Co(NH_3)_6^{++}$	7	9.0×10^{10}	(*33, 35*)
$[Cr(CrO_4)_3]^{3+}$	$[Cr(CrO_4)_2]^{++}$	7	2.1×10^{10}	(*31*)
$[Cr(en)_3]^{3+}$	$[Cr(en)_3]^{++}$	7	1.3×10^{11}	(*31, 36*)
Eu^{3+}	Eu^{++}		6.1×10^{10}	(*31, 36*)
Yb^{3+}	Yb^{++}		4.3×10^{10}	(*31, 36*)
Sm^{3+}	Sm^{++}		2.5×10^{10}	(*31, 36*)
Tm^{3+}	Tm^{++}		3.0×10^9	(*31, 36*)
Ho^{3+}	Ho^{++}		2.4×10^9	(*31, 36*)

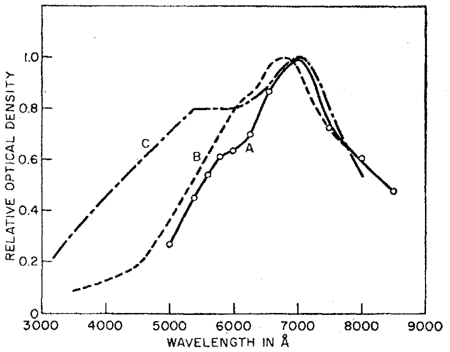


Fig. 6. Absorption spectra of hydrated and solvated electrons in (*A*) pure water irradiated by means of an electron pulse (*14*); (*B*) potassium chloride solution photolyzed by a light flash (*23*); (*C*) ethyl alcohol irradiated by means of an electron pulse (*25*).

trations and by a second-order process at high concentrations. These processes reveal two important reactions. The first-order decay is explained by reaction 3, and the second-order decay by

$$e^{-}_{\mathrm{aq}} + e^{-}_{\mathrm{aq}} \rightarrow H_2 + 2OH^{-}$$

and

$$e^{-}_{\mathrm{aq}} + H \rightarrow H_2 + OH^{-}$$

These hydrogen-forming reactions are of particular interest to radiation chemists, since they account for much of the hydrogen formed during radiolysis. The interaction of two hydrated electrons follows second-order kinetics and forms a molecule of H_2 instead of two freely diffusing H atoms (*28*). The reaction of e^{-}_{aq} with H to form H_2 is deduced from decay curves obtained in alkaline solutions (used to remove H_3O^{+} produced during irradiation) and in solutions containing OH-radical scavengers. This leaves H atoms as the major e^{-}_{aq} reactant, and the decay of the spectrum is due to $e^{-}_{\mathrm{aq}} + e^{-}_{\mathrm{aq}}$ and to e^{-}_{aq} + H (*29*).

Reactions with inorganic ions. Two general types of e^{-}_{aq} reactions occur. One is a dissociative capture, as in

$$H_2PO_4^{-} + e^{-}_{\mathrm{aq}} \rightarrow HPO_4^{--} + H,$$

and the other is nondissociative capture, as in

$$Cu^{++} + e^{-}_{\mathrm{aq}} \rightarrow Cu^{+}.$$

Some representative rate constants for inorganic anions and cations are given in Table 4. The high second-order rate constants as well as the reduction of Zn^{++}, Cd^{++}, and the rare earth ions attest to the high reactivity of e^{-}_{aq}. Transient absorption spectra attributed to the univalent ions Zn^{+}, Cd^{+}, Co^{+}, and Mn^{+} form in solutions containing divalent ions of these metals (*30*). Alkali and alkaline earth ions are unreactive (*13, 14*). Among the reactive ions there is great selectivity, although there is a rough correlation of rate constants with size of ion and character and degree of charge, as would be expected from the Debye equation. Positive ions are more reactive than negative ones, and the greater the charge, the higher the rate constant. In the series of rare earth ions, the elements showing stable divalent states are the most reactive, having rate constants in the range from 2.5 to 6.1 × 10^{10} $M^{-1}\mathrm{sec}^{-1}$. All other rare earth ions except Tm^{3+} and Ho^{3+} have rate constants of the order of 10^{8} M^{-1} sec^{-1} (*31*).

Reactions with organic molecules. As with inorganic ions, great variation in reactivity of e^{-}_{aq} with organic compounds is found. From rate constants ranging from $< 10^{7}$ $M^{-1}\mathrm{sec}^{-1}$ for alcohols, in which solvation occurs, to values for highly reactive compounds with $k > 10^{10}$ $M^{-1}\mathrm{sec}^{-1}$, much may be learned about the structure and reactivity of organic compounds.

The discovery of e^{-}_{sol} in irradiated pure ethanol confirms the unreactivity not only of the saturated hydroxyl group but also of saturated carbon hydrogen bonds (*25*). Saturated and unsaturated hydrocarbons, because of their limited solubility and low reactivity, cannot be effectively studied in water. The rate constants would, however, be less than 10^{7} $M^{-1}\mathrm{sec}^{-1}$, a value less by a factor of at least 10^{3} than that for the reactive compounds.

The rate constants for reaction of e^{-}_{aq} with some organic compounds are given in Table 4 (*32*). These data were obtained in solutions near neutrality and at $pH > 10$, usually with $10^{-3}M$ methanol added. For highly reactive compounds where solute is present in low concentrations, it is advisable to remove H^{+} and OH radicals. When methanol is used for removing the OH radical the resulting $\overset{\bullet}{C}H_2OH$ radical has a much lower reactivity with e^{-}_{aq} than the OH radical. Under these conditions pseudo first-order kinetics prevail, since $[e^{-}_{\mathrm{aq}}]$ is approximately $10^{-6}M$ and the solute concentration is greater than $5 \times 10^{-5}M$.

Table 5 shows that the reactive groups in nonaromatic compounds are the C—Cl, C═O, C═S, and S—S linkages and conjugated linkages such as C═C—C═C— and —C═C—C═O. Benzene, phenol, and hydroquinone are unreactive, but derivatives such as nitrobenzene, styrene, phthalic acid, and picric acid are very reactive. Of the chemicals of biological interest, purine, cytosine, thymine, cytidine, and uric acid are very reactive. The amino acids are unreactive, with the exception of cystine, the disulfide of cysteine. The sugars, arabinose and ribose, are unreactive too, and when combined with the parent purine and pyrimidine bases, in the cases of adenylic, cytidylic, guanylic, and thymidylic acids, they have little effect on the reactivity of these bases.

As with inorganic reactions, dissociative and nondissociative capture of e^{-}_{aq} may occur. Reactions 13 and 14 are representative of these two general reactions. Sometimes an intermediate negative ion transient is formed, and transient spectra, whether due to the negative ion or not, have been reported for thymine, cytosine, picric acid, and acrylamide.

At this time work has not progressed far enough to determine the significance of e^{-}_{aq} rate constants in organic reactions. However, in studies of aromatic

Table 5. Hydrated electron rate constants for organic compounds (*32*).

Compound	k($M^{-1}\mathrm{sec}^{-1}$)
Aliphatic	
Acetaldehyde	3.5×10^{9}
Acetone	5.9×10^{9}
Acrylamide	1.8×10^{10}
Carbon disulfide	3.1×10^{10}
Carbon tetrachloride	3.0×10^{10}
Chloroform	3.0×10^{10}
L-Cystine	3.4×10^{9}
Fumarate ion	7.5×10^{9}
Maleate ion	2.2×10^{9}
Methacrylate ion	8.4×10^{9}
Pyruvate ion	6.8×10^{9}
Tetracyanoethylene	1.5×10^{10}
Aromatic	
Aniline	$< 2 \times 10^{7}$
Benzene	$< 7 \times 10^{6}$
Benzoquinone	1.2×10^{9}
Hydroquinone	$< 1 \times 10^{7}$
Naphthalene	3.1×10^{8}
β-Naphthol	1.8×10^{9}
Nitrobenzene	3×10^{10}
Phenylalanine	$< 1 \times 10^{7}$
Phthalate ion	2×10^{9}
Picric acid	3.5×10^{10}
Styrene	1.3×10^{10}
Heterocyclic	
Adenosine	1.0×10^{10}
Cytidine	1.2×10^{10}
Hypoxanthine	1.7×10^{10}
5-Methylcytosine	1.0×10^{10}
Orotic acid	1.5×10^{10}
Purine	1.7×10^{10}
Pyridine	1.0×10^{9}
Thymine	1.7×10^{10}
Uracil	7.7×10^{9}
Thiophene	$\leq 6.5 \times 10^{7}$
Pyrrole	$\leq 6 \times 10^{5}$
Thiazole	2.5×10^{9}

derivatives the rate constant appears to be correlated with the electrophilic properties of the ring: the greater the net positive character, the greater the rate constant, as in the case of inorganic ions. It is possible that e^-_{aq} rate constants may provide the organic chemist with a fundamental new parameter for explaining the reactions he observes.

It is well to remember that e^-_{aq} rate constants obtained from spectral decay curves measure only the disappearance of e^-_{aq}. Sometimes an intermediate negative ion of appreciable lifetime forms, and the properties of this ion, too, may be studied. But even when such transients are not formed it is possible that the rate-determining step is the one following reaction or association of e^-_{aq} with the molecule or ion involved. For example, in the formation of H by way of reaction 4, an intermediate may be:

$$e^-_{aq} + H^+ \rightarrow (H^+)^-$$

The hypothetical species $(H^+)^-$ would account for the decay of the e^-_{aq} spectrum, but its conversion to a hydrogen atom by way of the reaction

$$(H^+)^- \rightarrow H$$

may be the rate-determining step. Evidence is, in fact, accumulating in support of the hypothesis that final product formation in the case of these reactions is delayed.

Future Developments

The positive identification of e^-_{aq} as the principal reducing species in irradiated water and the finding that e^-_{aq} is formed in photolysis has far-reaching consequences in science. Two aspects are the effect on the interpretation of chemical mechanisms and the future role of e^-_{aq} in chemistry and biology.

Since e^-_{aq} forms in radiolysis from thermalized electrons and in photolysis from excited ions, it must be considered an intermediate in reactions induced by ionizing radiations and by light. A reassessment of mechanisms proposed in these branches of chemistry is now required. And the use of precise rate constants in these mechanisms will be of great help in deciding on the rate-determining steps. In electrochemistry and radiation biology e^-_{aq} must be considered a possible reactive reducing species, especially in neutral and alkaline solutions. Particularly significant is the result that amino acids are nearly unreactive with e^-_{aq}, whereas the pyrimidine and purine bases present in nucleic acid are very reactive. And because e^-_{aq} is generated photochemically from dissolved organic molecules, it is apt to be an important intermediate in photosynthesis and in photobiology.

While reinterpretation of reaction mechanisms will be rewarding, by far the greatest promise offered by e^-_{aq} or, in general, by solvated electrons lies in the prospective deliberate use of these electrons in the investigation of chemical reactions. In this way information regarding the structure of compounds and of liquids will be obtained. Not only are the absolute rate constants revealing parameters in these studies but the absorption spectrum and electrical conductivity of e^-_{aq} are affected by the environment, facts well known from the behavior of solvated electrons in liquid ammonia. The theoretical chemist will find e^-_{aq} an intriguing entity because of its simplicity, its high reactivity, and the already impressive list of its rate constants, which can be correlated with the data available from thermal reactions. This newly discovered ion has already profoundly altered the course of radiation chemistry, and its further use will contribute to the development of other branches of chemistry and biology.

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