The foregoing reaction is just such an efficient reaction, and it requires only the presence of hydroxyl groups. Since these groups are present in large amounts within cells (for example, in sugars) and since increased resistance to radiation damage is shown by bacteria grown in a glucose medium (*3*), it is possible that this type of reaction plays a part in the high-dose radiation chemistry of cells.

P. E. Brown
M. Calvin
J. F. Newmark
Lawrence Radiation Laboratory, University of California, Berkeley

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12 November 1965

Mobility of the Hydrated Electron

Abstract: *The transient change in conductivity in diluted barium hydroxide solutions during and immediately after irradiation with single pulses of electrons from a 15-million-electron-volt linear accelerator was measured. Ionic mobility of the radiation-produced hydrated electrons was 1.84* $\times 10^{-3}$ *cm*^{2} *volt*$^{-1}$ *sec*$^{-1}$ $\pm$ *10 percent. This value corresponds to a diffusion constant of 4.75* $\times 10^{-5}$ *cm*^{2} *sec*$^{-1}$.

The hydrated electron, one of the prime objects of research in radiation chemistry (*1, 2*), has been firmly established as the main reducing species in water radiolysis. Its absorption spectrum is now well known, and its yield as well as the rate constants of its chemical reactions with numerous inorganic and organic species have been measured, mostly with spectrophotometric techniques. Also, some other physicochemical properties have been calculated theoretically (*3*) or estimated from experimental data (*1, 2*).

One of the aforementioned properties of the hydrated electron is its diffusion constant. This quantity, together with rate constants, is important for the calculation of yields in the diffusion model (*4*), by which method it may be possible to determine the initial spatial distribution of the primary species in the spurs. The diffusion constant D_{e-} is related to the ionic mobility μ_{e-} by the expression $D_{e-} = \mu_{e-}kT/q_{e-}$, where k is the Boltzmann constant, T is the absolute temperature, and q_{e-} is the charge on the electron. We therefore undertook to determine the diffusion constant of the hydrated electron by measuring its mobility, using a conductivity method.

If degassed water is irradiated with a pulse of ionizing radiation, a transient change of conductivity can be observed owing to the formation of hydrated electrons and the ionic species H_3O^+ and OH^-. In alkaline solution, practically all the H_3O^+ ions formed will immediately react with OH^- ions. Now, since the yield (G) of H_3O^+ is larger than that of OH^- [$G_{H_3O^+} = 3.6$ ions per 100 ev, $G_{OH^-} = 1.0$ ions per 100 ev (*5*)], we can expect a transient decrease in OH^- concentration during and immediately after the pulse, corresponding to a "negative yield" of -2.6 and thus approximately equal to electron concentration ($G_{e-} = 2.6$), and only a very slight increase in H_3O^+ concentration during the pulse. Therefore, the conductivity signal obtained will be strongly dependent on electron mobility.

We used approximately $4 \times 10^{-5}N$ $Ba(OH)_2$ solution (the highest concentration compatible with our technique) prepared by degassing triply-distilled water (*6*) and injecting a small volume of filtered $10^{-2}N$ $Ba(OH)_2$ solution. The exact concentration of the final solution and its carbonate content, the latter being about 5 μM, were determined by a conductometric titration technique. The samples were irradiated with single electron pulses of 4-μsec duration from a 15-Mev linear accelerator, in a quartz cell with 75-μ platinum foils as electrodes. The irradiation assembly and the electric circuit are shown in Fig. 1. The electron beam was collimated in a triple collimator so that a sufficiently homogeneous radiation field of 2.5-cm diameter was obtained. After passing through the cell, the beam was stopped in a Faraday cup. The current from the Faraday cup was integrated in a 10-microfarad capacitor (not shown in the figure), the voltage on which could be measured with a vibrating-reed electrometer. The electrometer reading was used for monitoring the dose; it had been calibrated previously by filling the cell with a Fricke dosimeter solution (*7, 8*) and establishing the relation between dose and electrometer reading. For measuring the transient conductivity signal, we used a symmetrical circuit (Fig. 1). This was necessary because part of the beam electrons are stopped in the cell, causing strong negative signals from both electrodes. These signals are several times as large as the conductivity signal. By properly adjusting the two channels of the differential amplifier (a Tektronix type CA plug-in unit with a separate type 132 power supply), these "charge-induced" signals could be canceled to a considerable extent. A change in conductance of the cell, however, resulted in a proportional voltage change across the differential amplifier; the voltage change was amplified and fed to the upper beam input of a Tektronix type 555 dual-beam oscilloscope equipped with two type L plug-in units. The lower beam input was connected to the Faraday cup for monitoring the beam pulse shape.

In order to minimize the effect of electrolysis and electrode polarization, the polarity of the batteries was reversed approximately every second by means of an automatic switching device. The resulting square-wave signal at the input of the differential amplifier could be eliminated by adjusting a compensating circuit consisting of two fixed 2-kilohm resistors and two 2-megohm variable resistors (marked "Compensation" in Fig. 1). Guard electrodes on both ends of the cell were kept at the same d-c (and slow a-c) potentials as the adjacent cell electrodes, thus eliminating the possible influence of radiation-induced conductivity in the cell windows. The linear accelerator could be triggered between any two polarity

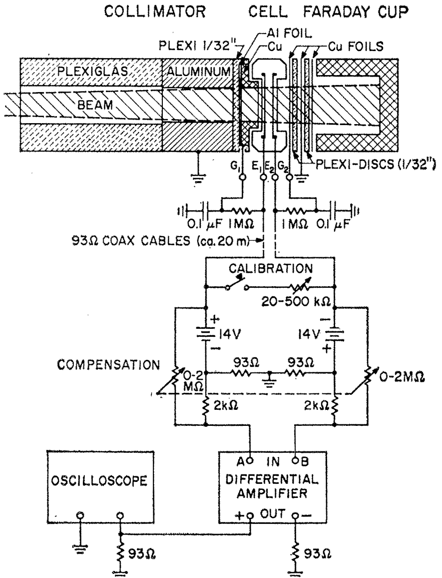

Fig. 1. Apparatus for transient conductivity measurements.

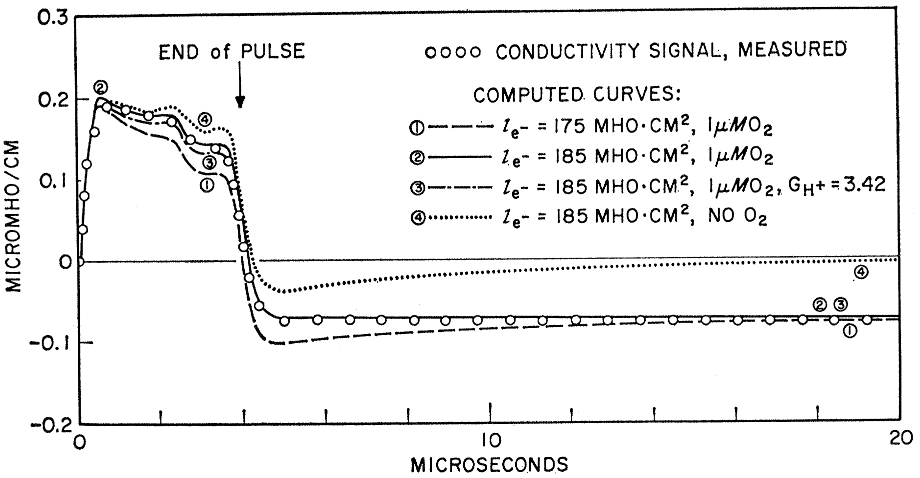

Fig. 2. Transient conductivity signal, obtained by irradiating a $Ba(OH)_2$ (about 4 × 10^{-5} *N*) solution with a 4-μsec pulse of electrons at an average dose rate of 4 × 10^{25} ev liter^{-1} sec^{-1}, and several computed signals.

reversals. For each measurement, two oscilloscope pictures at different battery polarities were taken. Since the nonbalanced portion of the charge-induced signals was independent of cell voltage, the "pure" conductivity signal could be derived by algebraical subtraction of the signals in the two pictures.

Figure 2 shows the conductivity signal (circles) obtained by subtracting two such traces. For evaluating the results, a CDC-3600 digital computer was used. A computer program had been written so that the concentrations of all chemical species involved and the change in conductivity as functions of time could be calculated from (i) the *G*-values for the molecular and radical products of water radiolysis; (ii) the rate constants for the reactions of these products with each other, published values (*9*), mostly determined by optical pulse-radiolysis techniques, being used; (iii) the mobilities of all ionic species (in this case the known values for H_3O^+ and OH^- and assumed values for e^-); (iv) the dose rate as a function of time, approximated by successive step functions.

Several conductivity signals thus computed are included in Fig. 2. As can be seen in this figure, the signals become negative after the pulse, an indication of transient decrease in conductivity which can be explained by a mobility of the electrons less than that of OH^-. The negative portion is strongly influenced by impurities such as O_2 which scavenge electrons and form negative ions of lower mobility (such as O_2^-). In order to fit the measured and the computed curve, we had to assume an oxygen content of the solution of 1 μM (compare curves No. 2 and No. 4). On the other hand, the positive portion depends strongly on electron mobility (compare curves No. 1 and No. 2), but relatively little on above-mentioned impurities, so that this portion was used as a criterion for the mobility. In order to show the influence of the H_3O^+ yield, about which there still is some uncertainty, we have also computed a curve for $G_{H_3O^+} = 3.42$ (5 percent lower than the value assumed to be correct) and correspondingly $G_{OH^-} = 0.82$ (curve No. 3). In Fig. 2 the best fit was obtained with curve No. 2, indicating an equivalent conductance, l_{e^-}, equal to 185 mho cm². Other measurements yielded slightly different values. As average values, we obtained for the hydrated electron the following results: the equivalent conductance, l_{e^-}, was 177 mho cm² ± 10 percent (*10*); the mobility ($\mu_{e^-} = l_{e^-}/F$, where F is the Faraday constant), μ_{e^-}, was 1.84×10^{-3} cm² volt^{-1} sec^{-1} ± 10 percent; the diffusion constant, $D_{e^-} = 4.75 \times 10^{-5}$ cm² sec^{-1} ± 10 percent. These values are about half the values previously estimated by Schwartz (*11*) and Platzman (*3*). Matheson (*2*) has used our value of the diffusion constant for calculating the diffusion-controlled rate constant for the reaction of the hydrated electron with oxygen, at the same time using an electron radius of 2.7 Å (*12*) and a radius for O_2 of 1.6 Å (*13*). The value obtained (2.33×10^{10} M^{-1} sec^{-1}) is consistent with the experimental value of 2×10^{10} (*9*).

KLAUS H. SCHMIDT
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60440
WARREN L. BUCK
Solid State Science Division

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A Search for Intergalactic Hydrogen in the Virgo Cluster

Abstract. *A fixed-horn antenna having a beam 10° by 10°, and a switched-load radiometer with traveling-wave-maser preamplifier were used to observe the 21-cm spectrum of the Virgo cluster of galaxies. An upper limit to the antenna temperature is 0.024°K relative to regions outside the cluster with filters whose width is 2 Mc/sec. If the excitation temperature of the intergalactic hydrogen is enough greater than the background continuum radiation so that absorption can be ignored, and if the velocity spectrum is that defined by the galaxies, the density of optically thin neutral hydrogen in the cluster does not exceed that outside of the cluster by an amount that gives 5.6 × 10^{12} solar masses in the cluster.*

Whether or not clusters of galaxies contain large masses of intergalactic material is an open question. See, for example, the opposing views of van den Bergh (*1*) and Holmberg (*2*). If this intergalactic material exists, it might be in the form of ionized hydrogen (*3*) or in another form. However, if the material is neutral atomic hydrogen, it may