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

Pulse Radiolysis Studies. II. Transient Spectra and Rate Processes in Irradiated Ethanol and Aqueous Ethanol Solution[1]

BY I. A. TAUB AND LEON M. DORFMAN

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The radiation chemistry of deaerated aqueous ethanol and deaerated liquid ethanol has been studied by the pulse radiolysis technique. The same transient absorption spectrum, showing a broad weak absorption at about 290 mμ and stronger narrow peaks at 266, 257 and 247 mμ, has been observed in both systems. It is concluded that the spectrum is that of the α-ethanol radical, $CH_3\dot{C}HOH$. The molar extinction coefficient in water is estimated to be $\epsilon_{2967} = 230 \pm 55\ M^{-1}$ cm.$^{-1}$. From the rate curves for the disappearance of the transient, determined by fast photoelectric spectrophotometry, the absolute rate constant for the bimolecular reaction of two α-ethanol radicals in water, at 23°, is found to be: $2k_b = (1.1 \pm 0.3) \times 10^9\ M^{-1}$ sec.$^{-1}$. The bimolecular rate constant in ethanol, at 23°, is found to be: $2k_b = (3.3 \pm 0.2) \times 10^6\ \epsilon'_{2967}\ M^{-1}$ sec.$^{-1}$, where ϵ'_{2967} is the molar extinction coefficient at 2967 Å. of the α-ethanol radical in ethanol. The radiation chemical yields of 2,3-butanediol and acetaldehyde have been determined in both systems, along with the hydrogen yields in heavy water solutions.

Introduction

The radiation chemistry of ethanol and of aqueous ethanol solutions has been studied from many different points of view, and experimental data obtained over a great variety of conditions have been reported. The reactive molecular fragments formed by irradiation of ethanol as a rigid solid at low temperatures have been examined by the electron spin resonance technique.[2-5] Similarly, e.s.r. spectra have been obtained for the species formed by hydroxyl radical attack upon solid ethanol and other alcohols.[6,7]

Liquid ethanol has been radiolyzed with a number of different types of radiation,[8-10] and extensive analytical data pertaining to the products are available. Isotopic studies with various deuterated ethanols[11,12] have attempted to obtain information about the nature of the chemical transients formed. An interesting investigation[13] of the radiolysis of solid ethanol followed by photolysis has demonstrated the photochemical decomposition of trapped transient species.

Radiolysis of aqueous solutions of ethanol,[14-16] where the attack on the ethanol molecule is principally indirect, provides an interesting comparison with the direct radiolysis. In aqueous solution, very recent studies[17,18] with deuterated ethanol molecules, in both water and heavy water, provide important information concerning the locus of attack on the ethanol molecule by the hydrogen atom from the water.

The present report is the second in a series of pulse radiolysis studies[19] of various organic and aquo-organic systems. This technique permits the observation of the ultraviolet absorption spectra of short-lived species in irradiated systems by synchronized flash absorption spectroscopy. The rate processes in which these species participate are then examined by fast photoelectric spectrophotometry. Deaerated liquid ethanol and deaerated aqueous ethanol solution have been radiolyzed and studied with this technique. In addition, a number of isotopic experiments with deuterated molecules have been carried out.

Experimental

The technical details of the pulse radiolysis method have been extensively described in the first report of this series.[19] A brief outline of the conditions pertaining to the present investigation follows.

Pulse Irradiation.—A 15-Mev. electron pulse from the linear accelerator was used throughout this work. Only the 5-μsec. pulse was used since accurate observations required the maximum concentration of species obtainable because of the relatively low molar extinction coefficient of the transient. The time profile of this pulse has been shown in the previous report.

The cross-section of the electron beam was roughly circular with an incident diameter of approximately 15 mm. The cross-sectional intensity distribution was homogeneous to within about ±10% over at least a 12-mm. diameter as determined by densitometer measurement of radiation discoloration on glass disks. The beam was slightly divergent to an emergent diameter of 25 mm. in a 4-cm. long cell. But the axial homogeneity in intensity (and hence in concentration of species) along the fourfold analyzing light beam was sufficiently good that second-order rate curves in a previous study gave the same constant within experimental error (±3 to 4%) in cells of 2 cm. length and 4 cm. length. Moreover, measurements of the initial optical density in irradiated ethanol showed the concentration of species in the 2- and the 4-cm. cell to be the same within ±4%.

The pulse was monitored on a relative basis in two different ways. In experiments not involving optical detection an aluminum block was placed behind the cell and the beam current absorbed in the block was measured with a current integrator. The beam was also monitored by a non-intercepting beam sensor[20] located within the drift tube just before the exit window of the accelerator. This sensor, which is normally used in positioning the beam, permitted the observation of the time profile of a single pulse on the oscilloscope screen. It was therefore used not only in

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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monitoring the pulse intensity but in determining the timing as well.

Solutions were irradiated in cylindrical quartz cells 4 cm. in diameter. Cells of 4-cm. length were used in most of the experiments, but a few determinations of rate curves were carried out with the 2 cm. long cell. Thus the total volume of liquid in the cell was 50 cc. in the larger cell.

Dosimetry.—The absolute dose was determined by means of a modified Fricke dosimeter for which the ferric ion yield[21,22] at these high dose rates is 15.6 molecules/100 e.v. This solution consists of 10^{-2} *M* ferrous ion and 0.8 *N* sulfuric acid. It is saturated with oxygen and contains no chloride ion. The ferric ion concentration was measured on a Beckman DU spectrophotometer at 25°. A molar extinction coefficient of 2200 at 304 mμ was used in the calculations.

Optical Detection.—The fourfold reflection system previously described[19] was used for optical detection, so that the absorption path length of the analyzing light beam in a 4-cm. cell was 16 cm. A Jarrell-Ash 2.25-m. grating spectrograph was used with a grating blazed at 370 mμ and a dispersion of 15 Å./mm.

The source of continuum for spectrophotographic recording was an end-window xenon spectroflash lamp fired from a 1 mfd. condenser charged to 14 kv. Eastman Kodak spectroscopic plates, type 103–0, were used exclusively. Absorption curves were determined from these plates with the aid of a Leeds and Northrup densitometer. Appropriate "H and D" corrections, from a representative curve, were applied to the densitometer tracings to determine the observed absorption curves which extend down to 240 mμ. The nature of the absorption spectrum was also checked spectrophotometrically at a few specific wave lengths by determining, from rate curves, the optical density at zero time after the pulse.

Fast spectrophotometric measurements were made by monitoring, with a 1P28 photomultiplier tube, the light from an Osram mercury lamp, type HBO 107/1 at specific wave lengths. A 1-mm. slit was placed in front of the multiplier tube. The direct coupled current amplifier used has a rise-time of less than 0.2 μsec. The circuit was checked for linearity of response.[19] Rate curves were enlarged 5-fold for numerical analysis by tracing, on graph paper, the projected image of the curve originally photographed from the oscilloscope screen.

Materials.—The water and the deuterium oxide used in this work were both triply distilled.[23] The deuterium oxide had an isotopic purity of 99.5% as determined by infrared analysis. The ethanol was reagent grade obtained from U. S. Industrial Chemicals Co., and was used without further purification. Ethanol-*d*, C_2H_5OD, was obtained from Merck and Co. (Montreal). Infrared analysis failed to show any hydroxyl hydrogen, indicating a content of less than 0.1%. 2,3-Butanediol was obtained from K and K laboratories. The acetaldehyde used was Eastman Kodak Co. analytical grade.

Ethanol samples for irradiation were degassed on a vacuum system by conventional pumping and freezing techniques with intermittent shaking of the liquid during pumping. In the process of degassing, approximately 5 cc. of an original liquid volume of 55 cc. was usually evaporated. Aqueous ethanol solutions were prepared by pipetting into a side-arm an appropriate amount of ethanol which was frozen at −195° while the water was being degassed. After the water was degassed, the ethanol was distilled into the main bulb to make up the solution. In all cases the cells were sealed off to avoid any contact with grease.

Analytical.—Analyses for reaction products in irradiated ethanol were carried out as follows. 2,3-Butanediol was determined in a Barber–Colman gas chromatograph using a flame ionization detector. A 5-ft. column of $^3/_{16}$ in. stainless steel packed with 7% didecyl phthalate on Haloport was used. The column temperature was 150° and the hydrogen flow rate was 12 ml./min. Under these conditions the retention time for 2,3-butanediol was $8^2/_3$ min. The irradiated sample was compared with a calibration curve obtained from standard samples in precisely the same concentration range, which was 10^{-3} *M*. The 2,3-butanediol could be identified uniquely since 1,4-butanediol showed a retention time of 19 min., and 1,3-butanediol showed a retention time of $15^2/_3$ min. Tests of the Raman spectrum and the freezing point of the standard 2,3-butanediol indicated that it probably consisted of the *d,l*-form, but may have contained some of the *meso*-form. The sample gave a single peak on the chromatograph.

The acetaldehyde produced in the ethanol was determined polarographically using a solution made up of 1 part of the ethanol sample to 9 parts of 0.1 *M* lithium hydroxide. Oxygen was not removed from the sample. The half-wave potential was −1.95 v. *versus* the saturated calomel electrode. The polarographic step-heights were compared with a number of standard acetaldehyde solutions made up volumetrically by pipetting at reduced temperature to avoid evaporation of the acetaldehyde.

Acetaldehyde in the aqueous ethanol solutions was determined colorimetrically using the dinitrophenylhydrazone technique.[24] The unknown sample was compared against a linear calibration curve by reading the optical density at 430 mμ each time at 9 min. after the reagent was added. The standard solution was made up volumetrically.

2,3-Butanediol in the aqueous system was determined by oxidation to acetaldehyde with periodate. The procedure was that given by Weiss[14] except that one-tenth the quantity of reagents suggested was used. The distillate was then diluted to 100 ml. and the acetaldehyde determined by the above method. This technique was checked with a standard solution containing ethanol and hydrogen peroxide in small amounts and gave a 10% high value.

The hydrogen product obtained in the isotopic experiments in aqueous solution was separated by means of a toepler pump. The amount was determined by pressure measurement with a McLeod gauge and was then analyzed mass spectrometrically.

Results and Discussion

The results obtained in both deaerated liquid ethanol and in deaerated neutral aqueous ethanol solutions consist of: (a) ultraviolet absorption spectra of the transient species, (b) rate curves for the disappearance of these transients, (c) radiolysis yields of some of the products and (d) isotopic data for hydrogen formation, principally in aqueous solution. A pulse intensity of approximately 1.9×10^{19} e.v./pulse in an irradiated volume of 13 cc. was used in most experiments. In these systems this produces an instantaneous total free radical concentration of approximately 10^{-4} *M*. This concentration is very much greater than the steady-state concentration produced in steady radiolyses.

Spectrophotographic.—The transient absorption spectrum observed in pure ethanol 5 μsec. after the pulse is shown in Fig. 1(a). It consists of a broad, weak absorption with a maximum at approximately 290 mμ, increasing to shorter wave lengths where two narrower peaks at 266 and 257 mμ are resolved. A further increase continues to the limit of our observations, at approximately 250 mμ. There is considerable uncertainty in the exact location of the weak maximum at 290 mμ, and particularly in the long-wave-length limit of the spectrum, the curve shown being an average of several determinations.

The transient absorption spectrum observed in 0.1 *M* aqueous ethanol solution, as well as in more dilute solutions, 5 μsec. after the pulse is shown in Fig. 1(b). It shows a similar broad absorption at approximately 290 mμ which is somewhat less well resolved than the spectrum in pure ethanol. The absorption increases to shorter

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wave lengths where three narrow peaks are resolved at 266, 257 and 247 mμ. The difference in over-all optical density between the curves in Fig. 1 is the result of a higher concentration of the transient in ethanol where the radical yield is somewhat higher than in aqueous solution.

The general similarity of the two spectra and the almost precise correspondence of the narrow peaks and minima can leave little doubt that the same reactive transient is being observed in both systems. In ethanol, where the transients may be formed by direct electron impact, a number of different species are possible. In aqueous solution, a specific assignment is more easily arrived at. The identical nature of the spectra in the two systems is an important observation in making this assignment.

Isotopic Data.—In aqueous solution the transient ethanol species is produced by the interaction of the ethanol with the hydroxyl radical from the water and with a hydrogen atom (in whatever forms it may exist in neutral solution). Indications from e.s.r. studies[6,7,25] and from consideration of the radiolysis products[14,15] are that the hydroxyl radical abstracts hydrogen from the α-carbon atom. Information about the locus of attack by the hydrogen atom has been obtained in simple isotopic experiments with C_2H_5OD in D_2O, similar to those reported[26] for methanol in D_2O. There are two objectives to these experiments. The first is to establish where the abstraction takes place in neutral solution. The second is to determine the radiolysis yield for hydrogen atoms which abstract (represented in this case by HD) as distinct from the total, some of which may react by recombination with themselves and more likely with the organic free radical at the very high dose rates of these experiments. This information is required for a determination of the concentration of the transient species produced.

Table I shows the isotopic distribution of the hydrogen obtained in neutral solution using a pulse intensity of 1×10^{19} e.v./pulse. The G-values, determined at a pulse intensity of 1.9×10^{19} e.v./pulse and a concentration of 0.1 M, are

$$G(\text{HD}) = 1.1 \text{ molec./100 e.v.}$$
$$G(D_2) = 0.43 \text{ molec./100 e.v.}$$

TABLE I

ISOTOPIC DISTRIBUTION OF THE HYDROGEN FORMED IN THE RADIOLYSIS OF C_2H_5OD IN NEUTRAL D_2O SOLUTION

Ethanol concn., m	Hydrogen, %			
	H_2	HD	D_2	HD/D_2
5×10^{-3}	1.2	45.0	53.8	0.84
4×10^{-2}	2.5	65.3	32.1	2.0
5×10^{-2}	3.1	65.1	31.8	2.0
7×10^{-2}	3.1	70.2	26.8	2.6
1×10^{-1}	3.7	70.0	26.3	2.7

The data show that the abstraction is virtually exclusively from the alkyl group and not from the hydroxyl group since the mixed isotopic molecule predominates, and more particularly since the observed $G(D_2)$ is only slightly in excess of the molecular yield.[18,27,28] This conclusion is in agreement with recent work of Riesz and Burr[18] and with the more detailed observations of Lifshitz and Stein[17] which also show that >90% of the abstraction by hydrogen atoms is from the α-carbon atom.

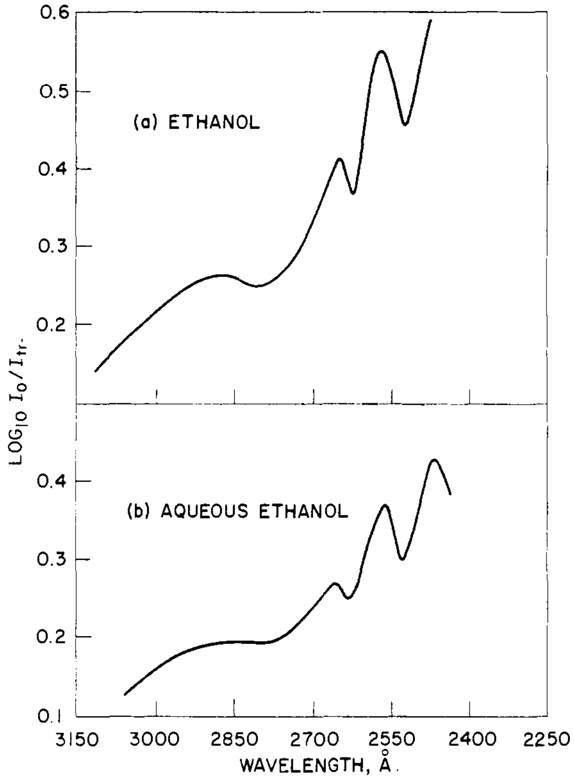

Fig. 1.—Absorption spectra of the transient species obtained 5 μsec. after the electron pulse: (a), deaerated ethanol; (b) deaerated aqueous ethanol solution.

Liquid ethanol-*d*, C_2H_5OD, has also been irradiated. The observed isotopic distribution of H_2 = 40.8%, HD = 56.2% and D_2 = 3.1% is in approximate agreement with the data of Burr.[11] But the interpretation[11] that the HD is formed by hydrogen abstraction from the hydroxyl group is not consistent with the foregoing observations in heavy water solution. Rather, it appears that the HD must be formed by molecular detachment and/or primary detachment of the hydroxyl deuterium atom followed by abstraction from the α-carbon atom as has been suggested.[9]

Product Yields.—In addition to hydrogen, the major products observed in both systems are 2,3-butanediol and acetaldehyde.

In 0.1 M aqueous ethanol solution irradiated with a total dose of 5.8×10^{20} e.v., the observed yields were

$$G(\text{2,3-butanediol}) = 1.33 \text{ molec./100 e.v.}$$
$$G(\text{acetaldehyde}) = 0.33 \text{ molec./100 e.v.}$$

The error limit in both these yields may be as high as 10%. The acetaldehyde yield is in close agreement with the value of Jayson, *et al.*,[14] in

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neutral solution. Assuming the acetaldehyde to be formed by disproportionation of α-ethanol radicals, the material balance may be written in the form

$$G_{\mathrm{OH}} + G^{\mathrm{S}}_{\mathrm{OH}} + G(\mathrm{HD}) = 2G(\text{butanediol}) + 2G(\text{acetaldehyde}) + G^{\mathrm{R}}(\text{ethanol}) \quad \text{(I)}$$

The terms on the left-hand side of eq. I represent the yields of the species which are the precursors of the α-ethanol radical; $G^{\mathrm{S}}_{\mathrm{OH}}$ is the yield of hydroxyl radicals within the spurs, included in this summation in view of two recent observations. The first[17] is that ethanol reacts 1.7 times as effectively with the hydroxyl radical as does the bromide ion. The second[29,30] shows that the scavenging action of bromide ion is efficient enough that scavenging of hydroxyl radicals occurs within the spurs. Taken together the data indicate that the scavenging of hydroxyl radicals within the spurs by ethanol at a concentration of 0.1 *M* may be very nearly complete. $G(\mathrm{HD})$ is the observed yield of deuterium hydride in our irradiations in heavy water solutions, discussed in the previous section.

The terms on the right-hand side of eq. I represent the sum of the yields of products formed from the organic free-radical; G^{R}(ethanol) is the yield of ethanol formed by association of an α-ethanol radical with a hydrogen atom. There are two independent observations which confirm the approximate magnitude of this yield.

Substituting our experimental yields in eq. I, and taking[31] $G_{\mathrm{OH}} = 2.4$ and $G^{\mathrm{S}}_{\mathrm{OH}} = 2G_{\mathrm{H_2O_2}} = 1.4$, we may estimate G^{R}(ethanol) = 1.6 molec./100 e.v. Assuming the observed hydrogen deficiency in these high intensity experiments to be due to recombination with the organic free radicals, we may also estimate this quantity from the relation $G^{\mathrm{R}}(\text{ethanol}) = G_{\mathrm{H}} - G(\mathrm{HD})$. Taking[33] $G_{\mathrm{H}} = 2.9$, we obtain G^{R}(ethanol) = 1.8 molec./100 e.v., in quite good agreement. The second observation providing quantitative support for this interpretation is obtained in the fast kinetic measurements and is presented in a subsequent section.

In liquid ethanol irradiation with a total dose of 3.6×10^{21} e.v., the observed yields were: G(2,3-butanediol) = 1.27 molec./100 e.v., G(acetaldehyde) = 1.88 molec./100 e.v. The error limit in both of these G-values is approximately 10%. The literature[8,9,32] shows considerable variation in these yields, and it has been variously suggested that trace impurities may have an important effect.

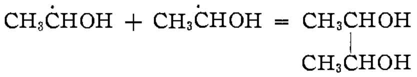
Spectral Assignment.—It is concluded from the over-all evidence that the transient spectra observed in irradiated ethanol and in irradiated aqueous ethanol solution are to be assigned to the α-ethanol radical, $\mathrm{CH_3\dot{C}HOH}$. This assignment for the aqueous system is based on the following observations: (1) E.s.r. spectra obtained by photolyzing hydrogen peroxide in a rigid matrix of various alcohols[6,7] show that in general abstraction by hydroxyl radical occurs at the α-carbon atom

$$\mathrm{OH + CH_3CH_2OH = CH_3\dot{C}HOH + H_2O} \quad (1)$$

(2) Isotopic data[14] relative to hydrogen formation in aqueous ethanol solution show that the hydrogen atom abstracts at the α-carbon atom

$$\mathrm{H + CH_3CH_2OH = CH_3\dot{C}HOH + H_2} \quad (2)$$

(3) The major product in aqueous ethanol solution is 2,3-butanediol with an observed yield in the present investigation of 1.33 molec./100 e.v. It is presumably formed in the association reaction



$$\mathrm{CH_3\dot{C}HOH + CH_3\dot{C}HOH = \begin{array}{l} CH_3CHOH \\ \quad | \\ CH_3CHOH \end{array}} \quad (3)$$

The kinetic data, as will be seen, show that the disappearance of the transient does indeed follow a second-order rate law.

In liquid ethanol, although the mode of formation of the observed transient is by no means understood, the following considerations lead to the same assignment: (4) The e.s.r. spectrum[3,4] obtained in irradiated solid ethanol at 77°K. is that of the α-ethanol radical. (5) 2,3-Butanediol is a major product in irradiated liquid ethanol where the decay of the transient is also found to follow a second-order rate law with a half-life comparable to that in aqueous solution. (6) Finally, and most important, the very close correspondence of the spectrum in ethanol with that in aqueous solution where the assignment is rather more clearly made indicates that the observed transient in ethanol is also the α-ethanol radical.

Kinetics.—The decay of the transient immediately after the electron pulse was observed by fast photoelectric spectrophotometry. Attempts to observe the formation rate curve of the transient in water as had been done in the case of the hydroxycyclohexadienyl radical,[19] were unsuccessful because of the experimental restrictions imposed by the low extinction coefficient of the transient; but the indication was that the rate constant for reaction 1 must be considerably in excess of 10^8 M^{-1} sec.$^{-1}$.

A typical decay curve covering a total time of 50 μsec., in this case in ethanol, is shown in Fig. 2. The U-shaped trace in the lower left is the pulse profile as monitored by the beam sensor. As may be seen, the recording of the decay curve begins directly at the end of the pulse. The optical density could not be monitored during the pulse because of extraneous current induced in the photomultiplier by the γ-ray burst. A large number of such decay curves, at a variety of wave lengths of the more intense mercury lines within the region of absorption of the transient, were obtained both in aqueous solution and in ethanol, mostly covering a time range of 50 and 100 μsec.

A test of the conformity of these rate curves to a second-order rate law may be made by using the integrated form of the bimolecular rate expression

$$-\,\mathrm{d[R]}/\mathrm{d}t = 2k_{\mathrm{b}}[\mathrm{R}]^2 \quad \text{(II)}$$

Expressing [R], the concentration of the transient, in terms of its optical density, the integrated form

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(29) A. O. Allen and R. A. Holroyd, *J. Am. Chem. Soc.*, **77**, 5852 (1955).

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(32) N. A. Bach and J. I. Sorokin, Symposium on Radiation Chem., *Acad. Sci., U.S.S.R.*, Vol. I, p. 135 (1955).

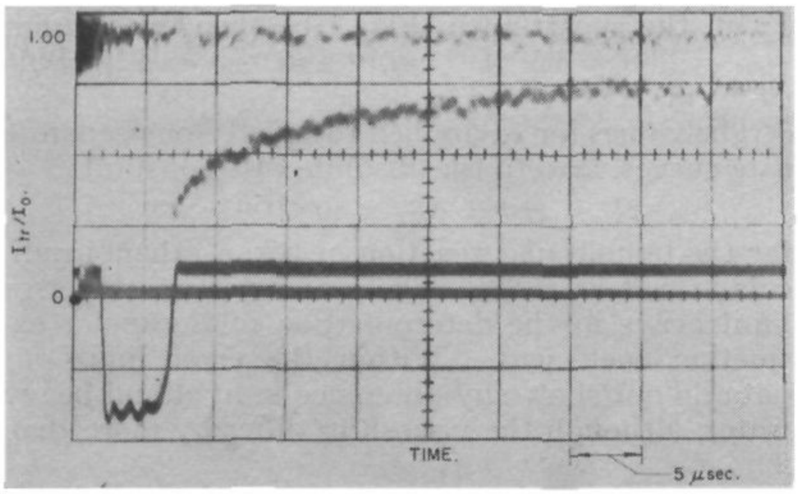

Fig. 2.—Rate curve for the disappearance of the transient in deaerated ethanol. The upper trace defines 100% transmission. The time-profile of the electron pulse is shown in the lower left.

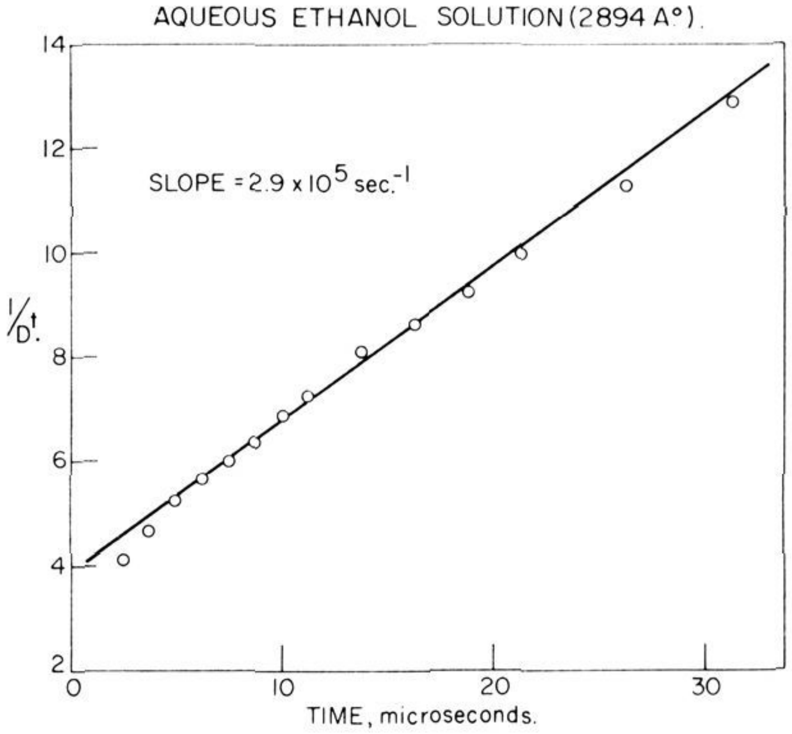

Fig. 3.—Test of second-order rate law for the disappearance of the transient in deaerated aqueous ethanol solution. The 2894 Å. line was used in observing the rate curve. The solvent was deuterium oxide. Zero time in this figure does not correspond precisely with the end of the pulse.

of eq. II reduces to

$$1/\log_{10}(I_0/I_{tr})_t = \left(\frac{2k_b}{\epsilon l}\right)t + 1/\log_{10}(I_0/I_{tr})_{t_0} \qquad (III)$$

where t is the time, ϵ is the molar extinction coefficient of the transient, l is the length of the absorption path of the analyzing light beam, and the rate constant for the bimolecular disappearance is written as $2k_b$. There is no observable permanent absorption in these systems at the wave lengths used in the spectrophotometric measurements.

Figure 3 shows a plot of the reciprocal of the optical density against time for a typical decay curve in aqueous solution. It is clear from this plot that the disappearance of the α-ethanol radical in water closely follows a second-order rate law over most of the observed rate curve. In view of the general considerations which have been discussed, the decay curve in aqueous solution is attributed to the bimolecular reaction of α-ethanol radicals with themselves principally in the association reaction 3 to form 2,3-butanediol, but also to a much lesser extent in the disproportionation reaction to form acetaldehyde. In the short period immediately after the pulse the experimental points clearly deviate from the straight line plot.[33] This deviation is attributed to the reaction

$$CH_3\dot{C}HOH + H = C_2H_5OH \qquad (4)$$

which may be expected to have a higher rate constant than reaction 3. As has been pointed out, comparison of the material balance of the organic products with the hydrogen deficiency in this work quantitatively supports this interpretation. Further confirmation may be obtained in the following way. The optical density at the end of the pulse obtained from the experimental decay curve in Fig. 2 represents the total number of radicals present which disappear in reaction 4 as well as by reaction with themselves. On the other hand, the optical density representing only those radicals which disappear by reaction with themselves may be obtained by extrapolation of the straight-line plots, as in Fig. 3, to the end of the pulse. The ratio of this number to the total number is found from these optical densities to be 0.6. The material balance data and the hydrogen deficiency both lead to ratios in the range of 0.5 to 0.6, again in very satisfactory agreement.

From the slope of the straight line plots typified in Fig. 3, and the value of the molar extinction coefficient, ϵ_λ, at the wave length appropriate for the particular rate curve, the absolute rate constant $2k_b$ may be determined. The data obtained, in both D_2O and H_2O at a number of wave lengths all at 23°, may be summarized by the following values expressed in terms of the molar extinction coefficients

$$\begin{array}{ll} D_2O & 2k_b = (4.6 \pm 0.2) \times 10^6\,\epsilon_{2967}\ M^{-1}\ \mathrm{sec.}^{-1} \\ & 2k_b = (4.8 \pm 0.5) \times 10^6\,\epsilon_{2894} \\ H_2O & 2k_b = (4.6 \pm 0.2) \times 10\epsilon\ \mathrm{S}_{3020} \\ & 2k_b = (5.7 \pm 1.1) \times 10^6\,\epsilon_{2967} \\ & 2k_b = (4.2 \pm 0.5) \times 10^6\,\epsilon_{2894} \end{array}$$

The rate curves in heavy water were determined in conjunction with the isotopic experiments and not because of any intrinsic interest in comparing the rate constants in light and heavy water.

The molar extinction coefficient may be estimated from the rate curves and the product yields in two separate ways. The initial concentration of the α-ethanol radicals which react only with themselves may be determined from the sum of the yields of 2,3-butanediol and acetaldehyde. The quantity $G^S{}_{OH} = 1.4$ has been subtracted from these yields on the assumption that the α-ethanol radicals formed by scavenging within the spurs will also react within the spurs in a time considerably shorter than 1 μsec. to form a correspondingmo lecular

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(33) ADDED IN PROOF.—Additional experiments in acidic solution (0.8N H_2SO_4), where the hydrated electron is converted to a hydrogen atom, show that this short initial deviation is completely eliminated and a precise second-order fit obtained. This short deviation is therefore associated with the hydrated electron, either through a contribution to the optical density or through a kinetic contribution in the analogous reaction

$$CH_3\dot{C}HCH + e^-{}_{aq} = C_2H_5CH + OH^- \qquad (4a)$$

The second order fit in acidic solution, moreover, has the same slope as in neutral solution, confirming the magnitude of the rate constant. These investigations will be reported subsequently.

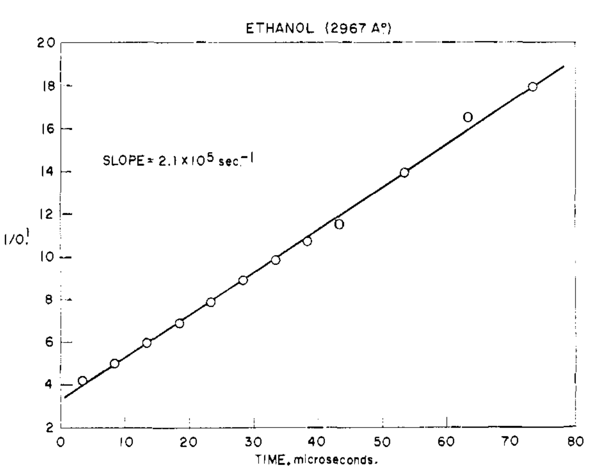

Fig. 4.—Test of second-order rate law for the disappearance of the transient in deaerated ethanol. The 2967 Å. line was used in observing the rate curve. *Zero time in this figure does not correspond precisely with the end of the pulse.*

yield and will not contribute to the optical density observed after the pulse. The optical density corresponding to the radical concentration determined from these product yields is that obtained by extrapolation of the straightline plots, as in Fig. 3, to the end of the pulse. Since this optical density corresponds to the radical concentration at $t = 5$ μsec., a correction has been applied for the disappearance of the radicals during the pulse by reaction with themselves. This correction involves our own measured value of $2k_b$ and hence requires the use of successive approximations in calculating the concentration at $t = 5$ μsec. The simplest calculation assumes instantaneous formation by reactions 1 and 2 and therefore gives a lower limit of $\epsilon_{2967} \geq 212\ M^{-1}$ cm.$^{-1}$. A more precise correction for the period of the pulse involves an expression for the concentration of the radical at $t = 5$ μsec. and does not assume formation by reaction 2 to be instantaneous. The rate constant for reaction 2 is not precisely known, but tests of the expression over a considerable range of values show a variation of only $\pm 10\%$ in the corrected radical concentration. The value estimated by this calculation is $\epsilon_{2967} = 245\ M^{-1}$ cm.$^{-1}$, and the considerations of initial optical density and material balance which have been discussed suggest this is probably an upper limit.

The molar extinction coefficient may also be estimated from the initial observable radical concentration determined from the sum of the yields of the precursors, $G_{\mathrm{OH}} + G(\mathrm{HD})$. The optical density corresponding to this concentration is that obtained from the initial absorption in the rate curves, as in Fig. 2, at the end of the pulse. From these data, assuming instantaneous formation and correcting for radical disappearance to $t = 5$ μsec. by reaction 3, a lower limit of $\epsilon_{2967} \geq 216\ M^{-1}$ cm.$^{-1}$ is obtained, in agreement with the value calculated from product yields.

From all the data the best value for the molar extinction coefficient of the α-ethanol radical in water is estimated to be $\epsilon_{2967} = 230 \pm 55\ M^{-1}$cm.$^{-1}$. From the spectrum in Fig. 1(b) then, we obtain: $\epsilon_{2894} = 260 \pm 65\ M^{-1}$ cm.$^{-1}$ and $\epsilon_{3020} = 210 \pm 53\ M^{-1}$ cm.$^{-1}$.

The values for ϵ_λ, applied to twenty-one separate rate curves, lead to the absolute rate constant

$$2k_b = (1.1 \pm 0.3) \times 10^9\ M^{-1}\ \text{sec.}^{-1}$$

for the bimolecular reaction of two α-ethanol radicals in water at 23°. The major part of the error limit arises in the determination of the molar extinction coefficient. Within the error limit our data do not show any difference in light and heavy water, although the viscosities differ by more than 20%.

The product yields in aqueous solution indicate that most of this disappearance is by association, reaction 3. If we assume that the lesser yield of acetaldehyde is due to disproportionation

$$\mathrm{CH_3CHOH + CH_3CHOH = CH_3CHO + C_2H_5OH} \quad (5)$$

the individual rate constants for association and disproportionation are indicated to be

$$2k_3 = (8.8 \pm 2.1) \times 10^8\ M^{-1}\ \text{sec.}^{-1}$$

and

$$2k_5 = (2.2 \pm 0.5) \times 10^8\ M^{-1}\ \text{sec.}^{-1}$$

Comparison of the value of $2k_b$ with estimates from diffusion theory[34,35] suggests that the reaction of two α-ethanol radicals in water occurs at a rate limited by diffusion. Alternatively, the theory may be tested by using the experimental value and assuming unity encounter efficiency.

In ethanol the disappearance of the α-ethanol radical closely fits a second-order rate law as may be seen from Fig. 4. The absolute rate constant for the bimolecular reaction at 23°, expressed in terms of ϵ'_{2967}, the molar extinction coefficient at 2967 Å. of the α-ethanol radical in ethanol, is

$$2k_b = (3.3 \pm 0.2) \times 10^6\ \epsilon'_{2967}\ M^{-1}\ \text{sec.}^{-1}$$

The following two considerations suggest that the molar extinction coefficient in ethanol may not be identical with that in water. First, if the assumption $\epsilon'_{2967} = \epsilon_{2967}$ is made, the absolute rate constant in ethanol turns out to be $2k_b = (7.5 \pm 0.5) \times 10^8$ M^{-1} sec.$^{-1}$, which seems surprisingly low compared with the value in water, in view of the fact that the estimated diffusion coefficients in the two media differ by only a few per cent. Second, if the assumption $\epsilon'_{2967} = \epsilon_{2967}$ is used to estimate the radiation chemical yield of the α-ethanol radical in ethanol, the value $G(\mathrm{CH_3\dot{C}HOH}) \cong 9$ molec./100 e.v. is obtained. Such a high value leads to a very serious material balance discrepancy with the products. The indications suggest that $\epsilon'_{2967} > \epsilon_{2967}$ by perhaps 30–40%.

A formation rate curve in ethanol was not observed. This indicates that the various precursors of the α-ethanol radical, such as the ethoxy radical or ionic species,[9] have lifetimes in ethanol which are too short for kinetic studies with our time resolution.

It is of interest to point out that the observations of Johnsen[13] which suggest the photochemical decomposition of a trapped transient species in irradiated solid ethanol, may be clearly understood

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in view of the absorption spectrum in Fig. 1(a). The α-ethanol radical shows a strong absorption at the 2537 Å. line of the mercury spectrum.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER, N. Y.]

Excitation Functions of the (p,pn) and (p,2p) Reactions on Te^{130} at 60–233 Mev.[1a]

BY DEAN W. MAURER[1b] AND EDWIN O. WIIG

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The cross sections of the reactions $Te^{130}(p,pn)Te^{129m}$, $Te^{130}(p,pn)Te^{129g}$ and $Te^{130}(p,2p)Sb^{129}$ have been determined for protons of 60, 120, 180 and 233 Mev. energy. The observed yields of Te^{129} and Sb^{129} are compared with those predicted by interpolation of Monte Carlo cascade calculations on Ru^{100} and Ce^{140} at 83, 238 and 368 Mev. followed by evaporation calculations based on data for Ce^{142}. There is good agreement in shape and absolute magnitude for the (p,pn) excitation function but poor agreement for the (p,2p) reaction. In the (p,pn) reaction the low-spin Te^{129g} isomer is found to be favored over high-spin Te^{129m}, in agreement with the predictions of Häller and Rudstam.

Introduction

The general shape of the excitation function for a given, simple spallation reaction brought about by moderate and high energy protons, results from the linear addition of the yields of the individual reaction steps which give rise to this product. The relative weight or importance of each reaction step and how this changes with the energy of the incoming particle depends upon various nuclear parameters such as the shape of the nuclear potential well, the distribution and density of nucleons in the nucleus, the interaction of the particles, etc. Recent Monte Carlo calculations[2] of the fast cascade phase of such reactions based on a crude model of the nucleus have made possible an estimation of the weight and variation with energy of the individual reaction steps. By comparing the resulting net excitation function for simple reactions, *i.e.*, those involving the loss of only a few nucleons, with experimental results, a much clearer picture of the reaction may be obtained. Furthermore, deviations from the experimental results may indicate changes to be made in the nuclear model.

An investigation of the (p,pn) and (p,2p) reactions on Te^{130} was undertaken to add to the meager data available[3,4] in the intermediate mass range for comparison of cross sections of such reactions with cross sections obtained from Monte Carlo and evaporation calculations. This region is of special interest since the only agreement in absolute value for the (p,pn) cross section was obtained here by Ware and Wiig[4] on Ce^{140}. Natural tellurium was used, since Te^{129} and Sb^{129} can arise only from the heaviest isotope, Te^{130}.

Experimental

Tellurium[5] in the form of metal powder was bombarded in the internal beam of the University of Rochester 130-inch synchrocyclotron. The targets, as described earlier,[6] were prepared by packing 75–100 mg. of Te powder into a 5 × 20 × 1 mm. box made of 0.75 mil high purity aluminum foil. Two 0.75-mil aluminum foils were placed in front and two in back of the target envelope to serve as monitors of the beam by the known cross section of the Al^{27} (p,3pn) Na^{24} reaction.[7] Only the two inner foils were used as monitors since the gain and loss of Na^{24} from these foils would be the same.

All irradiations were carried out for 1 hour after which the monitor foils were separated from the target and reserved for Na^{24} determination. In general, the tellurium target was dissolved in HCl and HNO_3 and a known amount of antimony carrier was added. The solution was boiled to dryness several times to expel HNO_3 and finally diluted to 100 ml. with 3 *N* HCl. A 25-ml. aliquot was taken and the remainder of the solution saved to determine the target weight. Holdback carriers of tin, cadmium, indium and palladium were added and tellurium precipitated with SO_2. The tellurium was purified by standard techniques, mounted as the metal and counted. The antimony, which had remained in solution, was then precipitated with H_2S, purified, mounted as the metal, and counted.

All the samples were counted on a methane-flow beta proportional counter. The decay was followed for a period of 12 to 18 months. Owing to the many isotopes of tellurium and antimony produced, the decay curves were quite complex. The routine resolution of these curves was done by the method of Perkel[8] after the composition has been determined by normal procedures. This method required the calculation of a large number of exponential terms. To facilitate the work an IBM-650 computer was programmed to do the tedious part of the calculation. The method allows one to resolve the 34-day isomer of Te^{129} from the tail of the decay curve, the 72-min. isomer from all the other activities and 4.6-hr. Sb^{129} from all the other antimony activities.

The aluminum monitor foils were counted directly on the proportional counter to determine Na^{24}. Resolution of the resulting decay curves was quite simple.

After the counting samples had decayed sufficiently and the decay curves had been analyzed, the samples were dissolved and analyzed spectrophotometrically to determine the chemical yield. The antimony was determined by the

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[1] (a) The investigation was supported in part by the U. S. Atomic Energy Commission. This report is based on a thesis submitted by Dean W. Maurer in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Rochester, 1959. (b) Bell Telephone Laboratories, Incorporated, Murray Hill, N. J.

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