J. Phys. Chem. **1986**, *90*, 5378-5382

Reaction of Hydrated Electrons with Alkali Metal Cations in Alkaline Aqueous Solutions

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(Received: March 14, 1986)

Confirming experiments of Walker et al. and Hart et al., we show by flash photolysis and pulse radiolysis that the decay of hydrated electrons in aqueous alkaline solutions leads to an intermediate which by illumination with soft UV light ($\lambda >$ 250 nm) revives hydrated electrons—even 100 ms after the primary electrons have disappeared. The formation of the intermediate is observed only at high alkali hydroxide concentration (pH > 11), where the first-order equilibrium reaction ($e^- + H_2O \rightleftarrows H + OH^-$) is blocked, and at low electron concentrations, where the normal second-order reaction ($2e^- + 2H_2O \rightarrow H_2 + 2OH^-$) is slow. Varying the pH and the concentrations of alkali metal cations M^+ and of primary hydrated electrons, we conclude that the intermediate is formed in the reaction $e^- + M^+ \rightarrow M^0$ (M = Na and Cs; $k = (2 \pm 0.5) \times 10^4\ M^{-1}\ s^{-1}$), it has the stoichiometry of a neutral alkali metal atom, it decays by a second-order process $2M^0 + 2H_2O \rightarrow H_2 + 2M^+ + 2OH^-$ ($k = (1.5 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$), and it has a light absorption maximum at 270 nm ($\epsilon(\max) = 4500 \pm 500\ M^{-1}\ cm^{-1}$).

Years ago Walker et al.[1] and Hart et al.[2] reported that in the decay of hydrated electrons in alkaline aqueous solutions an intermediate is formed which on irradiation with soft UV light ($\lambda > 250$ nm) revives hydrated electrons. Walker et al. suggested this intermediate to be a dimeric electron ($2e^- \rightarrow e_2^{2-}$ or $Na^+ + 2e^- \rightarrow Na^-$) as a transition state of the so-called bimolecular electron reaction 2 leading to molecular hydrogen. Hart et al., on the other hand, gave evidence that this intermediate is a product of an electron reaction with an alkali metal cation ($e^- + M^+ \rightarrow M^0$).

In a subsequent paper, Czapski et al.[3] on the basis of their pulse radiolytic work claimed all effects to be due to impurities because they could not detect any traces of light absorption in the wavelength range around 350 nm where according to Walker et al. this new intermediate has its light absorption maximum.

In our kinetic studies[4] on the electron reaction with water in liquid ammonia, we concluded for energetic reasons that an intermediate should be formed which might be identical with that postulated in the aqueous systems.[1,2] Therefore with the same but more refined experimental techniques as Walker (double-flash experiments) and as Czapski (pulse radiolysis), we have taken up their experiments and fully confirm the formation of an intermediate during the decay of hydrated electrons in aqueous alkaline solutions, give tentatively its kinetics of formation, further decay, and light absorption spectrum.[5] However we explicitly stated that we would not know what it is, but nevertheless we speculated that hydroxide ions might be involved. Now we know that this speculation was erroneous; in the following we will give all experimental results of our flash photolytic and pulse radiolytic work. From this we conclude that the intermediate is a species of the stoichiometry of an alkali metal atom as already postulated by Hart et al.[2] and as is known in nonaqueous systems.[6]

Experimental Section

Figure 1 displays the principle of the double-flash experiments similar to that already used by Walker et al.[1] The hydrated electrons were produced in the optical cell O (Suprasil, 40 cm long, 1.5 cm inner diameter) by photolysis ($OH^- \rightarrow e^- + OH$) with the hard UV light of the first flash lamp, F1 (quartz, 40 cm long). The second flash lamp F2 (Duran glass, 40 cm long; discharge energy of both lamps up to 1200 J, flash half-width up to 20 μs), the light of which was filtered by an additional 2-mm Duran glass filter G (light transmission below 250 nm < 0.1%), was triggered with a delay of 0.3–100 ms relative to the first flash: the signal of photodiode P2 responding to the scattered light of flash lamp F1 was fed to a delay circuit D which produced a 10 kV/1 μs pulse; this pulse fired via an auxiliary electrode, the spark gap S of the flash lamp F2. The second flash had no effect on the solution on its own because it contained no short-wave UV components, but it could revive hydrated electrons after their decay. The whole system was surrounded by a cylindrical glass tube (not shown in Figure 1) which on its inner side was covered with a thin layer of Teflon powder, acting as a very effective reflector for the UV light and thus enhancing the yield of the photochemical reactions. The flash lamps were filled with up to 10 Torr of argon and were connected with a capacitor of 4 μF charged up to 25 000 V. The system of course also could be used for normal flash light experiments.

The optical detection system was conventional. It consisted of a tungsten or xenon lamp L, a monochromator M, and the photocell P1 which was connected to a transient recorder T in connection with an *x–y* plotter or a desk computer.

After the usual purification steps, 100 °C water steam was blown for 24 h through the optical cell for final purification. It was then filled with 10^{-4}–0.3 M alkali hydroxide solution (reaction of metallic Cs or Na with water in the cell or direct introduction of commercial NaOH). Unwanted reactive radicals of the primary photolytic step were scavenged by hydrogen (1 bar) or added methanol (0.02 M). All reagents (but NaOH) purified by multiple distillation were introduced into the cell by a final distillation under high-vacuum condition.

Normal pulse radiolysis experiments were carried out with the Van de Graaff generator of the Hahn-Meitner-Institut in Berlin. The electron energy was 3.8 MeV, duration of the pulse was 5 μs, and the dose absorbed per pulse was 100 rad. The solutions prepared as before were contained in a 10-cm optical cell. The optical detection system was in principle the same as before. However, a sampling technique was allowed to average the signals of a series of irradiation experiments for better signal-to-noise ratio.

Experimental Results

According to the well-accepted reaction scheme of hydrated electrons in alkaline solutions[7] (rate constants are taken from

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(1) Basco, N.; Kenney, G. A.; Walker, D. C. *Chem. Commun.* **1969**, 917. Basco, N.; Kenney-Wallace, G. A.; Vidyarthi, S. K.; Walker, D. C. *Can. J. Chem.* **1972**, *50*, 2059.

(2) Gopinathan, C.; Hart, E. J.; Schmidt, K. H. *J. Phys. Chem.* **1970**, *74*, 4169.

(3) Meisel, D.; Czapski, G.; Matheson, M. S.; Mulac, W. A. *Int. J. Radiat. Chem.* **1975**, *7*, 233.

(4) Telser, Th.; Schindewolf, U. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 488.

(5) Telser, Th.; Schindewolf, U. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 1116.

(6) Edwards, P. P. *J. Solution Chem.* **1985**, *14*, 187.

(7) Hart, E. J.; Anbar, M. *The Hydrated Electron*; Wiley Inter-science: New York, 1970.

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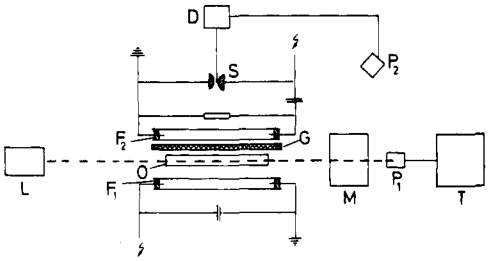

Figure 1. Schematic drawing of the double-flash apparatus: F1 and F2, flash lamps with full UV contribution and with $\lambda > 250$ nm only; G, Duran glass filter; P1 and P2, photodiodes; D, delay circuit; S, spark gap; O, optical cell; L, tungsten or xenon lamp; M, monochromator; T, transient recorder.

references 7–9), the only decay channels are the so-called monomolecular equilibrium reaction (first-order with respect to electrons), leading to H atoms

$$e^- + H_2O \rightleftarrows H + OH^- \tag{1}$$

$$k_1 = 880\ s^{-1}$$

$$k_{-1} = 1.8 \times 10^7\ M^{-1}\ s^{-1}$$

and the bimolecular reaction (second-order with respect to electrons), leading to H_2 molecules

$$2e^- + 2H_2O \rightarrow H_2 + 2OH^- \tag{2}$$

$$k_2 = 6 \times 10^9\ M^{-1}\ s^{-1}$$

H atoms formed in eq 1 react further by

$$e^- + H + H_2O \rightarrow H_2 + OH^- \tag{3}$$

$$k_3 = 2.5 \times 10^{10}\ M^{-1}\ s^{-1}$$

and

$$2H \rightarrow H_2 \tag{4}$$

$$k_4 = 1 \times 10^{10}\ M^{-1}\ s^{-1}$$

The reactive OH radicals, unwanted byproducts of the photolytic and radiolytic electron formation ($OH^- + h\nu \rightarrow OH + e^-$; $H_2O \rightsquigarrow H^+ + OH + e^-$), are scavenged by dissolved hydrogen

$$OH + H_2 \rightarrow H_2O + H \tag{5}$$

$$k_5 = 5 \times 10^7\ M^{-1}\ s^{-1}$$

followed by reactions −1, 3 and 4 or by added methanol which also removes H atoms

$$OH + CH_3OH \rightarrow H_2O + CH_2OH \tag{6}$$

$$k_6 = 5 \times 10^8\ M^{-1}\ s^{-1}$$

$$H + CH_3OH \rightarrow H_2 + CH_2OH \tag{7}$$

$$k_7 = 1.6 \times 10^6\ M^{-1}\ s^{-1}$$

The CH_2OH radicals dimerize and do not interfere in the reactions. The decay curves of the hydrated electrons in alkaline solutions of varying pH with H_2 or CH_3OH as scavengers will be evaluated according to the given decay scheme.

Normal Flash Experiments. In single-flash experiments at pH 10 and e^- concentrations below 4×10^{-9} M (flash energy = 10 J), we find the normal decay kinetics. In solutions with 0.02 M methanol as the scavenger, the electron decay follows a first-order reaction over five half times. Simple first-order kinetics according to reaction 1 is expected because at low e^- concentration reaction 2 is too slow to be observed and because the fast scavenging reactions 6 and 7 prevent all other parallel and consecutive reactions. The experimental half time $\tau = 0.55$ ms is slightly smaller than the literature value ($\tau_1 = \ln 2/k_1 = 0.79$ ms), indicating an impurity of low concentration.

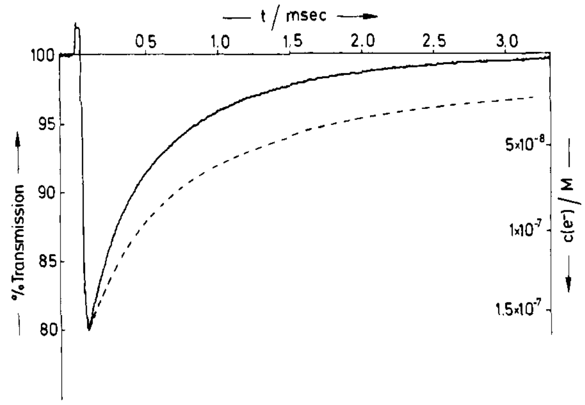

Figure 2. Time dependence of light transmission at 700 nm and hydrated electron concentration (right scale) after a single hard UV flash. Dashed line: calculated decay according to reaction 2. $c(NaOH) = 7 \times 10^{-2}$ M, $c(H_2) = 7 \times 10^{-4}$ M.

In solutions with 7×10^{-4} M hydrogen as the scavenger and otherwise identical experimental conditions, the electron concentration passes through a maximum about 0.5 ms after the flash due to additional electrons formed by scavenging reactions 5 and −1. The following electron decay is slow (half times up to 6 ms). Solving the coupled differential equations for the formation and decay of electrons and H atoms according to reactions 1, −1, 2, 3, and 4 (reaction 5 is complete already at the beginning of the observation 0.1 ms after the flash) with the proper rate constants and boundary conditions, we get a very good simulation of the decay curve when we again take into consideration an additional slow pseudo-first-order reaction with an impurity ($k_{imp} = 1.1 \times 10^2\ s^{-1}$).

At pH 12.8 the H-atom scavenging reaction −1 is so fast that with H_2 as scavenger the delayed electron formation cannot be observed any more in the time scale of our flash experiments. Therefore, we find no differences in the experimental curves using hydrogen or methanol as scavengers for the unwanted primary photolysis products. Furthermore reaction path 1 is not open for the decay of electrons because equilibrium 1 is shifted to the left side due to the high OH^- concentration. Consequently the electrons should decay only by the second-order process 2.

Figure 2 shows the decay curve observed after a 70-J flash with an initial electron concentration of 1.6×10^{-7} M. The decay is faster than expected (dashed line calculated according to reaction 2) and has a pronounced first-order contribution. The evaluation of data with the procedure of Walker[1] yields $k_2 = (5 \pm 1) \times 10^9\ M^{-1}\ s^{-1}$ in best agreement with literature and $(1 \pm 0.1) \times 10^3$ s as rate constant for a parallel pseudo-first-order process, which is an order of magnitude higher than the first-order contribution at low pH ascribed to electron reactions with impurities. This implies that at higher alkali hydroxide concentrations an additional reaction path for the decay of electrons is open in which the alkali hydroxide is the reaction partner, that the first-order process 1 still proceeds against expectation, or that an increased concentration of impurities is present. The impurity aspect will be discussed further below.

If the alkali hydroxide is the reaction partner of the hydrated electrons, then the first-order contribution to the overall decay should increase with the MOH concentration. Figure 3 displays the half time of the first-order decay contribution again calculated from the experimental parallel first- and second-order decay curves with the procedure as before: between 10^{-3} and 0.3 M CsOH (X) and NaOH (▽) the pseudo-first-order reaction half time decreases with increasing concentration. Below 10^{-3} M, however, the half time is constant due to the reaction with unidentified impurities of constant concentration.

The final question, which of the two components of alkali hydroxide, M^+ cations or OH^- ions, is the responsible reaction partner, is easily answered. Decreasing the OH^- concentration

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(8) Anbar, M.; Bambenek, M.; Ross, B. "Selected Specific Rates of Reactions of Transients of Water", Document NSRDS-NBS 43, U.S. Department of Commerce: Washington, DC, 1973.

(9) *Actions Chimiques et Biologiques des Radiations*; Haissinsky, M., Ed.; Masson et C^ie: Paris, 1966.

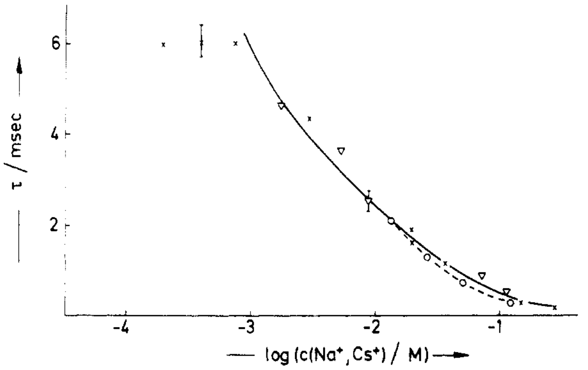

Figure 3. Half time τ of the first-order contribution of the decay reaction of hydrated electrons as a function of the alkali metal cation (Na^+ or Cs^+) concentration: X, CsOH; ▽, NaOH; ○, NaOH + $NaClO_4$.

at constant M^+ concentration by titration with perchloric acid in the pH range between 11 and 13 gives no change in the pseudo-first-order reaction rate (constant within 10%); however, increasing the M^+-ion concentration by addition of $NaClO_4$ at constant pH leads to the same decrease of the pseudo-first-order reaction half time (○ in Figure 3) as a corresponding increase of the alkali hydroxide concentration.

Thus, we can state undoubtedly that at high pH, but only then, an additional reaction channel for the electrons is open, namely, the reaction with alkali cations (and probably also alkali earth cations as we now can interpret Walkers experiments[1])

$$e^- + M^+ \rightarrow M^0 \qquad M = Cs \text{ and } Na \tag{8}$$

as already assumed by Hart.[2] Walker's[1] and our own failure[5] to detect the cation concentration dependence in the electron decay reactions was probably due to experimental reasons: the experiments were done at a pH too low to block the competing reaction 1.

Accepting that the additional reaction at high pH is that with alkali cations, we can get the rate constant for reaction 8

$$v = k_8[e^-][M^+] \tag{9}$$

with $k_8[M^+] = \ln 2/\tau_8$ and $1/\tau_{exp} = 1/\tau_8 + 1/\tau_{imp}$ and τ_{imp} = 6 ms due to impurities which we assume to have constant concentration (see Figure 3). The rate constant k_8 of course should be dependent on the ionic strength I of the solutions because we deal with a reaction between two charged species[10]

$$\log k_8 = \log k_8^0 - 1.02z(i)I^{1/2} \tag{10}$$

where $z(i)$ is the charge number of the reaction partner of the electrons and k_8^0 is the rate constant extrapolated to $I = 0$; the factor 1.02 is valid for aqueous systems at room temperature. The plot of k_8 vs. $I^{1/2}$ in Figure 4 definitely has a negative slope, i.e., $z(i)$ must be positive, and indicates $z(i) = 1$ (solid line; the dashed lines represent the scatter of the data: $z(i) = 0.8$ and 1.5, respectively). Thus, the kinetic salt effect at least is not incompatible with the assumption that the reaction partner of the electrons is an univalent alkali metal cation. The scatter of data in Figure 4 is understandable, since we assume a constant contribution in the first-order decay due to impurities of constant concentration—but very likely the impurity concentration will vary from sample to sample. Extrapolation of the data of Figure 4 to zero ionic strength yields $k_8 = (2.0 \pm 0.5) \times 10^4\ M^{-1}\ s^{-1}$. This constant is indeed below the upper limit $1 \times 10^5\ M^{-1}\ s^{-1}$ given in the literature[8] for the reaction between hydrated electrons and Na^+ ions. The more correct plot log k vs. $I^{1/2}/(1 + aI^{1/2})$ gives no decisive change in slope or rate constant.

Analyzing the decay curves of the hydrated electrons (observed at 700 nm) of course gives only indirect evidence for reaction 8. More direct evidence follows from the observation of the optical density in the near-UV. At low pH and low Na^+-ion concentration where reaction path 8 cannot compete with reaction path 1, no additional UV absorption is observed. At high pH, however, where path 1 is blocked, an absorption in the UV grows in within 1 ms after formation of hydrated electrons and decays within 100 ms. From these UV experiments, we could tentatively deduce the absorption spectrum[5] but not give kinetic data for the formation and decay of M^0 due to the instability of the UV lamp. More information follows from the double-flash and from the pulse radiolysis experiments.

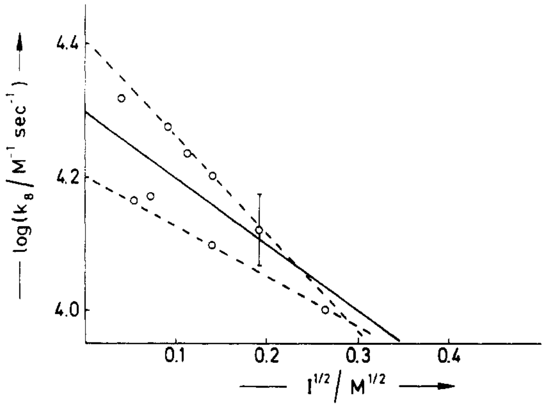

Figure 4. Dependence of the rate constant k_8 on the square root of the ionic strength I. The dashed lines envelop the experimental points; the solid line is the best fit with the theoretical slope of −1.

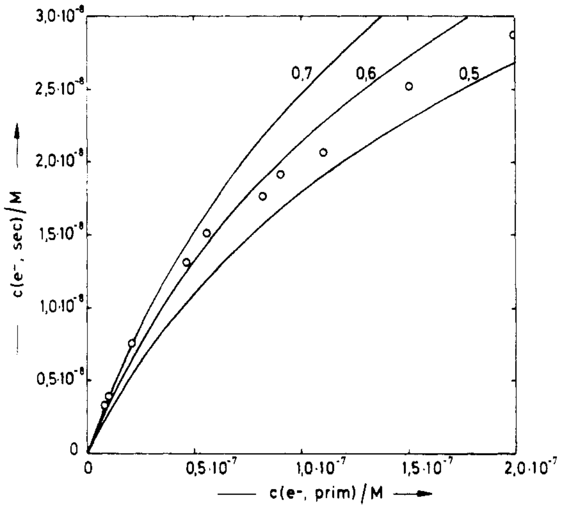

Figure 5. Concentration of secondary electrons vs. that of primary electrons in the double-flash experiments. The solid lines give the theoretical dependences with the proportionality factor a of eq 11 as parameter. $c(CsOH) = 4 \times 10^{-2}$ M; $c(CH_3OH) = 2 \times 10^{-2}$ M; delay time between flashes, 1.8 ms.

Double-Flash Experiments. As pointed out in the introduction, Walker et al.[1] assumed that the photoactive intermediate is a dimeric electron e_2^{2-} as a precursor of molecular hydrogen in reaction 2; in contrast Hart et al.[2] postulated in agreement with our results the intermediate to be formed with a M^+ cation as in reaction 8. We get further proof for this from the double-flash experiments.

At low alkali hydroxide concentrations where we find the normal electron decay reactions 1 and 2 (besides the reaction with an impurity), we never can produce secondary electrons by the delayed second flash no matter what the experimental conditions are; i.e., neither reaction 1 or 2 nor that with the impurity leads to the photoactive intermediate.

On the other hand at high alkali hydroxide concentration where we get the indirect evidence for the additional electron decay channel 8, the second flash revives secondary electrons after the primary electrons have decayed; i.e., the photoactive intermediate X is formed. Figure 5 displays the concentration of secondary electrons (1.7-ms delay of second flash of constant energy 600 J) as a function of the concentration of primary electrons (primary

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(10) Brönsted, J. N. *Z. Phys. Chem.* **1922**, *102*, 169; **1925**, *155*, 337.

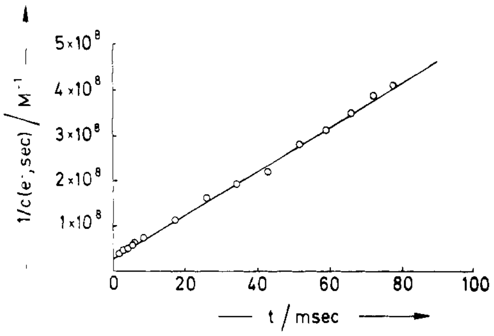

Figure 6. Time dependence of the secondary electron concentration (second-order plot). $c(\mathrm{CsOH}) = 4 \times 10^{-2}$ M; $c(\mathrm{CH_3OH}) = 2 \times 10^{-2}$ M; $c(\mathrm{e^-,prim}) = 1.8 \times 10^{-7}$ M; flash energies, 70 and 600 J, respectively.

flash varied within 10 and 100 J). Since the concentration of the secondary electrons is proportional to the concentration of X

$$c(\mathrm{e^-,sec}) = ac(\mathrm{X}) \qquad (11)$$

($a \leq 1$), we read from Figure 5 that the ratio $c(\mathrm{X})/c(\mathrm{e^-,prim})$ decreases with increasing primary electron concentration $c(\mathrm{e^-,prim})$. This excludes that the intermediate is formed in a second-order electron reaction (e.g., reaction 2 as suggested by Walker et al.[1] and already contradicted by Czapski[3]), which becomes predominant at high primary electron concentrations; i.e., it supports the conclusions of the preceding section that the intermediate is formed in a first-order electron reaction. An evaluation of Figure 5 will be given further below.

From the secondary electron concentration as a function of the delay time of the second flash and otherwise identical experimental conditions, we get the kinetics of the decay of the intermediate. The plot of $1/c(\mathrm{e^-,sec})$ vs. delay time in Figure 6 yields a straight line [$c(\mathrm{e^-,sec})$ decreases from 3×10^{-8} to 2.5×10^{-9} M within 80 ms] with no systematic deviation; i.e., the intermediate decays by a second-order process. This we would expect if indeed the intermediate has a stoichiometry of a neutral alkali metal atom $\mathrm{M^0}$ as we deduced in the preceding section. Thus, we formulate the decay reaction of the intermediate

$$2\mathrm{M^+} + 2\mathrm{H_2O} \rightarrow 2\mathrm{M^+} + 2\mathrm{OH^-} + \mathrm{H_2} \qquad (12)$$

If the intermediate were, according to Walker et al.,[1] a dimeric electron $\mathrm{e_2}^{2-}$, then for stoichiometric reasons it should decay by a first-order reaction.

From the slope of Figure 6 we read the rate constant $k_{12} = 2.5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ assuming the proportionality factor of eq 11 $a = 1$. But since very likely $a < 1$ and thus $c(\mathrm{M^0}) > c(\mathrm{e^-,sec})$, the real constant k_{12} will be smaller than $2.5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$.

With this information we can evaluate the experimental points of Figure 5 to get an estimate of the proportionality factor of eq 11 and thus of the true rate constant k_{12}. By the method of Runge and Kutta, we solved the coupled differential equations for the decay of hydrated electrons according to reactions 2 and 8 and the formation and decay of the intermediate $\mathrm{M^0}$ according to reactions 8 and 12 (reaction 1 can be neglected because at the high pH of the experiments it does not contribute to the electron decay; also reactions 3–7 can be excluded because of experimental conditions). The only parameter for the simulation of Figure 5 is factor a of eq 11; the rate constant k_{12} is smaller by the same factor than that read from Figure 6. The full lines of Figure 5 obtained with $a = 0.7$, 0.6, and 0.5 envelop the experimental points. Using $a = 0.6 \pm 0.1$, we finally have $k_{12} = (1.5 \pm 0.25) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$.

The systematic deviations of the experimental points from the simulated curves with constant a probably are due to the difficulties of reading the exact primary and secondary electron concentration at zero time from the original traces of the optical density vs. time: the stray light of the relatively long afterglow of the flashes does not allow the exact extrapolation of absorption to zero time.

Pulse Radiolysis. In the flash photolytic experiments, we observed a long-lasting absorption in the near-UV, peaking around 270 nm, which we think is due to the intermediate formed by reaction 8. To get better data for its absorption spectrum, we took up pulse radiolysis studies at the Hahn-Meitner Institut in Berlin.

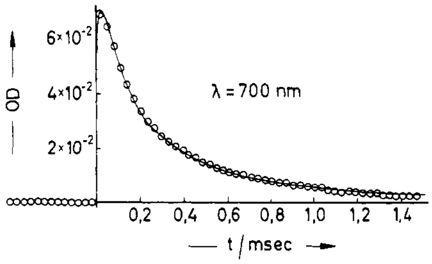

Figure 7. Time dependence of the optical density at 700 nm after a 100-rad electron pulse. $c(\mathrm{CsOH}) = 7 \times 10^{-2}$ M; $c(\mathrm{H_2}) = 7 \times 10^{-4}$ M; O, experimental points; solid line, calculated.

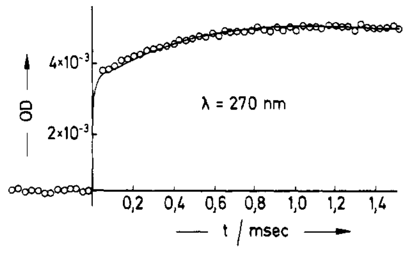

Figure 8. Time dependence of the optical density at 270 nm after a 100-rad electron pulse. $c(\mathrm{CsOH}) = 7 \times 10^{-2}$ M; $c(\mathrm{H_2}) = 7 \times 10^{-4}$ M; O, experimental points; solid line, calculated.

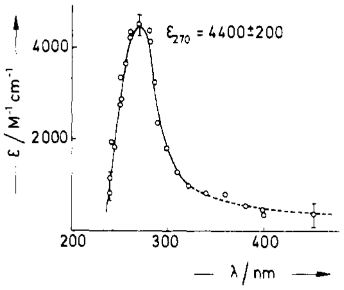

Figure 9. Absorption spectrum of $\mathrm{Cs^0}$. Experimental conditions as in Figure 7.

In Figures 7 and 8, the time dependence of the optical density at 700 and 270 nm, respectively, after an electron pulse is plotted (5-μs pulse, absorbed dose 100 rad). At 700 nm, where the hydrated electrons have their maximum absorption, the optical density after the pulse increases sharply due to prompt electrons and additional electrons formed in reactions 5 and −1 and then passes through a maximum and finally decays within 1.5 ms almost to zero. At 270 nm we also get an initial fast increase of the optical density due to the tailing absorption of the electron ($\epsilon(\mathrm{e^-},270\ \mathrm{nm}) = 700\ \mathrm{M^{-1}\ cm^{-1}}$) and then the optical density passes through a maximum about 1 ms after pulse, due to the growth of the intermediate $\mathrm{M^0}$, and decays to zero only after 0.1 s (not shown in Figure 8).

The full lines in Figures 7 and 8 are obtained by solving the coupled rate equations of all reactions involved with the rate constants given (including also those reactions which we neglected in the preceding section because of the slower time scale of the flash photolytic work). The only parameter we freely can choose is the extinction coefficient of $\mathrm{M^0}$ at 270 nm: we get the best fit with $\epsilon(\mathrm{M^0},270\ \mathrm{nm}) = 4400 \pm 200\ \mathrm{M^{-1}\ cm^{-1}}$. The agreement of the experimental data with the computer simulation is very good and confirms the kinetic data for $\mathrm{M^0}$ given before.

Evaluation of the curves taken at other wavelengths yields the absorption spectrum of the intermediate which is plotted in Figure 9. It has its maximum at 270 nm, falls off strongly below this (no data could be taken below 240 nm because of the too small intensity of the Xe lamp), and seems to tail off above 320 nm. However, we do not think this tail is real because above 320 nm the increasing absorption of the hydrated electron interferes with

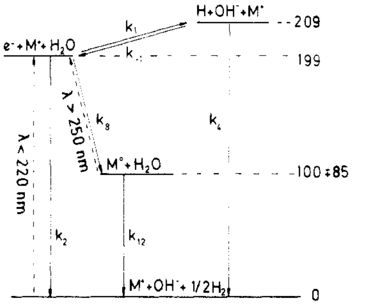

Figure 10. Schematic energy diagram of the intermediate species formed by the reactions of hydrated electrons in basic aqueous solutions: full arrows represent chemical reactions, dashed arrows photochemical transitions. The rate constants are given in the text. Energy scale on the right-hand side in kJ/mol.

that of the intermediate. The spectrum of M^0 obtained by pulse radiolysis is in best agreement with our tentative data obtained by flash photolysis[5] [λ(max) = 270 nm, ϵ(max) = 5000 M^{-1} cm^{-1}].

Conclusions

Our flash light and pulse radiolytic experiments fully confirm the experiments of Walker et al.[1] and Hart et al.[2] on a photoactive intermediate in the decay reaction of hydrated electrons in alkaline solutions and give additional information on the nature, the kinetics of formation and decay, and the absorption spectrum of the intermediate. The data are summarized in Figure 10 in the form of an energy diagram. The stable state of the alkaline aqueous system saturated with hydrogen ($M^+ + OH^- + {}^1/_2H_2$) can be excited by UV light ($OH^- + h\nu \rightarrow e^-$; λ(max,$OH^-$) = 193 nm) or by high-energy radiation ($H_2O \rightsquigarrow H_2O^+ + e^-$); the excited state after all other primary and secondary reaction products have been scavenged is the reactive hydrated electron ($e^- + M^+ + H_2O$).

Three reaction channels are open for the decay of hydrated electrons: (a) the known strongly exothermic second-order reaction 2 which directly leads to hydrogen and which is predominant at high electron concentrations, (b) the slightly endothermic first-order equilibrium reaction 1 leading to H atoms (because of unfavorable equilibrium this channel is blocked at high OH^- concentrations), and (c) reaction 8 with M^+ ions, observable only at high alkali hydroxide concentrations where reaction 1 is blocked and M^+ ions are available in high concentrations as a reaction partner.

Because neither reaction 8 nor 12 is an equilibrium reaction, we locate the intermediate state $M^0 + H_2O$ between the ground state and the excited state; i.e., reaction 8 is exothermic (the energy data given on the right of Figure 10 are obtained from thermodynamic considerations[11]).

In the many experiments done with dissolved CsOH and NaOH, we never could—within the limits of error—detect any differences in the kinetics or in the absorption of M^0. However, we think this cannot be used as an argument against our conclusions, for Zn^+, Cd^+, Co^+, Ni^+, Mn^+, etc., all known as primary products of hydrated electron reactions with the divalent cations, also have the same absorption spectra (λ(max) = 300 nm).[12]

We have one fact we cannot explain: in the experiments with heavy water we can neither revive hydrated electrons in the double-flash experiments nor detect any evidence for reaction 8 in the decay kinetics of the hydrated electrons in normal flash experiments: in heavy water the intermediate M^0 obviously is not formed. This of course is surprising, but in the literature we find experiments that hint into the same direction: in their pulse radiolytic studies with 0.2 M NaOH and 100 bar of H_2 as the scavenger, Matheson and Rabani[13] find, besides the expected second-order decay reaction 2, a pronounced first-order contribution. Since the first-order reaction 1 is blocked, the authors think the first-order contribution is due to an impurity. On the other hand doing the same experiments with the same experimental procedures in 0.2 M NaOD and 100 bar of D_2 in heavy water, Hart and Fielden[14] do not find any deviations from pure second-order decay kinetics. We cannot assume that in the Argonne Laboratory and in our laboratory the normal water will have the same impurities, and also in both laboratories the heavy water is free of these. Therefore, we think that Matheson and Anbar's deviations from a clean second-order kinetics are not due to an impurity reaction but to reaction 8, leading to the intermediate M^0. Of course the question remains open why M^0 should not be formed in heavy water or why should be there such as unexpected solvent isotope effect.

We have no general information on isotope effects of hydrated electron reactions in normal and heavy water. We only know that the diffusion-controlled reaction 2 has the same rate in both aqueous solvents.[8] On the other hand, the slow reaction 1 is in heavy water more than 10 times slower than in normal water;[8] i.e. it has a very pronounced isotope effect as does also our slow reaction 8. So presently we conclude that all non-diffusion-controlled electron reactions in aqueous solutions have a remarkable solvent isotope effect—perhaps as a consequence of stronger binding of the electrons in heavy water due to hydrogen bridging. Recently we showed that the reaction of sodium–ammonia solutions with water also has a very pronounced solvent isotope effect; in the fully deuterated system, it is about 5-fold slower than in the normal system.[4] Thus, we think that reaction 8 in heavy water is too slow to be detected—due to the solvent isotope effect.

Our experimental results on the kinetics of formation and on the absorption spectrum of the intermediate M^0 explain why Czapski[3] failed to detect it: because of conclusions by Walker et al.[1] that the photoactive intermediate is formed in the second-order reaction 2 and that it has a maximum light absorption around 350 nm, Czapski worked with high electron concentrations (>10^{-5} M) where reaction 2 is predominant, and he searched for the light absorption at 350 nm where according to Figure 9 the intermediate has at the best only a tailing absorption. Because of this failure, Czapski concluded all effects to be due to impurities.

Of course our work is not a final argument against impurities, and we think that no one ever can give one beyond any doubt. But we are sure we do not deal with impurities. First of all, Walker et al. in Canada, Hart et al. in the US, and we could revive solvated electrons after their decay by a photo flash. If we dealt with an impurity, then it should be an universal impurity of the same world-wide concentration, which is never present in heavy water. To exclude impurities, we used in our ≈50 experiments widely varying procedures of purification, we used reagents of different origins, and we used optical cells made of quartz and Suprasil—always getting the same results. We added impurities, e.g., oxygen which by repeated flashing is removed from the system, Ni^{2+} ions which in the basic solutions are completely precipitated, or Al^{3+} ions which form soluable oxo complexes: in no case could we find a photoactive species which could be detected in the double-flash experiments. Therefore, we think that reactions 8 and 12 really describe the observed effects.

Evidence for the formation of the neutral species Na^0 formed by electron reactions in basic water–methanol mixtures was also put forward by Sawamura et al.,[15] analyzing experimental data from Pikaev et al.[16]

Acknowledgment. We are grateful to Prof. A. Henglein and Dr. E. Janata for their cooperation and help in the pulse radiolytic experiments at the Hahn-Meitner-Institut in Berlin and to the Deutsche Forschungsgemeinschaft and to the Fonds der chemischen Industrie for financial support.

Registry No. CH_3OH, 67-56-1; NaOH, 1310-73-2; H_2O, 7732-18-5; CsOH, 21351-79-1; H_2, 1333-74-0; Na^+, 17341-25-2; Cs^+, 18459-37-5.

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