

CNC bending mode in the molecule) set at 249 and 540 cm.^{-1} in the so-called "300" and "600" models, comparable to CH_3NC .

For the calculation of the anharmonic sum of energy states, in analogy to part I, we have used again two anharmonic models characterized by anharmonicity con-

stants according to a "minimum" model 1 and a "maximum" model 2. The constants for a Morse-type expression for the energy and dissociation limits of the various bonds in CD_3NC are given in Table VI.

Other parts of the rate calculations were made as before.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY, ARGONNE, ILL.]

Pulse Radiolysis Studies. III. Elementary Reactions in Aqueous Ethanol Solution^{1,2}

BY LEON M. DORFMAN AND I. A. TAUB

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The kinetics of the elementary reactions of two transient species, the hydrated electron and the α -ethanol radical, have been observed in irradiated deaerated aqueous ethanol solution using the pulse radiolysis technique. Absolute rate constants at 23° have been determined for the reaction of the hydrated electron with a hydrogen ion and for the first-order decay of the electron: $e_{\text{aq}}^- + \text{H}_{\text{aq}}^+ = \text{H}$, $k_{e_{\text{aq}}^- + \text{H}^+} = (2.26 \pm 0.21) \times 10^{10} M^{-1} \text{sec.}^{-1}$; $e_{\text{aq}}^- + \text{H}_2\text{O} = \text{H} + \text{OH}^-$, $k_{e_{\text{aq}}^- + \text{H}_2\text{O}} \leq 4.4 \times 10^4 \text{sec.}^{-1}$. The molar extinction coefficient at 577–579 $m\mu$ of the hydrated electron in water, based on $G_{e_{\text{aq}}^-} = 2.7$ molecules/100 e.v., was determined as: $\epsilon_{577} = (9.7 \pm 1.5) \times 10^3 M^{-1} \text{cm.}^{-1}$. Experiments with $\text{C}_2\text{H}_5\text{OD}$ in strongly basic D_2O establish that the product of the bimolecular reaction of two hydrated electrons is a molecule of hydrogen: $e_{\text{aq}}^- + e_{\text{aq}}^- = \text{H}_2 + 2\text{OH}^-$. The isotopic data also give $G_{e_{\text{aq}}^-} = (2.9 \pm 0.3)$ molecules/100 e.v. in D_2O . The molar extinction coefficient of the α -ethanol radical at 2967 Å. was determined as: $\epsilon_{2967} = 240 \pm 45 M^{-1} \text{cm.}^{-1}$. The absolute rate constant for the bimolecular reaction of two α -ethanol radicals at 23° was determined as: $2k_b = (1.4 \pm 0.4) \times 10^9 M^{-1} \text{sec.}^{-1}$.

Introduction

This report in the series^{3,4} of pulse radiolysis studies of organic and aquo-organic systems is concerned with the elementary reactions in deaerated aqueous ethanol solution. Two aspects, in particular, of the radiation chemistry of this system are dealt with. The reaction kinetics of the hydrated electron, of which the absorption spectrum in irradiated water has recently been observed,^{5,6} have been studied. These reactions are of general importance in the radiation chemistry of aqueous systems. The kinetics of the disappearance of the α -ethanol radical, the absorption spectrum of which has already been reported,⁴ have now been studied in acid solution.

A number of isotopic experiments, involving $\text{C}_2\text{H}_5\text{OD}$ in D_2O over a pH range of 0.4 to 13, have been carried out. The results provide the basis for the determination of the molar extinction coefficients of both the hydrated electron and the α -ethanol radical. In the latter case, the molar extinction coefficient, which has been estimated in neutral solution,⁴ may be determined to a higher degree of certainty in acid solution. The isotopic data, furthermore, furnish definitive information concerning the nature of one of the reactions of the hydrated electron.

Experimental

The technical details of the pulse radiolysis method used in these fast reaction studies have been described in the first paper³ of this series. Only the particular conditions pertaining to the present investigation will be outlined.

Pulse Irradiation.—A 15-Mev. electron pulse from the linear accelerator was used throughout. The work on the α -ethanol radical was done with a 5- $\mu\text{sec.}$ pulse, with the exception of a few runs where a 3- $\mu\text{sec.}$ pulse was used. The kinetics of the hydrated electron were observed after a 0.4- $\mu\text{sec.}$ pulse. The time-profile of the pulse, which is very nearly rectangular, has been shown elsewhere.³

The electron beam used in this work was more nearly collimated than in the previous work, having an incident diameter of 16 mm. and an emergent diameter of about 18 mm. in a 4-cm. long cell.

Cylindrical quartz cells of various sizes were used in the irradiations. In those runs where it was desirable to define the irradiated

volume precisely, cells of 4 cm. length and inside diameter 15 mm., thus smaller than the actual beam diameter, were used. Cells of 4 cm. diameter were also used. In the determination of bimolecular rate constants, where a uniform concentration of transient species along the axis of the beam was highly desirable, a number of runs were carried out in cells of 2 cm. length to ensure that this condition would be satisfied. In the observations of the kinetics of the hydrated electron at high pulse intensity, a cell of only 1 cm. length was used because of the very high extinction coefficient of this species.

Dosimetry.—The pulse was monitored on a relative basis by integrating the current in the beam sensor⁷ which has been mentioned previously.⁴ The absolute dose was determined in two ways. The usual bulk dosimetry with the Fricke dosimeter containing $10^{-2} M$ ferrous ion and 0.8 N sulfuric acid was used. This solution was saturated with oxygen and contained no chloride ion. The yield of ferric ion in this solution at the high dose rates^{8,9} is 15.6 molecules/100 e.v. The ferric ion concentration was measured on a Beckman DU spectrophotometer. In addition a type of *in situ* dosimetry was used involving the optical detection system itself in a fast spectrophotometric measurement of the total ferric ion formation in the above dosimeter solution. This method was considered worthwhile in the determination of the molar extinction coefficients, where the actual concentration (or energy deposition) in the path of the analyzing light beam was the particular information required. This information was obtained by calculating the ferric ion concentration from the optical density corresponding to the plateau in the formation rate curve. This optical density represents the concentration of ferric ion formed from all reactions in the dosimeter, which in these experiments are completed within about 2 sec. after the pulse. The rate curve for ferric ion formation was determined at either 302 or 366 $m\mu$ depending upon the length of the irradiation cell. The ferric ion concentrations were calculated using $\epsilon_{302} = 2200 M^{-1}$ and $\epsilon_{302}/\epsilon_{366} = 8.57$. This ratio of the molar extinction coefficients was determined with a Cary spectrophotometer, type 14R, using a solution approximately $2 \times 10^{-4} M$ in ferric sulfate and 0.8 N in sulfuric acid.

Optical Detection.—The fourfold reflection system was used in most of the experiments. In a number of observations of the hydrated electron a twofold reflection was used for optical detection. The 2.25-m. spectrograph was used with two separate gratings. For detection in the ultraviolet region a grating blazed at 370 $m\mu$ with a dispersion of 15 Å./mm. was used. For the kinetic studies of the hydrated electron at 577–579 $m\mu$ a grating blazed at 600 $m\mu$ with a similar dispersion was used.

The steady light source in the fast spectrophotometric measurements was an Osram mercury lamp, type HBO 107/1, monitored with a 1 P28 photomultiplier tube. At 2967 Å., where the α -ethanol kinetics were observed, a 1-mm. slit was placed in front of the photomultiplier, giving a band width of 15 Å. For the hydrated electron, which exhibits a very broad absorption

(1) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963; see Abstracts of Papers, p. 11P.

(2) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(3) L. M. Dorfman, I. A. Taub, and R. E. Bühler, *J. Chem. Phys.*, **36**, 3051 (1962).

(4) I. A. Taub and L. M. Dorfman, *J. Am. Chem. Soc.*, **84**, 4053 (1962).

(5) J. W. Boag and E. J. Hart, *Nature*, **197**, 45 (1963).

(6) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962).

(7) K. Johnson, T. Klippert, and W. J. Ramler, *Nuclear Instr. Methods*, **14**, 125 (1962).

(8) J. Rotblat and H. C. Sutton, *Proc. Roy. Soc. (London)*, **A255**, 49 (1960).

(9) J. K. Thomas and E. J. Hart, *Radiation Res.*, **17**, 408 (1962).

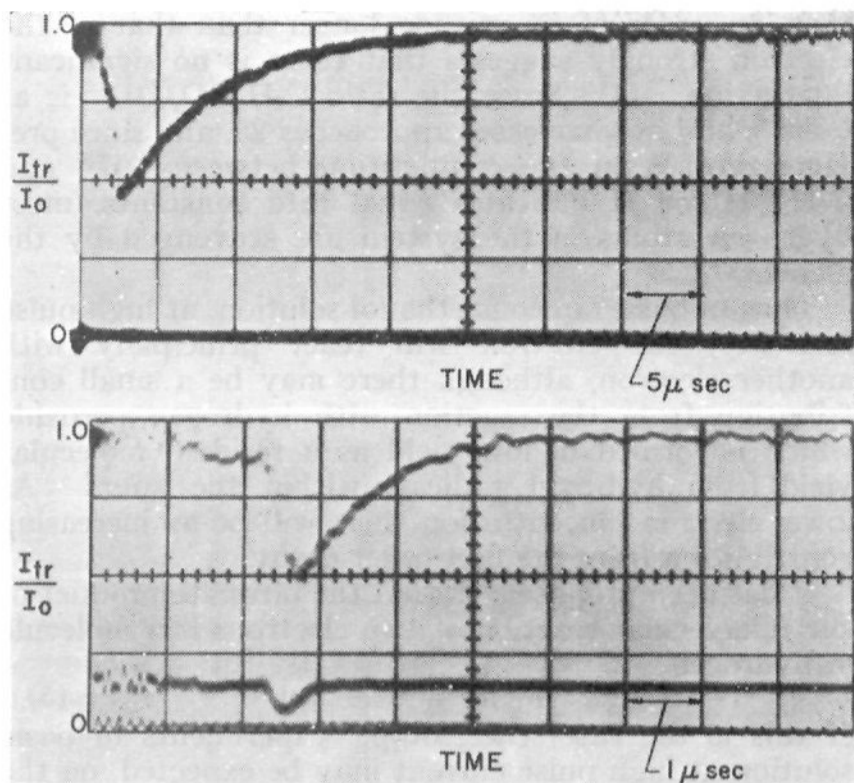


Fig. 1.—Rate curves for the disappearance of the hydrated electron absorption at 577 $m\mu$ in deaerated acidic aqueous ethanol solutions: a, top figure, $[H^+] = 0.8 \times 10^{-5} M$; b, lower figure, $[H^+] = 6 \times 10^{-5} M$. A simultaneously recorded time-profile of the pulse is shown just above the 0% transmission trace.

spectrum,^{5,6} a 5 mm. slit or 75 Å. band width was used at 577–579 $m\mu$.

Materials.—The water and the deuterium oxide were both triply distilled.¹⁰ The ethanol was reagent grade, obtained from U. S. Industrial Chemicals Co., and was used without further purification. A spectrophotometric check for benzene indicated that if any were present it must amount to less than 10^{-4} mole %. Ethanol-*d*, C_2H_5OD , was obtained from Volk Radiochemical Co. (Chicago, Ill.) where it was synthesized by the hydrolysis of sodium ethanolate in deuterium oxide. It was found to contain not more than 0.1% hydroxyl hydrogen.

The solutions to be irradiated, most of which were 0.5 *M* in ethanol, were degassed on a vacuum system by conventional pumping techniques with vigorous shaking of the liquid during pumping. The ethanol was introduced into the water before degassing. This technique was preferred to the side-arm technique previously used⁴ and appears to result in a more rigorously degassed solution, judging from the increased hydrogen yields.

A number of runs were carried out in basic solution at about pH 12 to 13. It was important that there be no contamination by any reactive impurities. The pH of these solutions was therefore adjusted approximately by adding to the degassed solution under vacuum, an appropriate quantity of sodium which had been vacuum distilled. The hydrogen formed by the interaction of the sodium with the water was, of course, pumped off. The pH was measured after the run. In the isotopic experiments in acid solution the pH was adjusted by introducing either sulfuric acid or deuterated sulfuric acid into the solution.

Analytical.—The analysis of the isotopic hydrogen was carried out by separating the hydrogen in a conventional vacuum system fitted with a toepler pump, followed by pressure-volume measurement using a McLeod gage and then mass spectrometric analyses. In those acid solutions used for the observation of the reaction of the hydrated electron with a hydrogen ion an accurate pH determination was required for the calculation of the rate constant. The pH was determined using a Beckman model G pH meter in the earlier runs and a Radiometer model 4 pH meter in the later runs.

In a few acid runs the yield of hydrogen peroxide was measured using the iodide technique.¹¹ An aliquot of the irradiated solution was mixed with dilute sodium hydroxide to bring the pH to approximately 7 before adding the iodide reagent. A calibration curve was constructed using the optical density of I_3^- at 350 $m\mu$, obtained after 3 min. from the time of mixing, developed in standard hydrogen peroxide solutions in the concentration range $5 \times 10^{-6} M$ to $6 \times 10^{-5} M$; prepared as previously described.³

Results and Discussion

The immediate precursors of the α -ethanol radical are the hydroxyl radical and the hydrogen atom, formed as transient species in the water. The α -ethanol radical is formed in the reactions

(10) E. J. Hart, *J. Am. Chem. Soc.*, **73**, 68 (1951).

(11) C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

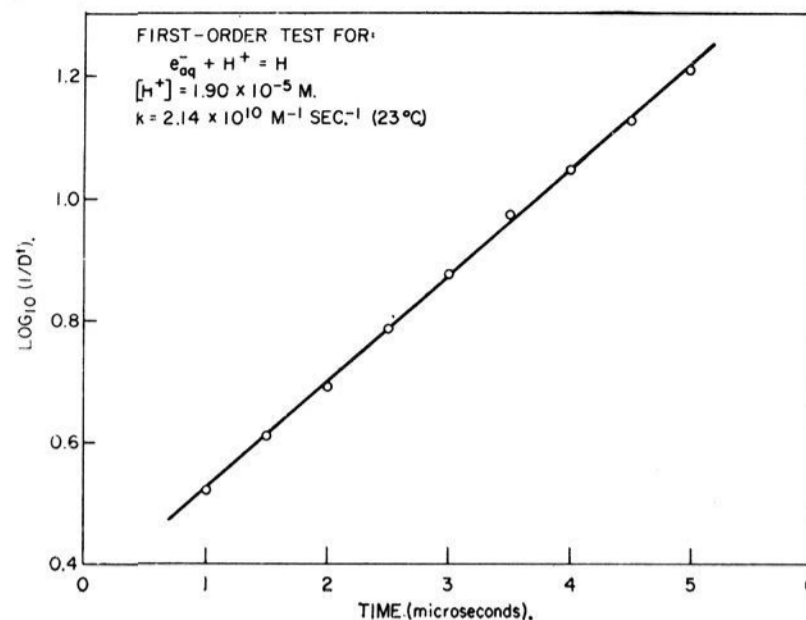


Fig. 2.—Test of the first-order rate law for the disappearance of the hydrated electron in deaerated acidic aqueous ethanol solution.



and



The hydrated electron, as will be shown, does not react with the ethanol in these high intensity irradiations. In strongly acid solution the fate of the hydrated electron is exclusively the reaction with the hydrogen ion



The hydrogen atom then reacts with the ethanol according to (2). The kinetics of the hydrated electron have been observed in both acidic and basic solution. The results lead to some important conclusions concerning the general behavior of this primary species. The kinetics of the α -ethanol radical have now been observed in acid solution.

Kinetics of the Hydrated Electron.—The absolute rate constant for reaction 3 was determined by observing the decay kinetics of the hydrated electron at 577–579 $m\mu$ following a 0.4- μ sec. pulse. The solutions contained 0.5 *M* ethanol so that the hydroxyl radical is effectively removed in reaction 1 and cannot therefore enter into any competitive reaction for the hydrated electron. The range of hydrogen ion concentration and the pulse current were selected so that $[H_{aq}^+]/[e_{aq}^-] \gg 10$. This could be readily accomplished because the high molar extinction coefficient of the hydrated electron permits observations at a very low concentration of this species. Under these conditions, reaction 3 is pseudo-first order in the hydrated electron.

Two typical decay curves are shown in Fig. 1a and 1b, the first at a hydrogen ion concentration of $0.8 \times 10^{-5} M$, and the second, showing a much higher rate at a hydrogen ion concentration of $6 \times 10^{-5} M$. Such curves precisely fit a first-order rate law, as may be seen in Fig. 2, which shows a plot of the logarithm of the optical density as a function of time, and is thus a representation of the integrated form of the differential rate expression for reaction 3. The absolute rate constant is obtained from the slope of the straight line and the known hydrogen ion concentration, corrected for the small additional amount formed by the pulse itself. In view of the general importance of reaction 3 in the radiation chemistry of aqueous systems, it seems worthwhile to present the data for the individual runs, which are shown in Table I. These data give an absolute rate constant of

$$k_3 = (2.26 \pm 0.21) \times 10^{10} M^{-1} \text{ sec.}^{-1} \text{ at } 23^\circ$$

It is of interest to compare k_3 with the rate constant for the proton reaction

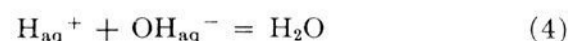


TABLE I
RATE CONSTANT FOR THE REACTION OF THE HYDRATED
ELECTRON WITH A PROTON AT 23°

Acid	Concn. of H ⁺ (M × 10 ⁵)	Pulse ^a current, mamp.	k _{eaq} ^{+H⁺} , M ⁻¹ sec. ⁻¹ × 10 ⁻¹⁰
H ₂ SO ₄	1.90	20	2.14
H ₂ SO ₄	1.90	20	2.43
H ₂ SO ₄	1.89	15	2.28
HClO ₄	2.89	15	1.85
HClO ₄	2.93	25	1.83
H ₂ SO ₄	3.68	23	2.65
H ₂ SO ₄	3.72	33	2.62
H ₂ SO ₄	3.72	33	2.45
HClO ₄	5.31	20	2.17
HClO ₄	5.34	30	2.35
HClO ₄	5.34	30	2.30
H ₂ SO ₄	6.01	30	1.82
H ₂ SO ₄	6.01	30	1.99
H ₂ SO ₄	6.01	30	2.06
H ₂ SO ₄	7.39	33	2.37
H ₂ SO ₄	7.39	33	2.17
H ₂ SO ₄	8.20	15	2.75
H ₂ SO ₄	8.17	7	2.34
H ₂ SO ₄	8.17	7	2.44

Mean^b 2.26 ± 0.21

^a A pulse current of 30 mamp. corresponds to an initial hydrated electron concentration of $\sim 3 \times 10^{-6}$ M. ^b S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas of this Laboratory independently find $(2.36 \pm 0.24) \times 10^{10}$ M⁻¹ sec.⁻¹.

for which Eigen and DeMaeyer¹² have obtained $k_4 = 1.3 \times 10^{11}$ M⁻¹ sec.⁻¹. They have explained this high rate constant in terms of a proton jump mechanism which results in a phenomenological interaction distance of approximately 8 Å. The fact that k_3 is fully 6-fold smaller than k_4 cannot be explained on the basis of a diffusion parameter since the diffusing proton is common to both reactions. It may be related to differences in the hydration structure surrounding the electron as compared with that around the hydroxyl ion. We are unable, at this point, to offer any meaningful interpretation of this substantial difference.

A number of isotopic experiments involving the system C₂H₅OD in D₂O, along with the fast kinetic studies, were carried out in basic solution in order to obtain information about the bimolecular reaction of two hydrated electrons. The following considerations apply to these experiments: (1) At a pH of about 12 the protons formed by the pulse cannot enter into a competitive reaction with the electron since the proton lifetime, in this strongly basic solution, is several orders of magnitude shorter than that of the electron because of the high value of k_4 . (2) The ethanol does not react with the electron in these high intensity pulse experiments, as we have found in neutral solution that increasing the ethanol concentration from 0.2 to 1 M fails to show any effect on the lifetime of the electron. This observation permits us to assign an approximate upper limit of 1×10^5 M⁻¹ sec.⁻¹ to the absolute rate constant for the reaction of the hydrated electron with ethanol. The value may, of course, be considerably lower. It is thus fully two orders of magnitude lower than the value suggested by Hummel and Allen¹³ on the basis of relative rate constant considerations. (3) The hydroxyl radical is effectively removed by hydrogen abstraction from the ethanol,¹³ the concentration of which is 0.5 M. The possibility exists, however, that the α-ethanol radical which is formed may react with the electron. Our observation that the lifetime of the α-ethanol radical in neutral solution is more

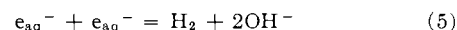
(12) M. Eigen and L. DeMaeyer, *Z. Elektrochem.*, **59**, 986 (1955).

(13) A. Hummel and A. O. Allen, *Radiation Res.*, **17**, 302 (1962).

than an order of magnitude longer than that of the electron strongly suggests that there is no significant interaction. (4) Since the ratio C₂H₅OD/OD⁻ is at least 5, and in some cases approaches 25, and since previous work¹⁴ on the competition between OH⁻ and C₂H₅OH for H indicates equal rate constants, most hydrogen atoms in the system are scavenged by the alcohol.

Thus in basic aqueous ethanol solution, at high pulse intensity, the electron will react principally with another electron, although there may be a small contribution from the reaction with hydrogen peroxide which is formed in low yield as a residual molecular yield from hydroxyl radicals within the spurs. At lower electron concentration there will be an increasing contribution from the first-order decay.

It has been proposed^{15,16} that the ultimate product of the bimolecular reaction of two electrons is a molecule of hydrogen.



If this is the case, the isotopic experiments in basic solution at high pulse current may be expected, on the basis of previously indicated yields of the hydrogen atom¹⁷⁻¹⁹ and the electron,^{16,20,21} to give

$$G(D_2) \cong 2 = G_{D_2} + \frac{1}{2}G_{e_{aq}^-} \quad (I)$$

and

$$G(HD) \cong 0.6 = G_D \quad (II)$$

where G_D is the deuterium atom portion of the total yield of reducing species appearing in the bulk of the solution. If, on the other hand, we make the assumption that free hydrogen atoms are formed in (5), we may expect

$$G(HD) \cong 3.5 = G_D + G_{e_{aq}^-} \quad (III)$$

and

$$G(D_2) \cong 0.5 = G_{D_2} \quad (IV)$$

The data shown in Table II were obtained using four 5-μsec., 80-mamp. pulses. The results in basic solution, $G(D_2) = 1.96$ and $G(HD) = 0.63$ molecule/100 e.v., clearly lead to the conclusion that the product of reaction 5 is indeed a molecule of hydrogen. Our value of

TABLE II
HYDROGEN YIELDS IN THE PULSE RADIOLYSIS OF DEAERATED
0.5 M C₂H₅OD IN D₂O AT 23°

Acidity adjustment	Total G(hydrogen), molec./100 e.v.	G(H ₂) ^b	G(HD)	G(D ₂)
0.8 N D ₂ SO ₄	3.87	0.15	3.36	0.36
.8 N H ₂ SO ₄	3.75	.24	3.28	.24
.8 N H ₂ SO ₄	3.87	.22	3.39	.26
.8 N H ₂ SO ₄	4.25 ^a	4.25	0	0
...	3.32	0.16	2.71	0.45
...	3.17	.11	2.64	.42
...	3.27	.10	2.76	.41
Na ^d	2.61	.05	0.66	1.89
Na	2.84	.06	.67	2.11
Na	2.45	.03	.55	1.87

^a This is the only run with C₂H₅OH in H₂O. ^b A large part of the H₂ may be accounted for on the basis of direct absorption in the C₂H₅OD. No corrections have been made for the small isotopic impurity in the D₂O. ^c The deuterium ion concentration in neutral D₂O is about 0.5×10^{-7} M. ^d A weighed amount of sodium was added to the D₂O solution to bring the OD⁻ concentration to 0.1 M. This adjustment was roughly checked using a glass electrode which most often indicated a pH near 13.

(14) J. T. Allan, M. G. Robinson, and G. Scholes, *Proc. Roy. Soc. (London)*, **A270**, 381 (1962).

(15) E. Hayon and J. Weiss, *Proc. Second Intern. Conf., Geneva*, **29**, 80 (1958).

(16) J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962).

(17) J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).

(18) J. Rabani, *J. Am. Chem. Soc.*, **84**, 868 (1962).

(19) C. Lifshitz, *Can. J. Chem.*, **40**, 1903 (1962).

(20) F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc. (London)*, **A267**, 443 (1962).

(21) G. Czapski and A. O. Allen, *J. Phys. Chem.*, **66**, 262 (1962).

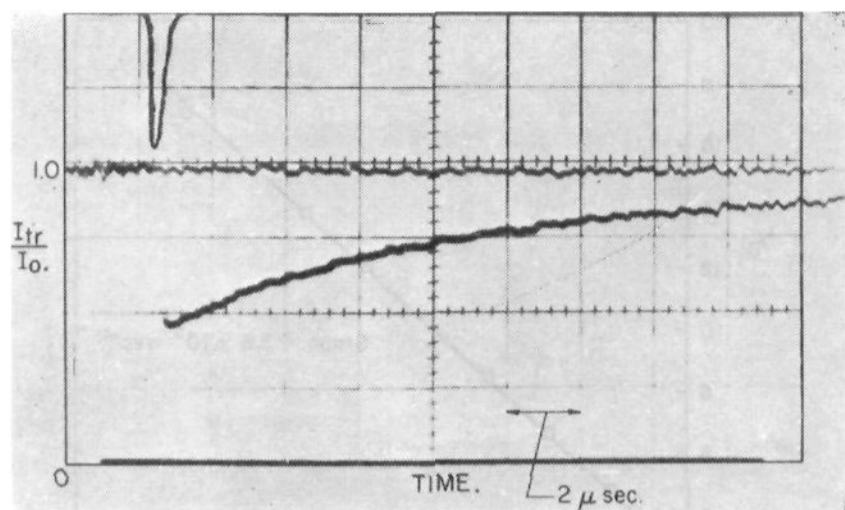
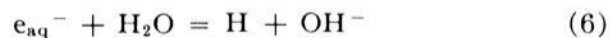


Fig. 3.—Rate curve for the disappearance of the hydrated electron absorption at 577 $m\mu$ in a deaerated strongly basic aqueous ethanol solution. The time-profile of the pulse is shown above the 100% transmission trace.

$G(\text{HD}) = 0.63$ is in close agreement with the recent value of Lifshitz,¹⁹ obtained using electron scavengers. Taking $G_{\text{D}_2} = 0.5$ and inserting the data into eq. I, we obtain $G_{e_{\text{aq}}^-} = (2.9 \pm 0.3)$ molecules/100 e.v. at $[\text{OD}^-] = 0.1 M$ which may be compared with other values in the literature.^{16,20}

The decay curve of the hydrated electron in these basic solutions was observed following a 0.4- μsec . pulse. A typical curve at pH 13 is shown in Fig. 3. A second-order test of such a curve is shown in Fig. 4. This is a plot of the reciprocal of the optical density as a function of time and is thus a representation of the integrated form of the differential rate expression for reaction 5. The electron decay closely follows a second-order rate law over that portion of the curve which corresponds to the disappearance of at least 65% of the initially formed hydrated electrons. There is then a deviation from the second-order fit.

We may obtain only an upper limit for k_5 from the linear portion of the curve in Fig. 4, since there may be small contributions to the rate of electron disappearance by processes other than reaction 5. One of these is the reaction of the electron with the small amount of hydrogen peroxide formed as a residual molecular yield. Analysis of five runs in acid solution indicates an approximate hydrogen peroxide yield of 0.3 molecule/100 e.v. with a 50% error limit. Another process is the smaller contribution from the unimolecular decay of the hydrated electron,^{16,22,23} about which more will be said later.



Any contribution by (6) is obviously a decreasing function of pulse intensity.

From the slope of the straight line in Fig. 4 we obtain

$$2k_5 \leq (1.32 \times 10^6) \epsilon_{577} \text{ at } 23^\circ$$

where ϵ_{577} is the molar extinction coefficient of the hydrated electron at the indicated wave length.

The molar extinction coefficient of the hydrated electron at 577–579 $m\mu$ may be determined from the initial optical densities taken from the rate curves in basic solution along with the appropriate yield of the electron. From several values already in the literature,^{16,17,20,21} along with our own determination of 2.9 in basic deuterium oxide solution, it would appear that $G_{e_{\text{aq}}^-} = 2.7 \pm 0.2$ molecules/100 e.v. is an appropriate value for the hydrated electron yield in aqueous solution. The initial observable optical density was, of course, corrected for the electron disappearance during the pulse. This correction is small, since the half-life of the hydrated electron in basic solution is almost an

(22) R. L. Platzman, "Basic Mechanisms in Radiobiology," U. S. Natl. Acad. Sci. Publ. No. 305, 1953, p. 34.

(23) G. Czapski and H. A. Schwarz, *J. Phys. Chem.*, **66**, 471 (1962).

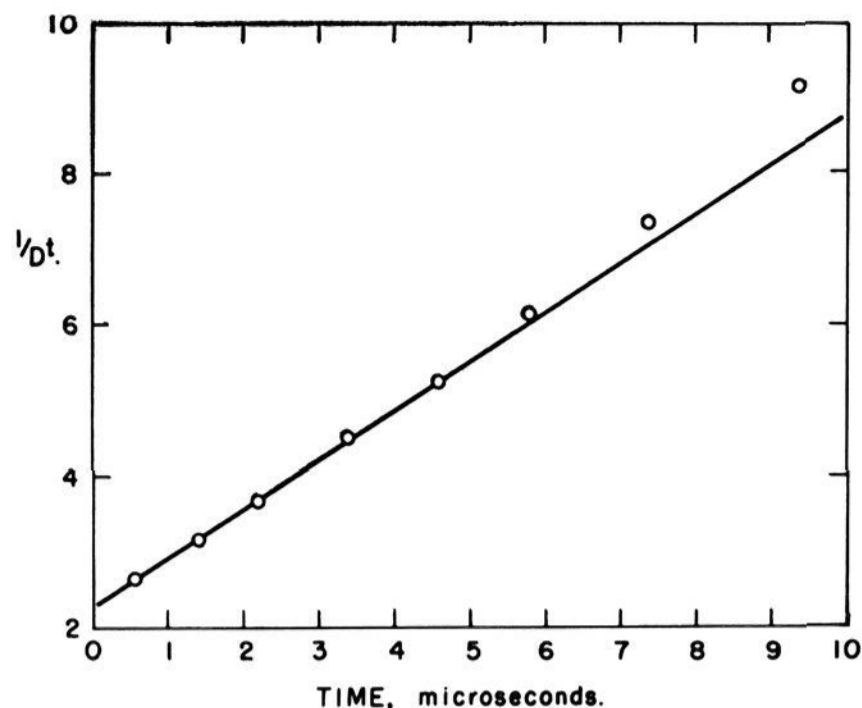


Fig. 4.—Test of the second-order rate law for the disappearance of the hydrated electron in a deaerated strongly basic aqueous ethanol solution.

order of magnitude greater than the pulse width. The value obtained for the molar extinction coefficient in aqueous solution is

$$\epsilon_{577} = (9.7 \pm 1.5) \times 10^3 M^{-1} \text{ cm.}^{-1}$$

Thus the upper limit for the rate constant for reaction 5 is

$$2k_5 < (1.3 \pm 0.2) \times 10^{10} M^{-1} \text{ sec.}^{-1} \text{ at } 23^\circ$$

where k_5 is defined by the expression

$$-d[e_{\text{aq}}^-]/dt = 2k_5[e_{\text{aq}}^-]^2$$

It should be noted that there is a minor discrepancy in neutral solution between the observed values for $G(\text{HD})$ and $G(\text{D}_2)$ and the values expected on the basis of the rate constants k_3 and k_5 , the observed $G(\text{D}_2)$ being only slightly in excess of the molecular yield. This discrepancy would nearly vanish, however, if $G(\text{D}_2)$ is actually slightly higher (the error limit for the G -values is ± 6 –8%) and if k_5 is lower than indicated by the upper limit.

In order to observe the first-order decay of the electron, reaction 6, experiments were done at a pulse current fully 20-fold lower than the highest currents used in observing reaction 5. Decay curves were observed

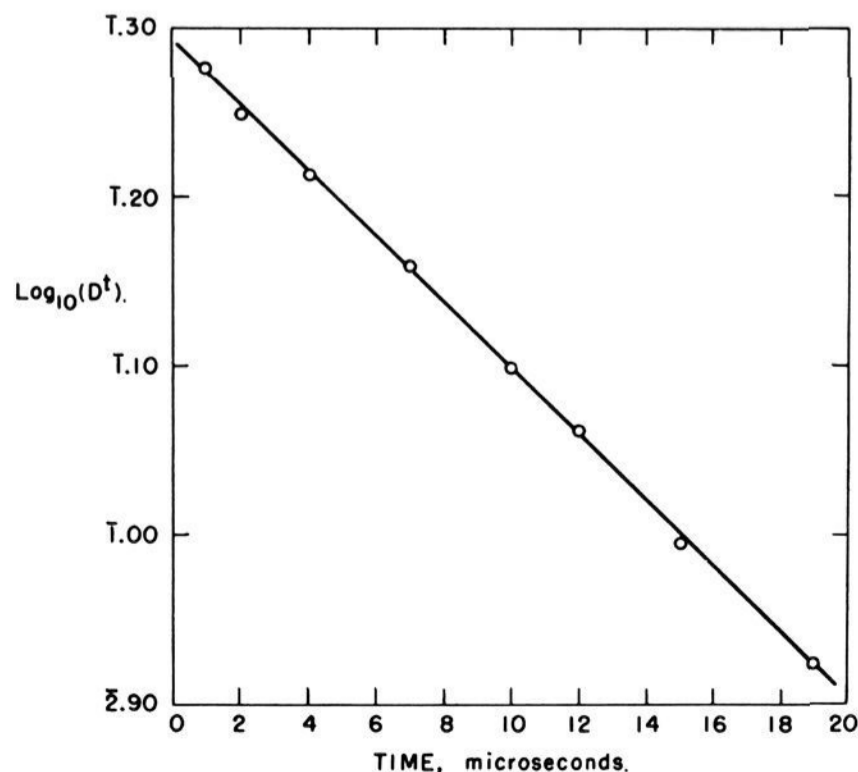


Fig. 5.—Test of the first-order rate law for the disappearance of the hydrated electron at low concentration in a deaerated strongly basic aqueous ethanol solution.

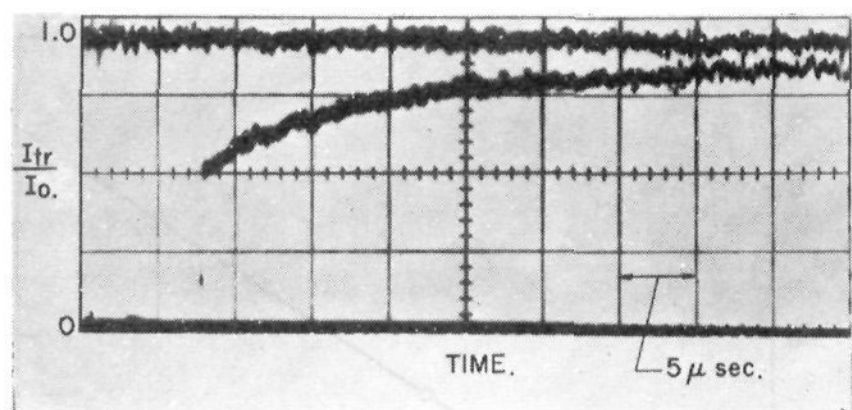


Fig. 6.—Rate curve for the disappearance of the α -ethanol radical absorption at 2967 Å. in deaerated highly acidic aqueous ethanol solution.

at pulse currents as low as 10 mamp. A first-order test of such a decay curve is shown in Fig. 5. The entire decay curve fits a first-order rate law. From the slope of the straight line we obtain

$$k_6 \leq 4.4 \times 10^4 \text{ sec.}^{-1} \text{ at } 23^\circ$$

or, expressed as a bimolecular rate constant

$$k_6 \leq 8.0 \times 10^2 M^{-1} \text{ sec.}^{-1} \text{ at } 23^\circ$$

Again, in this case, we feel justified in reporting only an upper limit for k_6 for the following reasons. The observations were carried out at an initial concentration of the hydrated electron of less than $1 \mu M$ in order to minimize any contribution from reaction 5. At this low electron concentration, trace impurities (such as oxygen) at a concentration level of less than $0.1 \mu M$ may make a significant contribution to the observed rate. The accurate determination of such low impurity levels and hence the assessment of any trace impurity contributions is an objective which will clearly be most difficult to attain. The indicated value for k_6 may be the true value, but it is presented here only as an upper limit. This value, it will be noted, is approximately 3-fold lower than the limiting value indicated in recent¹⁶ relative rate constant determinations, relating these now to the present value of $k_3 = 2.3 \times 10^{10} M^{-1} \text{ sec.}^{-1}$.

Kinetics of the α -Ethanol Radical.—The rate of disappearance of the α -ethanol radical, which had previously⁴ been determined only in neutral solution, has been observed in acid solution. The absorption spectrum which is observed in $0.8 N$ sulfuric acid solution is similar to that in neutral solution.

A typical decay curve is shown in Fig. 6. This curve precisely fits a second-order rate law, as may be seen in Fig. 7. As has been pointed out,⁴ the initial short deviation from a second-order law, which was observed in neutral solution, is completely eliminated in acid solution. This initial deviation in neutral solution apparently results from a contribution by the hydrated electron to the optical density at 2967 Å.

From data such as Fig. 7, the absolute rate constant for the bimolecular reaction of two α -ethanol radicals is found to be

$$2k_b = (5.8 \pm 0.3) \times 10^6 \epsilon_{2967} M^{-1} \text{ sec.}^{-1} \text{ at } 23^\circ$$

where ϵ_{2967} is the molar extinction coefficient of the α -ethanol radical at the indicated wave length.

The molar extinction coefficient may be determined from the optical density obtained from the rate curves and the radical yield obtained from the isotopic experiments in acid solution. The initial yield of the α -ethanol radical is given by

$$G(\text{CH}_3\dot{\text{C}}\text{HOH}) = G_{\text{OD}} + 0.9G(\text{HD}) \quad (\text{V})$$

where $G(\text{HD})$, the observed yield in the isotopic scavenging experiments, is corrected by a factor of 0.9 on the basis of the α/β hydrogen abstraction ratio de-

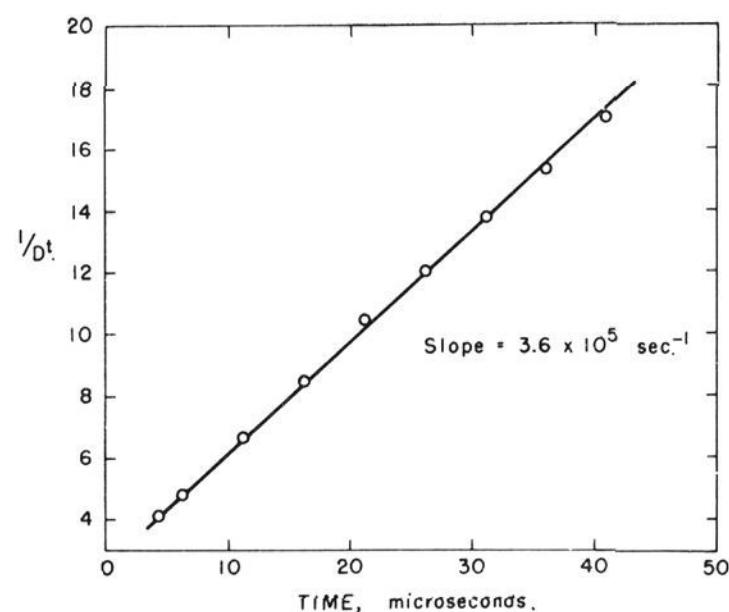


Fig. 7.—Test of the second-order rate law for the disappearance of the α -ethanol radical in deaerated acidic ($0.8 N \text{ H}_2\text{SO}_4$) aqueous ethanol solution at 2967 Å. Zero time in this figure does not coincide precisely with the end of the pulse.

termined by Lifshitz and Stein²⁴; $G_{\text{OD}} = 3.1$ is the hydroxyl yield²⁵ in D_2O .

The correction for the disappearance of α -ethanol radicals during the pulse is rather more straightforward in acid solution. Since the formation reactions 1 and 2 are essentially instantaneous in $0.5 M$ ethanol solution, and the time-profile of the pulse is rectangular, the rate of formation of the α -ethanol radical is linear in time. The differential rate equation for the α -ethanol radical was integrated and the concentration at the end of the pulse obtained by successive approximations. The average value for ϵ_{2967} obtained from a number of different runs is

$$\epsilon_{2967} = 240 \pm 45 M^{-1} \text{ cm.}^{-1}$$

This gives

$$2k_b = (1.4 \pm 0.4) \times 10^9 M^{-1} \text{ sec.}^{-1} \text{ at } 23^\circ$$

This value does not differ significantly from the value estimated in neutral solution. It does, however, have a higher degree of certainty.

Mechanism.—On the basis of the foregoing information, the following may be said in summary concerning the radiation chemistry of deaerated aqueous ethanol solution. The fate of the hydrated electron in the bulk of the solution in these high intensity experiments is principally its disappearance in reaction 3. This is true not only in acid solution, but in neutral solution as well because of the high value of k_3 and the hydrogen ion concentration formed by the pulse itself. The α -ethanol radical is formed in reactions 1 and 2 and disappears in a bimolecular reaction which has been discussed.⁴

In the steady radiolysis, at much lower intensity, the first-order decay of the electron, reaction 6, will become more important with a smaller contribution by reaction 3, depending upon the intensity.

In basic solution, depending upon pH, reaction 3 will play a lesser or negligible role, and reactions 5 and 6 will occur competitively, depending upon intensity.

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(24) C. Lifshitz and G. Stein, *J. Chem. Soc.*, 3706 (1962).

(25) H. A. Mahlman and J. W. Boyle, *J. Am. Chem. Soc.*, **80**, 773 (1958).