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Abstract

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M. A. PROSKURNIN, V. A. SHARPATYI, V. I. SMIRNOVA,
N. M. POMERANTSEV, G. N. KUZMINCEVA and T. A. SIMONOVA

TRANSFORMATION OF THE OXIDIZING COMPONENT OF RADIOLYSIS IN THE NITRATE-WATER SYSTEM

(Presented by Academician A. N. Frumkin, 25 February 1961)

To elucidate the role of OH radicals in the process of radiolytic reduction of the nitrate ion in alkaline solutions, the kinetics of accumulation of H_2O_2 and O_2 were investigated; these, it may be assumed, are formed by reactions of dimerization and disproportionation of free hydroxyl (¹), the oxidizing component of water radiolysis.

Solutions prepared from chemically pure reagents and twice-distilled water were irradiated; sodium nitrate was recrystallized twice beforehand. Radioactive Co^{60} preparations with a dose rate in the irradiated volume of 20–750 rad/sec were used as the radiation source.

Table 1

G	~ 14	11.4	8	5	3	2.7	2.1
$G_{H_2O_2}$	—	0.3	0.1	0.1	0.1	0.1	0.1
G_{O_2}	0.8	0.6	0.8	0.7	1.2	1.2	0.8
G_{OH}^*	0	3.9	3.5	3.7	4.1	3.8	5.3
$\sum G_{OH}$	3.2	6.9	6.9	6.7	9.1	8.8	8.7

* OH used for the oxidation of nitrite.

Analysis of the radiolysis products (nitrite ion, H_2O_2 , O_2 , and H_2) was carried out by known methods (²⁻⁴); the nitrite ion was determined with an accuracy of up to 2%, hydrogen peroxide to 10%; the accuracy of determining gaseous radiolysis products was $\pm 3\%$.

The principal results of the study of the kinetics of accumulation of H_2O_2 and O_2 in solutions are summarized in Table 1. Table 1 presents the results of experiments in which one-molar alkaline sodium nitrate solutions (1 M NaOH)

were irradiated, with analysis of the gaseous products being carried out both in alkaline and in acidified solutions, and analysis for hydrogen peroxide only after the solution had been brought to $\text{pH} \sim 5$.

Acidification of the solutions to the required pH values was carried out either directly at the moment irradiation was stopped, or some time after irradiation had been stopped. The time of taking samples for analysis of nitrite ion and hydrogen peroxide after acidification was also varied. It was found that, upon irradiation of strongly alkaline (1 M NaOH) sodium nitrate solutions, hydrogen peroxide, analyzed immediately after cessation of irradiation and acidification of the solution to pH about 5, is liberated with a yield of ~ 2.2 ; at the same time, in the alkaline solutions themselves, H_2O_2 is not detected. The sum of the transformation yields of the reducing (H radicals) component of radiolysis for the alkaline solution (1 M NaOH) is equal to 9.2 equiv/100 eV, while that of the oxidizing component, as is seen from Table 1, is considerably lower. With an increase in the nitrate-ion content in the solution by a factor of 2–5, under the same irradiation and analysis conditions, the balance with respect to G_{OH} and G_{H} diverges approxi-

by 50%. In solutions acidified after irradiation (down to pH values of 11.4–2), the nitrite ion, as it turned out, is present in a lower concentration than in the solutions before acidification. In this case, at $\text{pH} \sim 2\text{--}3$, convergence of the balance for the products of transformation of H- and OH-radicals is observed if it is assumed that the loss of nitrite in solutions of this acidity is associated with its interaction with products of transformation of the oxidizing component. Under these same acidification conditions, $G_{\text{H}_2\text{O}_2}$, like G_{O_2} , remains approximately constant regardless of the pH of the solution analyzed. It is possible that the relatively high content of H_2O_2 in the solution ($G_{\text{H}_2\text{O}_2} = 2.2$), found upon direct (rapid) acidification of the solution to pH about 5 (in the analysis for H_2O_2), on the one hand, and, on the other hand, the loss of nitrite ion in the solution upon acidification to pH values 2–1.14, have one and the same cause. From this one might conclude that, upon irradiation of strongly alkaline solutions, OH radicals, undergoing certain transformations in the presence of nitrate ions, are capable of existing for some time and, under certain conditions, affect the yield of the final products.

There are indications in the literature of the possible participation in radiolytic reactions of peroxide-type compounds formed by the interaction of primary radical products from water with anions of oxygen-containing acids (of the type NO_3^- , SO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^-). Thus, for example, the increase in the “yield of water decomposition” in an acidic medium (0.8 N H_2SO_4), compared with a neutral one (⁵), is attributed to the removal by SO_4^{2-} ions of OH radicals from the reverse reactions of oxidation of H_2 and H_2O_2 . There is, moreover, a report of the formation in nitric acid, upon irradiation with accelerated electrons, of an unstable compound which decomposed with a half-life characteristic of peroxide compounds (⁶). It is assumed that peroxide-type compounds, stable for a long time, are also formed during the radiolysis of potassium dichromate solutions

(⁷). It is possible that in the case of the system we studied, under the conditions described, higher oxygen compounds are likewise formed.

In irradiated frozen solutions of the composition described, radicals whose formation is associated with the interaction of OH with nitrate ions (⁸) were directly detected by the EPR method. It was established that the nitrate ion stabilizes the OH radical (especially in the presence of the OH⁻ ion). Such an OH · NO₃²⁻ radical can exist up to a temperature of -100°. It was assumed that in this temperature region the OH · NO₃²⁻ radical dimerizes. In irradiated pure ice the usual OH radical rapidly disappears already at a temperature of about -160°. Qualitative experiments by magnetic static weighing showed that irradiated solutions at temperatures above -100° possess paramagnetism, and in different temperature intervals the magnetic susceptibility of the sample is different. As in the case of the liquid phase, in frozen solutions a discrepancy in the balance due to the oxidizing component of radiolysis was found in alkaline (1 M NaOH) solutions of sodium nitrate (1 ÷ 5 M) from 20 to 60%; upon acidification of the solutions to pH ~ 2–3, disappearance of part of the nitrite is likewise observed. The analogy in the kinetics of formation of the final products in liquid and frozen solutions apparently indicates a commonality of the intermediate stages of radiolysis. Nevertheless, with the aid of the EPR method we were unable to record radical products at higher temperatures (from -90° to 25°). It is possible that in liquid alkaline solutions the initially formed OH · NO₃²⁻ radicals dimerize, and then, upon acidification, may, depending on conditions, either lead to the formation of H₂O₂ or oxidize the nitrite ion.

In order to approach an understanding of the properties of the proposed products, we measured the magnetic susceptibility of irradiated sodium nitrate solutions of various concentrations, and also investigated a series

properties of the irradiated solutions by the method of nuclear magnetic resonance (NMR). Experiments on magnetic weighing of solutions with concentrations of 1 and 5 M were carried out by the Gouy method at various magnetic-field strengths (from 7 to 11 thousand oersteds) at room temperature. To determine the apparent change in weight in the magnetic field, VM-20 microbalances (without ferromagnetic parts) with a sensitivity of 0.01 mg per scale division were used. The gram magnetic susceptibility of the samples (χ_g) was determined. The values of χ_g for parallel measurements of the same sample were reproduced with an accuracy of ±0.4–0.5%.

To exclude possible paramagnetism associated with the formation of O₂ in this system under the action of radiation, nitrogen was bubbled through the solutions before weighing.

Table 2

Sample	$\chi_g \cdot 10^6$ of irradiated solution, pH ~ 14	$\chi_g \cdot 10^6$ of irradiated solution, pH 2	$\chi_g \cdot 10^6$ of unirradiated solution, pH ~ 14	$\chi_g \cdot 10^6$ of unirradiated solution, pH 2
5M NaNO ₃	-0.581	-0.594	-0.602	-0.602
1M NaNO ₃	-0.687	-0.692	-0.696	-0.696

It was found that irradiation of strongly alkaline sodium nitrate solutions leads to an apparent increase in the weight of the sample in a magnetic field (χ_g decreases) as compared with unirradiated solutions. The principal data (averages of several experiments) on the change in the gram magnetic susceptibility of irradiated (for about 5 hours at a dose rate of 750 rad/sec) and unirradiated solutions are given in Table 2.

From these data it may be concluded, first, that the irradiation effect (the apparent decrease in diamagnetism) is manifested to a greater extent in the more concentrated solutions: for 5M NaNO₃ at pH ~ 14 , $\Delta\chi_g = 0.021 \cdot 10^{-6}$; for 1M NaNO₃ at pH ~ 14 , $\Delta\chi_g = 0.009 \cdot 10^{-6}$. Second, when the irradiated solutions are acidified to pH 2, an apparent increase in diamagnetism (a decrease in paramagnetism) is observed: for 5M NaNO₃, for example, $\Delta\chi_g = 0.013 \cdot 10^{-6}$. If it is assumed that the products of transformation of the oxidizing component of radiolysis are paramagnetic and that, upon acidification of the solution, they enter into reaction with the nitrite ion, then the results obtained by the magnetic-weighing method are in qualitative agreement with the data from the balance method for radiolysis products.

In connection with the limited accuracy of the methods used for recording the comparatively small irradiation effects, it seemed advisable to carry out a series of experiments to detect the paramagnetic particles by an independent method. For this purpose we used the NMR method, which, as is known, makes it possible to detect paramagnetic particles in solution and to determine their concentration⁽⁹⁾. The sensitivity of the technique used to the presence of paramagnetic particles was estimated with the aid of copper sulfate solutions. The spectrometer used in the work reliably recorded the presence of paramagnetic copper ions in solution at a concentration somewhat below 0.01 M.

Using an NMR apparatus⁽¹⁰⁾, by the saturation method⁽¹¹⁾, an estimate was made of the spin-lattice relaxation time (T_1) of irradiated and unirradiated sodium nitrate solutions in the concentration range described. The estimate of T_1 was made relative to the protons of water. As before, before and after irradiation the alkaline solutions were freed of oxygen.

Comparison of the proton relaxation times of pure water and unirradiated sodium nitrate solutions showed that T_1 for these samples was identical within

the accuracy of the experiment. Irradiation of NaNO_3 solutions causes a change in the proton relaxation time, and the observed changes in the amplitudes of the NMR signals corresponded to a decrease in T_1 by a factor of 2–3. Heating the samples during irradiation to 70–80° preserves the irradiation effect. (Of course, these measurements should be regarded as qualitative, since the presence of paramagnetic particles in the solution somewhat changes the Q -factor of the coil of the measuring circuit.) Upon acidification of the solutions

to $\text{pH} \sim 2$, the relaxation time increased to a value comparable with T_1 for unirradiated samples (and, consequently, for water). It is evident from this that both the method of static magnetic weighing and the NMR method “detect” parallelism in the change in the properties of paramagnetic particles formed during radiolysis in the given system.

In conclusion, we note that the totality of the data obtained by the three methods of studying irradiated aqueous alkaline solutions of sodium nitrate may indicate the formation in the liquid phase of intermediate paramagnetic, comparatively stable products of radiolysis. The formation and existence of these products is apparently associated with the interaction of the oxidizing component of water radiolysis with nitrate and alkali ions.

Physicochemical Institute
named after L. Ya. Karpov

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