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SOLVATED ELECTRON IN ETHANOL AND METHANOL

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Pulse Radiolysis Studies of the Reactivity of the Solvated Electron in Ethanol and Methanol

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By means of the pulse radiolysis technique a short-lived transient species has been observed in irradiated de-aerated ethanol and methanol, exhibiting an optical absorption throughout the visible and near infra-red. This transient is suggested to be the solvated electron on the basis of the nature of the spectrum, the reactivity with hydrogen ion and with various organic electron acceptors, and the formation of mononegative ions of some of these acceptors.

The absolute rate constants have been determined for the reactions of the solvated electron with hydrogen ion, oxygen and benzyl chloride in ethanol and methanol. The diphenylide ion was found to be short-lived in ethanol. The absolute rate constant for the first-order decay of the diphenylide ion has been determined.

The theoretical considerations of electron solvation in polar liquids such as ammonia¹ and water² apply to other polar liquids. Thus in ethanol and methanol, for which the values of the static dielectric constant at room temperature are 25 and 33 respectively³ (large compared to unity) one may expect *a priori* that the physical process of electron solvation will take place. Measurements of the dielectric dispersion in these alcohols,⁴ which indicate that both liquids have a relatively high atomic polarization, as does water, lead to this conjecture.

The natural lifetime of the solvated electron, if solvation does occur, will then be determined largely by the specific rate of removal of the electron in chemical reactions with the solvent. The rates of these reactions with the solvent may vary widely from one liquid to another, as is evident from a comparison of the natural lifetime of the solvated electron in ammonia⁵ and in water.⁶ If this lifetime is sufficiently long the species may be amenable to direct observation.

Some evidence for electron solvation in organic glasses,⁷ consisting of compounds having lower dielectric constants than the alcohols, has been obtained in flash photochemical experiments with solutions of the alkali metals. These experiments have been extended to the liquid state.⁸ Observation of an optical absorption and formation of mononegative ions of solute molecules in γ -irradiated organic glasses,⁹ including ethanol, has been presented as evidence for electron solvation.

The possible role of electron solvation in the radiation chemistry of liquid ethanol has been discussed,¹⁰ and a mechanism involving negative polarons has been suggested. Recently, experimental evidence¹¹ indicating that the solvated electron is a precursor of hydrogen in the radiolysis of methanol, has been obtained by the use of scavengers which are effective electron acceptors.

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The present paper is concerned with the application of the pulse radiolysis technique^{12, 13} to this question in the case of liquid ethanol and methanol. The primary objective has been the determination, by this fast reaction method, of the specific reactivity of an observed transient which, from its spectral and chemical characteristics is suggested to be the solvated electron.

EXPERIMENTAL

The technical details of the pulse radiolysis method have already been presented.¹³ Some additional details are given in the later reports^{14, 6} on ethanol and aqueous ethanol solutions. Only the briefest description will be presented here, along with those experimental conditions which are unique to the present investigation.

PULSE IRRADIATION

A 15 MeV electron beam from the linac was used throughout. In the spectrophotographic experiments a 5 μ sec pulse was used. In the spectrophotometric experiments, in which some of the rate curves had a total duration of 2 μ sec or less, a 0.4 μ sec pulse was used. The pulse currents were in the range 40-150 mA. A 0.4 μ sec pulse at 100 mA delivers a dose of approximately 1.4×10^{17} eV/g. The electron beam had an incident diameter of 16 mm and an emergent diameter of about 18 mm for a 4 cm long cell. The cells used were cylindrical quartz cells as in previous work.

SPECTROPHOTOGRAPHY

The four-fold reflection system with collinear analyzing light beam and electron beam¹³ was used throughout. The Jarrell-Ash 2.25 m grating spectrograph, $f/24$ was used. Eastman-Kodak spectroscopic plates, type 103-F, were used over the region 450-670 m μ . A single flash of the xenon flash lamp was sufficient to produce satisfactory spectra on these plates. Over the region 550-850 m μ , Eastman Kodak spectroscopic plates, type I-N, were used. These plates were sensitized in aqueous ammonia followed by an alcohol wash and air-dried with a blower. Considerable difficulty was encountered in obtaining sensitized plates of uniform density, without blotching. Five flashes of the spectroflash lamp were needed to obtain spectra of satisfactory density with these plates for use on the densitometer.

SPECTROPHOTOMETRY

A 1 P28 photomultiplier tube was used to monitor the light from the steady lamp, which was an Osram mercury lamp, type HBO 107/1. The visible absorption was usually monitored at 5461 Å, although a few runs were also done at 5770-5790 Å. Since the absorption is extremely broad, a 5 mm aperture in front of the photomultiplier was used, giving a band width of 75 Å.

MATERIALS

The ethanol was U.S.I. Absolute Pure Ethyl Alcohol, U.S.P.-N.F. Reagent Quality, obtained from U.S. Industrial Chemicals Co. The methanol was Anhydrous Methyl Alcohol, Analytical Reagent, obtained from Mallinckrodt Chemical. The methanol was fractionally distilled in the following manner. About 1 l. methanol, to which had been added 1 ml of concentrated sulphuric acid and 4 to 5 g of 2,4-dinitrophenylhydrazine, was placed in the still pot of a Hasteloy B (#1979) Podbielniak still, 8 mm $\times$ 12 in. After refluxing for about 1 h the still was run at maximum take-off rate and the first 110 ml were discarded. The next 500-600 ml were collected and used. This purification was found to be necessary since the distillation substantially increased the half-life of the solvated electron in degassed neutral solution. In the purified methanol, the half-life of the transient

was fully an order of magnitude longer than for the rate curves for reaction with added solutes. The ethanol, in most runs, was used without further purification on the basis of the observed, relatively long, half-life of the transient in neutral solution. Some ethanol was purified with a drying agent prepared from 5 g of magnesium powder, 60 ml of ethanol and 0.5 g of iodine. To this was added 900 ml of ethanol which was then refluxed for 1 h and then distilled. This procedure reportedly reduces the water content to less than 0.02 %. In the one case in which runs were carried out with this purified ethanol there was no difference in the measured rate constant.

Other compounds used in this work were: benzyl chloride, CP Baker's Analyzed Reagent; diphenyl from Matheson Co.; naphthalene, Baker's Analyzed Reagent; anthracene, Scintillation Grade from Reilly Tar and Chemical Corp.

The degassing technique was the same as described previously,⁶ which involved sealing off the cells under vacuum, except for the experiments with oxygen in solution. For the solutions containing oxygen, for which it was necessary to determine the concentration of dissolved oxygen, it was desirable to use a cell having no gaseous volume. Consequently, cells having capillary leads and ground glass caps, adapted from a description of an irradiation syringe,¹⁵ and using the degassing method described there, were used exclusively in the rate studies with oxygen.

The solutions containing oxygen were made up by admitting a known pressure of oxygen to the degassed alcohol maintained at about -78°C . The solution was then brought back to room temperature and the cells, which had previously been flushed with helium were filled by forcing the liquid from the degassing bulb¹⁵ into the cells under helium pressure. These cells had no gaseous volume, being filled entirely with the alcohol solution.

Acidified alcohol solutions, which were used in determining the rate of reaction of the solvated electron with the hydrogen ion, were made up from HCl and H_2SO_4 in the following manner. Anhydrous HCl was bubbled through ethanol for about 15 min and through methanol for about 5 min to make up stock solutions which were roughly 1-2 M. Solutions were then made up by micro-pipetting from this stock solution to give solutions in the concentration range 10^{-4} - 10^{-5} M. Sulphuric acid stock solutions were made up from a weighed quantity of concentrated acid. There was thus an uncertainty of a few percent in the sulphuric acid content. The solutions for kinetic studies were similarly made up by micro-pipetting from the stock solution. In all cases, appropriate corrections were applied to the degassed solutions for volume loss during degassing.

The benzyl chloride stock solutions were made up both gravimetrically and volumetrically. In calculating the concentration of benzyl chloride in the dilute solutions the volume correction for solvent loss in degassing was taken into account.

ANALYTICAL

The oxygen content of the oxygenated solutions was determined by extraction of the gas from the alcohol in a vacuum system, followed by analysis on a gas chromatograph. The oxygen and dissolved helium were removed by means of a Toepler pump and forced into a U-tube between two stopcocks. This gas was then analyzed chromatographically on a column packed with molecular sieve 13X which separated oxygen and nitrogen. The amount of nitrogen was an indication of the extent of air leakage into the cell. This generally amounted to less than 5×10^{-6} M O_2 . In several runs, duplicate cells were filled and the oxygen concentration determined both before and after a run.

The acid content of the stock solutions was determined by diluting the stock solution 100-fold in water (the resulting aqueous solution being roughly 2×10^{-2} M) and determining the pH with a Radiometer model 4 pH meter.

RESULTS AND DISCUSSION

The experimental observations which have been carried out at the time of preparation of this paper include the spectrophotographic recording of the transient

spectrum in deaerated ethanol and methanol, the determination of the absolute rate constants for the reactions of the transient with hydrogen ion, oxygen and benzyl chloride in both alcohols, and an investigation of the reactions in solutions containing electron acceptors such as naphthalene and diphenyl. In the last system, these studies involve not only the primary transient but also observation of transient species formed from the solute molecules.

SPECTRUM

Spectrophotographic observations made during, and within 2 or 3 μsec after a 5 μsec electron pulse (current ~ 80 mA) show a transient optical absorption in deaerated ethanol extending from about 350 $m\mu$ to our long-wavelength limit of observation at about 860 $m\mu$. The spectrum shows a broad peak at about 696 $m\mu$ with a shoulder at about 520 $m\mu$ as determined from densitometer tracings. The location of these maxima must be regarded as approximate since "H and D" corrections have not been applied to the plates. Moreover, the peak is not at all sharp and the most obvious feature of the spectrum is the absence of any pronounced structure. Deaerated methanol also shows a strong absorption in the visible, but the location of any maximum has not yet been established.

The half-life of the transient in deaerated neutral ethanol following a 0.4 μsec pulse at 110 mA (which corresponds to 1.5×10^{17} eV/g) is approximately 3 μsec . The decay curve under these conditions is shown in fig. 1. This curve undoubtedly contains a contribution from the reaction with the counter-ion. The lifetime in basic solution is considerably longer, as indicated in a single experiment, but a complete investigation of the natural lifetime in strongly basic solution, such as we have reported for the hydrated electron,⁶ has yet to be carried out. From the rate curves we estimate the product of the molar extinction coefficient at 5461 Å and the G -value, $\epsilon G_{e_{\text{sol}}}$. These estimates give:

ethanol	$\epsilon G_{e_{\text{sol}}} = 1 \text{ to } 1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \text{ mol./100 eV}$
methanol	$\epsilon G_{e_{\text{sol}}} = 0.8 \text{ to } 1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \text{ mol./100 eV}$

In the absence of information on $G_{e_{\text{sol}}}$ we are unable to estimate the oscillator strength.

The region of the absorption spectrum and the maximum at about 696 $m\mu$ are very similar to the absorption spectrum of the hydrated electron in water.^{16, 17} The transient absorption is eliminated in acidic alcohol solutions. Moreover, the specific reactivities of the transient with hydrogen ion and with oxygen are nearly identical to the reactivities of the hydrated electron^{6, 18} with these stable species. The transient reacts rapidly with electron acceptors such as benzyl chloride, naphthalene and diphenyl. For diphenyl, which has been studied in detail, the product has been identified as the mononegative ion. These observations indicate that the transient is the solvated electron, e_{sol} .

RATE CONSTANTS

The absolute rate constants which have been determined are shown in table 1. In all cases, the rate curves have been observed at a concentration of the added reactant such that the decay rate of the electron is fully an order of magnitude faster than in the absence of the reactant, and is furthermore pseudo-first-order.

TABLE 1.—ABSOLUTE RATE CONSTANTS FOR REACTIONS OF THE SOLVATED ELECTRON IN ETHANOL AND METHANOL AT 23°C

reaction	solvent	rate constant, $M^{-1} \text{ sec}^{-1} \times 10^{10}$
$e_{\text{sol}} + H^+_{\text{sol}}$	C_2H_5OH	2.1 ± 0.4
$e_{\text{sol}} + O_2$	C_2H_5OH	2.0 ± 0.3
$e_{\text{sol}} + C_6H_5CH_2Cl$	C_2H_5OH	0.53 ± 0.13
$e_{\text{sol}} + H^+_{\text{sol}}$	CH_3OH	3.7 ± 1.0
$e_{\text{sol}} + O_2$	CH_3OH	2.1 ± 0.4
$e_{\text{sol}} + C_6H_5CH_2Cl$	CH_3OH	0.57 ± 0.12

The reaction of the solvated electron in ethanol with oxygen,

has been determined over a concentration range of oxygen from 4×10^{-5} to 11×10^{-5} M. The initial electron concentration was varied 2-fold. Typical decay curves are shown in fig. 2 and fig. 3 for the reaction in ethanol. A typical first-order rate law test of such rate curves is shown in fig. 4 in which is presented a plot of the logarithm of the optical density as a function of time. This is a representation of

$$\log_{10} D' = k't/2.303,$$

the integrated form of the pseudo first-order differential rate expression, where $D' = \log_{10} (I_0/I_t)$ and k' is the pseudo first-order rate constant. The results give rate constants of $(2.0 \pm 0.3) \times 10^{10} M^{-1} \text{ sec}^{-1}$ and $(2.1 \pm 0.4) \times 10^{10} M^{-1} \text{ sec}^{-1}$ at 25°C for the reactions in ethanol and methanol respectively. The slightly larger error limit with methanol stems largely from the fact that only three separate determinations were made compared with ten with the ethanol. These rate constants are essentially the same as that of the hydrated electron with oxygen, for which a value of $1.9 \times 10^{10} M^{-1} \text{ sec}^{-1}$ has been reported.¹⁸

The rate of reaction with hydrogen ion was determined over a concentration range of the hydrogen ion of 0.24×10^{-4} to 1.2×10^{-4} M in ethanol and 0.4×10^{-4} to 1×10^{-4} M in methanol using HCl. A somewhat smaller range was covered using H_2SO_4 . The hydrogen ion concentration in the HCl solutions was calculated on the assumption of complete dissociation¹⁹ of this acid in the alcohols at the low concentrations used. In ethanol the absolute rate constant for reaction of the electron with hydrogen ion is found to be $(2.1 \pm 0.4) \times 10^{10} M^{-1} \text{ sec}^{-1}$. The sulphuric acid solutions, on the assumption of only the first dissociation to H^+ and HSO_4^- , give $(2.2 \pm 0.3) \times 10^{10} M^{-1} \text{ sec}^{-1}$ in agreement with this value. The rate constant for the reaction in methanol was found to be $(3.7 \pm 1.0) \times 10^{10} M^{-1} \text{ sec}^{-1}$. We cannot explain the apparent higher rate constant for the reaction with the hydrogen ion in methanol. A small correction for the contribution by counter-ion, amounting to about 3%, was applied here as well as to the reaction rates with oxygen.

The electron reacts rapidly with benzyl chloride. The rate constants in ethanol and methanol were found to be $(5.3 \pm 1.3) \times 10^9 M^{-1} \text{ sec}^{-1}$ and $(5.7 \pm 1.2) \times 10^9 M^{-1} \text{ sec}^{-1}$, respectively, at 23°C. In these solutions we find the benzyl radical as an intermediate, as established by its transient absorption spectrum, in agreement with previous work.²⁰ The reactions of this transient are under investigation in our laboratory. In solutions of triphenyl chloromethane we similarly find the triphenyl methyl radical.

AROMATIC ANIONS

The transient absorption spectra and kinetics in ethanol solutions of aromatic molecules such as naphthalene, diphenyl and anthracene are being investigated.

The initial objective was to obtain supporting evidence for the identity of the solvated electron through the observation of the mononegative ions of the hydrocarbons, which are presumably formed (as for the diphenylide ion) in the reaction:

The ultra-violet and visible absorption spectra of these mononegative ions are known.^{21, 22} The solvated electron reacts rapidly with these electron acceptors, and with the diphenyl we have identified the diphenylide ion from the peak at 400 m μ and the wide band in the visible showing two peaks at 610 and 635 m μ . This corresponds with the spectrum published,²³ in which peaks are shown at 400, 617 and 637 m μ . As expected, since the electron is the precursor, these transients are eliminated in acid solution.

In the experiments with diphenyl and naphthalene, the simultaneous decay of the absorption at 5461 Å and the formation of a second transient at 3130 Å has been recorded using a double photomultiplier arrangement. Such simultaneous disappearance and appearance curves are shown in fig. 5. The decay curve at 5461 Å contains a contribution from both the solvated electron and the diphenylide ion, the former presumably predominating at low concentration of diphenyl, *ca.* 10⁻⁵ M, with an increasing contribution by the diphenylide ion as the concentration is increased. The formation curve at 3130 Å consists primarily of an absorption of a transient formed from the diphenylide ion, probably by proton capture from the solvent to form a hydrogen adduct. Such a process has been suggested to occur in methanol solution.¹¹ The near identity in the rates of the formation and disappearance curves in fig. 5 clearly establishes the precursor relationship of the transients.

The observation, made both spectrographically and spectrophotometrically at 4047 Å, that the diphenylide ion in ethanol is short-lived is in contrast with the long lifetime of the aromatic anions in solvents such as tetrahydrofuran. This difference in lifetime is attributed to the protonic character of the ethanol. The decay of the diphenylide ion in ethanol is first-order. The rate constant for the reaction, $\text{C}_{12}\text{H}_{10}^- + \text{C}_2\text{H}_5\text{OH}$, determined at diphenyl concentrations greater than 10⁻³ M, was found to be $(4.1 \pm 0.7) \times 10^5 \text{ sec}^{-1}$ at 23°C expressed as a first-order constant. Work on the protonation reactions of other aromatic anions is continuing.

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FIG. 1.—Rate curve for the disappearance of the solvated electron in deaerated pure ethanol at 5461 Å following a 0.4 μsec electron pulse.

FIG. 2—Rate curve for the reaction of the solvated electron with oxygen in ethanol following a 0.4 μsec pulse at 60 mA. The initial oxygen concentration was 4.6×10^{-5} M. The rate curve was obtained at 5461 Å.

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FIG. 4 — Test of first-order rate law for the reaction of the solvated electron with oxygen in ethanol. This is a logarithmic plot of the optical density as a function of time.

FIG. 5 — Simultaneous disappearance and formation curves, following a $0.4 \mu\text{sec}$ pulse, at $5461 \text{ \AA}$ (upper curve) and $3130 \text{ \AA}$ (lower curve) in ethanol solution of diphenyl. The upper curve contains a contribution from both the electron and the diphenylide ion. The lower curve represents a transient formed from the diphenylide ion.

FIG. 3.—Rate curve for the reaction of the solvated electron with oxygen in ethanol. The sweep-rate is 1 μ sec large division. The curve was obtained at 5461 Å. The pulse current is approximately 80 mA.

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