Research Potentials of the Hydrated Electron

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In the hydrated electron the kineticist's dream is realized. Designated e_{aq}^- in order to distinguish it from a subexcitation or thermal electron e_{aq}^- is not only the simplest negative aqueous ion, but it is also a highly reactive and useful one. Its broad, intense optical absorption band centered at 715 nm provides an unexcelled means of delving into its kinetic and structural properties and, although its natural lifetime is less than 10^{-3} sec, the current pulse radiolysis[1-5] and flash photolysis techniques[6-9] are ideal for its study. However, these pulse methods are unneccessary for research with e_{aq}^- since ^{60}Co γ rays or ultraviolet light readily generates it in suitable systems. How e_{aq}^- may be used as a new reagent in chemical research will be revealed by a brief treatment of its structure and some of its chemical reactions and finally how it is prepared and used in actual practice. For more complete discussions consult a number of reviews.[10-15] Pertinent too is Dye's recent paper on solvated electron reaction rates in amines.[16]

The hydrated electron will find applications in many branches of chemistry. Were e_{aq}^- found only in irradiated water, its usefulness to chemistry would be quite restricted, but not only is it a common product of aqueous photochemical reactions, it is also present in many chemical reactions. In a recent review Walker[14] showed that e_{aq}^- is a primary product when sodium amalgam or certain inorganic ions such as U^{3+} dissolve in water. Furthermore, under some conditions cathodic reduction involves e_{aq}^-. It has also been generated by photoemission from immersed metals. Another important method of producing e_{aq}^- is from hydrogen atoms in alkaline solutions. Certainly in these broad areas of chemistry the possible participation of e_{aq}^- must be considered, and as a guide to the nature of these reactions the extensive literature on reactions of the ammoniated electron ($e_{NH_3}^-$) is most helpful.[17]

Structure

While the fine structural details of e_{aq}^- remain a mystery as for many aqueous ions, broadly it may be described as an electron in a cavity with its charge more than 99% compensated by the surrounding protons.[18]

This simple structure is supported by a comparison of its optical and epr properties with those of the well-known F centers in alkali halides and with the ammoniated electron, $e_{NH_3}^-$, which it closely resembles. Electrons trapped in crystals or in vacancies in solvents have been thoroughly studied by optical and epr spectroscopic methods. There is little question but that the electron in an alkali halide vacancy in the crystal[19] is the primary F center. In Figure 1[20-26] the optical

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(8) K. Schmidt and E. J. Hart, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 267.
(9) G. Stein, *Actiones Chim. Biol. Radiations*, **13**, in press.
(10) E. J. Hart, *ibid.*, **10**, 1 (1966).
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(14) D. C. Walker, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 49.
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(16) J. L. Dye, *Accounts Chem. Res.*, **1**, 306 (1968).

(17) H. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, New York, N. Y., 1963, p 151.
(18) L. Onsager, *Radiation Res. Suppl.*, **4**, 13 (1964).
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(20) E. J. Hart in "Radiation Chemistry of Aqueous Systems," G. Stein, Ed., Weizmann Science Press, Jerusalem, 1968, p 73.
(21) K. Schmidt, B. D. Michael, and E. J. Hart, unpublished results.
(22) M. Gold and W. L. Jolly, *Inorg. Chem.*, **1**, 818 (1962).
(23) E. M. Fielden and E. J. Hart, *Trans. Faraday Soc.*, **63**, 2975 (1967).
(24) B. G. Ershov and A. K. Pikaev, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 1.
(25) K. Eiben and I. A. Taub, *Nature*, **216**, 782 (1967).
(26) G. Nilsson, H. C. Christensen, J. Fenger, P. Pagsberg, and S. O. Nielsen, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 71.
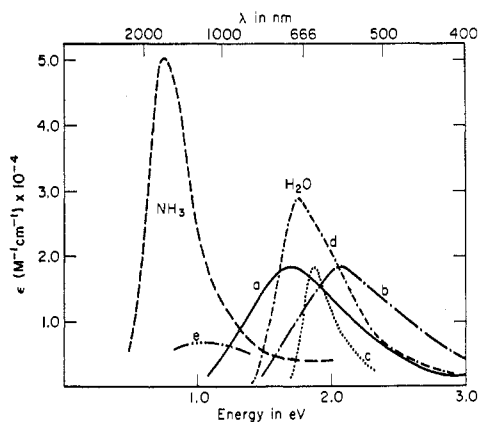
Figure 1. Comparison of solvated and hydrated electron absorption spectra. Ammonia, liquid at $-48°$;[20,22,23] water (a) liquid at 25°; (b) 10 M NaOH glass at $-194°$;[24] (c) crystalline ice at $-194°$[25] (ϵ_{max} assumed equal to that of liquid water); (d) crystalline ice at $-10°$ (ϵ based on an oscillator strength of 0.65);[26] (e) liquid at 313°[21] (ϵ_{max} arbitrary).

spectrum of e_{aq}^- (a) is compared with those of the ammoniated and trapped electrons (e_{tr}^-) in crystalline ice (d and c) and in an alkaline aqueous glass (b). Furthermore the shape of the e_{aq}^- absorption band does not depend on pH in the range 4–13.[20,21] Plotted on this same scale the F center in KBr would have a band centered at 1.97 eV with a molar extinction coefficient of 10^5 M^{-1} cm^{-1}. Its half-width is 0.4 eV. Notice the similarity of all these bands. They have a comparatively sharp low-energy edge and a broader one on the high-energy side. Further detailed comparisons between e_{aq}^- and e_{tr}^- confirm this close relationship.

Raising the temperature broadens the absorption band of the e_{aq}^- and shifts λ_{max} from 715 nm to longer wavelengths[21] in a manner similar to that of F centers and $e_{NH_3}^-$.[22,27,28] Since there is substantially no loss in intensity of the e_{aq}^- band as the temperature is raised from 4 to 90° we conclude that the number of hydrated electrons formed by a given dose of radiation is independent of temperature.[21,29] Even at the much higher temperature of 313° electrons hydrate. The pulse radiolysis of liquid D$_2$O reveals a broadened optical band with λ_{max} near 1000 nm (see curve e of Figure 1). The decay of e_{aq}^- at this temperature is so rapid that its spectrum can only be observed during the electron pulse.[21] Nevertheless this result convincingly demonstrates the ability of the electron to create its own trap in liquid water, as Onsager suggests.[18]

At low temperatures in ice, however, preformed traps or cavities are necessary. In a low-temperature aqueous alkaline glass where there are a large number of imperfections there are also plenty of available sites for trapping electrons released by γ rays. In pure crys-

talline ice where very few traps exist, the yield of trapped electrons is vanishingly small at low temperatures.[25] Curve d for crystalline ice, shown in Figure 1, was obtained at $-10°$ by a pulse radiolytic method,[26] and like e_{aq}^- has only a short lifetime. Thus we confidently conclude that e_{aq}^-, like these other solvated electrons, consists of an electron trapped in a cavity. The environment, however, differs in these cases, and in the liquids solvated electrons show high mobility.

In one major respect these electrons trapped in glassy ice differ from F centers. Figure 2 shows the effect of photoannealing of alkaline and water–alcohol glasses.[24] In F centers, bleaching by light symmetrically lowers the band, showing the structural uniformity of vacancies in the crystal. Similar bleaching of the glasses (shown in Figure 2) by monochromatic light shifts the band center to shorter wavelengths. This shows that the fine structure of the optical band of e_{tr}^- is an envelope of many electron absorption lines differing in electron-trapping energies,[24] and because of the similarity of the absorption spectra of e_{tr}^- and e_{aq}^- I assume that if a similar experiment could be carried out with e_{aq}^- it, too, would show this selective bleaching.

The epr spectrum of e_{aq}^- consists of a single line with a g factor of 2.0002 $\pm$ 0.0002 and a narrow line of less than 0.5 G.[30] The motion of the hydrogen atoms of water lining the e_{aq}^- cavity delocalizes e_{aq}^- to such an extent that interactions with definite protons no longer occur.

The simple dielectric model satisfactorily accounts for the thermodynamic and optical properties of $e_{NH_3}^-$.[31,32] This model fits e_{aq}^- too, although its unknown cavity size is treated as an adjustable parameter. But with a cavity radius, R_0, equal to 1.45 Å, the oxygen–oxygen distance in liquid water, the calculated 1s–2p transition energy is 1.65 eV (1.73 eV observed). For this model the radius of charge distribution is 2.8 Å, which indicates an appreciable leakage of electron charge density outside the cavity.[32,33] In more detailed models the tetrahedral structure of four water molecules has been used. This model not only explains the experimental results in ice but also those in water.[34–36]

Most instructive in gaining an insight to the structure of molecules have been the pictorial studies of molecular orbital densities produced by Wahl,[37] and, by using the Jortner, Rice, Wilson[31] equation for the energy, E_{1s}, of the 1s state, the electron density of e_{aq}^- may be computed. For the self-consistent field (SCF) dielectric model with cavity of radius R_0, the equation for E_{1s} is given by

(27) D. M. Gruen, M. Krumpelt, and I. Johnson in Proceedings of a Symposium on the Characteristics of Molten Salts, Marcel Dekker, in press.

(28) J. Corset and G. Lepoutre in "Metal-Ammonia Solutions," G. Lepoutre and M. J. Sienko, Ed., W. A. Benjamin, Inc., New York, N. Y., 1964, p 186.

(29) W. C. Gottschall and E. J. Hart, J. Phys. Chem., 71, 2102 (1967).

(30) E. C. Avery, J. R. Remko, and B. Smaller, J. Chem. Phys., 49, 951 (1968).

(31) J. Jortner, S. A. Rice, and E. G. Wilson in ref 28, p 222.

(32) J. Jortner in ref 20, p 91.

(33) J. Jortner, Radiation Res. Suppl., 4, 24 (1964).

(34) M. Natori and T. Watanabe, J. Phys. Soc. Japan, 21, 1573 (1966).

(35) M. Natori, ibid., 24, 913 (1968).

(36) L. Kevan in ref 20, p 21.

(37) A. C. Wahl, Science, 151, 961 (1966).

$$E_{1s} = \left[\frac{X^2}{2R_0^2} - \frac{\gamma_D}{2R_0} + \frac{\gamma_D}{R_0}(1+X)e^{-2X} - \frac{\gamma_D}{2R_0}e^{-4x}\left(1 + \frac{21}{8}X + \frac{5}{2}X^2 + X^3\right)\right]\frac{e^2}{a_0}$$

where $X = \lambda R_0$; $\gamma_D = 1 - (1/D_s)$; and λ satisfies the condition $dE_{1s}/dX = 0$. For $R_0 = 1.4$ Å and a dielectric constant of 78, $\lambda = 0.53$.

The parameter λ is obtained by minimizing the energy, and for a value of 0.53 the mean radius of charge distribution of e_{aq}^- is 2.8 Å, just between the limits of 2.5–3.0 Å usually ascribed to e_{aq}^-.[38,39] Wahl[40] calculated the charge density distribution of e_{aq}^- using the equation for E_{1s} for $\lambda = 0.53$. His results are displayed in Figure 3 as a two-dimensional contour diagram automatically drawn by the CDC-3600 computer.[41] According to this picture, e_{aq}^- consists of a symmetrical
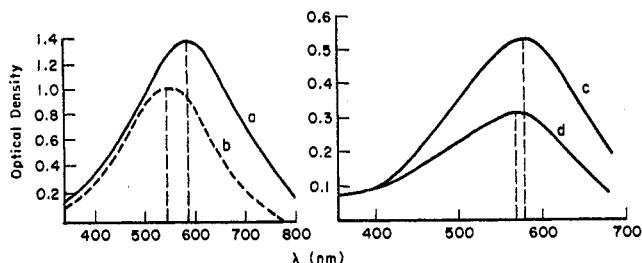

Figure 2. Absorption spectra of trapped electrons in 10 M KOH (a, b) and in H_2O–CH_3OH mixture (c, d) before partial photoannealling (a, c) and after partial annealling (b, d) by monochromatic light at wavelength 700 (b) and 650 (d) nm. Temperature $-194°$.[24]

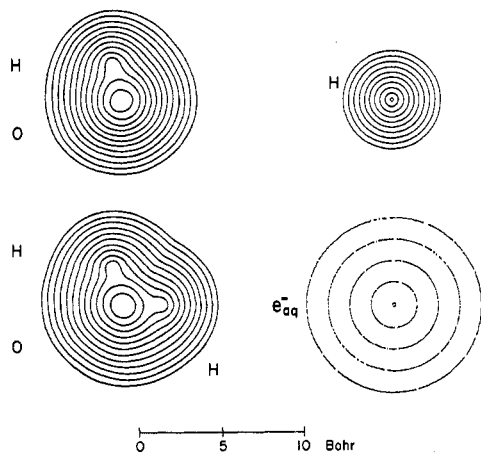Figure 3. Electron density contours for the polaron model of e_{aq}^-; comparison with the hydrogen atom, hydroxyl radical, and water molecule.[41] In OH and H_2O the innermost contour corresponds to a probable electron density of 1.0 e^-/bohr³ (0.25 in H) and each successive outer contour decreases by a factor of 2 down to 0.00049 e^-/bohr³. In the e_{aq}^- diagram the innermost contour corresponds to an electron density of 0.0077 e^-/bohr³ and the outermost to 0.00049 e^-/bohr³.

spherical charge of increasing density as the center is approached. Figure 3 shows the electron density along the equatorial plane, the innermost contour of which corresponds to an electron density of 0.0077 e^-/bohr³ and the outermost contour to 0.00049 e^-/bohr³.

How does this diffuse electron cloud density compare with those of other simple molecules? Displayed on the same scale in Figure 3 are the contour densities of the H atom, the OH radical, and the H_2O molecule.[41] From this figure it is clear that the electron charge density of the relatively large e_{aq}^- overlaps that of the water molecules lining its cavity, as has been suggested by Marcus[42] and Jortner.[32] Figure 3 provides only a primitive picture of e_{aq}^-, but it must do until a more sophisticated model incorporating both long- and short-range interactions can be treated mathematically.

Reactions and Rate Constants

Although e_{aq}^- has only been known for 10 years some 600 of its rate constants have already been measured: more than the combined sum of the H and OH rate constants.[43] Most of these have been obtained by following the decay of the e_{aq}^- absorption band by the technique of pulse radiolysis where conditions for setting up pseudo-first-order kinetics for reactions are simple. Its reactions may be studied at 10^{-5} or even 10^{-6} M solute concentrations since the decay of e_{aq}^- may be followed from initial concentrations of 10^{-7}–10^{-8} M down to 10^{-9} M. The details of these methods have been described elsewhere,[1,2,3,10] but they will be dealt with later in this paper.

As data accumulate our ability to understand e_{aq}^- reaction mechanisms is enhanced and the theoretical chemist is provided with the results needed to work out electron-transfer processes. As will be brought out next, the unique feature of e_{aq}^- reactions is that it disappears during its reactions, many of which are diffusion controlled. Marcus also points out that because its wave function is spread out over several water molecules, unlike other ions, its reactions are sensitive to their orientation fluctuations.[42]

Created along with e_{aq}^- in water by a pulse of ionizing radiation are H, OH, H^+, OH^-, H_2O_2, and H_2. All except OH^- and H_2 react with e_{aq}^-, so this complicated group of chemical reactions must first be understood before e_{aq}^- may be used as a probe for unravelling the mechanisms of other reactions. Indeed, e_{aq}^- has been most helpful in sorting out the complex kinetics of irradiated water.

Table I lists these reactions in H_2O and compares them with similar ones of the deuterated electron (e_d^-) in D_2O.[44,45] All of them except the equilibrium reaction (eq 1) possess rate constants of the order of 10^{10}

(38) M. S. Matheson, Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 45.

(39) M. Anbar and E. J. Hart, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 79.

(40) A. C. Wahl, private communication.

(41) A. C. Wahl and U. Blukis, J. Chem. Educ., 45, 787 (1968).

(42) R. A. Marcus, Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1968, p 138.

(43) M. Anbar and P. Neta, Intern. J. Appl. Radiation Isotopes, 18, 493 (1967).

(44) E. J. Hart and E. M. Fielden, J. Phys. Chem., 72, 577 (1968).

(45) E. M. Fielden and E. J. Hart, Radiation Res., 33, 426 (1968).

Table I
Rate Constants of Some Hydrated and Deuterated Electron Reactions[44,45]

Reactions[a]	Rate constant, M^{-1} sec^{-1}	
	H_2O	D_2O
$e_{aq}^- + H_2O \rightarrow H + OH^-$	16	1.25
$OH^- + H \rightarrow e_{aq}^- + H_2O$	2.0×10^7	2.0×10^7
$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-$	6.0×10^9	6.0×10^9
$e_{aq}^- + H \rightarrow H_2 + OH^-$	2.5×10^{10}	2.8×10^{10}
$e_{aq}^- + OH \rightarrow OH^-$	3.0×10^{10}	2.8×10^{10}
$e_{aq}^- + H^+ \rightarrow H$	2.1×10^{10}	1.7×10^{10}
$e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$	1.2×10^{10}	1.2×10^{10}

[a] For reactions in D_2O substitute e_d^- for e_{aq}^- and D for H in the reactions listed.

$$e_{aq}^- + H_2O \underset{b}{\overset{a}{\rightleftharpoons}} H + OH^- \qquad (1)$$
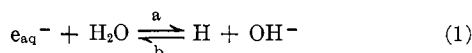
M^{-1} sec^{-1}, essentially that of diffusion-controlled reactions. Each reaction except 1a shows little or no isotope effect. Notice in particular that reactions of e_{aq}^- with itself and with the hydrogen atom liberate H_2; its reaction with OH and H^+ form OH^- and H, respectively. According to Table I an OH^- is the reaction product with H_2O_2, but the simplicity of this reaction and others proves deceiving. In each case some intermediate species such as e_{aq}^{2-}, H^-, H_3O, and $(H_2O_2)^-$ may be involved. Such an intermediate is not expected in the case of the OH radical where a vacant orbital exists. Here the reaction is simply

$$e_{aq}^- + \cdot\ddot{O}{:}H \longrightarrow {:}\ddot{O}{:}H^-$$
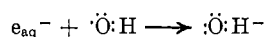
The rate constants for the reactions given in Table I were determined by the disappearance of e_{aq}^-, but it is dangerous to assume that they express the rate for the over-all reaction as was noted above. In many cases reaction rates are so rapid that detection on the microsecond time scale is impossible. All we can say of these reactions is that they are complete in less than 10^{-6} sec. A good example is the reaction of N_2O

$$N_2O + e_{aq}^- \xrightarrow{H_2O} N_2 + OH^- + OH$$
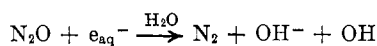
where the OH^- forms within 0.2×10^{-6} sec, a fact brought out by recent pulse conductivity data.[46] For this molecule a possible intermediate, N_2O^-, must rapidly decompose into an OH^- ion. After the electron pulse the rapid return to the original conductivity takes place with the usual neutralization, $H^+ + OH^- \rightarrow H_2O$, rate constant 1.4×10^{11} M^{-1} sec^{-1}. Different, however, is the behavior of H_2O_2 in slightly alkaline solutions. After the electron pulse a long-lived negative ion of lower mobility than OH^- remains. Unlike the submicrosecond life of N_2O, the H_2O_2 ion decays with a half-life of about 0.4 sec.

Of particular interest in Table I is the slowness of the e_{aq}^- reactions with H_2O and D_2O.[47] These reactions are 10^{-9} and 10^{-10} fold slower than the corresponding ones with H^+ and D^+. Because of this inertness, measurements of these rate constants require the elimination of

the reactive H^+, H_2O_2, and O_2 scavengers, at least to concentrations in the 10^{-9} M range. Removal of H_2O_2 and O_2 to this level is achieved by irradiating slightly alkaline H_2 saturated solutions (pH about 9.0) either with steady γ rays or with feeble 1–10-rad microsecond X-ray pulses. In the presence of dissolved H_2 the OH radicals created by the radiation change first to hydrogen atoms (by eq 2) and then by reaction 1b back to e_{aq}^-.

$$OH + H_2 \longrightarrow H_2O + H \qquad (2)$$
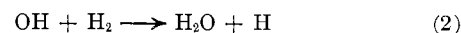
The principal mode of decay of e_{aq}^- in these lightly irradiated solutions after removal of impurities is by reaction 1a, although reaction 3 becomes important at

$$e_{aq}^- + e_{aq}^- \longrightarrow H_2 + 2OH^- \qquad (3)$$
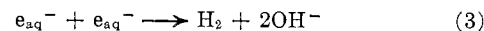
concentrations of the order of 10^{-8} M. In the case of e_d^-, with its second-order rate constant of 1.2 M^{-1} sec^{-1}, initial concentrations as low as 2×10^{-9} M e_d^- were used.[45] Under these conditions the initial incidental e_{aq}^- scavengers must be eliminated. The practical limit is about 0.5×10^{-9} M H_2O_2.

Reaction 3, rapid in H_2O and D_2O, is negligible in liquid ammonia solutions containing $e_{NH_3}^-$. This puzzling behavior of $e_{NH_3}^-$ has never been explained. If it were as fast as the e_{aq}^- reaction the characteristic deep blue color of metal–ammonia solutions would disappear within a microsecond.

Some representative reactions of e_{aq}^- with inorganic molecules and ions appear in Table II. The hydrated

Table II
Comparison of e_{aq}^- and Hydrogen Atom Rate Constants[43]

	k, M^{-1} sec^{-1} [a]	
	e_{aq}^-	H atom
Ag^+	3.2×10^{10}	1.1×10^{10}
Cd^{2+}	5.2×10^{10}	$<1.0 \times 10^5$
$Co(NH_3)_6^{3+}$	8.0×10^{10}	1.7×10^6
O_2	1.9×10^{10}	1.9×10^{10}
N_2O	5.6×10^9	$\sim 10^5$
MnO_4^-	3.0×10^{10}	2.6×10^{10}
Zn^{2+}	1.4×10^9	$<1.0 \times 10^5$
Eu^{3+}	6.1×10^{10}	
CH_3COCH_3	6.0×10^9	$\sim 10^6$
C_2H_5OH	$<10^5$	1.6×10^7
C_3H_7I	3.0×10^{10}	
$C(NO_2)_4$	5.4×10^{10}	$(0.55–2.6) \times 10^9$
C_6H_6	1.4×10^7	1.1×10^9
$C_6H_5COO^-$	3.0×10^9	
$1,3\text{-}C_6H_8$	1.0×10^9	7.5×10^9
$1,4\text{-}C_6H_8$	$<7.5 \times 10^6$	4×10^9
C_6H_{10}	$<1.0 \times 10^6$	3×10^9

[a] Rate constants of $1,3\text{-}C_6H_8$, $1,4\text{-}C_6H_8$, and C_6H_{10} are given in ref 51.

electron lowers the charge on the positive ion by one unit. Thus Ag^+ and Cu^{2+} form Ag^0 and Cu^+, respectively. In negative ions, such as MnO_4^-, the product is MnO_4^{2-}, and in ions having vacant orbitals final products, except for possible ligand equilibration to the new charge, result. In other cases because of the change in charge the structure of the ion may be unstable. Examples of such unstable ions are Zn^+,[48] Au(I), and

(46) K. Schmidt and S. Ander, private communication, 1968.
(47) E. J. Hart, S. Gordon, and E. M. Fielden, *J. Phys. Chem.*, **70**, 150 (1966).
(48) G. E. Adams, J. H. Baxendale, and J. W. Boag, *Proc. Chem. Soc.*, 241 (1963).

Au(III).[49] Here the intermediate formed undergoes disproportionation which leads to the final product. Of the rare earth ions, those possessing stable bivalent states have high rate constants; those with no stable bivalent states have low rate constants. Much remains to be learned from the simple reaction of e_{aq}^- with inorganic ions whose resulting unstable valency states frequently last long enough to study.

While atomic H is a powerful reducing agent, e_{aq}^- with its standard potential of 2.7 V is a better one.[50] Not only are its reactions faster as in the case of N_2O and acetone, but reduction of Zn^{2+} and Cd^{2+} will only take place by e_{aq}^-. Table II compares some of these e_{aq}^- and hydrogen atom rate constants for a few inorganic and organic compounds. Notice the highly specific action of e_{aq}^- toward the 1,3- and 1,4-cyclohexadienes.[51]

The hydrated electron behaves as an ideal nucleophilic reagent in its reactions with organic compounds. In a series of organic halides and a variety of aromatic compounds the e_{aq}^- rate constants correlate satisfactorily with the Taft and Hammett functions of these molecules.[52,53] Again as in the case of inorganic compounds, while the rate constants have been measured, in but a few cases has it been shown that the products formed according to Table II are the primary ones. However in the reactions

$$e_{aq}^- + C_3H_7I \longrightarrow C_3H_7 + I^-$$
$$e_{aq}^- + C(NO_2)_4 \longrightarrow C(NO_2)_3^- + NO_2$$
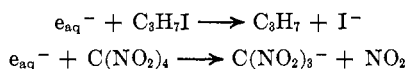
e_{aq}^- disappearance and I^- and $C(NO_2)_3^-$ appearance are simultaneous in the microsecond time range.[54,55] In most cases one assumes that an intermediate ion exists. Note in this table that substitution of COO^- in the aromatic structure drastically increases the rate constant. This is a manifestation of the redistribution of electron density induced by the substitution of groups in the aromatic nucleus.
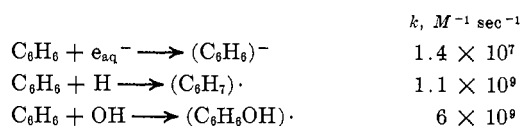
The purine and pyrimidine constituents of nucleic acid are highly reactive. Adenosine, cytidine, 5-methylcytosine, purine, and thymine possess rate constants of the order of 10^{10} M^{-1} sec^{-1}.[43] Consequently they attest to their diffusion-controlled nature and that reaction occurs on each encounter. On the other hand the amino acid constituents of the protein possess low (but sometimes high) reactivity. The simple amino acids, such as glycine, alanine, proline, etc., have rate constants less than 10^7 M^{-1} sec^{-1}. However substituted amino acids such as phenylalanine, histidine, and those with sulfur groups, such as cysteine and cystine, have reactivities of the order of 10^8 and 10^{10} M^{-1} sec^{-1}. Consequently in any aqueous medium containing proteins the probable point of attack will be on these sub-

stituted amino acids or on the sulfur or disulfide bonds of the protein. The importance of e_{aq}^- in radiation-induced biological damage needs further assessment. However, a knowledge of its rate constants with the constituents of large molecules and even of the large molecules themselves and their correlation with protein studies will help solve this perplexing problem.[56]

Reaction with C_6H_6

Above I stressed the fact that while many rate constants involving e_{aq}^- were known, relatively few studies have been followed through by product analysis. In order to rectify this shortcoming I have recently undertaken a detailed study of the radiolysis of aqueous benzene.

Benzene reacts with e_{aq}^-, H, and OH according to the following reactions and rate constants

	k, M^{-1} sec^{-1}
$C_6H_6 + e_{aq}^- \longrightarrow (C_6H_6)^-$	1.4×10^7
$C_6H_6 + H \longrightarrow (C_6H_7) \cdot$	1.1×10^9
$C_6H_6 + OH \longrightarrow (C_6H_6OH) \cdot$	6×10^9

Note that e_{aq}^- reacts with benzene over two orders of magnitude slower than does H or OH. In order to avoid the complex reactions of these two radicals we irradiate benzene in an alkaline solution at pH 13 under high-pressure hydrogen.[57] In this case the hydrogen atom changes into e_{aq}^- according to (1b) with its rate constant of 2×10^7 M^{-1} sec^{-1} and the OH radical, actually the O^- radical ion at pH 13, changes into e_{aq}^- by reaction 2b, followed by reaction 1b. Thus by irradi-

$$O^- + H_2 \longrightarrow H + OH^- \qquad (2b)$$
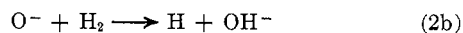
ating the solution at pH 13 under 2000 psi H_2 pressure (0.10 M) conversion of H and OH into e_{aq}^- approaches 100%. If the concentration of C_6H_6 is kept below 40 μM, then less than 5% of the OH radicals react with benzene. Furthermore the equilibrium constant of reaction 1 is 8×10^{-7} at pH 13; the ratio $(H)/(e_{aq}^-) = 4.4 \times 10^{-4}$. Consequently hydrogen atom reactions are drastically suppressed. In this way we nearly isolate the reactions of e_{aq}^- with C_6H_6.

The reduction of C_6H_6 proceeds successively through 1,4-C_6H_8 to C_6H_{10}, to C_6H_{12} when 25 μM C_6H_6–0.1 M H_2 solution is irradiated at pH 13. As is the case in alkali metal–ammonia reductions of benzene no 1,3-C_6H_8 appears. Figure 4 shows the development of these products in the irradiated solution. While it is possible that 1,4-C_6H_8 forms to the exclusion of its 1,3 isomer, pulse radiolysis studies reveal that the rate of e_{aq}^- reaction with 1,3-C_6H_8 is at least a thousandfold greater than with its 1,4 isomer[51] (see Table II). The low rate constants of 1,4-C_6H_8 and C_6H_{10} with e_{aq}^- and their high reactivity with hydrogen atoms indicate that reduction of these species even at pH 13 is unquestionably through hydrogen atoms.

Similar irradiations of dilute D_2O–benzene solutions

(49) A. S. Ghosh-Mazumdar and E. J. Hart, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 193.
(50) J. H. Baxendale, *Radiation Res. Suppl.*, **4**, 139 (1964).
(51) B. D. Michael and E. J. Hart, in preparation.
(52) M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964).
(53) M. Anbar and E. J. Hart, *J. Phys. Chem.*, **69**, 271 (1965).
(54) J. K. Thomas, *ibid.*, **71**, 1919 (1967).
(55) J. Rabani, W. A. Mulac, and M. S. Matheson, *ibid.*, **69**, 53 (1965).

(56) R. Braams and M. Ebert, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 464.
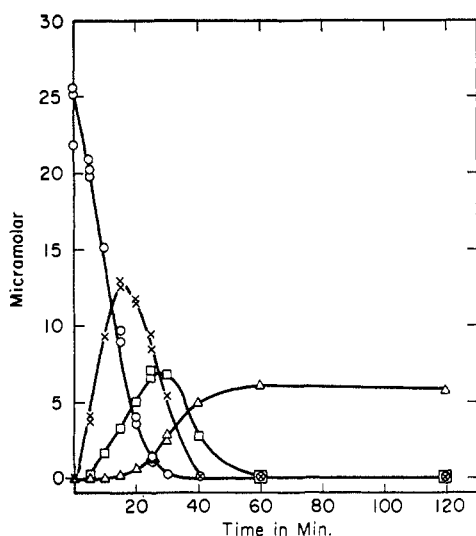(57) M. H. Studier and E. J. Hart, *J. Amer. Chem. Soc.*, in press.

Figure 4. The reduction of dilute benzene solutions at pH 13 by ^{60}Co γ rays:[57] (○) C_6H_6, (×) 1,4-C_6H_8, (□) C_6H_{10}, (△) C_6H_{12}. Dose rate = 1.15 krad/min.

demonstrate appreciable exchange in addition to reduction.[57] Note in Table III that $C_6H_2D_4$ is the most abundant deuterated benzene, and since deuteration takes place it is clear that disproportionation is important. However the reaction

$$\dot{C}_6H_7 + e_{aq}^- \xrightarrow{H_2O} C_6H_8 + OH^-$$
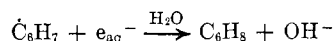
producing 1,4-C_6H_8 is probably diffusion controlled. Note the further appreciable deuteration of cyclohexene and cyclohexane.

A chromatographic separation of the benzene-extractable nonvolatile products reveals nine reduced dimers. After proving that dicyclohexyl elutes first and diphenyl last beyond our group of compounds, we assume that those eluting at intermediate stages consist of the unsaturated components from $C_{12}H_{14}$ to $C_{12}H_{20}$, each of which further reduces to $C_{12}H_{22}$. As evidence for this conclusion we find masses corresponding to these compounds on spectrographic analysis. While highly speculative we assume that the first steps of benzene radiolysis are[57]
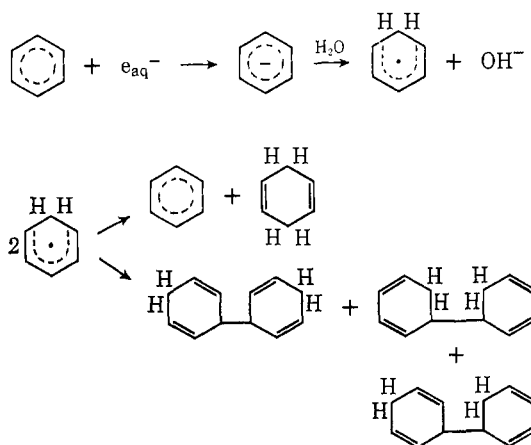
Unquestionably the reduction of benzene at pH 13 involves not only e_{aq}^- but also H atoms. Table II

Table III
Deuteration of Benzene and Its Reduction Products at pH 13[57]

Compd	Most abundant	Most D
C_6H_6	C_6H_6	$C_6H_2D_4$
C_6H_8	$C_6H_6D_2$	$C_6H_3D_5$
	$C_6H_5D_3$	
C_6H_{10}	$C_6H_7D_3$	$C_6H_5D_5$
	$C_6H_6D_4$	
C_6H_{12}	$C_6H_8D_4$	$C_6H_6D_6$
	$C_6H_7D_5$	

compares these rate constants for C_6H_6, 1,3- and 1,4-C_6H_8, and C_6H_{10}. With the low reactivity of e_{aq}^- toward unconjugated double bonds, H atom reactions dominate in the advanced stages of reduction of both C_6 and C_{12} compounds.

Apparatus

Expensive linear accelerators are unnecessary for e_{aq}^- studies. Research on this ion is within the reach of all laboratories possessing ultraviolet light sources or X-rays operating either in pulse or steady-state modes. Below I briefly describe some of the methods used in e_{aq}^- research.

Pulsed Light Source. A simple photoflash apparatus has been designed especially for e_{aq}^- research.[8] The apparatus consists of a xenon flash lamp producing a light pulse of about 45-μsec half-width, a mercury ultraviolet lamp, and a supersil quartz irradiation cell. The light transmission system consists of a tungsten lamp, a multiple reflection optical system, red filters to isolate the 700-nm band, a photomultiplier, and an oscilloscope. Because of its high molar extinction coefficient (1.85 × 10^4 M^{-1} cm^{-1}), research with nanomolar concentrations of e_{aq}^- is feasible. Typical e_{aq}^- decay curves are shown in Figure 5.[58] The top curve illustrates the natural decay of 92 nM e_{aq}^- in a pH 11 H_2-saturated solution. When scavengers such as O_2 are added the half-life and initial e_{aq}^- concentration diminish. The lowest curve with its half-life of about 0.3 × 10^{-3} sec indicates that the O_2 concentration is 107 nM. With steady uv irradiation for 15 sec the middle curve with a half-life of 1.8 × 10^{-3} sec reveals the effect of the 11 nM O_2 remaining in the solution.

A flash of uv light generates e_{aq}^- in a H_2-saturated solution at pH 11 by the reaction $OH^- + h\nu \rightarrow OH + e_{aq}^-$, but the OH radical is later converted into e_{aq}^- by reactions 1 and 2. Thus this alkaline solution provides an excellent source of e_{aq}^- in a medium containing only the inert Na^+ and OH^- ions. It is ideal for measuring first- and second-order rate constants. In addition it has considerable potential in analytical chemistry.[8,10,59]

Steady Light Source. Built into the photogeneration apparatus described above is a steady uv lamp controlled by a shutter. This light source generates e_{aq}^- which reacts with O_2, H_2O_2, and other e_{aq}^- scaven-

(58) B. Hickel, private communication.
(59) E. J. Hart and E. M. Fielden, Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 253.
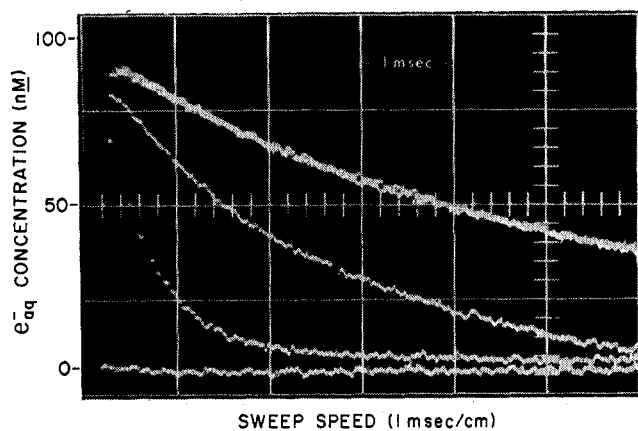
Figure 5. Typical e_{aq}^- formation and decay curves of photogeneration unit for a hydrogen-saturated 0.001 N NaOH solution:[58] (top curve) decay of a 92 nM e_{aq}^- solution free from scavengers; (lower curve) effect of adding 100 nM O_2; (middle curve) partial "cleanup" by steady uv light with 17 nM O_2 left.

gers present in the solution. In operating this system it is standard practice to "clean up" the solution by steady preirradiation before adding the e_{aq}^- scavenger to be tested. For example, if 10^{-6} M O_2 is added to a solution having an original half-life of 4.2 $\times$ 10^{-3} sec, the expected half-life is $\tau_{1/2}$ = $0.693/(2 \times 10^{10} \times 10^{-6})$ = 0.035×10^{-3} sec. Since our e_{aq}^- dose is only 0.05 μM no signal may be seen when the original solution is flashed with light. On the other hand the steady light source produces e_{aq}^- which scavenges O_2 and converts it into H_2O by the over-all reaction $O_2 + 4e_{aq}^- \rightarrow 2O^{2-}$. As this reaction proceeds the O_2 diminishes, and when its concentration reaches about 10^{-7} M e_{aq}^- signals appear. Figure 5 shows the successive development of this signal as the concentration of O_2 is progressively lowered. Eventually the original half-life of 4.2 msec is restored.

Steady γ-Ray Source. The penetrating γ rays of ^{60}Co provide a better source of e_{aq}^- than a steady ultraviolet light source. With γ rays, studies may be carried out in high-pressure cells under conditions where the radicals and transient species are generated homogeneously throughout the irradiated volume. The disadvantages are that H, OH, and H_2O_2 also form. However, as described above, by irradiating an alkaline solution at high pressure H_2, H, and OH are converted to e_{aq}^- and essentially pure e_{aq}^- results. Scavengers such as methanol and ethanol eliminate H and OH radicals. Their reactions produce the $\cdot CH_2OH$ and $CH_3\dot{C}HOH$ radicals, and if they do not interfere with the reaction this atmospheric pressure system is simpler than the more unwieldy high-pressure one.

Pulsed Electron Beams. These are mainly used in the study of short-lived species and in the determination of rate constants.[1-5] Electron pulse intensities generating of the order of 10^{-6} M e_{aq}^- are customarily employed. The optical scans obtained are similar to those of Figure 5.

In the measurement of e_{aq}^- rate constants it is absolutely essential to remove e_{aq}^- scavengers. For this reason, scavengers at high concentrations are usually injected into a preirradiated "matrix" solution consisting of the components necessary to produce the desired pH. Since the matrix contains dissolved H_2 and no scavenger, it may be preirradiated until the oxygen concentration is reduced to <0.05 μM. Now when a concentrated solution of the compound to be tested is injected, the O_2 contamination that it carries is relatively small. Another problem to avoid is the creation in the solution of appreciable quantities of H_2O_2 resulting from electron pulses used to generate e_{aq}^-. The H_2O_2 forms not only from the molecular H_2O_2 created in the "spur" but also from the reaction OH + OH $\rightarrow$ H_2O_2, resulting from the high OH concentration introduced by the electron pulse. While the molecular H_2O_2 cannot be avoided, the high-intensity H_2O_2 is eliminated by using lower dose rates. For this reason "cleanup" of the solution *in situ* is done by converting the electrons to X-rays. In an alkaline H_2-saturated solution the H_2O_2 is reduced to water. Once these conditions are achieved, no simpler method of measuring free-radical rate constants has ever been devised. Has not the kineticist's dream been realized?

Concluding Remarks

The full impact of e_{aq}^- on the several branches of chemistry has by no means been realized. But since it commands the attention of an increasing number of chemists it will not be long before its experimental and theoretical potentials will be recognized and exploited. By my simple treatment of the structure, of some of its chemical reactions, and how it is used I hope to stimulate new research at the experimental and theoretical levels.