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Abstract

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THE E.P.R. SPECTRUM OF THE HYDRATED ELECTRON IN IRRADIATED FROZEN ALKALINE SOLUTIONS

The formation of the hydrated electron, e_{aq}^{-}, during the radiolysis of water and aqueous solutions was postulated as early as 1953 (^{1}). Later, as a result of kinetic studies, some evidence was obtained for the participation of two kinds of "hydrogen atoms" in radiation reactions occurring in aqueous solutions (^{2}). The properties of the hydrated electron (or "polaron," in the terminology of the author of the cited work) were discussed in an article (^{3}). Recently (^{4,5}) it was shown that "hydrogen atoms" of one of the two kinds have a negative charge equal to unity. Finally, in work (^{6}) the existence of e_{aq}^{-} was proved by methods of optical spectroscopy.

By the method of electron paramagnetic resonance (e.p.r.), H atoms and OH and HO_2 radicals were found in frozen irradiated acids and neutral water ($^{7-10}$). In these objects the hydrated electron apparently interacts with hydrogen ions, being converted into atomic hydrogen:

$$e_{aq}^{-} + H_3O^{+} \rightarrow H + H_2O \tag{1}$$

and therefore does not appear in the e.p.r. spectrum. Obviously, in alkaline ice e_{aq}^{-} should be stabilized and should give an e.p.r. signal.* For this purpose we investigated the e.p.r. spectra of frozen irradiated alkaline solutions of various concentrations and at various temperatures.

The source of ionizing radiation was a direct-acceleration electron tube (^{12}). The electron energy was 0.9 MeV. The e.p.r. spectra were recorded on an RE 1301 radiospectrometer. In all experiments twice-distilled water was used. Heavy water (D_2O content–99.8%) was purified by preliminary irradiation and redistillation. The alkalis used were of "chemically pure" grade. Before use, hydrogen peroxide was distilled in vacuum.

Samples of the solutions studied, of volume 0.05 ml, were placed in ampoules made of special glass, which gave almost no e.p.r. signal upon irradiation, were slowly frozen, and were transferred into a special device intended for their irradiation at the temperature of liquid nitrogen. This device consisted of a massive copper block with grooves for the ampoules; the lower end of the block was immersed in a wide Dewar vessel with liquid nitrogen. The thermal stability

Fig. 1. EPR spectra of irradiated water and KOH solutions

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of the products formed upon irradiation was studied with the aid of a cryostat, in which samples with irradiated ice were kept for 10 min at a specified temperature. In all cases the e.p.r. spectra were recorded at −196°.

The absorbed dose rate was determined with the aid of a cerium dosimeter. A $2 \cdot 10^{-3}$ M solution of ceric sulfate in 0.4 M H_2SO_4 was used, which after irradiation was diluted with 0.4 M H_2SO_4 the required number of times. The value $G(Ce^{3+})$ for a Ce^{4+} solution of this concentration was taken to be 2.5 ions/100 eV ([13,14]). The dose rate was usually $3.5 \cdot 10^{17}$ eV/ml • sec.

Figure 1 shows the EPR spectra of irradiated frozen water and alkaline solutions. In the case of H_2O, the EPR spectrum of ice irradiated at liquid-nitrogen temperature consists of a doublet belonging to the OH radical and a broad band assigned, according to ([7]), to the H_2O^+ ion (Fig. 1a). In irradiated D_2O ice, the triplet of the OD radical is observed (Fig. 1b).

Fig. 1. EPR spectra of irradiated water and KOH solutions:
a –H_2O at −196°; *b* –D_2O at −196°; *v* –H_2O at −150°; *g* –H_2O_2 solution in water at −150°; *d* –1 M KOH solution at −196°; *e* –5 M KOH solution at −196°; *zh* –10 M KOH solution at −196°; *z* –1 M KOH solution at −150°; *i* –5 M KOH solution at −150°; *k* –10 M KOH solution at −150°. The dose is approximately $3 \cdot 10^{20}$ eV/ml. The vertical line indicates the position of the EPR signal for DPPH.

After thawing the water samples to a temperature of −150°, a weak signal remains, attributable to the HO_2 radical (Fig. 1v). The intensity of this signal increases sharply in a hydrogen peroxide solution (Fig. 1g). All these results are in complete agreement with the literature data ([7]-[10]). Figure 1d, e, zh shows, respectively, the EPR spectra of 1, 5, and 10 M KOH solutions irradiated at liquid-nitrogen temperature.* As can be seen from these figures, already in a 1 M frozen KOH solution a new broad line appears with a *g*-factor approximately equal to 2.04, and its intensity increases substantially as the concentration of KOH in the ice is increased. At the same time, a decrease is observed in the intensity of the lines belonging to the OH radical, and the appearance of a new narrow line with a *g*-factor corresponding to the *g*-factor of the free electron. Along with this, as the KOH concentration increases,

* When the present work was nearing completion, a communication appeared ([11]), the authors of which assigned one of the lines in the e.p.r. spectrum of irradiated alkaline ice to e^-_{aq}. However, this line apparently belongs to the hydrated ion-radical $O^- \cdot nH_2O$.

* Frozen irradiated NaOH solutions give an analogous EPR spectrum. Pure KOH irradiated at low temperature gives no EPR signal under these conditions.

Fig. 2

Figure 2: Fig. 2

the color of the irradiated ice changes from blue to dark blue. After samples of alkaline ice are kept for 10 min at a temperature of −150°, the lines of the OH radical disappear completely for all the KOH concentrations studied (Fig. 1, ,); two lines remain: a broad one (g-factor 2.04, line width $\Delta H = 40$ Oe) and a narrow one (g-factor about 2.002, $\Delta H = 13$ Oe). Complete disappearance of the EPR signal occurs at a temperature of approximately −110°. At the same time the color of the irradiated alkaline ice also disappears.

In the EPR spectrum of concentrated KOH solutions irradiated at a temperature of 196°, there are also observed a doublet with splitting of 500 Oe in the case of H_2O (Fig. 2a) and a triplet with a distance between components of 78 Oe in the case of D_2O (Fig. 2), belonging to H and D atoms, respectively.

We assign the broad line to the hydrated ion-radical $O^- \cdot nH_2O$, arising as a result of the reaction:

$$OH + OH^- + (n-1)H_2O \rightarrow O^- \cdot nH_2O. \tag{2}$$

It should be noted that the formation of the ion-radical O^- was postulated in work (^{15}) in explaining radiation reactions in alkaline solutions. Earlier this line had been found in the EPR spectrum of an alkaline $NaNO_3$ solution irradiated at a temperature of −145° (^{16}). The authors of the cited work also assigned it to the hydrated ion-radical $O^- \cdot nH_2O$. In analogous solutions and under the same conditions this line was also observed by us. However, in a sufficiently concentrated alkaline solution of hydrogen peroxide it disappears. Apparently, the nitrate ion reacts with OH or O^- very slowly, whereas for hydrogen peroxide such reactions are quite characteristic. In addition, according to (^{16}), the line assigned to $O^- \cdot nH_2O$ is not observed in a frozen alkaline $NaNO_3$ solution with additions of such effective acceptors of OH radicals as glycerin and ethyl alcohol. All these data indicate that the appearance of the broad line with g-factor about 2.04 is connected with the fate of the OH radical. Like the authors of work (^{16}), we believe that the considerable shift of the g-factor and the broadening of the line are due to the presence of a residual orbital moment in the O^- ion and to the action upon it of intracrystalline fields.

Fig. 2. EPR spectra of irradiated 10 M KOH solutions: a –in H_2O at −196°; –in D_2O at −196°; –in D_2O at −150°. The dose is approximately $3 \cdot 10^{20}$ eV/ml.

The narrow line, in our opinion, belongs to the hydrated electron, e^-_{aq}, or to a polaron. In favor of this assumption speaks, first, the fact that the g-factor for this line is close to the g-factor of the free electron. It should be noted that the g-factor of the EPR signal in the case of ammonia solutions of alkali metals, for which the presence of solvated electrons or polarons has been shown by many methods, also

is close to the *g*-factor of the free electron (17). The paramagnetic-resonance lines of such solutions are extremely narrow (of the order of tenths of an oersted). However, their width depends on the concentration of the solution and on temperature*.

Second, evidence for the presence of e_{aq}^- in irradiated alkaline ice may be provided by the results of our experiments on the investigation of the e.p.r. spectra of irradiated frozen 10 M KOH solutions in heavy water (Fig. 2b, c). Analysis of the spectrum shown in Fig. 2b indicates that it is a superposition of a triplet belonging to the D atom, a singlet of the ion-radical $O^- \cdot nD_2O$, and a narrow line of e_{aq}^-**. After holding the sample for 10 min at −150°, the triplet of the D atom disappears and, as in the case of H_2O, two singlets remain, attributable to $O^- \cdot nD_2O$ and e_{aq}^- (Fig. 2c). In the case of D_2O, the width of the line attributed to $O^- \cdot nD_2O$ is the same as for H_2O. This confirms our assumption that the unpaired electron in this ion-radical is localized on the oxygen atom. At the same time, the line belonging to e_{aq}^- narrows ($\Delta H = 7$ oersted). The latter is apparently due to the interaction of the electron with the spins of the surrounding nuclei and to the difference in the magnitudes of the magnetic moments of the H and D nuclei. Third, alkaline ice containing relatively small additions of hydrogen peroxide does not become colored upon irradiation. However, the $O^- \cdot nH_2O$ line still appears in the e.p.r. spectrum of this solution. Evidently, hydrogen peroxide accepts e_{aq}^- more efficiently than $O^- \cdot nH_2O$. Fourth, with increasing KOH concentration there is an increase in the yield of radicals in ice irradiated at −196° (see Table 1). This can be explained by stabilization of e_{aq}^- and conversion of OH into $O^- \cdot nH_2O$, and by the consequent decrease in the probability of recombination processes of radical products during irradiation. It cannot be excluded, however, that in these solutions the electron is stabilized at low temperature in the form of an *F*-center.

Table 1

Dependence of the radical yield on KOH concentration at temperatures −196 and −150°

Temp., °C	KOH conc., M	G, radicals/100 eV
−196	0	0.55
−196	1	0.6
−196	5	1.1
−196	10	1.6
−150	0	negligible
−150	1	0.2
−150	5	0.8
−150	10	1.6

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* According to (11), the width of the e.p.r. signal line in a sodium-ammonia solution at −196° is 11 oersted.

** The concentration of OD radicals in this case is very small. Therefore they do not appear in the e.p.r. spectrum.

Note: Figure translations are in progress. See original paper for figures.