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Reactions of the Hydrated Electron*

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The rate constants for the reaction of the hydrated electron e_{aq}^- with a number of solutes and with radicals formed in water radiolysis are reported. Hydrated electrons were formed in the electron pulse irradiated solutions at concentrations in the range from 1 to 10 μ M. Their reaction was followed by the decay of the optical absorption of e_{aq}^- at 5780 Å. Generally a 0.4 μ sec pulse of 15 MeV electrons was used. In the absence of e_{aq}^- scavengers, second-order kinetics prevailed owing to the dominance of the reactions, $e_{aq}^- + e_{aq}^-$, $e_{aq}^- + H$, and $e_{aq}^- + H_2O_2$ when OH radical scavengers were present in alkaline solution. An analysis of the decay curves leads to values for $k_{e_{aq}^- + e_{aq}^-}$ and $k_{e_{aq}^- + H}$ of 0.9×10^{10} and $3 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, respectively. With scavenger present in excess over $[e_{aq}^-]$, pseudo first-order kinetics were found and rate constants for a number of inorganic and organic compounds are reported. The agreement of these and other rate constants with diffusion-controlled reaction theory is discussed.

It is natural to assume that ionizing radiation, i.e., fast charged particles, will produce positive ions and electrons in passing through liquid water. However, as was pointed out by Weiss^{1a} the radiation chemistry of aqueous systems could be fairly adequately explained by assuming the formation and reaction of the intermediates H and OH. The H and OH were presumed to be produced very rapidly from the electron and the positive ion^{1b} according to the following reactions:

Because of the success of the H and OH radical theory in correlating experimental aqueous radiation chemistry, and because it was suggested that the low-energy secondary electrons were recaptured in about 10^{-13} sec in the parent spur,² the electron largely ceased to exist as a significant species in mechanisms advanced by radiation chemists to explain their experimental results. Nevertheless, Platzman³ on the basis of theoretical calculations predicted that most secondary electrons in water would escape the parent spur, and be trapped by polarization of the water in a potential well of about 2 eV (6200 Å). Later, work by Hayon and Weiss,^{4a} Baxendale and Hughes,^{4b} and Barr and Allen⁵ indicated the existence of two reducing species in aqueous radiation chemistry, one of which might be the hydrated electron, e_{aq}^- . The most convincing proof that the major reducing species in neutral water is e_{aq}^- came from competitive scavenger studies by Czapski and Schwarz⁶ and

* based on work performed under the auspices of the U.S. Atomic Energy Commission.

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Johnson, Dainton, Smith and Tazuke⁷ showing that the relative rate constants for reaction of this species with scavengers depend upon the ionic strength of the solution in a manner predicted by the Brønsted theory for a reactant of unit negative charge.

The hydrated electron was observed by Hart and Boag^{8,9} who photographed the absorption induced in aqueous systems by an intense pulse of energetic electrons. They found a broad intense absorption band extending from the near ultra-violet into the infra-red with a peak at 700 Å, not too far from the value predicted by Platzman. From its behaviour with various electron scavengers they attributed this absorption to the hydrated electron. This discovery made possible the measurement of hydrated electron rate constants by means of the pulsed radiolysis technique.¹⁰⁻¹⁵ In addition to the high rate constants measured in this work for reactions with known electron scavengers other evidence that the visible absorption spectrum of Boag and Hart is due to the hydrated electron has been obtained. For example, Gordon *et al.*¹⁰ showed that the variation with ionic strength of the rate constant for the reaction of absorbing species with ferricyanide ion is that expected if the absorbing species has unit negative charge. Further, Boag¹⁶ has shown the electrical conductivity in pulse irradiated water decays with the same half-life as the decay of light absorption.

In this paper measurements of rate constants for reactions of e_{aq}^- with various scavengers and with other radiation chemical intermediates is described. In particular, the decay of light absorption at 5770-5790 Å in the aqueous systems containing ethanol, methanol or ferrocyanide is interpreted in terms of these rate constants. The rate constants and their significance for diffusion kinetics are also discussed.

EXPERIMENTAL

TECHNIQUE OF PULSED RADIOLYSIS

The apparatus used was developed by Matheson and Dorfman.¹⁷ Since this apparatus has previously been described¹⁸ only essential features and new modifications will be mentioned here. An Applied Radiation Corporation linear accelerator supplied a 13 MeV electron pulse at currents of 10-160 mA and with a pulse duration of 0.4-5 μsec. The 0.4 μsec pulse was used because of the short half-life of the hydrated electron and because the high extinction coefficient of this species made it easily observable even with low currents and short pulses. The beam emerging from the accelerator window was roughly circular in cross section and diverged very slightly. Cylindrical cells were aligned axially with the electron beam at a sufficient distance from the accelerator window that the front cell window was uniformly irradiated. This area of uniformity was checked by densitometry of the darkened areas of Pyrex glass plates placed in the beam. For bimolecular reactions, cylindrical cells 2 cm int. diam. and 1 cm int. length were used. Dosimetry with ferrous sulphate showed nearly equal intensities in 1 and 2 cm cells and showed lower intensity in the 4 cm cells. For the pseudo first-order rate constants it was necessary to use low intensities in order to minimize the second-order reactions. Since irradiation uniformity is not important in this case, 4 and occasionally 6 cm long cells were employed. The cell windows were made of 0.5 mm Suprasil (high-purity fused silica) which resists radiation discoloration. With these cells no interference in the visible region due to fused silica luminescence was observed when the cells were filled with 0.1 N H₂SO₄. Also 2-cm thick fused silica did not give a signal when irradiated in the cell position.

Cells were filled with solutions to be irradiated by the apparatus shown in fig. 1. This apparatus was held in a suitable mount so that solutions could be replaced in the cell without removing it from its position for irradiation. The syringe was filled with degassed

test solution by the method described by Senvar and Hart.¹⁹ To replace solution, the liquid in the cell was forced out through the 3-way stopcock by argon pressure, then the 3-way stopcock was turned to allow fresh solution from the syringe to fill the cell which was maintained under slight argon pressure.⁸ The solution lubricated all joints and stopcocks. The argon was a pure grade free of oxygen and other impurities reactive toward e_{aq} .

As has been described¹⁸ the optical arrangement passed the light from the constant intensity d.c. high-pressure mercury-arc source (usually an Osram HBO 100 W/1) either 2 or 4 times through the length of the cell, so that the light path could be varied from 2 to 16 or even up to 24 cm. The light beam after passing through the cell entered the slit of a Jarrell-Ash 2.25-m grating spectrograph (or a Bausch and Lomb 0.5-m grating monochromator) where a selected wavelength (generally the mercury lines at 5770-5790 Å) impinged on a 1P28 photomultiplier. The amplified signal was displayed on a Tektronix 551 dual-beam oscilloscope and recorded by photographing on Polaroid type 3000 film.¹⁸ The photographs were enlarged 4 times for measurements. The response of the over-all circuit was linear within experimental error (about 2 %) and re-checked with neutral density filters of optical density 0.1-1.0, whose transmission at 5770-5790 Å had previously been measured on a Cary model 14 R spectrophotometer. In a few experiments, filters including an interference filter, were used to isolate wavelengths near 6830 Å (width at half-intensity 130 Å), and this beam was then monitored with an RCA 7326 photomultiplier tube. The rise time of the overall recording circuit was less than 0.2 μ sec.

The deposition of energy in the cells was measured with the modified Fricke dosimeter (no chloride ion and saturated with oxygen)²⁰ using a $G(Fe^{3+})$ of 15.6 and a molar extinction coefficient of 2196 $M^{-1} cm^{-1}$ at 3020 Å (25 %) for the ferric ion. By setting the sweep time on the oscilloscope for 50 sec full scale, the production of ferric could be followed *in situ* with the above multiplier detection after filling the cell in fig. 1 with oxygenated ferrous sulphate solution and replacing the argon with oxygen. A molar extinction coefficient for e_{aq} of 11,400 $M^{-1} cm^{-1}$ at 5780 Å (21 %) using $G_{e_{aq}}$ of 2.5, was reported.¹⁰ But by using a value²¹ of 2.7 for $G_{e_{aq}}$, a revised extinction coefficient of 10,400 at pH 10 and at 5780 Å was calculated.

MATERIALS

Triply distilled water²² was used to prepare solutions. Cells, syringes and other containers were thoroughly cleaned and baked out at $\sim 500^\circ C$ before each use. Because carbonate apparently reacts with OH radicals to give a long-lived visible absorption, care was taken to use carbonate-free alkaline solutions. These solutions were prepared by (a) dissolving metallic sodium in water under an argon atmosphere, (b) using barium hydroxide (Baker Analyzed Reagent), or (c) washing sodium hydroxide (Mallinckrodt Analytical Reagent) with air-free water and using the residue on the assumption the carbonate would be principally in the outer layers. All three solutions gave the same results in the range used (pH 10-12.5). Of the alcohols used as OH scavengers, the ethanol was U.S. Industrial Chemical absolute reagent quality and the methanol was purified by a fractional distillation from a mixture of methanol and the sulphuric acid salt of 2,4-dinitro phenyl hydrazine. In the determination of the rate constants of the hydrated electron with O_2 , N_2O , NO and CO_2 the gases were always liquefied or solidified. The liquids were pumped and a middle fraction used in the reaction solution. Buffalo Electrochemical Co. 99 % hydrogen peroxide was diluted as required. Other chemicals were reagent grade and used without further purification.

RESULTS

RATE CONSTANT EQUATIONS

Fig. 2 shows the oscilloscope screen photograph of a typical experiment. The upper trace represents zero light taken with shutter closed; the bottom horizontal

trace is I_0 , the light intensity transmitted in the absence of absorbing species; while the intermediate curve represents I_t , showing the sudden decrease in transmitted light when the electron pulse strikes the cell and the subsequent decay of absorption. By Beer's law

$$\log_{10} (I_0/I_t) = \epsilon C t = D_t, \quad (4)$$

where D_t = optical density at time t , ϵ = molar extinction coefficient, C = concentration of absorbing species in moles/l., and l = the light path in cm.

For a first-order reaction in which only the reactant (C_t) absorbs,

$$\ln D_t = -kt + \ln D_0. \quad (5)$$

Thus a plot of $\ln D$ against t should give a straight line with slope equal to the negative of the rate constant k . For a single second-order reaction where non-absorbing products are formed

$$1/D_t = 2kt/\epsilon l + 1/D_0, \quad (6)$$

so that a plot of $1/D_t$ against t gives $2k$, the second-order rate constant for disappearance of C , divided by ϵl .

Our experimental plots of $1/D$ against t (see fig. 3-6) are not linear since several reactions occur. However, the initial curve is nearly linear and its slope represents " k "/ ϵl , where

$$"k" \cong 2k_{12} + \sum_i k_{e_{aq}} \cdot X_i \frac{[X_i]_0}{[e_{aq}]_0} \quad (X_i \text{ is not } e_{aq}). \quad (7)$$

$[X_i]_0$ and $[e_{aq}]_0$ are the initial concentrations of the reactants, X_i and e_{aq} respectively.

HYDRATED ELECTRON REACTIONS

The radiation chemical intermediates presently accepted are those on the right hand side of eqn. (8):

and the reactions of e_{aq}^- with other intermediates are indicated in eqn. (9)-(13):

The constants k_9 and k_{13} can be readily measured by adding excess H_2O_2 or excess $H_3O_{aq}^+(H_2SO_4)$, since the e_{aq}^- then reacts by pseudo first-order reactions. The measured first-order rate constants are $k_9(H_2O_2)$ and $k_{13}(H_3O_{aq}^+)$ where the concentrations of H_2O_2 and $H_3O_{aq}^+$ are known. This technique of measuring bimolecular rate constants as pseudo-first order rate constants is applicable to a large number of stable compounds or ions. But the pseudo-first-order reaction (14),

must also be considered or minimized. A list of rate constants so determined for the hydrated electron are given in table I.

TABLE I. RATE CONSTANTS FOR REACTIONS e_{aq}^- WITH SOLUTES AT 20-22°C.^a

Solute	Concentration range, μ M	pH	k (M ⁻¹ sec ⁻¹)
H ⁺ ^b	10-100	4-5	$2.36 \pm 0.24 \times 10^{10}$
H ₂ O ₂ ^b	60-200	7	$1.23 \pm 0.14 \times 10^{10}$
O ₂ ^b	35-120	7	$1.88 \pm 0.2 \times 10^{10}$
NO ^c	22-200	7	$3.14 \pm 0.2 \times 10^{10}$
N ₂ O ^c	50-300	7	$8.67 \pm 0.6 \times 10^9$
CO ₂ ^c	50-200	7	$7.67 \pm 1.1 \times 10^9$
HCO ₂ ⁻	1,000,000	~ 10	$< 10^6$
CH ₃ CO ₂ ⁻	1,000,000	~ 10	$< 10^6$
HCO ₂ H ^d	1,100-21,000	5-9	$1.43 \pm 0.1 \times 10^8$
CH ₃ CO ₂ H ^d	1,000-10,000	5-4	$1.76 \pm 0.3 \times 10^8$
HCHO	200	7	$< 10^7$
(CH ₃) ₂ CO	60-200	7	$5.9 \pm 0.2 \times 10^9$
CH ₃ CHO	100	11	3.5×10^9
H ⁺			
CH ₂ =C	100	7	1.8×10^{10}
CON ₂			
CHCl ₃	70-200	7	$2.0 \pm 0.05 \times 10^{10}$
CCl ₄	60	7	3.1×10^{10}
CS ₂	50-200	7	$3.10 \pm 0.15 \times 10^{10}$
Fe(CN) ₆ ³⁻	60-200	7 and 10-3	$3.0 \pm 0.4 \times 10^9$
CuSO ₄	20-100	7	$3.3 \pm 0.3 \times 10^{10}$
Ag ⁺	20-100	7	$3.6 \pm 0.4 \times 10^{10}$
NO ₃ ⁻	60-200	7	$1.1 \pm 0.1 \times 10^{10}$
e_{aq}^-	~ 10	10-13	1×10^{10} (for $2k_{12}$)
H	~ 2	10-9	$\sim 3 \times 10^{10}$
OH	~ 10	11	$\sim 3 \times 10^{10}$

^a initial $[e_{aq}^-]$, 1 to 3 μ M; ^b with and without 1 mM methanol present; ^c 1 mM methanol present; ^d contribution of unionized acid alone; ^e extrapolated to zero ionic strength (0.025 M methanol present).¹⁰

SECOND-ORDER RATE CONSTANTS

If no scavenger is present, the reactions (9)-(13) as well as the fast reactions, $H + H$, $H + OH$, $OH + OH$, and $H + OH$, will affect the rate of the e_{aq}^- decay in irradiated water. On the other hand, the slow reactions, $H + OH$, $H + H_2O_2$, $OH + H_2$ and $OH + H_2O_2$, may be neglected. Consequently, $1/D_t$ against t will not be linear as for a single bimolecular reaction. Because of the complexity of this mechanism, it is necessary to reduce the number of reactions taking place when k_{10} and k_{12} are estimated from the experimental data. In alkaline solutions, (13) is suppressed since reaction (15),

is very fast,²¹ with a rate constant of 1.4×10^{11} M⁻¹ sec⁻¹.

Three hydroxyl radical scavengers, ethanol, methanol and potassium ferrocyanide were used to eliminate reaction (11) and other hydroxyl radical reactions outside the "spur". Hydroxyl radicals react with ferrocyanide, ethanol and

hydrogen with rate constants of 4×10^9 , 1×10^9 and $4.5 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$, respectively.²⁴⁻²⁶ If we assume that $k_{\text{OH} \cdot \text{CH}_3\text{OH}}$ has the intermediate value of $1 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ or higher, then reaction (11) may be neglected in 0.025 M methanol, 0.5 M ethanol, 0.002 M ferrocyanide solutions at dose rates supplying 10^{-4} M OH and e_{aq} . Furthermore, in 0.5 M ethanol, H atoms are also effectively scavenged.

From the two rate constants, $k_{\text{H} \cdot \text{O}_2}$ of $2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ ²⁷ and $k_{\text{H} \cdot \text{CH}_3\text{OH}} = 2 \times 10^6$, $k_{\text{H} \cdot \text{C}_2\text{H}_5\text{OH}} = 2 \times 10^7$ and $k_{16} = 4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ can be calculated.²⁸

Thus, in 0.5 M ethanol at pH 10-11, reactions (9), (12) and (14) only should be included. In the methanol and ferrocyanide solutions, reaction (10) as well as $\text{H} + \text{H}$ must be added. Since ferricyanide is also a reaction product in the ferrocyanide irradiations, we must also consider reactions (16) and (17).

Fig. 3-5 show the agreement of calculations with experimental plots of $1/D$ against t for the ethanol, methanol and ferrocyanide systems, respectively, at pH 10.9. The rate constants and radiolysis yields used are listed under each figure. The curves in the figures were generated from the appropriate differential equations for the disappearance of e_{aq} using the Argonne analogue computer PACE and the indicated G values and rate constants. The calculated reciprocal of optical density was then obtained from $[e_{\text{aq}}]$ using eqn. (4). Integrals of the individual reactions were also obtained in order to determine the relative amounts of e_{aq} disappearing in each reaction. The requirement that the sum of these integrals be 1.0, the normalized value of $[e_{\text{aq}}]_0$, was used as a check on the calculation. The integrals obtained for the curves plotted in fig. 3-5 are given in table 2.

TABLE 2.—RELATIVE AMOUNTS OF e_{aq} DISAPPEARING IN AQUEOUS SOLUTIONS

0.5 M ETHANOL FOR CONDITIONS OF FIG. 3				
REACTIONS INTEGRATED				
curve	(12)	(9)	(14)	H ₂ O ₂ remaining
A	0.498	0.160	0.341	0.0248
B	0.643	0	0.355	0
C	0.803	0.187	0	0.0018

0.025 M METHANOL FOR CONDITIONS OF FIG. 4							
REACTIONS INTEGRATED							
curve	(12)	(9)	(10)	(14)	(18)	(19)	(20)
A	0.335	0.190	0.229	0.244	0.0	0.022	0.180
B	0.407	0.211	0.203	0.177	0.0	0.015	0.144
C	0.612	0.250	0.134	0.0	0.0	0.008	0.035
D	0.375	0.205	0.131	0.0	0.288	0.008	0.046

0.00193 M POTASSIUM FERRICYANIDE							
REACTIONS INTEGRATED							
(12)	(9)	(10)	(17)	(16)	(19)	final H ₂ O ₂	final ferricyanide
0.328	0.155	0.130	0.388	0.048	0.01	0.104	0.723

In the calculations of the ethanol results, the reaction of the hydrated electron with the radiolysis products, acetaldehyde and butanediol, may be neglected since aliphatic alcohols have little or no reactivity with e_{aq} ,¹¹ and $k_{e_{\text{aq}} \cdot \text{CH}_3\text{CHO}}$ is 3×10^9

$M^{-1} \text{ sec}^{-1}$ (see table 1). Besides only 10% of the ethanol radicals form acetaldehyde by a relatively slow reaction (17). We also neglected the possible reaction of e_{aq}^- with the ethanol radicals. This assumption is justified since the value for $2k_{12}$ of $0.85 \pm 0.15 \times 10^{10}$ which is found in the ethanol results, is in agreement with the methanol and ferrocyanide experiments. Also experiments run at 100 atm H_2 pressure and at pH 13, where H atoms are converted to e_{aq}^- by reaction (21) gave $2k_{12} = 1 \times 10^{10} M^{-1} \text{ sec}^{-1}$ (30, 31). The pseudo first-order reactions, (14) or (18) with impurities,

had to be included in order to get a fit in fig. 3. The results cannot distinguish between (14) and (18) since the kinetics is unchanged.

In fig. 4 with methanol the increased initial rate (over fig. 3) is attributed to $e_{aq}^- + H$ as discussed above. Other reactions taken into account are

In this case formaldehyde formed by the disproportionation of $\dot{C}H_2OH$ radicals is unreactive toward e_{aq}^- (see table 1). Taking the same conditions as for curve A, but replacing (14) with (18) assuming no H atoms being formed in (18) gave the curve, D, essentially coincident with B, the variation being due to the difference in the amount of $e_{aq}^- + H$ occurring. At pH 12, H atoms are converted to e_{aq}^- by reaction (21),

as was demonstrated by Jortner and Rabani³⁰ and confirmed by others.³¹ A decrease in the effective rate constant, " k ", from 1.9×10^{10} to $1.3 \times 10^{10} M^{-1} \text{ sec}^{-1}$ is found in 0.025 M methanol solutions as the pH is increased from 10 to 12. We interpret this result as a suppression of reaction (10) because of the conversion of H atoms into hydrated electrons by (21). In fig. 5 the observed rate of disappearance of e_{aq}^- in ferrocyanide solutions is satisfactorily fitted with our set of rate constants. However, the inclusion of (14) gives too high a rate. Because of the large number of reactions in the ferrocyanide work one cannot attach much importance to this finding.

TABLE 3. INITIAL " k " FOR e_{aq}^- DISAPPEARANCE AS FUNCTION OF pH IN 0.5 M AQUEOUS ETHANOL

pH	initial D_0 extrapolated	$k \times 10^{10}$
7	0.22 ± 0.05	3.5
8.8	0.24 ± 0.05	2.8
9.9	0.24 ± 0.02	1.6
10.9	0.25 ± 0.02	1.3
11.5	0.24 ± 0.02	1.3
11.6 ^b	0.25 ± 0.02	1.2
11.5 ^{b, c}	0.25 ± 0.02	1.2
12	0.25 ± 0.02	1.6
12.5	0.28 ± 0.02	1.3

^a in units $10^{10} M^{-1} \text{ sec}^{-1}$; ^b NaOH used; in all others Ba(OH)₂ used; ^c NaOH = $0.8 \times 10^{-3} M$ Na₂SO₄.

In fig. 6, we present the experimental $1/D$ against t curves in 0.5 M ethanol at pH 7.0, 8.8, 9.9 and 11.5. In table 3, " k " calculated from the initial slopes of these and similar curves are given for pH 7 to 12.5. The higher rate of disappearance of e_{aq} in fig. 6 and table 3 as the pH is decreased is due to reaction (13). The results indicate independence of " k "/ ϵl and k_{12} on pH in the region 9.9–12.5. Within our experimental error, ionic strength has no effect although a small salt effect was found in aqueous methanol when many experiments were carried out.¹⁰ The constancy of the initial D as the pH is changed between 7 and 12.5 indicates that ϵGe_{aq} does not depend on pH in this region.

The general conclusion from fig. 3–6 and tables 2–4 is that the rate constants of table 1 account for the observed results. The rate constant for (14) $e_{aq} + H_2O$ as derived from these results is, however, uncertain. An upper limit of $4 \times 10^4 \text{ sec}^{-1}$ has been given,^{10, 11} and indeed Dorfman and Taub¹¹ have measured a first-order disappearance of the electron at low pulse intensities at pH 13. Fig. 3 and 4 suggest $2 \times 10^4 \text{ sec}^{-1}$ and fig. 5 suggests a lower value for k_{14} . Further work will be necessary to establish the value of k_{14} and to determine whether we are presently measuring a reaction with impurities.

DISCUSSION

Many of the rate constants for the hydrated electron given in table 1 are fast, being about $2.3 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. In table 4 a few of these rate constants are

TABLE 4.—COMPARISON OF DIFFUSION-CONTROLLED AND EXPERIMENTAL RATE CONSTANTS (25°C)

τ_{AB}^a	D_{AB}^a	$k(\text{calc})^{b,c}$	$k(\text{expt})^d$
(H ₂ O _{aq} ⁺ + OH _{aq} ⁻)			
0	14.7 ^d	7.95	14 ^e
2.7	14.7 ^d	8.4	14 ^e
7.5	14.7 ^d	12.9	14 ^e
(H ₂ O _{aq} + e_{aq})			
2.7	10 ^f	5.7	2.3 ^g
2.7	20 ^h	11.4	2.3 ^g
5.0	10 ^f	7.05	2.3 ^g
5.0	20 ^h	14.1	2.3 ^g
(e_{aq} + e_{aq})			
2.7	20 ^h	0.86	0.45 ^g
5.0	20 ^h	3.47	0.45 ^g
7.5	20 ^h	6.88	0.45 ^g
(e_{aq} + O ₂)			
2.7	11.4 ^f	2.32	1.88 ^g
5.0	11.4 ^f	4.32	1.88 ^g

^a in units $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$; ^b calc. from eqn. (22) setting l as 80; ^c in units $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$; ^d Ertl and Gerischer, *Z. Elektrochem.*, 1962, **66**, 560; ^e ref. (23); ^f $D_H = 9.5 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ from ionic mobility of ref. (32) so $D_{AB} = 10$ essentially puts $D_e = 0$; ^g k_{12} was used for encounter rate not $2k_{12}$; ^h assumes $D_e = 10 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, ref. (33); ⁱ $D_e = 10 \cdot 10^{-5}$ and $D_{O_2} = 1.4 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, the latter from *Landolt-Börnstein Tabellen*, 5. Auflage, 2. Ergänzungsband, p. 198.

compared with the diffusion-controlled encounter rate calculated from eqn. (22), the Debye equation.³²

$$k = \frac{4\pi r_{AB} D_{AB} N}{1000} \cdot \left\{ \frac{Z_A Z_B e^2}{r_{AB} E k T} \left(\exp \left[\frac{Z_A Z_B e^2}{r_{AB} E k T} \right] - 1 \right) \right\} \quad (22)$$

The first term on the right is the encounter rate for uncharged species A and B whose total diffusion coefficient is D_{AB} and whose encounter radius is r_{AB} . N is Avogadro's number. The bracketed term is the Debye correction on the encounter rate if A and B have charges $Z_A e$ and $Z_B e$, the force between them is coulombic, and the effective dielectric constant of the solution is E . T is the absolute temperature, k is the Boltzmann constant and e is the charge on the electron. Eigen and DeMaeyer²³ have calculated the rate constant for neutralization (table 4) and find agreement between experimental and calculated rate constants, if the interaction distance r_{AB} is large, 7.5 Å. Reaction is presumed to occur by proton transfer across several hydrogen-bonded water molecules. For $e_{aq}^- + H_3O_{aq}^+$, however, the calculated rates are all too high. Eqn. (22) contains three uncertain quantities as far as e_{aq}^- reactions are concerned; the encounter distance, the diffusion coefficient, and (if the encounter distance is small) the effective dielectric constant. It does not appear that a reasonable combination of r_{AB} , D_{AB} and E can be chosen to reduce sufficiently the calculated value of k_{13} for agreement with experiment. Schwarz³³ has assumed the electronic mobilities in water and ammonia will be in the same ratio as the ionic mobilities, and thus deduces a diffusion coefficient D for e_{aq}^- of $10 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. This is probably a reasonable value. For the reaction of two negative species, $e_{aq}^- + e_{aq}^-$, and of e_{aq}^- with the neutral species, O_2 , the rates do appear to be diffusion controlled if the assumption of a small encounter distance (2.7 Å) is correct. It may be noted that the rate constant for $e_{aq}^- + NO_3^-$ (table 1) is about twice the rate constant k_{12} , even though the diffusion coefficient for NO_3^- is about 1/5 the value used for e_{aq}^- . A more certain value of the diffusion coefficient of e_{aq}^- (or of its mobility) would allow more definite conclusions. Activation energies for these reactions also are needed to determine whether they are indeed diffusion controlled. The reaction $e_{aq}^- + H_3O_{aq}^+$ may involve an activation energy, since there are no vacant ground-state orbitals for $H_3O_{aq}^+$ and since a bond must be broken in the reaction.

In table 1 the known electron scavengers, $H_3O_{aq}^+$, H_2O_2 , O_2 , NO , N_2O and CO_2 are seen to have high rate constants as expected. The organic electron scavengers acetone, $CHCl_3$ and CCl_4 are also very rapid and perhaps diffusion controlled. It is noted that the organic acids acetic and formic, react moderately fast, but that their ions do not.

For diffusion-kinetics calculations of molecular and free-radical G values, one needs the rate constants for all the reactions between the chemical species, the radius of distribution of each species in the cluster, and the diffusion coefficients of each. The rate constants for these reactions are no longer variable parameters. All the necessary rate constants have now been determined for e_{aq}^- , and values for the reactions of the other intermediates have also been reported by Fricke and Thomas²⁷ and Schwarz.³³ Some of the diffusion coefficients and the radii of distribution remain to be determined more precisely. One expects all radii of distribution to be the same, except for e_{aq}^- where the radius should be larger.¹² The

high rate constant for $e_{aq}^- + H_3O_{aq}^+$ supports the suggestion that some or all of $G_H = 0.5^{21}$ is due to this reaction. The neutralization reaction (15) will also have to be included in calculations as it is very fast and several reactions of e_{aq}^- yield OH_{aq}^- .

Finally, the results reported here will eventually have significance in other fields than radiation chemistry. Specifically, the study of the rate constants of the hydrated electron, its mobility, and its absorption spectrum in water, and the comparison of these properties with the corresponding properties of the electron in liquid ammonia should increase our understanding of metal-ammonia solutions and of the structure and molecular motions of water.

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FIG. 1.—Irradiation assembly.

FIG. 3.—Second-order plots of $1/D$ against t for 0.5 M aqueous ethanol, pH 10.9; ●, expt. points for 3 different experiments. Curves calculated with computer: curve A, $G_{e_{aq}} = 2.7$, $G_H = 0.5$, $G_{H_2O_2} = 0.5$, $2k_{12} = 0.85 \times 10^{10}$, $k_9 = 1.23 \times 10^{10}$, $k_{14} = 2.43 \times 10^4 \text{ sec}^{-1}$. Curve B is the same as A except $G_{H_2O_2} = 0$, $2k_{12} = 1.08 \times 10^{10}$. Curve C is the same as A except $2k_{12} = 1.07 \times 10^{10}$, $k_{14} = 0$.

FIG. 4.—Second-order plots of $1/D$ against t for 0.025 M aqueous methanol, $\text{pH} = 10.8$ (NaOH); $\bullet$, expt. points. Curves calculated: curve A, $G_{\text{aq}} = 2.7$, $G_{\text{H}} = 0.5$, $G_{\text{H}_2\text{O}_2} = 0.7$, $2k_{12} = 0.85 \times 10^{10}$, $k_9 = 1.23 \times 10^{10}$, $k_{10} = 3 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, $k_{20} = 1.92 \times 10^6$, $2k_{19} = 1.5 \times 10^{10,27}$, $k_{14} = 3.36 \times 10^4 \text{ sec}^{-1}$. Curve B is the same as A except $2k_{12} = 0.9 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, $k_{14} = 1.92 \times 10^4 \text{ sec}^{-1}$. Curve C is the same as A except $2k_{12} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, $k_{14} = 0$. Curve D is the same as A except $k_{14} = 0$ and $k_{18} = 3.36 \times 10^4 \text{ sec}^{-1}$.

FIG. 5.—Second-order plots of $1/D$ against t for $0.00193 \text{ M K}_4\text{Fe(CN)}_6$, $\text{pH} = 10.9$; $\bullet$, expt. points. Calculated curve: $G_{e_{\text{aq}}} = 2.7$, $G_{\text{OH}} = 2.7$, $G_{\text{H}} = 0.5$, $G_{\text{H}_2\text{O}_2} = 0.7$, $2k_{12} = 1.01 \times 10^{10}$, $k_{10} = 2.7 \times 10^{10}$, $k_{16} = 5.4 \times 10^9$, $k_9 = 1.08 \times 10^{10}$, $k_{17} = 4.5 \times 10^9$, $2k_{19} = 1.35 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$.

FIG. 6.—Disappearance of e_{aq}^- at different initial pH in 0.5 M ethanol. pH adjusted with Ba(OH)_2 . A = pH 11.5 (results similar for pH 12.0 and 12.5); B = pH 9.9; C = pH 8.8; and D = pH 7.

FIG. 2. Hydrated electron decay curve for 0.5 M ethanol at pH 12.

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