ISSN 1070-4272, Russian Journal of Applied Chemistry, 2012, Vol. 85, No. 1, pp. 71–75. © Pleiades Publishing, Ltd., 2012. Original Russian Text © E.S. Bobkova, A.A. Isakina, V.I. Grinevich, V.V. Rybkin, 2012, published in Zhurnal Prikladnoi Khimii, 2012, Vol. 85, No. 1, pp. 75–79.

> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

## Decomposition of Aqueous Solution of Acetic Acid under the Action of Atmospheric-Pressure Dielectric Barrier Discharge in Oxygen

E. S. Bobkova, A. A. Isakina, V. I. Grinevich, and V. V. Rybkin

Ivanovo State University of Chemical Engineering, Ivanovo, Russia

Received December 3, 2010

**Abstract**—Decomposition of an aqueous solution of acetic acid under the action of an atmospheric-pressure dielectric barrier discharge in oxygen in a flow-through reactor was studied. A mechanism of chemical reactions is suggested, which describes the decomposition of the acid and formation of the reaction products observed.

DOI: 10.1134/S1070427212010144

The problem of water treatment to bring its quality to the potable water level is one of the most topical issues. The commonly used methods of water purification, such as chlorination, ozonation, UV irradiation, are comparatively expensive and fail to always provide the required efficiency [1]. That is why purification techniques based on high-energy chemical methods, radiative, photochemical, and plasmochemical have been intensively studied recently [2, 3]. In fact, the ozonation and UV irradiation are processes of this kind because both ozone and UV light are produced by some gas discharge.

The energy efficiency of these methods is poor because they use only a small part of opportunities furnished by a discharge, which yields a large number of active species capable of effective decomposition of organic impurities. These are radicals, excited atoms and molecules, electrons, and ions. Their use requires a special organization of the process because, as a rule, these species are short-lived. Therefore, various kinds of gas discharges that are in direct contact with a solution being processed are promising.

A large number of designs of this kind have been developed. For example, these are the corona discharge burning over the surface of a solution [4], dc discharge in a fluid [5], pulsed streamer discharge in solution [6], and dielectric barrier discharge (DBD) [7]. Decomposition products are of particular interest because, even upon full decomposition of the main substance, they will determine the purification quality. However, data of this kind cannot be found in the overwhelming majority of known reports and the efficiency of a particular type of treatment is judged from the decrease in the concentration of the main organic contaminant [8]. Only in [5, 7, 9], it was noted that carboxylic acids accumulate in the course of time in aqueous solutions in destruction of phenol and its oxy derivatives.

In this study, we examined the decomposition of an aqueous solution of acetic acid in a DBD in order to find whether it is possible and advisable to use the discharge both in removal of the acid itself and in processes in which the acid is a reaction product.

## EXPERIMENTAL

The experimental installation was described in detail in [7]. The reactor for DBD generation had the form of a vertical Pyrex tube with an outer diameter of 12 mm and wall thickness of 1.7 mm, which served as the dielectric barrier for the discharge. An aluminum alloy electrode with a diameter of 8 mm was coaxially mounted within the tube. The electrode was coated with a hydrophilic glass fabric with a thickness of about 1 mm. The discharge zone length L was 12 cm. A solution was introduced through radial orifices in the upper part of the internal electrode and flowed down

in the film mode over the surface of the glass fabric under the gravity force. The volumetric flow rate of the solution was controlled, with the time  $\tau_L$  of its residence with the discharge zone varied approximately from 2 to 12 s. The value of  $\tau_L$  was calculated by

$$\tau_L = \pi D h L/Q,$$

where D is the diameter of the glass fabric coating; h, thickness of the solution film; and Q, volumetric flow rate of the solution.

The solution film thickness was estimated using the expression valid for a smooth laminar flow in the gravity force field [10]:

$$h = \{(3\nu/g)[Q/(\pi D)]\}^{1/3},$$

where v is the kinematic viscosity, and g, the gravitational constant.

A 16-kV mains-frequency voltage was applied between the internal electrode and an aluminum foil electrode deposited onto the outer tube. Under these conditions, the discharge current was 0.56 mA, and the specific power introduced into the discharge, 0.93 W cm<sup>-3</sup>. Technical-grade oxygen (99.8%) served as the plasma-forming gas with a flow rate of 3.2 cm<sup>3</sup> s<sup>-1</sup>. The oxygen was delivered in the direction opposite to that of the solution. The initial concentration of the acid solution was  $55 \times 10^{-6}$  M.

After the stationary process mode was attained, the gas leaving the reaction zone was passed during a fixed time through an absorbing vessel or through a bed of a GTT catalyst which effectively converts carbon monoxide molecules to carbon dioxide [11]. The absorbing solution was filled with distilled water or an ammonia solution of barium chloride. The resulting solutions and the discharge-treated solution were analyzed. The content of acetic acid was found from the optical density at the absorption peak of colored solutions ( $\lambda = 400 \text{ nm}$ ) produced by the reaction of the acid with ammonium meta-vanadate [12]. The optical density was measured with a Hitachi U-2001 spectrophotometer (Japan). The aldehyde concentration was measured by the photoluminescent method. A luminescing compound was formed by the reaction of the aldehyde with 1,3-cyclohexanedione in the presence of ammonium ions. A Flyuorat-02 fluorimeter (Russia) was used. The CO<sub>2</sub> concentration in the gas phase was determined using the following scheme of reactions [13]:

$$BaCl_{2} \cdot 2H_{2}O + 2NH_{4}OH + 2CO_{2}$$

$$\rightarrow Ba(HCO_{3})_{2} + NH_{4}Cl + 2H_{2}O,$$

$$Ba(HCO_{3})_{2} + BaCl_{2} \cdot 2H_{2}O + 2NH_{4}OH$$

$$\rightarrow 2BaCO_{3}\downarrow + 2NH_{4}Cl + 4H_{2}O,$$

$$BaCO_{3} + 2HCl \rightarrow BaCl_{2} + CO_{2}\uparrow + H_{2}O,$$

$$HCl + NaOH \rightarrow NaCl + H_{2}O.$$

A sample of an ammonia solution of  $BaCl_2$  through which  $CO_2$  was passed was boiled on a water bath to provide complete precipitation of  $BaCO_3$ . The precipitate was filtered off and dissolved in a certain amount of hydrochloric acid. The excess amount of the acid was titrated with sodium hydroxide.

Figure 1 shows how the concentration of acetic acid and degree of its decomposition depend on the time of residence of the solution with the discharge zone. The degree of decomposition, obtained in this case, is fairly high ( $\sim$ 70%). It is noteworthy that a  $\sim$ 14% degree of decomposition of the acid was achieved in [14] in a similar reactor, with air used as the plasma-forming gas. The fact that the degree of decomposition reaches saturation means that either the process is limited by the generation rates of active species, or there occur inverse reactions that form the acid from its interaction products. The second hypothesis seems to be more substantiated for the following reasons.

The specific action of the electric discharge on the



Fig. 1. Concentration *c* of acetic acid and degree  $\alpha$  of its decomposition vs. the time  $\tau$  of residence between the solution and the discharge zone.

solution consists in that its surface is bombarded with high-energy particles. In particular, the cathode potential drops in atmospheric-pressure discharges reach several hundred electronvolts [15]. Therefore, it would be expected that the discharge must have an effect similar to that produced on water by radiation [16], i.e., formation of OH, H<sup>-</sup>, and O<sup>-</sup> radicals as primary active species. Just this assumption was made in studies concerned with the decomposition of phenol in a streamer corona reactor [6] and formation of hydrogen peroxide in a dc discharge with an electrolyte cathode [17]. Primary active species are formed in the following reactions:

$$H_2O + discharge \rightarrow OH + H^{-} and H_2 + O^{-}$$
.

The first of these reactions is more probable because of the lower energy expenditure.

The radicals formed interact with each other to give both molecular and radical products:

$$H' + H' \rightarrow H_2,$$
  

$$O' + OH \rightarrow O_2 + H',$$
  

$$OH + OH \rightarrow H_2O + O,$$
  

$$OH + OH \rightarrow H_2O_2.$$
 (1)

Thus, the OH, O, and H radicals are active species capable of interacting with the acid. The following reactions are energetically possible:

$$CH_{3}-(C=O)-OH+O \rightarrow CH_{2}-(C=O)-OH+OH, \quad (2)$$

$$CH_3-(C=O)-OH+OH \rightarrow CH_2-(C=O)-OH+H_2O, \quad (3)$$

$$CH_3-(C=O)-OH + H \rightarrow CH_2-(C=O)-OH + H_2, \quad (4)$$

$$CH_3-(C=O)-OH+OH \rightarrow CH_3-(C=O)+H_2O_2.$$
(5)

Let as estimate the formation rates of the H<sup>·</sup> and OH radicals. According to [18], the yield of H<sup>·</sup> and OH radicals per mole of electrons under the action of discharge is approximately 10. At a discharge current of 0.56 mA, this gives a total formation rate of radicals of  $5.8 \times 10^{-8}$  mol s<sup>-1</sup>. Taking the time of contact with the solution to be, for the sake of certainty,  $\tau_L = 2$  s and having calculated the solution volume being treated,  $V = 0.46 \times 10^{-3}$  l, we find that the formation rate of radicals is  $1.4 \times 10^{-4}$  M s<sup>-1</sup>. The decomposition rate of the acid,

found from the initial portion of the kinetic curve (Fig. 1 at  $\tau_L \rightarrow 0$ ), was  $2.4 \times 10^{-5}$  M s<sup>-1</sup>. Consequently, formation of active species cannot be the rate-determining factor for decomposition of the acid and its regeneration reactions

$$\label{eq:CH2-(C=O)-OH+H} \begin{array}{l} \to \ \mathrm{CH}_3-(\mathrm{C=O})-\mathrm{OH}, \\ \\ \mathrm{CH}_3-(\mathrm{C=O})^{\cdot} + \cdot \mathrm{OH} \rightarrow \mathrm{CH}_3-(\mathrm{C=O})-\mathrm{OH} \end{array}$$

may occur.

Let us evaluate the rate constant of the reaction between 'OH radicals and the acid. Among their loss reactions, reaction (1) has the maximum rate constant of  $5.5\times10^{10}\,M^{-1}$  s^{-1} [6]. Equating the rate of this reaction to the rate of radical formation, we obtain [OH] = $4.9 \times 10^{-8}$  M. Apparently, this value is the upper-bound estimate. Taking the experimental value of the acid decomposition rate and assuming that the acid reacts with OH radicals, we find that the rate constant of this reaction is  $9 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>. In view of the fact that the value of this constant is the lower-bound estimate, it is in good agreement with the constant of  $1.6 \times 10^7 \text{ M}^{-1}$ s<sup>-1</sup>, obtained in [19]. Because the same species are involved in both initiation and inverse reactions, a 100% decomposition, observed for phenols [7], is hardly expected in the case under consideration.

The main transformation product of the acid is the aldehyde in the liquid phase (Fig. 2), and  $CO_2$  and CO molecules in the gas phase (Fig. 3). The aldehyde and acid molecules hardly pass into the gas phase (Fig. 4). The concentration ratio between  $CO_2$  and CO molecules is approximately 1 : 1. Consequently, one molecule each of  $CO_2$  and CO must be formed from a molecule of the acid, which requires that the bond between the methyl and carboxy groups should be ruptured. With consideration for the initiation reactions written above, this may occur as a result of the following possible reactions:

$$\begin{array}{l} \cdot \mathrm{CH}_2-(\mathrm{C=O})-\mathrm{OH}+\mathrm{O} \rightarrow \cdot \mathrm{OCH}_2-(\mathrm{C=O})-\mathrm{OH},\\ \cdot \mathrm{OCH}_2-(\mathrm{C=O})-\mathrm{OH} \rightarrow \cdot (\mathrm{C=O})-\mathrm{OH}+\mathrm{CH}_2\mathrm{O},\\ \cdot (\mathrm{C=O})-\mathrm{OH}+\cdot \mathrm{OH} \rightarrow \mathrm{H}_2\mathrm{CO}_3 \rightarrow \mathrm{H}_2\mathrm{O}+\mathrm{CO}_2,\\ \mathrm{CH}_2\mathrm{O}+\mathrm{OH} \rightarrow \mathrm{H}\cdot \mathrm{CO}+\mathrm{H}_2\mathrm{O},\\ \mathrm{H}\cdot \mathrm{CO}+\mathrm{OH} \rightarrow \mathrm{CO}+\mathrm{H}_2\mathrm{O}. \end{array}$$

The acetaldehyde can be formed by the scheme

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 85 No. 1 2012



Fig. 2. Concentration c of acetic aldehyde in solution vs. the time  $\tau$  of residence between the solution and the discharge zone.



**Fig. 3.** Concentration *c* of carbon(II) oxide in the gas phase vs. the time  $\tau$  of residence between the solution and the discharge zone. (1) Without a catalyst and (2) with a catalyst.



**Fig. 4.** Concentration c of (1) acetic aldehyde and (2) acetic acid in the gas phase vs. the time  $\tau$  of residence between the solution and the discharge zone. (1) Without a catalyst and (2) with a catalyst.

$$CH_{3}-(C=O)-OH+ OH \rightarrow CH_{3}-(C=O)+H_{2}O_{2},$$
$$CH_{3}-(C=O)+H \rightarrow CH_{3}-(C=O)H.$$

Calculations of the amount of carbon in the products and in the undecomposed acid demonstrated that at contact durations of 3, 4, and 5.5 s its contents are 80, 86, and 96%, respectively, relative to the content of carbon contained in the starting acid. Despite that the difference from 100% is within the balance calculation error (~20%), the systematic improvement of the balance with increasing contact duration suggests that an additional product, undetected by the methods used, is formed at a short contact duration. The concentration of this product must exceedingly strongly depend on the contact duration. Possibly, the product of this kind could be methanol formed by the scheme

$$CH_3$$
-(C=O) + O →  $CH_3$  +  $CO_2$ ,  
 $CH_3$  +  $OH$  →  $CH_3OH$ .

A similar scheme, but with H atoms involved, could yield methane. However, methane must give carbon oxides in the gas phase, which would be detected in the balance.

## CONCLUSIONS

(1) The transformation of an aqueous solution of acetic acid by active species formed under the action of an atmospheric-pressure dielectric barrier discharge on water was studied. It was shown that the conversion of the acid reaches a value of 70%, with the main conversion products being  $CO_2$  and CO molecules in the gas phase and acetaldehyde in the liquid phase.

(2) It was suggested the fundamental aspects of formation of acetic acid decomposition products are common to monobasic carboxylic acids.

(3) It was found that, in destruction of an aqueous solution of acetic acid, not only oxidation occurs in the aqueous solution, but also reduction of acetic acid and products of its decomposition.

## REFERENCES

 Trapido, M., Munter, R., and Veressinina, Y., Proc. Int. Conf. Int. Ozone Association of the European-African-Asian-Australasian Group in Conjunction with Acwatech, Moscow, 1998, May 26–28, pp. 519–523.

- 2. Pikaev, A.K., *Khim. Vysok., Energ.*, 2000, vol. 34, no. 2, pp. 83–102.
- 3. Lerouge, S., Fozza, A.C., Wertheimer, M.R., et al., *Plasmas Polymers*, 2000, vol. 5, no. 1, pp. 31–46.
- Grabowski, L.R., Van Veldhuizen, E.M., Pemen, A.J., and Rutgers, W.R., *Plasma Chem. Plasma Proc.*, 2006, vol. 26, no. 4, pp. 3–17.
- Jinzhang Gao, Yongjun Lin, Wu Yang, et al, *Plasma Sources Sci. Technol.*, 2003, vol. 12, pp. 533–538.
- Grymonpre, D.R., Sharma, A.K., Finney, W.C., and Locke, B.R., *Chem. Eng. J.*, 2001, vol. 82, pp. 189–207.
- Bubnov, A.G., Burova, E.Yu., Grinevich, V.I., et al., *Plasma Chem. Plasma Proc.*, 2006, vol. 26, no. 1, pp. 19– 30.
- Malik, M.A., *Plasma Chem. Plasma Proc.*, 2010, vol. 30, no. 1, pp. 21–31.
- Bubnov, A.G., Burova, E.Yu., Grinevich, V.I., et al., *Plasma Chem. Plasma Proc.*, 2007, vol. 27, no. 2, pp. 177–187.
- Bird, R.B., Stewart, W.E., and Lightfoot, E.N., *Transport Phenomena*, New York: Wiley, 1960, p. 37.
- 11. Egorova, G.V., Voblikova, V.A., Tkachenko, S.N., et al., *Zh. Fiz. Khim.*, 2003, vol. 77, no. 11, pp. 1966–1971.

- 12. Lur'e, Yu.Yu., *Analiticheskaya khimiya promyshlennykh stochnykh vod* (Analytical Chemistry of Industrial Wastewater), Moscow: Khimiya, 1984.
- Hillebrand, W.F. and Lundell, G.E.F., *Applied Inorganic Analysis*, John Wiley & Sons Inc., New York; Chapman & Hall Ltd, London, 1953, 2nd ed.
- Ognier, S., Iya-sou, D., Fourmond, C., and Cavadias, S., *Plasma Chem. Plasma Proc.*, 2009, vol. 29, no. 4, pp. 261–273.
- Titov, V.A., Rybkin, V.V., Maximov, A.I., and Choi, H.S., *Plasma Chem. Plasma Proc.*, 2005, vol. 25, no. 5, pp. 503–518.
- Pikaev, A.K., Kabakchi, S.A., and Makarov, I.E., Vysokotemperaturnyi radioliz vody i vodnykh rastvorov (High-Temperature Radiolysis of Water and Aqueous Solutions), Moscow: Energoatomizdat, 1988.
- 17. Chumadova, E.S., Shikova, T.G., Rybkin, V.V., and Titov, V.A., Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 2008, vol. 51, no. 11, pp. 29–32.
- Gangal, U., Srivastava, M., and Sen Gupta, S.K., *Plasma Chem. Plasma Proc.*, 2010, vol. 30, no. 2, pp. 299–310.
- Karpel Vel Leitner, N. and Dore, M., J. Photochem. Photobiol. A. Chem., 1996, vol. 99, nos. 2–3, pp. 137– 143.