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Abstract

Full Text

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THE EFFECT OF THE CONCENTRATION OF SODIUM NITRATE IN AQUEOUS SOLUTION ON THE DEGREE OF ITS RADIOLYTIC TRANSFORMATION

(Presented by Academician A. N. Frumkin on 5 VI 1958)

The appearance of products of radiolytic reactions in aqueous solutions is due primarily to the interaction of H and OH radicals with molecules of the dissolved substances. By combining the irradiation conditions and the composition of the solution, it is possible to obtain a yield of reaction products corresponding to the complete utilization of the radiolyzed water molecules (of the order of 12–13 molecules per 100 eV) (^{1}).

Fig. 1. Dependence of $G_{\mathrm{NaNO_2}}$ (g-eq/100 eV) on the concentration of $\mathrm{NaNO_3}$ in an alkaline solution (pH = 14)

We studied the dependence of the yield of nitrite accumulation in alkaline solutions (pH = 14) of sodium nitrate on the concentration of the latter (from 10^{-7} to $6M$, Fig. 1, curve 1)*. The curve for the dependence of $G_{\mathrm{NO_2^-}}$ on $[\mathrm{NaNO_3}]$ has four clearly expressed regions. In the concentration interval of $\mathrm{NaNO_3}$ from 10^{-7} to $5 \cdot 10^{-4}$ M, $G_{\mathrm{NO_2^-}}$ increases with increasing content of nitrate ion in the solution, reaching a certain constant value (~ 4.3 eq/100 eV) in the region of sodium nitrate concentrations $5 \cdot 10^{-4} \div 10^{-2}$ M. In more concentrated solutions of sodium nitrate, a further increase in $G_{\mathrm{NO_2^-}}$ is observed, proportional to the logarithm of the concentration of $\mathrm{NaNO_3}$, which was also observed by Mahlman and Schweitzer in 0.1-5 M solutions of $\mathrm{NaNO_3}$ (^{2}). In 1 M and more concentrated solutions of $\mathrm{NaNO_3}$, $G_{\mathrm{NO_2^-}}$ remains constant (~ 9 eq/100 eV).

The introduction into a nitrate solution of the conjugate acceptor of OH radicals, glycerin (^{3}) [10^{-3} M], under the same irradiation conditions, does not change the course of the dependence of $G_{\mathrm{NO_2^-}}$ on $[\mathrm{NaNO_3}]$ in the initial portion of the curve up to values of the $NaNO_3$ concentration of $5 \cdot 10^{-4}$ M. However, the presence of glycerin in the solution reduces the magnitude of the gently sloping portion of the curve. At $NaNO_3$ concentrations in the solution exceeding $5 \cdot 10^{-3}$ M, the curve of the dependence $G_{NO_2^-}$—[$NaNO_3$]

has a greater steepness than in the absence of glycerin (Figs. 1, 2). In $1 \div 6M$ solutions of $NaNO_3$ containing glycerin, a higher limiting value of $G_{NO_2^-}$ is reached (~ 12 equiv/100 eV).

Comparison of the yields of gaseous products in $1M$ sodium nitrate solutions without glycerin and with glycerin shows that G_{H_2} decreases from 0.06 mol/100 eV to 0.04 mol/100 eV, and the oxygen yield, correspondingly, from 0.40 to 0. The experimental data presented agree well with the assumption that coupled reactions of glycerin oxidation and sodium nitrate reduction occur in aqueous solutions, and they confirm the possibility of additional involvement of H and OH radicals in the reactions of nitrate reduction and glycerin oxidation from recombination reactions.

It should be noted that the obtained value of the limiting yield of nitrate-ion reduction by H atoms in the presence of glycerin, 12 equiv/100 eV in $1 \div 6M$ $NaNO_3$ solutions (assuming that the same number of OH radicals participates in glycerin oxidation), corresponds to the utilization of 12 pairs of radicals in oxidation-reduction reactions (12 water molecules). This value coincides with the results of Firestone ($G_{\text{H and OH}} = 11.7 \pm 0.6$) ([4]), who studied radiation-initiated isotopic exchange between H and D atoms in water vapor. Under these experimental conditions, compared with the liquid phase, where the Frank-Rabinowitch cage effect is manifested, there is a significant decrease in the density of the reaction medium and, consequently, a marked increase in the diffusion rate of H and OH radicals formed upon excitation of water molecules. Thus, the degree of participation of free radicals in exchange reactions increases.

In the concentration range of $NaNO_3$ $10^{-4} \div 10^{-2}$ M (Fig. 1, 1), constancy of $G_{NO_2^-} \simeq 4$ equiv/100 eV is reached, evidently associated with the practically complete scavenging by nitrate ions of H radicals formed from ionized water molecules. The concentration of NO_3^- required for complete scavenging of H atoms somewhat exceeds the value of the local concentration of H atoms in the track of the ionizing particle, which depends on the reactivity of NO_3^- with respect to the H atom. In works ([6],[7]) it was shown that, for solutions of some compounds, the range of these limiting concentrations may vary from 10^{-5} to 10^{-2} M. $G_{NO_2^-} = 9$ equiv/100 eV, and its constancy in $2 \div 6M$ nitrate solutions, exceeding the utilization of radical products from ionized water molecules, cannot be due only to the direct action of γ-rays on NO_3^-* (as was shown earlier

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* In the work a source of γ-rays, Co^{60}, of 30 g-eq Ra was used; the yield of $NaNO_2$ was determined from the initial portions of the curves for the accumulation of $NaNO_2$ versus dose (in the interval 0–25,000 r). NO_2^- was determined colorimetrically by the diazotization reaction of phenol with sulfanilic acid.

([3],[8]) by freezing $NaNO_3$ solutions of the same concentrations during irradiation). $G_{NO_2^-}$ due to the direct action of γ-radiation under these conditions cannot exceed 10-15% of the total yield of nitrate-ion reduction. This conclusion is confirmed by experiments with melts of crystalline hydrates of nitrate salts ([5]), where the concentration of NO_3^- was of the order of $10M$. Under these irradiation conditions, the effect of direct action of γ-rays on NO_3^- acquires considerable weight, and at the same time $G_{NO_2^-}$ falls to 1-1.5 equiv/100 eV.

As indicated above, introduction of glycerin into dilute $NaNO_3$ solutions ($10^{-7} \div 10^{-5}\ M$) does not affect the course of the dependence of $G_{NO_2^-}$ on $[NaNO_3]$ (curves 1 and 2 in Fig. 1 coincide). Such coincidence may be due to insufficient accuracy in determining NO_2^- in dilute solutions ($\sim$ 20%). Under these conditions, one should expect attainment of a constant yield (4 equiv/100 eV) at lower concentration values

* Malman and Schweitzer explain the increased yield of NO_2^- in acidic nitrate solutions ($0.1 \div 5M$) by the direct action of radiation on the NO_3^- ion.

NO_3^- in solution, since glycerin ($1 \cdot 10^{-3}\ M$) should have facilitated the involvement of H atoms in the reaction.

In conclusion, we note that the method used in this work—varying the concentration of the dissolved substance ($NaNO_3$) and introducing a coupled acceptor (glycerin)—made it possible to distinguish the radiolysis conditions under which the action of ionized and excited water molecules is manifested.

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