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Abstract

Full Text

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PROOF BY THE E.P.R. METHOD OF THE PARTICIPATION OF THE TRAPPED ELECTRON IN RADIATION-CHEMICAL REACTIONS IN FROZEN AQUEOUS SOLUTIONS

Earlier, by the e.p.r. method, we showed (^{1}) the presence of a hydrated (more precisely, trapped) electron in irradiated frozen aqueous solutions of alkalis. In communications (^{2,3}), its formation under these conditions was detected by methods of optical spectroscopy. Many dissolved substances (for example, nitrite or nitrate ions) are effective acceptors of this intermediate product of radiolysis. Therefore it may be assumed that the introduction of such acceptors into an alkaline solution in sufficiently high concentrations will cause the formation of the corresponding ion-radical products. For this purpose, in the present work an investigation was made of the e.p.r. spectra of irradiated frozen aqueous solutions of sodium nitrite and nitrate in acidic, neutral, and alkaline media. The procedure for irradiation and measurement of the e.p.r. spectra is described in our work (^{1}). Nitrite was determined colorimetrically with the Griess reagent (^{4}).

Fig. 1. E.p.r. spectra of irradiated $NaNO_2$ solutions at −150° (absorbed dose $\sim 2 \cdot 10^{20}$ eV/ml):
a −1 M $NaNO_2$ solution; *b* −1 M $NaNO_2$ solution in alkaline medium (5 M KOH). The vertical line indicates the position of the e.p.r. signal of polycrystalline DPPH.

The e.p.r. spectra of aqueous solutions of $NaNO_2$ and $NaNO_3$ irradiated at

$-196°$ in acidic and neutral media are a superposition of the doublet of the OH radical, formed by the action of radiation on water, and of the lines of radicals arising from nitrite or nitrate ions. The e.p.r. spectrum of alkaline solutions is also the result of superposition of the lines of several radicals formed both from water and from the dissolved substance. However, in alkaline solution, as we showed earlier (^{1}), the OH radical is transformed into the thermally more stable ion-radical $O^- \cdot nH_2O$. The ratio of the line intensities of the OH and $O^- \cdot nH_2O$ radicals is determined by the alkali concentration.

The OH radicals disappear at a temperature of approximately $-160°$, whereas radicals arising from nitrite or nitrate ions, as well as the ion-radicals $O^- \cdot nH_2O$ (in the case of alkaline solutions), are stable at this temperature; moreover, the concentration of these radicals does not change noticeably on heating to $-140°$.

The EPR spectra of irradiated frozen aqueous solutions of nitrite ions in acidic and neutral media are identical. The EPR spectra of radicals remaining after the disappearance of OH radicals, as well as their interpretation, are shown in Figs. 1 and 2. The principal characteristics of their lines are presented in Table 1. It should be noted that the general form of the EPR spectra at $-150°$ obtained by us coincides with those given in works (5, 6). However, our interpretation of some lines differs from the interpretation of the authors of those works.

Table 1

Radical number	Number of components of the hyperfine structure	Distance between the outer components, Oe	g-factor	Proposed radical
I	3	116	~ 2.00	NO_2
II	3	85	~ 2.00	NO_2
III	3	~ 60	~ 2.00	NO_2^{2-}
IV	3	64	~ 2.00	NO_3^{2-}
V	1	–	2.015	NO_3
VI	1	–	~ 2.04	$O^- \cdot nH_2O$

As analysis shows, lines of radicals I and II in the EPR spectra of frozen solutions of nitrite and nitrate ions are always present. The main characteristics of the lines of radical I coincide with the characteristics available in the literature for the lines of the NO_2 radical. For example, according to data (7), the distance between the outer components of the triplet of this radical, obtained as a result of irradiation of KNO_3 powder, is 113 Oe. Radical II is always associated with radical I. The intensity of the triplet of radical II is small compared with the intensity of the triplet of radical I. Therefore, in the case of neutral, and especially alkaline, $NaNO_3$ solutions, when the intensity of the triplet of radical I is very small, the lines of radical II are scarcely manifested. The ratio of the

Fig. 2. EPR spectra of irradiated NaNO3 solutions at −150° (absorbed dose $\sim 10^{20}$ eV/ml): a–0.9 M NaNO3 + 0.1 M HNO3 solution; –1 M NaNO3 in an alkaline medium (5 M KOH); –1 M NaNO3 solution

Figure 2: Fig. 2. EPR spectra of irradiated NaNO3 solutions at −150° (absorbed dose $\sim 10^{20}$ eV/ml): a–0.9 M NaNO3 + 0.1 M HNO3 solution; –1 M NaNO3 in an alkaline medium (5 M KOH); –1 M NaNO3 solution

intensities of the lines of radicals I and II remains constant during irradiation of samples of frozen $NaNO_2$ and $NaNO_3$ solutions and upon thawing them. This indicates that they apparently belong to one and the same radical, namely the NO_2 radical. Probably the difference in their spectra is due either to a different configuration of the NO_2 molecule or to different sites of its localization. In work (8) it was shown that the appearance of the EPR spectrum of the NO_2 radical at 4.2° K is affected by the position in the crystal lattice of the matrix (Ar, CO_2, or CH_4) in which this radical is localized.

Fig. 2. EPR spectra of irradiated $NaNO_3$ solutions at −150° (absorbed dose $\sim 10^{20}$ eV/ml): **a**–0.9 M $NaNO_3$ + 0.1 M HNO_3 solution; **b**–1 M $NaNO_3$ in an alkaline medium (5 M KOH); **c**–1 M $NaNO_3$ solution.

From Fig. 1 it is seen that in the EPR spectrum of an irradiated frozen alkaline nitrite solution, in addition to radicals I and II, a triplet of radical III and a singlet of radical VI (*g*-factor about 2.04) are also observed. Earlier (1), on the basis of analysis of the EPR spectra of irradiated frozen alkali solutions, we assigned this singlet to the ion-radical $O^- \cdot nH_2O$. The triplet of radical III, in our opinion, belongs to the ion-radical NO_2^{2-},

arising from the addition of a hydrated electron to the ion NO_2^-:

$$NO_2^- + e_{aq}^- \rightarrow NO_2^{2-}. \tag{1}$$

The occurrence of reaction (1) was postulated by some authors for the radiolysis of an aqueous nitrite solution at ordinary temperature (^{9,10}). The formation of NO_2^{2-} ion-radicals upon irradiation of KCl and KBr crystals with additions of KNO_2 was observed by the EPR method in work (^{11}).

In the EPR spectra of neutral and alkaline sodium nitrate solutions radical IV is present. The relative intensity of its lines increases with increasing alkali concentration. In an acidic medium this radical is absent. Apparently, this radical should be assigned the structure NO_3^{2-}. The possibility of formation of the radical NO_3^{2-} was indicated in work (^{11}). In work (^{12}), triplets of radicals in irradiated crystalline nitrate in the presence of small amounts of NO_2^- were assigned, respectively, to NO_2 and NO_3^{2-}. In the EPR spectrum of an alkaline nitrate solution, as in the case of a nitrite solution, there is singlet VI, which, as already stated earlier, belongs to the ion-radical $O^- \cdot nH_2O$. The formation of radical V is associated with the fate of the OH radical, as was found earlier in works (^{5,6}). Fig. 3 clearly shows that the disappearance of OH radicals is accompanied by the appearance of radical V—a singlet with *g*-factor 2.015. In our opinion, this singlet should be assigned to the NO_3 radical, in which the unpaired electron is localized on the nucleus of the oxygen atom ($I = 0$). Formation of such a radical was observed in work (^{7}) upon irradiation of crystalline KNO_3.

Thus, the results we obtained indicate that the EPR spectra of irradiated solutions of nitrite and nitrate ions depend strongly on the acidity of the medium. This, in our view, indicates that the formation of radicals from the dissolved substance occurs mainly as a result of interaction of the dissolved substance with radicals arising from water. The nature of the latter, as is known, depends on the pH of the solution.

In our case the radical NO_3^{2-}, apparently, is formed as a result of the reaction:

$$NO_3^- + e_{aq}^- \rightarrow NO_3^{2-}. \tag{2}$$

Fig. 3. Change in the appearance of the EPR spectrum of a $1\,M$ $NaNO_3$ solution irradiated at −196°, during thawing: *a*—solution irradiated at −196°; *b* —solution kept for 10 min at −180°; *v*—the same at −170°; *g*—the same at −160°.

The intensity of the lines of the NO_3^{2-} ion-radical increases with increasing alkali concentration. However, in acidic solutions, where e_{aq}^- is effectively converted into H atoms, NO_3^{2-} radicals are not formed. Apparently, for the same reason the triplet lines of the NO_2^{2-} radical are absent from the EPR spectra of frozen $NaNO_2$ solutions in acidic and neutral media. According to (^{13}), the formation of NO_2 upon irradiation of aqueous NO_3^- solutions occurs as a result of the reaction of NO_3^- with H atoms:

$$NO_3^- + H \rightarrow NO_2 + OH^-. \tag{3}$$

Therefore, in an acidic medium, instead of NO_3^{2-} only NO_2 radicals arise.

OH radicals, as indicated, are transformed in an alkaline medium into ion-radicals $O^- \cdot nH_2O$. However, in neutral and acidic media in nitrate solutions they can react with NO_3^- ions:

$$NO_3^- + OH \rightarrow NO_3 + OH^-. \tag{4}$$

The possibility of such a reaction during the radiolysis of aqueous NO_3^- solutions was indicated in works (^{14,15}).

In the EPR spectra of alkaline solutions of $NaNO_2$ and $NaNO_3$, irradiated at a temperature of −196°, a doublet of the H radical is observed (in the case of H_2O) and a triplet of the D atom (in the case of D_2O), with a separation between the outer components of ∼ 500 and ∼ 156 oersteds, respectively. With increasing concentration of the dissolved substance they disappear.

Table 2

Composition of solution and saturating gas	G, radicals/100 eV, −196°	G, radicals/100 eV, −150°	$G(NO_2^-)$, ions/100 eV
$1M$ $NaNO_2$ (air)	0.7	0.6	–
$1M$ $NaNO_2$ + $5M$ KOH (air)	1.6	1.6	–
$1M$ $NaNO_3$ (air)	1.0	0.6	0.6
$5M$ $NaNO_3$ (air)	2.3	2.2	1.1
$1M$ $NaNO_3$ + $1M$ KOH (air)	1.3	0.9	0.5
$1M$ $NaNO_3$ + $5M$ KOH (air)	1.6	1.6	1.0
$1M$ $NaNO_3$ + $1M$ KOH (argon)	1.1	0.9	0.8
$1M$ $NaNO_3$ + $5M$ KOH (argon)	2.2	2.2	1.45

With an increase in the concentration of dissolved $NaNO_2$ and $NaNO_3$, as well as KOH, the yield of radicals increases. At the same time the yield of nitrite ions in thawed $NaNO_3$ samples also increases (see Table 2). This phenomenon is apparently associated with a decrease in the probability of recombination processes of radicals formed from water during irradiation, and, in the case of high concentrations of $NaNO_2$ and $NaNO_3$, to some extent also with the direct action of radiation on the dissolved substance.

Irradiated $NaNO_3$ solutions in acidic and neutral media are colored bluish*, whereas $NaNO_2$ solutions and alkaline $NaNO_3$ solutions are colorless. The absence of the dark-blue color characteristic of the trapped electron stabilized in an alkaline medium (^{1}) also confirms our hypothesis that, under these conditions, e_{aq}^- interacts with NO_2^- and NO_3^- (reactions 1 and 2).

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* This coloration is probably due to NO_3 radicals.

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