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Abstract

Full Text

PHYSICAL CHEMISTRY

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RADIATION-CHEMICAL OXIDATION OF POTASSIUM IODIDE IN SOLUTIONS SATURATED WITH NITROUS OXIDE

(Presented by Academician A. N. Frumkin, 26 XII 1964)

It is known ([1]) that the reaction of nitrous oxide with atomic hydrogen in the gas phase proceeds according to the equation

$$N_2O + H \rightarrow N_2 + OH. \tag{1}$$

Apparently, an analogous interaction with atomic hydrogen should occur in aqueous solutions.

On the basis of the experimental data obtained, it is accepted in the literature that a significant fraction of the reducing radicals formed during the radiolysis of water are, by their nature, hydrated thermalized electrons ($e^- \cdot nH_2O$). The literature has discussed the question ([2]) of the specificity of the interaction of the hydrated electron with nitrous oxide as compared with atomic hydrogen. The hydrated electron can interact with N_2O by one of the following reactions:

$$N_2O + (e^- \cdot nH_2O) \rightarrow N_2 + O^-_{aq}; \tag{2}$$

$$N_2O + (e^- \cdot nH_2O) \rightarrow N_2 + OH + OH^-_{aq}. \tag{3}$$

In this case the ion-radical O^-_{aq}, formed in reaction (2), apparently has oxidation-reduction properties different from those of the OH radical, since O^-_{aq} does not oxidize J^- in solutions to free iodine ([3]), but disappears as a result of interaction in other reactions. On the other hand, the OH radicals arising under the action of radiation and by reactions (1) and (3) at high pH ($10 \div 14$) can probably be converted into O^-_{aq} by the reaction

$$OH + OH^- \rightarrow O^-_{aq}. \tag{4}$$

Consequently, in strongly alkaline solutions hydroxyl radicals will react mainly in the form O^-_{aq}. Then, if the hydrated electron reacts with N_2O according to reaction (2), in solutions of KJ saturated with nitrous oxide there should be two regions on the plot of the dependence of the yield of free iodine on pH in which $G(J_2)$ changes. The first—at pH $2 \div 4$—is due to competition between

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nitrous oxide and the hydroxonium ion for the hydrated electron. The second—pH $10 \div 14$—is associated with the dissociation of hydroxyl radicals by reaction (4).

Conversely, if the interaction of the hydrated electron with N_2O proceeds with the formation of hydroxyl radicals, the influence of pH should be manifested only in alkaline solutions and will be due to the occurrence of reaction (4). A similar picture will occur if the primary reducing particle is a hydrogen atom.

In the present work the influence of the pH of the solution on the yields of free iodine and nitrogen during irradiation with γ-rays from Co^{60} of KJ solutions with concentrations of 0.05 and $\sim 0.5\ M$, saturated with N_2O at atmospheric pressure, was investigated. Nitrous oxide of medical grade was purified from oxygen by passing it through an alkaline solution of pyrogallol. The concentration of nitrous oxide was $\sim 0.025\ M$. The solutions were prepared with twice-distilled water from chemically pure reagents recrystallized three times; the pH of the solutions was established by adding twice-distilled H_2SO_4 or KOH of reagent-grade purity.

Chemapol (Czechoslovakia). Irradiation was carried out in glass spheres of diameter ~ 25 mm. The dose rate was $\sim 1.5 \cdot 10^{14}$ eV/cm$^3 \cdot$ sec, and the total dose was $(2 \div 8) \cdot 10^{17}$ eV/cm$^3 \cdot$ sec. The experimentally determined dependence of the yield of free iodine on pH is shown in Fig. 1. As can be seen from the figure (curve 1), when the pH is varied from 2.5 to 10 the yield of J_2 remains constant and equal to 3.00 ± 0.15 molecules per 100 eV. With a further increase in pH the yield drops sharply, reaching at pH 14 a value of 0.4 ± 0.1 molecule/100 eV. That the change in yield in alkaline solutions is indeed due to competition between reaction (4) and the reaction

$$J^- + OH \rightarrow J + OH^- \tag{5}$$

is confirmed by experiments in which the concentration of J^- was increased tenfold ($\sim 0.5\,M$). As can be seen from Fig. 1 (curve 2), under these conditions the curve of the dependence on pH is shifted toward higher concentrations of OH^- by one unit. Assuming that reactions (1) or (3), (4) and (5), and the reaction

(Figure: Figure 1 graph: yield of free iodine versus pH)

Fig. 1. Yield of free iodine as a function of the pH of the solution: 1—0.05 M, 2—0.5 M

$$O^- + OH \rightarrow OH^- + O, \tag{6}$$

$$O + J^- \rightarrow JO^- \tag{7}$$

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occur in the irradiated solutions, one can write the following expression for the yield

$$G(J_2)_{obs} = \frac{1}{2}(G_{red} + G_{OH}) \frac{k_5(OH)(J^-)}{2k_4(OH)(OH^-) + k_5(OH)(J^-)} = \frac{G(J_2)_{max}}{1 + 2k_4(OH^-)/k_5(J^-)}. \quad \text{(I)}$$

Transforming it into a form convenient for graphical solution, we obtain

$$1 + \frac{2k_4}{k_5}\frac{(OH^-)}{(J^-)} = \frac{G(J_2)_{max}}{G(J_2)_{obs}}. \quad \text{(II)}$$

Figure 2 presents the graphical solution of equation (II) from the data of Fig. 1. The experimental points for both solutions lie well on a single straight line with slope $k_4/k_5 = 0.025 \pm 0.045$. Thus, the results obtained confirm the assumption that the decrease in the yield of free iodine at high pH is associated with dissociation of the OH radical. The absence of any changes in $G(J_2)$ in the pH range $2.5 \div 7$ indicates that the hydrated electron formed upon irradiation, on reaction with N_2O, gives the same radical as is formed when radiation acts on water and by reaction (I). Obviously, the result obtained is entirely understandable if the reducing particle is the H atom.

The system under study makes it possible to calculate the yields of reducing radicals and OH radicals, as well as the observed yield of water decomposition in neutral and alkaline solutions. To obtain a complete material balance in these solutions, the yields of hydrogen peroxide, gaseous products, and possible products of nitrogen and iodine oxidation were determined. These quantities, and the water-decomposition yields calculated from them, are given in Table 1.

Table 1

Yields	KJ			
	0.05 M neutral solution	0.5 M pH 14	neutral solution	pH 14
$G(N_2)$	3.15 ± 0.25	3.28 ± 0.25	3.23 ± 0.25	3.20 ± 0.4
$G(H_2)$	0.40 ± 0.03	0.28 ± 0.03	0.37 ± 0.06	0.27 ± 0.01
$G(O_2)$	0.22 ± 0.05	0.16 ± 0.035	0.24 ± 0.08	0.13 ± 0.01
$G(H_2O_2)$	0.53 ± 0.05	–	0.27 ± 0.06	0.12 ± 0.02
$G(NO_2^-)$	–	0.04 ± 0.02	–	0.04 ± 0.02
$G(JO_4^-)$	–	0	–	0
G_{rec}	3.15 ± 0.25	3.28 ± 0.25	3.23 ± 0.25	3.20 ± 0.4
G_{OH}	2.45 ± 0.4	–	2.55 ± 0.34	–
$G(-H_2O)$	$3.95 \pm 0.3^*$	3.84 ± 0.30	3.97 ± 0.37	3.74 ± 0.42
$G(-H_2O)$	$4.37 \pm 0.33^{**}$	–	4.32 ± 0.43	–

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* $G(N_2) + 2G(H_2)$.

** From the material-balance equation.

Gaseous products were determined by gas-analysis methods. The dose rate in these experiments was $(4 \div 5) \cdot 10^{15}$ eV/cm^3·sec, and the total dose was $(5 \div 9) \cdot 10^{19}$ eV/cm^3.

Hydrogen peroxide was determined iodometrically and polarographically on a mercury dropping electrode. Periodate was determined polarographically [4]. Sodium nitrite was determined with Griess reagent.

(Figure: Fig. 2. Graphical solution of equation (II) from the data of Fig. 1: a –curve 1, b–curve 2)

Fig. 2. Graphical solution of equation (II) from the data of Fig. 1: *a*–curve 1, *b*–curve 2

Spectrophotometric determinations showed that, in strongly alkaline solutions, in the region where the yield of free iodine decreases, JO^- and JO_3^- ions are formed. Both ions give an absorption maximum at $\lambda = 263$ mμ, and therefore it was not possible to separate them. Meanwhile, in a photochemical study of such a system in the indicated region, the evolution of gaseous O_2 was observed [3] in amounts equivalent to the difference between the maximum and the observed yields of J_2 at the given pH. It is possible that the formation of considerable amounts of O_2 upon photolysis of alkaline KJ solutions is explained by efficient photochemical decomposition of JO^- and JO_3^- ions.

The yield of water decomposition was previously determined in solutions of Fe^{3+} ions (pH $1 \div 3$) and nitrate (pH ~ 6.5), saturated with hydrogen under pressure [5], and was found to be 4.2 ± 0.2 molecules/100 eV. For the present system, as is seen from the data of Table 1, it is close to this value. Consequently, it may be concluded that in the pH range $1 \div 14$ the yield of water decomposition remains practically constant.

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CITED LITERATURE

1. C. P. Fenimore, G. W. Jones, *J. Phys. Chem.*, **63**, 1154 (1959).
2. F. S. Dainton, D. B. Peterson, *Proc. Roy. Soc. A*, **267**, 443 (1962).
3. F. S. Dainton, G. Sills, *Proc. Chem. Soc.*, 1962, 223.
4. P. Souchay, *Anal. chim. acta*, **2**, No. 1, 17 (1948).

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5. V. N. Shubin, P. I. Dolin, Z. L. Krylova, *Collected Proceedings of the II All-Union Conference on Radiation Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1962, p. 129.

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

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