ISSN 0018-1439, High Energy Chemistry, 2014, Vol. 48, No. 1, pp. 60–61. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © E.S. Bobkova, A.V. Sungurova, 2014, published in Khimiya Vysokikh Energii, 2014, Vol. 48, No. 1, pp. 82–83.

PLASMA CHEMISTRY
SHORT COMMUNICATIONS

Formation of Formaldehyde in Aqueous Solution under Atmospheric-Pressure Direct-Current Discharge

E. S. Bobkova and A. V. Sungurova

Research Institute of Chemical Thermodynamics and Kinetics, Ivanovo State University of Chemical Technology, pr. F. Engel'sa 7, Ivanovo, 153000 Russia

e-mail: esbobkova@isuct.ru

Received June 10, 2013; in final form, August 30, 2013

DOI: 10.1134/S0018143914010044

The possibility of degradation of organic compounds in water by treatment with discharges of various types has become a subject matter of intensive research. Regardless of the discharge type, the common products of decomposition of a variety of organic compounds (phenol, synthetic surfactants, carboxylic acids) are aldehydes and carbon dioxide [1, 2]. By plasma treatment of water, not only species having a high oxidizing power (OH radicals), but also good reducing agents (H radicals) are generated [3]. Thus, it may be assumed that reduction reactions can occur along with the oxidative degradation processes. The purpose of this study was to test this hypothesis using distilled water as the object of treatment.

Analyses showed that water has pH ~ 6.8, and its potentiometric titration with hydrochloric acid revealed the presence of hydrogen carbonate ions at a concentration of 16.6 mg/L. That is, the acidity is due to the presence of dissolved CO_2 in the water.

The experimental setup was described earlier [4]. An atmospheric-pressure air dc discharge was excited by applying dc voltage across a metal anode and the surface of the solution. The anode–electrolyte surface distance was 4 mm. The discharge current was 40 mA. The volume of the electrolyte (distilled water) was 80 mL. After a certain time of discharge treatment, the solution was analyzed for formaldehyde. A fresh portion of the solution was used for each run.

The aldehyde concentration was determined by measuring the intensity of fluorescence, excited at the maximum absorption band, with a Fluorat-02 fluorometer (Russia). The luminescent compound was the product of the formaldehyde reaction with 1,3-cyclohexanedione in the presence of ammonium ions. The random error was determined for five measurements using a confidence level of 0.95. The error did not exceed 10%.

The figure (curve *1*) shows the kinetics of formaldehyde formation in water by the action of the discharge. The concentration of formaldehyde increases to 0.24 mg/L as the treatment time increases to 6 min; then, its degradation begins, which results in CO_2 and H_2O as the final product [5]. The shape of the kinetic curve indicates that there is a competition of the synthesis and degradation of formaldehyde and different active species are involved in these the processes. The hydrogen carbonate ion concentration measured in distilled water prior to treatment was 16.6 mg/L, which is quite sufficient for the formation of formaldehyde in the amount found.

The next step of the research was to study the influence of the amount of dissolved CO_2 on the concentration of formaldehyde. For this purpose, the water was preliminarily either boiled and purged with argon to reduce the concentration of dissolved carbon dioxide or saturated with CO_2. In the former case, both the rate of formation and the amount of formaldehyde decreased (curve *2*) as compared with the untreated water. In the latter case (curve *3*), the formaldehyde concentration and formation rate increased. Thus, the source of formaldehyde was dissolved CO_2 indeed.

The formaldehyde formation process can involve the following well-known reactions:

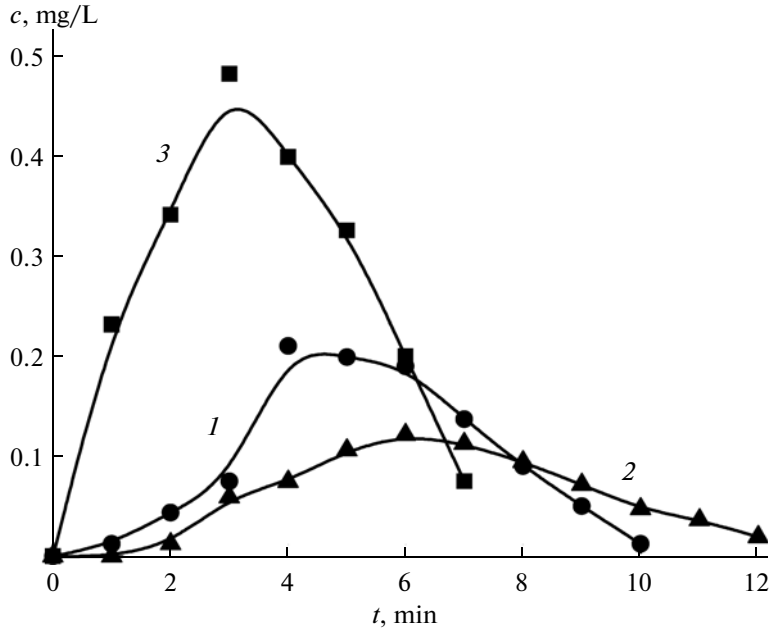
$$H_2O + \text{discharge} \rightarrow {}^{\cdot}OH + {}^{\cdot}H,$$

$$CO_2 + {}^{\cdot}H \rightarrow CO + {}^{\cdot}OH,$$

$$CO + {}^{\cdot}H \rightarrow {}^{\cdot}COH,$$

$${}^{\cdot}COH + {}^{\cdot}H \rightarrow HCOH.$$

In summary, this type of discharge ensures the synthesis of formaldehyde in water in the presence of dissolved carbon dioxide. Moreover, the CO_2 content



Dependence of the formaldehyde concentration upon the discharge treatment time: (*1*) distilled water, (*2*) after purging with argon, and (*3*) after saturation with carbon dioxide for 10 min.

determines the concentration of resulting formaldehyde.

This work was supported by the 2009–2013 Federal Target Program "Scientific Research and Academic Personnel for Innovative Russia," state contract no. 14.V37.21.0763.

REFERENCES

1. Bobkova, E.S., Krasnov, D.S., Sungurova, A.V., Shishkina, A.I., and Shikova, T.G., *High Energy Chem.*, 2013, vol. 47, no. 2, p. 53.
2. Bobkova, E.S., Grinevich, V.I., Ivantsova, N.A., and Rybkin, V.V., *Plasma Chem. Plasma Process.*, 2012, vol. 32, no. 1, p. 97.
3. Grymonpre, D.R., Sharma, A.K., Finney, W.C., and Locke, B.R., *Chem. Eng. J.*, 2001, vol. 82, nos. 1–3, p. 189.
4. Bobkova, E.S., Shikova, T.G., Grinevich, V.I., and Rybkin, V.V., *High Energy Chem.*, 2012, vol. 46, no. 1, p. 56.
5. Bobkova, E.S., Grinevich, V.I., Isakina, A.A., and Rybkin, V.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2011, vol. 54, no. 10, p. 85.

Translated by S. Zatonsky