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Abstract

Full Text

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PHYSICAL CHEMISTRY

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ON THE MECHANISM OF RADIOLYSIS OF DILUTE AQUEOUS SOLUTIONS OF NITRATES

Many works are known that are devoted to the study of radiolytic transformations in aqueous nitrate solutions. However, they mainly consider questions of the radiolysis of concentrated solutions. In this connection, the investigation of the mechanism of the action of ionizing radiation on dilute nitrate solutions, where the chemical transformations of NO_3^- ions are due chiefly to e_{aq}^- , H, and OH, is of unquestionable interest.

A source of γ -radiation, Co^{60} , was used. The absorbed-dose rate was determined by ferrous sulfate dosimetry ⁽¹⁾ and was $2.8 \cdot 10^{16}$ eV/ml · sec. The reagents used were of “chemically pure” grade. In addition, sodium nitrate was purified by recrystallization from triply distilled water. For preparing the solutions, water subjected to special purification was used. Triply distilled water was irradiated to a dose of $\sim 10^{21}$ eV/ml, and then, to decompose the H_2O_2 formed, it was exposed to ultraviolet light. The solutions were deaerated by passing purified argon through them for 30–40 min. The nitrite concentration over the entire pH range was determined colorimetrically with the Griess reagent ⁽²⁾. Hydrogen peroxide was measured spectrophotometrically: in neutral medium by the method of Ghormley-Schwartz ^(3,4), and in the case of acidic and alkaline solutions by reaction with Ce^{4+} ions in 0.4 M H_2SO_4 . Hydrogen was determined chromatographically on an KhT-2M instrument.

Fig. 1. Dependence of $G(\text{NO}_2^-)$ on pH for a $5 \cdot 10^{-3} M$ solution of NaNO_3 : 1—deaerated solution; 2—solution saturated with air.

Figure 1 presents the obtained dependence of $G(\text{NO}_2^-)$ on pH^* . It is seen from Fig. 1 that $G(\text{NO}_2^-)$ in a deaerated neutral solution is approximately 0.6–0.7. The yield of hydrogen (Fig. 2) under these conditions is 0.4, i.e., almost equal to $G_{\text{H}_2}^{**}$. This indicates complete involvement of hydrated electrons in reaction with the dissolved substance.

In our opinion, the formation of nitrate proceeds through the stage of formation of the ion-radical NO_3^{2-} :

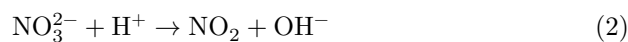


This ion was detected by us in the study of the ESR spectra of irradiated frozen aqueous solutions of NaNO_3 (5). It then converts

* All determinations of $G(\text{NO}_2^-)$ and $G(\text{H}_2\text{O}_2)$ were carried out at doses of $(3-6) \cdot 10^{17}$ eV/ml.

** The fact that $G(\text{H}_2)$ is somewhat less than G_{H_2} (0.45) is due to the scavenging effect.

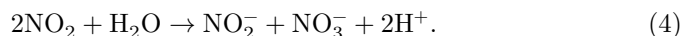
to nitrite as a result of the reactions:



or



and further



From the set of reactions (1–4) it may be concluded that two e_{aq}^- are consumed in the formation of one NO_2^- ion. Under the condition of complete utilization of hydrated electrons in the nitrate-ion reduction reaction, $G(\text{NO}_2^-)$ should be equal to $1/2 G_{e_{\text{aq}}^-}$, i.e., 1.35–1.45. This fact, as well as the observed dependence of $G(\text{NO}_2^-)$ on dose, indicates that some of the nitrite formed is oxidized by OH radicals:

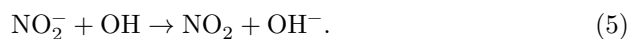
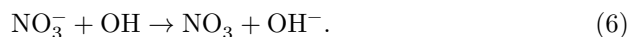
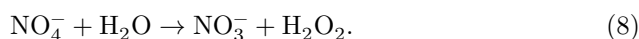
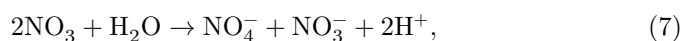


Fig. 2. Dependence of $G(\text{H}_2)$ on pH for a $5 \cdot 10^{-3}$ M solution of NaNO_3 (dose $1.7 \cdot 10^{18}$ eV/ml, solutions saturated with argon)

In addition, OH radicals also interact with NO_3^- ions*:



The formation of the NO_3 radical was shown in a study of the EPR spectra of irradiated frozen aqueous solutions of NaNO_3 in acidic and neutral media⁽⁵⁾. This is also indicated by the fact that $G(\text{H}_2\text{O}_2)$ in deaerated neutral NaNO_3 solutions exceeds $G_{\text{H}_2\text{O}_2}$ and is approximately 0.95 (Fig. 3). Apparently, an additional amount of hydrogen peroxide is formed by the reactions:



The possibility of formation of peroxidic nitrate compounds was indicated in works^(6–10).

Then, proceeding from the set of reactions (1–8), $G(\text{NO}_2^-)$ should be equal to:

$$G(\text{NO}_2^-) = \frac{1}{2}G_{e_{\text{aq}}^-} - \frac{1}{2}G_{\text{OH}} + \\ + G(\text{H}_2\text{O}_2) - G_{\text{H}_2\text{O}_2}. \quad (9)$$

The value obtained from this equation, $G(\text{NO}_2^-) \simeq 0.55$, is very close to the experimental values of $G(\text{NO}_2^-)$ **.

Fig. 3. Dependence of $G(\text{H}_2\text{O}_2)$ on pH for a $5 \cdot 10^{-3} M$ solution of NaNO_3 : 1 – deaerated solution; 2 – solution saturated with air.

In dilute aqueous solutions of NaNO_3 saturated with air or oxygen, a decrease in the yields of nitrite ion is observed when the concentration of NaNO_3 is lowered. At the same time, an increase in the yields of

* The assumption expressed in work⁽⁶⁾ concerning the dependence of $G(\text{NO}_2^-)$ on dose rate at its low values (10^{14} – 10^{17} eV/ml · sec) was not confirmed by our experiments.

** The initial yields of the products of water radiolysis were taken as: $G_{e_{\text{aq}}^-} = 2.9$; $G_{\text{OH}} = 2.3$; $G_{\text{H}_2\text{O}_2} = 0.7$ ⁽¹¹⁾.

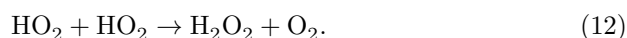
hydrogen peroxide. The data obtained are shown in Fig. 4. They indicate that under these conditions reaction (1) competes with the reaction:



Fig. 4

Figure 2: Fig. 4

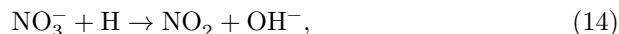
the final result of reaction (10) being the formation of an additional amount of H_2O_2 :



Using the steady-state method, one can obtain an equation relating the concentrations of NO_3^- , O_2 , and the yields of NO_2^- , H_2O_2 :

$$\frac{1}{1 + \frac{K_{10}[\text{O}_2]}{K_1[\text{NO}_3^-]}} = \frac{G_{e_{\text{aq}}^-} + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} - 2G(\text{H}_2\text{O}_2) + G(\text{NO}_2^-)}{2G_{e_{\text{aq}}^-}}. \quad (13)$$

The value k_{10}/k_1 calculated from this equation is 0.2 ± 0.03 . Upon acidification of a nitrate solution, the yields of nitrite and hydrogen peroxide decrease substantially. This is due mainly to two causes. First, in an acidic medium e_{aq}^- , interacting with the H^+ ion, is converted into an H atom. The latter, although it reduces the NO_3^- ion:



has a lower reactivity toward nitrate than e_{aq}^- . This is confirmed by the increased yield of molecular hydrogen in an acidic medium as compared with a neutral one. Thus, $G(\text{H}_2)$ is equal to 0.55* at pH 0.3 and 0.7 (Fig. 2). In other words, in a $5 \cdot 10^{-3} \text{ M}$ solution of NaNO_3 the reaction of reduction of the NO_3^- ion by H atoms competes with the recombination reaction of H atoms formed in different tracks. Secondly, in an acidic medium a nonradiation reaction between radiolysis products occurs:

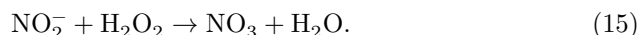


Fig. 4. Dependence of $G(\text{H}_2\text{O}_2)$ (1, 2, 3) and $G(\text{NO}_2^-)$ (4, 5, 6) on the concentration of the NaNO_3 solution at pH 5.5: 1, 4 –deaerated solution; 2, 5 – solution saturated with air; 3, 6 –solution saturated with oxygen.

This reaction, to explain the radiolysis of acidic NaNO_3 solutions, was postulated in works (7,12). We investigated the kinetics of this reaction, occurring in

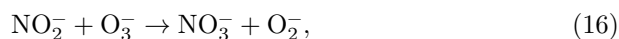
$5 \cdot 10^{-3} M$ NaNO_3 solutions in an acidic medium (pH 2.3 and 1.2) after irradiation. Calculations by the formula derived in work ⁽¹³⁾ give an average value of the rate constant of this reaction of $1.34 \cdot 10^5 \text{ l}^2/\text{mol}^2 \cdot \text{sec}$. This value agrees well with the value obtained in work ⁽¹³⁾ in studying the kinetics of nonradiation oxidation of nitrous acid by hydrogen peroxide.

Investigation of radiolytic transformations in alkaline $5 \cdot 10^{-3} M$ NaNO_3 solutions showed that $G(\text{NO}_2^-)$ increases with increasing pH. Thus, at pH 13.2, $G(\text{NO}_2^-)$ is 1.9–2.0 (see Fig. 1). The yield of molecular hydrogen in an alkaline medium changes almost not at all. It is equal to 0.35–0.40 (Fig. 2). Such a substantial increase in $G(\text{NO}_2^-)$ is due, first, to dissociation of the OH radical in an alkaline medium.** The ion-radical formed—

* This value agrees with the value reported in work ⁽¹²⁾.

** Formation of the O^- ion-radical in irradiated alkaline ice was shown by us ^(14,15) using the EPR method.

the radical O^- oxidizes NO_2^- ions much less effectively. Secondly, this is also explained by the increase of $G_{e_{\text{aq}}^-}$ in alkaline medium. Indeed, taking G_{H_2} to be 0.45 and considering that at pH 13.2 $G(\text{NO}_2^-) = \frac{1}{2}G_{e_{\text{aq}}^-}$, we obtain $G_{e_{\text{aq}}^-} = 3.7\text{--}3.8$ and $G_{-\text{H}_2\text{O}} = 4.6\text{--}4.7$. These yield values agree with those found in work ⁽¹¹⁾ in the study of the radiolysis of N_2O solutions. In a deaerated $5 \cdot 10^{-3} M$ solution of NaNO_3 in alkaline medium, a decrease in $G(\text{H}_2\text{O}_2)$ is observed (see Fig. 3). This is probably associated with the fact that the ion-radical O^- partially decomposes H_2O_2 . In the presence of air, $G(\text{H}_2\text{O}_2)$ is somewhat higher. This phenomenon is explained by competition between reactions of e_{aq}^- with NO_3^- and O_2 , as well as by the formation in such solutions of the ozonide ion O_3^- —a product of the interaction of O^- with oxygen (16). This ion, reacting with nitrite:



gives an additional amount of H_2O_2 . The occurrence of reaction (16) is supported by the fact that $G(\text{NO}_2^-)$ in alkaline solutions containing oxygen is substantially lower than in deaerated solutions (see Fig. 1).

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