Russian Journal of General Chemistry, Vol. 71, No. 10, 2001, pp. 1536–1537. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 10, 2001, pp. 1622–1623.
Original Russian Text Copyright © 2001 by Piskarev.

Redox Processes in Water, Initiated by Electric Discharge over Its Surface

I. M. Piskarev

Skobel'tsyn Research Institute of Nuclear Physics, Moscow State University, Moscow, Russia

Received January 13, 2000

Abstract — The yields of oxidation and reduction in a flash corona discharge between a solid cathode and the water surface are compared. As the cathode was used a system of five aluminum electrodes. As the gas medium were tested air, oxygen, and nitrogen. The models of processes in the discharge suggest formation of atomic hydrogen in water vapor: $H_2O \rightarrow H + OH$. However, the reduction yield is equal to the Faraday value irrespective of the gas composition. In the presence of oxygen, oxidation prevails. The yield of Fe^{2+} oxidation in oxygen is about 190 reaction events per electron passed in the circuit; in air it is lower by a factor of 2, and in nitrogen the yield is equal to the Faraday value.

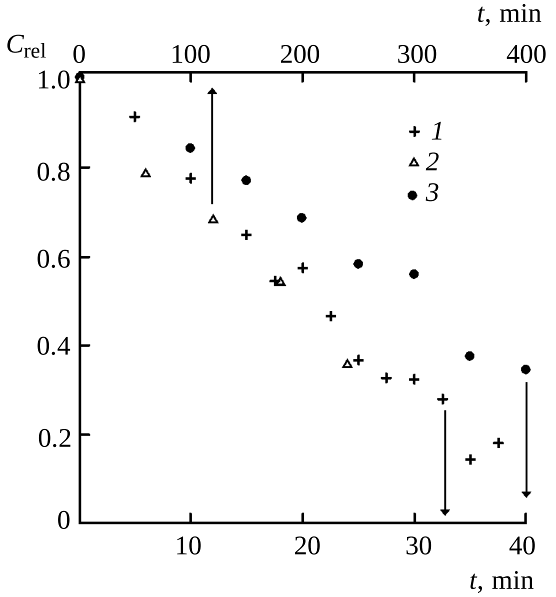
Processes initiated by electric discharge or ionizing radiation involve generation of reactive species exhibiting both reductive and oxidative power. By the law of charge conservation, the number of oxidation equivalents is equal to the number of reduction equivalents; in particular, in radiolysis of water the yields of reducing and oxidizing species are equal [1]. Generation of oxidants and reductants was discussed in [2].

The models of processes occurring under definite kinds of electric discharge, discussed in [3–5] and consistent with the experiment, suggest decomposition of water molecules: $H_2O \rightarrow OH + H$, i.e., formation of oxidants (OH radicals) and reductants (H atoms).

The goal of this work was comparative evaluation of the roles of oxidation and reduction in chemical reactions initiated by a specific kind of electric discharge: flash corona discharge in various gases (pure oxygen, pure nitrogen, or air) in the presence of water vapor. The experimental conditions were similar to those in [6, 7]. The reaction was performed in a 2-l glass vessel; the volume of the treated liquid was 100 ml. The flash mode of the corona discharge was generated by a system of five aluminum electrode. Each electrode was fed independently through 11-MΩ ballast resistors; the total discharge current from all electrodes was 0.5 mA, the voltage between each electrode and the liquid surface was 10 kV, with minus on electrodes. Diagnostics of the discharge conditions was performed similarly to [7]. Tests were performed with solutions of an oxidant and a reductant in equivalent concentrations. The oxidant was a 0.00417 M solution of potassium dichromate, and the reductant, a 0.025 M solution of Mohr's salt in 0.4 M H_2SO_4. Chemically pure grade chemicals and distilled water were used. Prior to the reaction in oxygen or nitrogen, the vessel was purged with the respective gas for 5 min, and this gas was fed in the course of the reaction at a rate of 0.8–1 l h^{-1}. In the case of air, there was no additional gas feeding. The content of potassium dichromate was determined by direct titration with Mohr's salt in acid solution [8], and the content of the Mohr's salt, by back-titration.

Potassium dichromate was treated with an electric discharge for 6 h separately in air and in pure oxygen, and also for 1.5 h in nitrogen, after which its content in the sample was determined. The content of dichromate decreased by ~4% in 6 h in air and oxygen and by ~1% in 1.5 h in nitrogen. This corresponds to the reduction yield of ~1/6 mol of dichromate per mole of electrons, i.e., practically to the Faraday yield, as the equivalent of dichromate is 6. The reduction yield of potassium dichromate in a common electrolysis under conditions when both electrodes are immersed in a liquid is also close to the Faraday value. The decrease in the dichromate content after electrolysis for 16 h with a current of 0.5 mA was 5%.

A different pattern was observed with oxidation of Fe^{2+} in Mohr's salt. The variation of the Fe^{2+} content with time is shown in the figure. It is seen that, when the discharge is performed in air or in oxygen, the Fe^{2+} content linearly decreases. This fact suggests that the active species generated by the discharge are practically completely consumed for oxidation of Fe^{2+}. It is seen from the figure that during discharge in oxygen Fe^{2+} in Mohr's salt is com-



Relative content of Fe^{2+} in Mohr's salt C_{rel} = $[Fe^{2+}]_t/[Fe^{2+}]_0$ as a function of time *t* of treatment with electric discharge (*V* –10 kV, current 0.5 mA). Initial concentration and atmosphere: (*1*) 0.025, oxygen; (*2*) 0.25, oxygen; and (*3*) 0.025, air.

pletely consumed in ~45 min. The yield of Fe^{2+} oxidation is about 190 mol per mole of electrons, i.e., no less than 190 oxidation equivalents is generated per electron passed in the circuit (which is accompanied by consumption of 10 keV). As the Mohr's salt concentration is increased by a factor of 10 (0.25 M), the oxidation yield remains the same. This means that the concentration of Fe^{2+} is sufficiently high and that the active species are not lost in reactions with each other. The results of the experiments with a 0.25 M Mohr's salt are plotted in the same figure, with the time scale changed by a factor of 10 (upper abscissa).

The rate of iron oxidation in Mohr's salt during discharge in air is lower; iron is completely consumed in approximately two times longer time, ~90 min. When the discharge is performed in nitrogen, the decrease in the Fe^{2+} concentration in 1.5 h does not exceed 1%, which corresponds to the oxidation yield of ~1 mol of iron per mole of electrons, i.e., to the Faraday yield, similarly to the yield of potassium dichromate reduction under the same conditions.

Thus, in the case when the gas phase contains oxygen, the main process is oxidation. This result can be understood in terms of the model [9] according to which the presence of oxygen and its transformation into ozone cause transformation of active radicals into OH radicals, which are oxidants, so that oxidation becomes the prevailing process. The active species themselves decay with a low probability, primarily with consumption of ozone. In the case when the gas medium contains no oxygen or ozone, active species primarily decay by reactions with each other, forming oxygen and water. Therefore, in nitrogen the yields of oxidation and reduction are equal to the Faraday yield.

REFERENCES

1. Pikaev, A.K., *Sovremennaya radiatsionnaya khimiya. Radioliz gazov i zhidkostei* (Modern Radiation Chemistry. Radiolysis of Gases and Liquids), Moscow: Nauka, 1986, p. 76.
2. Fioshin, M.Ya. and Smirnova, M.G., *Elektrosintez okislitelei i vosstanovitelei* (Electrochemical Synthesis of Oxidants and Reductants), Leningrad: Khimiya, 1981, p. 194.
3. Piskarev, I.M., *Kinet. Katal.*, 1999, vol. 40, no. 4, pp. 505–511.
4. Piskarev, I.M., *Indian J. Chem., Sect. A*, 1999, vol. 38, pp. 280–285.
5. Akishev, Yu.S., Deryugin, A.A., Kochetov, I.V., Napartovich, A.P., and Trushin, N.I., *Fiz. Plazmy*, 1994, vol. 20, no. 6, pp. 585–592.
6. Piskarev, I.M., *Zh. Fiz. Khim.*, 1998, vol. 72, no. 11, pp. 1976–1983.
7. Piskarev, I.M., *Zh. Tekh. Fiz.*, 1999, vol. 69, no. 1, pp. 58–63.
8. *Standard Methods for the Examination of Water and Wastewater*, Washington: APHA–AWWA–WEF, 1995.
9. Piskarev, I.M., *Zh. Fiz. Khim.*, 2000, vol. 74, no. 3, pp. 546–551.