Absorption Spectrum of the Hydrated Electron in Water and in Aqueous Solutions[1]

BY EDWIN J. HART AND J. W. BOAG

A transient absorption band with peak at 7000 Å. has been found in de-aerated water and in various aqueous solutions produced a pulse of 1.8 Mev. electrons. This band is attributed to the hydrated electron. The rate of decay of the absorption and the effect of various anions, cations, and dissolved gases have been studied. Similar absorption spectra produced irradiation have been found in concentrated aqueous solutions of ammonia and of methylamine, which resemble the known absorption spectra of solvated electrons in liquid ammonia or in liquid methylamine.

Introduction

When pure de-aerated water is irradiated with a pulse of 1.8 Mev. electrons, a transient absorption band appears which has a peak near 7000 Å. and a long tail extending through the visible.[2] The same band appears with somewhat greater intensity in aqueous solutions of some of the salts of the alkali metals. The facts (1) that this band is very similar in form to the absorption spectra of the solvated electron in solutions of the alkali metals in liquid ammonia[3] or in methylamine[4]; (2) that it decays in a time of the order of 10 microseconds, and (3) that its intensity is reduced by small concentrations of electron scavengers such as O_2, CO_2, or N_2O, lead us to attribute the absorption to the "hydrated electron," whose probable existence and properties were predicted by Platzman[5] and more recently discussed by Weiss,[6] under the name "Polaron."

Experimental evidence for the existence of two transient reducing species in the radiation chemistry of aqueous solutions has accumulated from kinetic studies and has been summarized by Allen[7] and by Matheson.[8] Recent evidence[9,10] has shown that one of these species carries a unit negative charge.

Previous attempts to detect solvated electrons in irradiated liquids have been made by Roberts and Allen,[11] who irradiated liquid ammonia and looked for any change in conductivity, and by Linshitz,[12] who irradiated water and looked for optical absorption, but in neither case was a positive result obtained. Keene[13] recently has found absorption in the visible region in pure water during and immediately after exposure to a pulse of 4 Mev. electrons. Stein and Jortner[14] reported an absorption peak

at about 9500 Å. when potassium was dissolved in water at $-5°$: they attributed this to the transient existence of trapped electrons in water. Schulte-Frohlinde and Eiben[15] have recently detected trapped electrons in frozen alkaline solutions by their e.s.r. spectrum and by their optical absorption spectrum, which showed a peak near 5750 Å.

Experimental Procedures

Electron Beam.—The electron beam was produced in a linear accelerator[16] giving two microsecond pulses of approximately 1.8 Mev. electrons, the peak current in the pulse being variable up to 0.5 ampere. In the work described here the electron beam was focussed into a flat horizontal ribbon by means of a single quadrupole lens, and this ribbon emerged through a 50 micron thick aluminum window and impinged on the entrance window of the quartz cell some 2.5 cm. away.

Irradiation Cell.—The quartz cell used is illustrated in Fig. 1. It was 6 cm. long, and the side through which the electrons entered was 0.3 mm. thick. The end windows of the cell were made of "super-pure" quartz, and were shielded from the direct electron beam by brass end posts, to obviate any possible absorption arising from transient color centers formed in the quartz by irradiation. The dose distribution along and through the cell is illustrated in Fig. 2. In the experiments described below a mean dose per pulse between 4 and 12 kilorads was used. The cell was provided with 5/20 standard taper cones at either end, the upper one of which was connected to a supply of pure argon for back flushing, and the lower one to a two-way glass stopcock provided with 5/20 cones, through which it could be connected to a syringe for filling, or to an exit tube for flushing out. Samples of de-aerated solutions were taken after flushing through the cell, and were kindly checked for oxygen content by Dr. L. H. Gray, using the Hersch cell technique.[17] Oxygen concentrations below one micromolar were generally found in such checks.

Preparation of Solutions.—All solutions were prepared from triply distilled water[18] in glassware previously heated to 520°. The solutions were degassed during a five-minute shaking period, and forced into a 100 ml. syringe, in a manner described by Senvar and Hart.[19] Nitrogen passed through a solid carbon dioxide trap was used to force these solutions into the syringe. Solutions of different concentrations were prepared by diluting the degassed stock solution with degassed water in ratios usually of 0.3 to 1, and 0.1 to 1. The solution was mixed inside the syringe with the aid of a flat Pyrex disc by repeated inversion of the syringe. The degassing technique proved to be very effective for the removal of dissolved oxygen, which was reduced to a concentration of less than 0.1 micromole per liter. About 4 micromolar carbon dioxide was left in neutral water, but less than 1 micromolar carbon dioxide remained in acid

(1) Based on work supported in part by the U. S. Atomic Energy Commission and in part by the British Empire Cancer Campaign.

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(3) R. C. Douthit and J. L. Dye, *J. Am. Chem. Soc.*, **82**, 4472 (1960).

(4) G. Hohlstein and U. Wannagat, *Z. für anorg. u. allgem. Chem.*, **288**, 193 (1957).

(5) R. L. Platzman, "Basic Mechanisms in Radiobiology," U. S. Nat. Acad. Sci. Pub. No. 305, 1953, p. 34.

(6) J. Weiss, *Nature*, **186**, 751 (1960).

(7) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Systems," D. Van Nostrand Co., New York, N. Y., 1962.

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(11) R. Roberts and A. O. Allen, *J. Am. Chem. Soc.*, **75**, 1256 (1953).

(12) H. Linschitz, "Basic Mechanisms in Radiobiology," U. S. Nat. Acad. Sci. Pub. No. 305, 1953, p. 39.

(13) J. P. Keene, *Nature*, in press.

(14) G. Stein and J. Jortner, *Nature*, **175**, 893 (1955).

(15) D. Schulte-Frohlinde and K. Eiben, *Z. für Naturforschung*, **17a**, 445 (1962).

(16) J. W. Boag and C. W. Miller, *Proc. 2nd UN Geneva Conf.*, **14**, 437 (1958).

(17) D. L. Dewey and L. H. Gray, *J. Polarographic Soc.*, **7**, 1 (1961).

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

(19) C. B. Senvar and E. J. Hart, *Proc. 2nd UN Geneva Conf.*, **29**, 19 (1958).
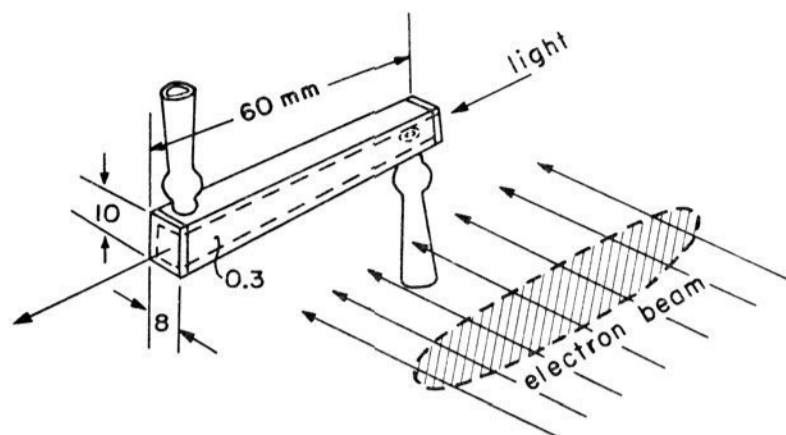
Fig. 1.—Dimensions of quartz irradiation cell with 0.3 mm· thick entrance window for electrons, and with super-pure end windows (mm.).
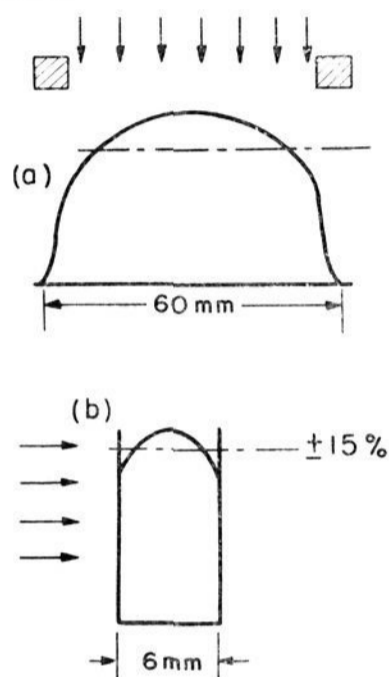

Fig. 2.—Dose distribution in the irradiated quartz cell: (a) along the cell; (b) through the cell in the direction of the electron beam.
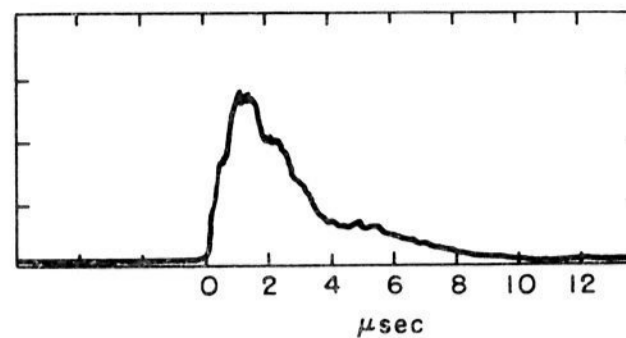

Fig. 3.—Duration of light flash from the underwater spark source.

Fig. 4.—Typical spectra on hypersensitized Kodak IIL emulsion through glass optical system: (a) flash before irradiation through 0.5 M Na_2CO_3 solution; (b) flash simultaneous with electron pulse; (c) flash 30 sec. after electron pulse.

solutions degassed by our technique. Solutions of oxygen, nitrous oxide and carbon dioxide were prepared by saturating the degassed solutions with the gases previously passed through a solid carbon dioxide trap. The stock solution was prepared at a concentration obtained by saturating at about 70 cm. pressure, and then forcing the saturated solution into the syringe at a pressure slightly above atmospheric. Analar grade of chemicals supplied by B.D.H. of sodium carbonate, potassium carbonate, sodium chloride, potassium chloride, ammonium chloride, sulfuric acid, sodium sulfate, sodium bicarbonate, sodium hydroxide and sodium pyrophosphate, and reagent grades of lithium carbonate, cesium carbonate, lithium chloride, calcium chloride, magnesium chloride, barium chloride and sodium dihydrogen phosphate were used without further purification. Anhydrous ammonia (I.C.I.) and methylamine (B.O.C.) were each passed through a sintered glass filter tube in water, and then directly into the evacuation chamber, which was cooled in an ice bath. Degassing was effected by bubbling these gases through the solutions for 30 minutes after saturation. These solutions were then forced into the 100 ml. syringes by the use of nitrogen. The concentration was determined by titration with standard hydrochloric acid.

Light Source.—The light source used was an underwater spark between uranium electrodes[20] fed by a 0.05 μf. low-inductance condenser charged to 20 kv. A series-connected air spark-gap with a trigger electrode allowed the underwater spark to be triggered either simultaneously with the electron pulse, or at any desired delay after the latter. Delay was introduced by means of a Tektronix Type 162 and 163 wave form generator. The spark duration (Fig. 3)

(20) J. W. Boag, Proc. 2nd Inter. Cong. Photobiology, Minerva, p. 109 (1957).

was some 4 microseconds. This light source gave a good continuum, the only lines present being absorption lines from the OH radical formed in the steam around the spark channel. These served as a convenient wave length marker in the ultraviolet (Fig. 4). Successive sparks varied somewhat in total light output, but the spectral distribution varied very little. Densitometer traces from a series of typical control spectra taken before and after irradiation are shown in Fig. 5. Small vertical translations of the densitometer curves bring all these control spectra into very close correspondence.

Spectrograph.—Two spectrographs were used in the work. The first was a Hilger intermediate spectrograph E. 486 with quartz optics. The second was a Hilger 517 F/4 spectrograph with glass optics.

Photographic Technique.—The absorption band studied was first discovered on a Kodak P 1200 plate, but in all the subsequent work Kodak scientific plates were used with emulsion type 2N, or more frequently type 2L, whose sensitivity extended to 8800 Å. To build up an adequate optical density for analysis in the infrared region of the spectrum, two, four, or (in the case of the E. 486 spectrograph) eight successive pulse-flash experiments had to be made, without moving the plate. Plates were developed for 2.5 minutes in Johnsons' Universal developer at 20°, and subsequently were fixed, washed and dried in the usual way. The 2L emulsion was hypersensitized by immersion for one minute in a 0.5 molar solution of ammonia in water.

The plate density was evaluated on a Joyce–Loebl Microdensitometer (Model MKIIIB) using calibrated grey wedges of density gradients 0.043, 0.083, or 0.13 cm.$^{-1}$. The optical density (O.D.) is plotted as a function of wave length (λ) in Figs. 5–15.

Evaluation of the Spectrograms.—The shape of the absorption band is determined readily by comparison of the spectra taken prior to and during the electron pulse. The absolute value of the absorption, however, is rendered uncertain by variations in total light output between the "prior" and "simultaneous" sparks. In an attempt to overcome this difficulty, when assessing the effect of various solutes on the intensity of the absorption, we have arbitrarily brought the densitometer traces into coincidence at 5000 Å., where the emulsion sensitivity has a minimum. The difference curves obtained in this way show only the part of the absorption band lying at λ 5000 Å., but its shape is not affected. The quantitative data presented below on suppression or enhancement of the band by different solutes are generally based on this way of evaluating the data. In a few cases, where the light output from successive sparks remained relatively constant throughout an experiment, the whole curves are presented.

The densitometer curves which are given in the present paper have not been corrected for non-linearity of the emulsion response curve nor for the variation of the emulsion gamma with wave length. The absorption in the irradi-
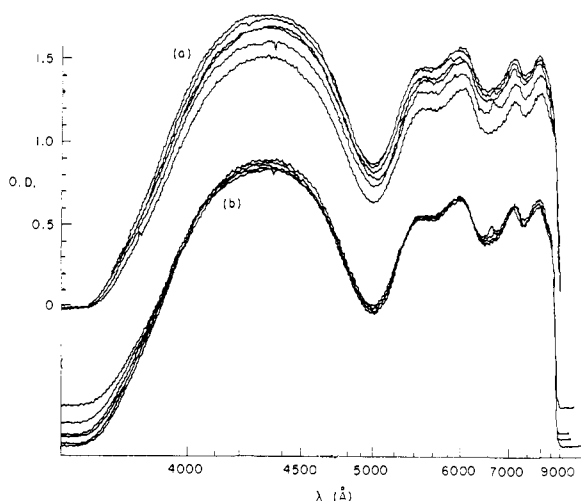
Fig. 5.—Variations in total light output between successive sparks: (a) series of comparison spectra taken before and after irradiation (all from a single plate); (b) the same spectra brought into coincidence at 5000 Å. by small vertical translations of the separate curves.
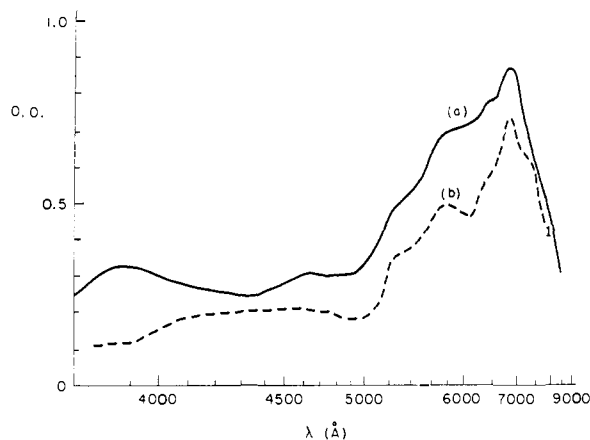

Fig. 6.—Absorption band due to the hydrated electron in irradiated aqueous solutions: (a) 0.05 M solution of Na_2CO_3 (deaerated) given a mean dose of 7 kilorads; (b) pure water (deaerated) exposed to a mean dose of 7 kilorads.
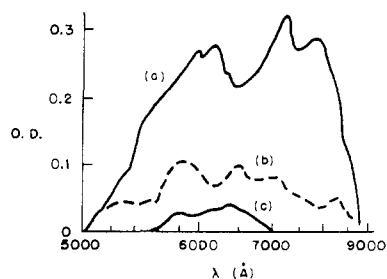

Fig. 7.—Decay of absorption in a 0.5 M sodium carbonate solution: (a) spectrogram simultaneous with electron pulse; (b) spectrogram delayed 15 μsec.; (c) spectrogram delayed 25 μsec.

ated solution frequently gave an optical density of 0.4 to 1.0 at the 7000 Å. peak, and in view of the erratic variation in emulsion sensitivity in this region of the spectrum due to the sensitizing dyes used, it was almost impossible to keep strictly to the linear part of the log-exposure *vs.* optical-density curve of the emulsion. The ripples on many of the
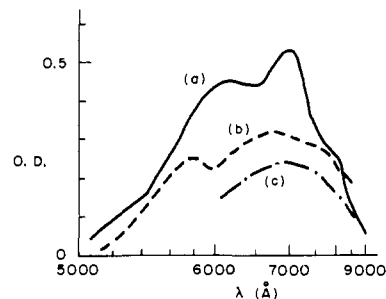

Fig. 8.—Absorption in 0.05 M solutions of alkali metal carbonates: (a) K_2CO_3; (b) Cs_2CO_3; (c) Li_2CO_3.
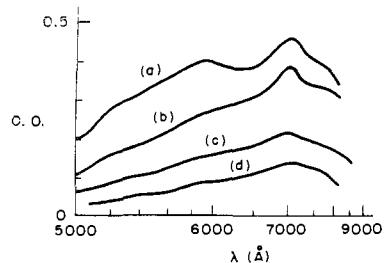

Fig. 9.—Absorption in pure water—effect of adding oxygen: (a) de-aerated; (b) 14 μM oxygen; (c) 47 μM oxygen; (d) 141 μM oxygen.
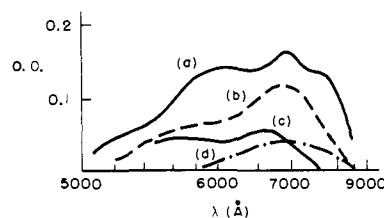

Fig. 10.—Absorption in pure water—effect of adding CO_2: (a) de-aerated water; (b) 31 μM CO_2; (c) 103 μM CO_2; (d) 1.03 mM CO_2.

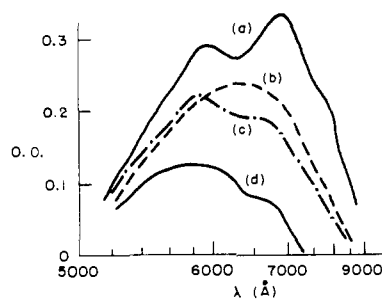
Fig. 11.—Absorption in 0.05 M solution of sodium carbonate—effect of adding oxygen: (a) de-aerated solution; (b) 8.7 μM oxygen; (c) 29 μM oxygen; (d) 87 μM oxygen.

curves are attributable in part, and probably entirely, to these causes.

Results

Water.—The absorption band found in pure de-aerated water exposed to a mean dose of 7 kilorads per pulse is shown in Fig. 6, together with the band obtained in a 0.05 M solution of sodium carbonate. In both cases the spark was triggered simultaneously with the electron pulse. The ripples on the curves cannot be considered significant at this time. They probably arise from the
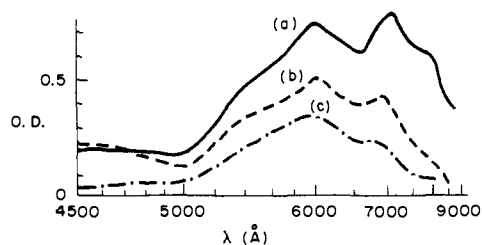
Fig. 12.—Absorption in 0.05 M solution of sodium carbonate—effect of producing H_2O_2 in the solution by pre-irradiating with various numbers of electron pulses: (a) 4 pulses; (b) 10 pulses; (c) 302 pulses.
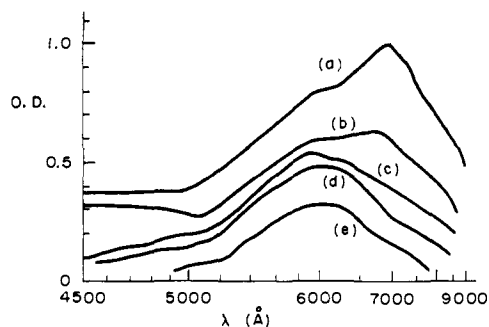

Fig. 13.—Absorption in 0.05 M solution of sodium carbonate—effect of adding nitrous oxide. (a) de-aerated solution; (b) 58 μM N_2O; (c) 190 μM N_2O; (d) 580 μM N_2O; (e) 1.9 mM N_2O.

variations in response of the sensitizing dyes in the emulsion, coupled with some nonlinearity in the gamma curve of the emulsion.

Lifetime of the Absorption—Only preliminary results on the lifetime will be reported here. A more exact study by means of a photomultiplier is in progress.

Figure 7 shows one set of delayed spectra in 0.5 M sodium carbonate. The height of the absorption peak (reckoned from an origin at 5000 Å.) has fallen greatly in 15 μsec., and is very small 25 μsec. after the electron pulse. All subsequent figures are shown with zero delay.

Several other plates confirm that the absorption band in pure water or in sodium carbonate solution has practically disappeared in a time of about 20 μsec., but they do not yield sufficiently accurate data to plot a decay curve. In 12 M and in 6.5 M aqueous solutions of methylamine the very strong absorption found with zero delay on the spark (Fig. 15) had practically vanished in a spectrogram taken with 30 μsec. delay, and entirely vanished in 300 μsec. The behavior at shorter times is more accurately studied by a photomultiplier.

Effect of Alkali Metal Ions.—Figure 8 shows the absorption peaks obtained in 0.05 M potassium, cesium and lithium carbonates. The differences in curve shape are unlikely to be significant.

Effect of Different Anions.—The absorption band found in sodium carbonate was also present in solutions of the sulfate, hydroxide, and chloride. No absorption was found in solutions of sodium bicarbonate or of formate.
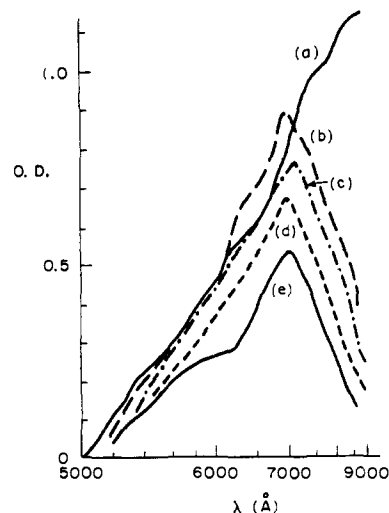

Fig. 14.—Absorption in aqueous solutions of ammonia given a mean dose of 7 kilorads: (a) 12.2 M NH_3; (b) 1.2 M NH_3; (c) 0.12 M NH_3; (d) 0.012 M NH_3; (e) pure de-aerated water.
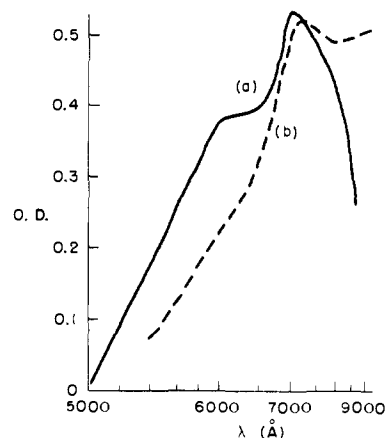

Fig. 15.—Absorption in aqueous solutions of methylamine given a mean dose of 12 kilorads: (a) 6.25 M CH_3NH_2; (b) 12.5 M CH_3NH_2.

Effect of Dissolved Gases and of H_2O_2.—Figure 9 shows the reduction in the absorption intensity in pure water which is produced by various concentrations of dissolved oxygen, while Fig. 10 shows the similar effect of dissolved CO_2 in water. Oxygen is also effective in reducing the absorption in a 0.05M solution of Na_2CO_3 (Fig. 11). Because of the instability of H_2O_2 in alkaline solutions its effect was studied by producing it by pre-irradiation of the de-aerated solution immediately before the test spectrogram was taken. For this plate (Fig. 12) we required two flashes to give adequate density on each spectrum, and so two pulses of about 12 kilorads each was the minimum number to which the solution was exposed during an experiment. In this experiment, the solution also received 2 accidental pulses before the test was made, so that the curves in Fig. 12 correspond to the amounts of H_2O_2 formed by 4, 10, or 302 pulses of 12 kilorads, (approximately 10 μM H_2O_2 per pulse as initial yield). It is clear that the reduction in intensity caused by a single pulse

is small, and our technique of using 2 or even 4 pulses for each spectrum cannot lead to any serious error. The effect of nitrous oxide in 0.05 M sodium carbonate is shown in Fig. 13.

Ammonia and Methylamine.—The absorption spectra measured in ammonia solutions of various concentrations are presented in Fig. 14. It can be seen that up to 1.2 M the absorption band is not significantly different from that found in pure water or other aqueous solutions tested. In the 12 M solution, however, the peak at 7000 Å. is absent, and no peak appears within the wave length range covered by this emulsion. The admission of air completely eliminated the absorption in the 12.2 M solution.

Figure 15 shows similar results for methylamine at concentrations of 6.25 and 12.5 M. The 7000 Å. peak is still present in the 12.5 M solution, but it is superimposed on an absorption which is increasing toward longer wave lengths.

Discussion

The existence of solvated electrons in solutions of alkali metals in liquid ammonia, in methylamine, or ethylamine, has been recognized for many years. A review of the properties of such solutions is given by Yost and Russell.[21] Evidence for the solvated electron in these solutions is provided, among other things, by their high conductance, their paramagnetic susceptibility and their e.s.r. spectrum, and also by the shape and location of their optical absorption spectra. In liquid ammonia the absorption spectrum has a peak at 14500 Å.[3] and in methylamine it has a peak at 7000 Å.[4]

In mixtures of liquid ammonia and liquid methylamine the absorption spectrum of the solvated electron shows a complicated variation with the proportions of the two solvents in the mixture. A peak at 7000 Å. occurs when more than 70% of CH_3NH_2 is present, and a broad peak near 13000–15000 Å. is usually also present.

The identification of the absorbing species in our irradiated solutions as the hydrated electron depends chiefly on the nature of the absorption spectrum. Experiments on conductivity are in preparation, but e.s.r. studies would be more difficult in view of the short lifetime of the species and the technical difficulty of irradiating aqueous samples in the spectrometer cavity. The evidence from the various absorption spectra presented is, however, very strong support of our conclusion.

The absorption found by us (Fig. 14) in a 12 M aqueous solution of NH_3 resembles the tail of the absorption spectrum of the solvated electron in liquid ammonia, and the peak at 7000 Å. in our 12.5 M solution of methylamine is very similar to that found by Hohlstein and Wannagat in methylamine solutions.[4] Moreover, the observed absolute intensity of absorption agrees quantitatively, within a factor of two or three, with that to be expected theoretically for the hydrated electron. (We are indebted to Dr. R. L. Platzman for a rough calculation of the expected values.)

The fact that the absorption spectrum in aqueous

(21) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Chapter 4, Prentice Hall, Inc., New York, N. Y., 1944.

solutions is affected in intensity but not in character by the type of anions or cations present indicates that the absorbing species is common to all the solutions. The short lifetime of the absorption band, and its attenuation by small concentrations of electron acceptors such as O_2, CO_2 or N_2O, are strong confirmation that we are, in fact, observing the hydrated electron.

The absorption band we find in aqueous solutions has a peak near 7000 Å., whereas Schulte-Frohlinde and Eiben[15] report that the "solvated" electron in alkaline ice has an absorption peak at 5750 Å. There is, however, no conflict between these findings. The term "hydrated electron" was used by Platzman[5] to describe an electron trapped in a potential well formed by polarized water molecules which had oriented themselves under the influence of the electronic charge. This process of orientation can hardly occur in ice at low temperature, and the trapped electrons in ice must, therefore, be bound in somewhat different potential wells— resembling more closely color centers in crystals.

In this paper we have presented the experimental data without drawing detailed quantitative conclusions on the lifetime of the hydrated electron in the presence of the various scavengers used. The fact that the lifetime of the hydrated electron, particularly in the presence of scavengers, is probably comparable to or less than the duration of the analyzing light flash, implies that any time-dependent variation in the spectral distribution during the light flash itself could lead to changes in the form and intensity of the observed absorption. We do not, therefore, at this stage wish to attribute significance to the changes in the position of the absorption peaks which appear, for instance, in Figs. 7, 11, 12, and 13.

According to Platzman, the kinetic energies of secondary electrons produced in water are reduced to thermal magnitude in a time of the order of 10^{-13} second, and these thermalized electrons are hydrated in about 10^{-11} second.[5] While it is possible for unhydrated thermalized electrons to react with certain solute molecules in 10^{-11} second, there is good chemical evidence supporting the reaction of hydrated electrons with solute, before conversion to hydrogen atoms occurs, in times as long as microseconds. The thermalized unhydrated electron (e^-) will not react with water according to

$$H_2O + e^- \longrightarrow H_2O^-$$
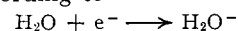
since the electron shells of the atoms in the water molecule are filled, and therefore it is impossible for a single water molecule to accept another electron. Furthermore the single reaction

$$e^- + H_2O \longrightarrow H + OH^-$$
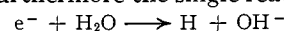
will not have time to take place, since e^- will not be localized long enough for the hydration of the OH^- to occur, which hydration is necessary to make the reaction energetically favorable. Therefore, one arrives at Platzman's conclusion, that the reaction with water requires the hydrated electron, thus

$$e_{aq}^- + H_2O \longrightarrow H + OH_{aq}^-$$
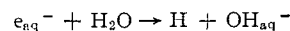
Over the past several years chemists have realized that there is more than one reducing species in irradiated water. Matheson[8] recently has presented an excellent review on the subject of

intermediates in irradiated water, and no attempt will be made to cover this complex subject here. Clear evidence that one of these species is a negatively charged one has been obtained recently by Czapski and Schwarz,[9] and by Collinson, Dainton, Smith and Tazuké.[10] We use the terminology of Platzman and call this species the hydrated electron, and designate it by e_{aq}^-. While our work is still only in a preliminary state, it is nevertheless possible to draw some conclusions of interest to radiation chemists.

Since the spectra we have obtained are identical in neutral water and in alkaline solutions up to pH 12, it is clear from our results that the hydrated electron exists for microseconds in the pH range from 7 to 12, even at dose rates of 12 kilorads per pulse. And since the spectrum is faint at best in acid solutions, we deduce that the major fraction of hydrated electrons reacts with hydrogen ions in less than a microsecond according to

$$e_{aq}^- + H_3O_{aq}^+ \longrightarrow H + H_2O$$
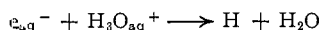
Other reactions readily occurring in neutral and alkaline solutions are of the hydrated electron with oxygen, carbon dioxide, nitrous oxide, hydrogen peroxide and the formate ion.

The results presented above show that the revealing method of spectroscopy can be used for the investigation of the physical and chemical properties of the hydrated electron. The solvated electron may also be produced by ionizing radiation in ammonia and the alkyl amines, and so this method may be used for studies of its properties in these media too.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 20, N. Y.]

The Migration Aptitude of Benzyl vs. Methyl in Carbonium Ion Reactions of the 2,2-Dimethyl-3-phenyl-1-propyl System[1]

BY PERCY WARRICK, JR., AND WILLIAM H. SAUNDERS, JR.

The rearrangement of 2,2-dimethyl-3-phenyl-1-propyl p-toluenesulfonate (Ia) by refluxing in formic acid and in acetic acid and of 2,2-dimethyl-3-phenyl-1-propylamine (Ib) by treatment with sodium nitrite in acetic acid yielded mixtures of olefins and esters. The mixtures, after treatment with lithium aluminum hydride, were analyzed by gas chromatography and infrared and ultraviolet spectroscopy. Migration aptitudes of methyl/benzyl of 3.5, 3.2 and 2.1 were obtained for acetolysis, formolysis and deamination, respectively. Benzyl has an electron-withdrawing inductive effect relative to methyl, and this is probably the main reason for its lower tendency to migrate.

We undertook a careful study of the migration aptitude of benzyl because the behavior of this group should shed special light on the mechanism of migration of alkyl groups. In migrations to oxygen, benzyl migrates considerably better than other primary alkyl groups, which suggests that it possesses some carbonium-ion character in the transition state.[2] Whether a similar situation obtains in carbonium-ion rearrangements was not clear. House[3] found that methyl migrates better than benzyl in the diazomethane–ketone reaction and in amino alcohol deamination. A number of other reactions are reported to give the opposite result,[4] though the methods available to these early workers were insufficiently quantitative to permit reliable conclusions.

For these reasons, we chose to re-examine the system with 2,2-dimethyl-3-phenyl-1-propyl.[4b] This neopentyl-like carbon skeleton would be ex-

pected to undergo complete rearrangement to stable products in a carbonium-ion reaction with minimum opportunity for steric complications at the migration terminus. The reactions studied were formolysis and acetolysis of the tosylate, and nitrous acid deamination of the amine. The product mixtures were analyzed by means of gas chromatography and ultraviolet and infrared spectroscopy.

The starting materials were synthesized by the following scheme. Methyl isobutyrate and benzyl chloride were condensed using sodium hydride as the base.[5] The resulting ester, methyl 2,2-dimethyl-3-phenylpropionate, was reduced with lithium aluminum hydride and the alcohol Ic was treated with p-toluenesulfonyl chloride in pyridine to produce Ia. Hydrolysis of methyl 2,2-dimethyl-3-phenylpropionate, followed by treatment with thionyl chloride and ammonium hydroxide in subsequent steps, gave 2,2-dimethyl-3-phenylpropionamide. Reduction of the amide with lithium aluminum hydride produced 2,2-dimethyl-3-phenyl-1-propylamine (Ib).

Since product analysis was to be done by gas chromatography, reference samples of the various

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(4) (a) M. Tiffeneau and J. Lévy, *Bull. soc. chim. France*, [4] **49**, 1647 (1931); (b) A. Haller and P. Ramart, *Compt. rend.*, **174**, 1211 (1922).

(5) The method of alkylation is adapted from B. E. Hudson and C. R. Hauser, *J. Am. Chem. Soc.*, **62**, 2457 (1940).