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TRANSLATION

MECHANISM OF DIRECT ACTION OF RADIATION ON PERCHLORIC U.C. ACID

By

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BY: L. T. Bugayenko

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MECHANISM OF DIRECT ACTION OF RADIATION ON PERCHLORIC U.C. ACID

L. T. Bugayenko

Earlier it was shown that the perchlorate ion is reduced only as a result of direct action of radiation [1,2]. Neither atoms of hydrogen nor hydroxyl radicals interact with perchlorate ion. The mechanism of direct action appeared complicated, proceeding through several intermediate steps [3]:

$$ClO_4^- \rightsquigarrow ClO_4 + e, \ (ClO_4^-)^* \qquad (1)$$

$$ClO_4 \rightarrow ClO_2 + O_2 \qquad (2)$$

$$ClO_2 + OH \rightarrow ClO_3^- + H^+ \qquad (3)$$

$$ClO_2 \xrightarrow{H} ClO_2^- \xrightarrow{2H} ClO^- \xrightarrow{H_2O_2} Cl^- \qquad (4)$$

Excited perchlorate, ions most probably, dissipate their energy during collisions, but to a certain extent the disintegration of excited ions by the reaction

$$(ClO_4^-)^* \longrightarrow ClO_3^- + {}^1/_2\, O_2 \qquad (5)$$

is possible.

In this work we continued investigation of the mechanism of transformation of perchlorate, ions studying the influence of ions of bivalent iron and molecules of organic compounds (ethyl alcohol and acetone) on yields of reduction of perchlorate ion and yields of reduction products of perchlorate ions.

Preparation, experiment, and analyses were conducted as described in [2,3]. Irradiation was produced by x-rays with maximum energy of 70 kv.

It was found that in oxygen saturated solutions of iron perchlorate in 2.5 M $HClO_4$, the yield of reduction of perchlorate ion in the interval of concentrations of Fe^{2+} ion, 0.005 - 0.06 M, maintains a constant value of 1.20 ± 0.05 ions per 100 ev of absorbed energy. It was found that the yields of formation of ions of chlorate and chloride depend on the concentration of Fe^{2+} ion. These data are shown in Fig. 1. The observed dependence of $G(ClO_3^-)$ on $[Fe^{2+}]$ shows that in the formation of chlorate ion reaction (3), not reaction (5) plays the main role, since the yield of formation of chlorate as a result of disintegration of excited perchlorate ions should not depend on the concentration of dissolved substances.

In Fig. 2 is shown a change of the ratio $G(ClO_3^-)/G(Cl^-)$ with increasive concentration of iron. Such a sharp drop of the curve is connected, first of all, with competition between dioxide of chlorine and the Fe^{2+} ion for radical OH and, secondly, with the very fast reaction:

$$ClO_2 + Fe^{2+} \rightarrow ClO_2^- + Fe^{3+} \qquad (6)$$

The formed ion of chlorite quickly is reduced by iron ions to the chlorine ion:

$$ClO_2^- + 4Fe^{2+} + 4H^+ \rightarrow Cl^- + 4\,Fe^{3+} + 2H_2O \qquad (7)$$

In Fig. 3 is shown the change of the yield of formation of Fe^{3+} ion as a function of concentration of Fe^{2+} ion.

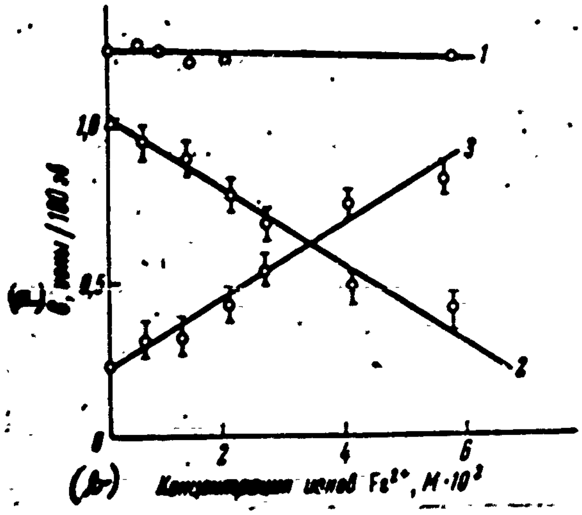

Fig. 1. Dependences of the yield of disentegration of ion of perchlorate (1), of yields of formation of ion of chlorate (2) and of ion of chlorine (3) on the concentration of perchlorate of bivalent iron in 2.5 M $HClO_4$.
KEY: (a) G, ions/100 ev; (b) Concentration of Fe^{2+} ions, $M\cdot 10^2$.

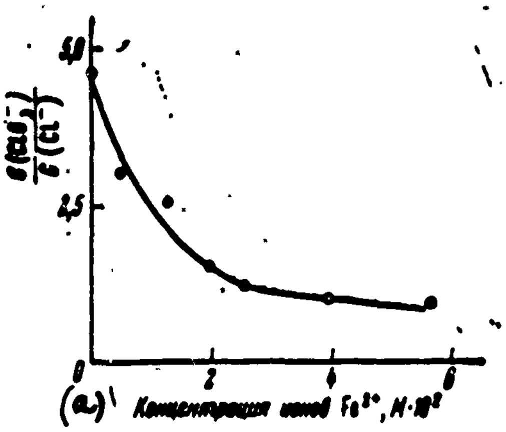

Fig. 2. Dependence of ratio of yields of ions of chlorate and ions of chlorine on the concentration of iron in 2.5 M HClO. KEY: (a) Concentration of Fe^{2+} ions, $M \cdot 10^2$.

Experimental points lie on a straight line. If we extrapolate this straight line to the y-axis, we will obtain the value of yield of oxidation of iron under conditions when it has practically no influence on the yield of reduction products of ion of perchlorate. The extrapolated value of yield of oxidation of iron equals 17 ± 1 ion per 100 ev. We will make an attempt to calculate the value of yield of oxidation of ion of iron in these conditions, assuming the known values of yield of products of radiolysis of water. We will consider that the yield of products of transformation of water are the same as in 0.4 M H_2SO_4 [4]. The electronic fraction of water in 2.5 M $HClO_4$ equals 0.8; therefore we will have the following values of yield $G_H = 3.00$; $G_{OH} = 2.50$ and $G_{H_2O_2} = 0.60$. The electron appearing during direct action of radiation on the ion of perchlorate, according to Lee [5], will cause formation of one H radical:

$$H_2O + e \rightarrow H_2O^- \rightarrow H + OH^-. \quad (3)$$

As was shown above, the fraction of the reaction (5) is small; therefore for calculation we will assume that 1.25 electrons will be formed and, consequently, 1.25 additional atoms of hydrogen per 100 ev. Radical OH oxidizes ions of iron and dioxide of chlorine. For the fraction of ions of iron will be obtained G_{OH} - $G(ClO_3^-)$= 1.50 radicals of OH per 100 ev. Since there is oxygen in solution, the atoms of hydrogen will be converted into radicals of HO_2. The latter very effectively interact with ions of Fe^{2+}, the concentration of which is significantly greater than the concentration of dioxide of chlorine.

Therefore in the presence of ions of iron the reduction of ClO_2 will be produced not by radicals HO_2, but by ions of Fe^{2+} by reactions (6) and (7).

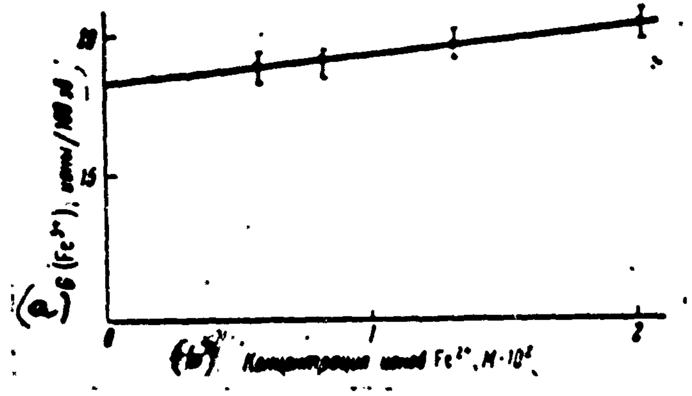

Fig. 3. Dependence of yield of oxidation of iron on the concentration of perchlorate of iron in 2.5 M $HClO_4$.
KEY: (a) $G(Fe^{3+})$, ions/100 ev. (b) Concentration of ions Fe^{2+}, M $HClO_4$.

The yield of formation of ions of chlorine equals 0.22 ions per 100 ev. Full yield of oxidation of ions of iron will be equal to:

$$G(Fe^{3+}) = 3G_H + 2G_{H_2O_2} + G_{OH} - G(ClO_3^-) + 5G(Cl^-). \quad (9)$$

Substituting the above calculated values of yields, we obtain G (Fe^{3+}) = 16.5 ions per 100 ev. This magnitude is in good agreement with the value of yield of oxidation of iron found by extrapolation of experimental data

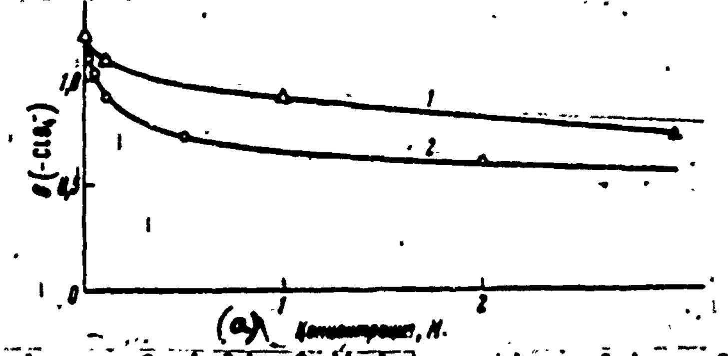

Fig. 4. Dependence of yield of disintegration of ion of perchlorate on the concentration of ethyl alcohol (1) and acetone (2). Concentration of perchloric Acid – 2.5.
KEY: (a) concentration, M.

Increase of G (Fe^{3+}) during increase of concentration of ions of Fe^{2+} occurs due to an increase of fraction of reaction (6) and the corresponding decrease of fraction of reaction (3) and, possibly, as a result of involvement, in the reaction of oxidation of iron, of a certain fraction of excited molecules of water.

On addition of an organic substance to the irradiated solution of inorganic compound usually is observed an increase of yield of transformation of inorganic compound. Such effects were observed during the irradiation of mixtures of organic compounds with sodium nitrate [6], cerium sulfate [7], sulfate of iron [8], bichromate of potassium [9], et al. During an irradiation of solutions of ethyl alcohol and acetone in 2.5 M $HClO_4$ we detected a decrease of yield of reduction of iron of perchlorate that was the greater the higher the concentration of organic compound (Fig. 4). In Fig. 5 is shown the dependence of yield of reduction of ion of perchlorate on the cube root of the concentration of organic compound. In this case the curve of yields of reduction becomes a straight line in the area of concentrations not exceeding 1 M, and is described by the following equations:

$$G(-\mathrm{ClO}_4^-) = 1{,}25 - (0{,}61 \pm 0{,}05)\sqrt[3]{[\mathrm{C_2H_5OH}]}$$

$$G(-\mathrm{ClO}_4^-) = 1{,}25 - (0{,}32 \pm 0{,}01)\sqrt[3]{[\mathrm{CH_3COCH_3}]}\,.$$

In the presence of organic compound the accumulation of no other products of reduction of ion of perchlorate, besides ions of chloride and chlorate is detected; it follows from this that decrease of yields of reduction of ion of perchlorate occurs at the primary stage of decomposition. The observed decrease of yield of reduction probably, is caused by reaction between radicals of perchlorate formed as a result of direct action and molecules of organic compound:

$$\dot{\mathrm{ClO}}_4 + \mathrm{RH} \rightarrow \mathrm{ClO}_4^- + \mathrm{H}^+ + \mathrm{R}. \qquad (10)$$

Recently was detected a similar reaction [10,11] between acetonitrile and a radical of perchlorate appearing during anodic oxidation of perchlorate of silver.

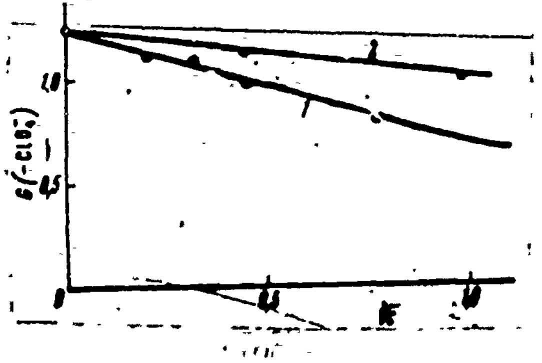

Fig. 5. Dependence of yield of disintegration of ion of perchlorate on the cube root of the concentration of ethyl alcohol (1) and acetone (2). Concentration of $HClO_4$ - 2.5 M.

One should note that molecules of investigated organic compounds in relation to the radical of perchlorate are more active, than the ion Fe^{2+} (for 0.06 M solutions no less than 10 times). This is not surprising, since it is known that in relation to the radical OH, which will behave analogously to the radical ClO_4, the ion Fe^{2+} is several times less active than certain organic compounds, for example butyl alcohol [12].

The process of disintegration of radical ClO_4 by reaction (2) apparently has a very high rate. Therefore it is possible to assume that reaction(2) proceeds in places of high density of ionization, in spurs. Reaction (10), should thus also proceed in spurs. Probability of collision between radical ClO_4 and the molecule of organic compound will then depend not on the concentration of organic molecules in the entire volume, but on the linear concentration; consequently it will be equal to the cube root of the concentration in the volume. This explains the dependence of G $(-ClO_4^-)$ on the cube root of the concentration of acetone and alcohol. The considered dependence is analogous to the dependence of molecular yield of hydrogen on the concentration of sodium nitrate [13] and of molecular hydrogen peroxide on the concentration of chloride and bromide of potassium [14].

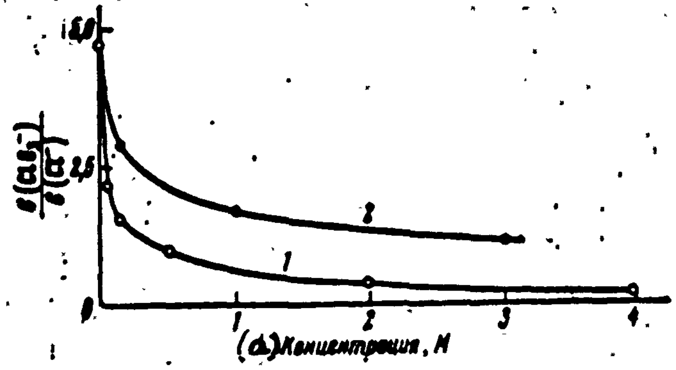

Fig. 6. Dependence of ratio of ion yields of chlorate and chlorine ions on the concentration of ethyl alcohol (1) and acetone (2). Concentration of $HClO_4$ - 2.5M.
KEY: (a) concentration, M.

In Fig. 6 is shown the change of ratio G (ClO_3^-)/ G (Cl^-) during increase of concentration of organic compounds in the solution. On addition of ethyl alcohol and acetone, good acceptors of OH radicals, the ratio of yields is decreased. It is possible to note that the lowering of the ratio of yields occurs significantly more slowly, than in the presence of ions Fe^{2+}. This is connected, probably, with the fact that molecules of organic compounds do not reduce the dioxide of chlorine, and the decrease of yield of chlorate occurs due to capture of radicals OH by molecules of organic compounds.

In conclusion I would like to thank V. N. Belevskiy and Wu Tsi-lan for their help in carrying out the experiments, and Professor N. A. Bakh for discussion and valuable advice concerning carrying out of the given work.

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