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PLASMA CHEMISTRY

Kinetics of DC Discharge-Induced Degradation of Nitrophenol in Aqueous Solution

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Abstract—The kinetics of degradation of nitrophenol and buildup of its products in the liquid cathode (doubly distilled water) of atmospheric-pressure dc discharge in air have been experimentally studied. It has been shown that the main products are formaldehyde and carboxylic acids. It has been found that the discharge treatment is accompanied by the formation of nitric acid in the liquid phase. The kinetic characteristics of the nitrophenol degradation process and its energy efficiency have been determined.

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Water quality impairment in natural sources and toughening the standards for drinking water call for development of novel, innovative water treatment processes. An effective method of removal of various aromatic hydrocarbons, synthetic surfactants, and carboxylic acids from aqueous solutions is the use of gas discharge excited either directly in the solution or over its surface. Investigation of the mechanism of these processes in plasma–solution systems and determination of their reaction routes are of great importance for both pure science and practical purposes, in particular, for the development of technology and the design of devices for use in potable water pretreatment and wastewater treatment processes. Various types of electric discharge are use for these purposes.

For example, high-voltage pulse discharge is effective in removal of organic compounds from aqueous solutions, especially, highly toxic liquids such as solutions containing organic dyes [1, 2], tributyl phosphate [3], and 4-chlorophenol [4]. Dielectric-barrier discharge (DBD) shows good results in the destruction of synthetic detergents [5], formaldehyde and acetone [6], and carboxylic acids [7]. The degradation of phenol in atmospheric-pressure dc discharge is documented quite well [8, 9]. However, data on the application of high-energy chemistry methods to decomposition of nitroaromatic compounds are quite scanty. These toxic compounds are indispensable raw materials and intermediate products in the manufacture of dyes, pesticides, medicinal drugs, and explosives. Being toxic to microorganisms, they do not undergo biodegradation [10]. The biodegradation of nitro compounds is hampered by a high strength of the bond of the NO_2 group with the aromatic ring [11]. Simple physical methods, including adsorption and membrane filtration are ineffective in reducing the toxicity of nitrophenols. On the other hand, chemical methods, such as chlorination and permanganate oxidation, lead to the formation of toxic intermediates because of incomplete decomposition. Therefore, it is important to explore whether electric discharges of various types can be used for cleaning aqueous solutions of nitroaromatic compounds. Hao et al. [12] studied the degradation of *p*-nitrophenol in a pulsed corona combined with ozonation. This method has proved effective in the degradation of the test compound (96%); carboxylic (formic and acetic) acids and nitrate ions were found as products.

The aim of this work was to study the kinetics of decomposition of nitrophenol and identify the products of its transformation in an electrolytic-cathode dc discharge, which had not been investigated in relation to the degradation of nitrophenol.

EXPERIMENTAL

The experimental setup was described in [13]. An atmospheric pressure direct-current discharge in air was excited by applying dc voltage across the metal anode and the surface of the solution. The distance between the anode and the electrolyte surface was 4 mm; the discharge current, 40 mA; and the electrolyte volume, 80 mL. A solution of *p*-nitrophenol with a concentration of 75 mg/L in doubly distilled water was used. After a certain discharge time, the pH of the solution and concentrations of nitrophenol, phenol, carboxylic acids, aldehydes, and nitrate and nitrite ions were measured. A fresh portion of the solution was used for each treatment time. The concentration of nitrophenol was determined by measuring absorbance of the solution at a wavelength of 350 nm on a Hitachi U-2001 spectrophotometer (Japan). The con-

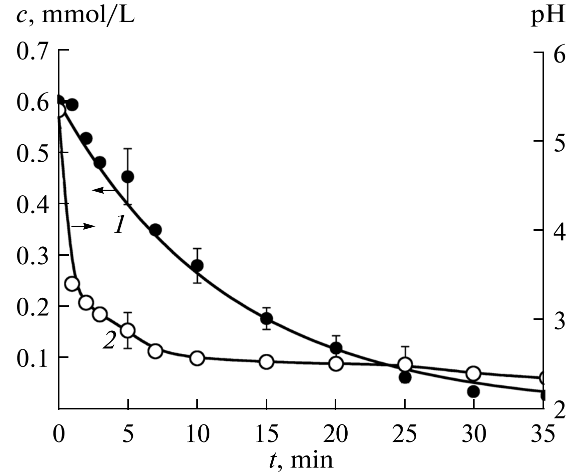

Fig. 1. Plots of (*1*) nitrophenol concentration and (*2*) pH of the solution as a function of time of atmospheric-pressure dc discharge treatment of nitrophenol in aqueous solution.

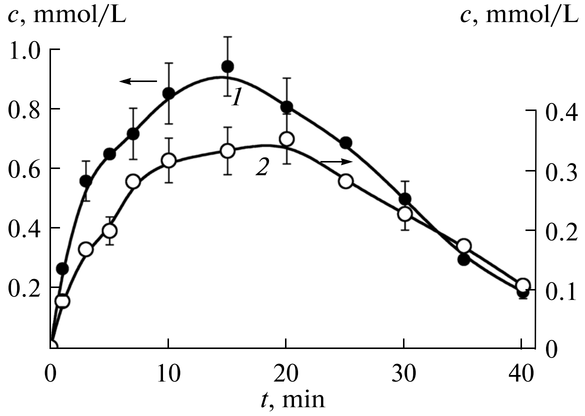

Fig. 2. Dependence of the concentration of (*1*) carboxylic acids and (*2*) aldehydes on the time of atmospheric-pressure dc discharge treatment of nitrophenol in aqueous solution.

centrations of phenol and aldehydes were found by measuring the intensity of fluorescence, excited at the absorption band maximum, with a Fluorat-02 fluorometer (Russia). Phenol was extracted with butyl acetate and re-extracted with an aqueous solution followed by acidification of the aqueous extract. In the case of aldehydes, a luminescent compound was the product of their reaction with 1,3-cyclohexanedione in the presence of ammonium ions. The concentration of carboxylic acids was determined from the absorbance at 400 nm of the compound produced by the reaction of an acid with ammonium metavanadate. The procedure for the determination of nitrate ions was based on their reaction with sodium salicylate in the presence of sulfuric acid to form the salt of nitrosalicylic acid, which absorbs at a wavelength of 400 nm. The method used for determining nitrite ions was based on their ability to diazotize sulfanilic acid to form a reddish violet dye of the diazo compound with 1-naphthylamine. Random error was verified in five measurement runs using a confidence level of 0.95. On average, the concentration determination error did not exceed 15%.

RESULTS AND DISCUSSION

Figure 1 illustrates the kinetics of the discharge-induced degradation of nitrophenol. It can be seen that the rate curve is described well by the first-order law in nitrophenol $c = c_0 \exp(-Kt)$ with an effective rate constant of 0.073 ± 0.006 s^{-1} (pair correlation coefficient 0.98). These data allowed us to calculate the energy efficiency of decomposition of nitrophenol. Under the given conditions, the impedance drop is 920 V, which corresponds to the power input to the discharge of 37 W. Calculation gave a G-value of 4.2 molecules per 100 eV at a treatment time of $t \rightarrow 0$, i.e., at a rate of $\left.\frac{dc}{dt}\right|_{t\rightarrow 0} = -c_0K$. Under the same treatment conditions, this energy yield was 0.003 molecule per 100 eV for phenol [10] or 0.001 molecule per 100 eV for Sulfonol [14]. The discharge in question has quite a high energy efficiency with respect to the degradation of nitrophenol compared to other benzene ring-containing organic compounds.

Considering the possible nitrophenol degradation products, it was logical to assume that the detachment of the nitro group would result in phenol as the main product, but this was not the case. The absence of phenol in the degradation products of nitrophenol subjected to treatment in a positive pulsed discharge was noted in [12]. We failed to detect hydroxylated phenols (hydroquinone, catechol); it is likely that they rapidly decompose into carboxylic acids and aldehydes. This fact was confirmed by Wang et al. [15], who studied the pulsed discharge treatment of a soil solution for removal of nitrophenol. Grymonpre et al. [18] studied the decomposition of resorcinol, catechol, and 1,4-hydroquinone solutions. They found that the degradation products are carboxylic acids and CO_2, with the degradation rate of dihydroxybenzenes being higher than that of phenol. In addition, the balance of carbon in the initial nitrophenol solution and the nitrophenol degradation products we have found (carboxylic acids and aldehydes) holds accurate to ~10% (Fig. 2). For example, at a treatment time of 15 min, the acid contains 1.8 mmol/L of carbon atoms (on acetic acid basis), the aldehyde contains 0.3 mmol/L (on formaldehyde basis), and the residual nitrophenol has 1.2 mmol/L versus the initial carbon content of 3.6 mmol/L. The small deficit of carbon in the products may be due to the formation of carbon dioxide, which is released to the gas phase.

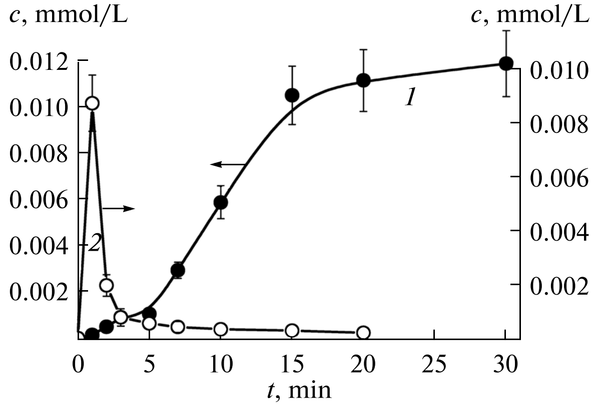

Fig. 3. Dependence of the concentration of (*1*) nitrate and nitrite (*2*) ions on the time of atmospheric-pressure dc discharge treatment of nitrophenol in aqueous solution.

As follows from the data in Fig. 2, which shows the time dependence of the concentration of carboxylic acids and aldehydes, these products are intermediate and undergo degradation. In [16] it was found that the DBR treatment of aqueous solutions of carboxylic acids results in aldehydes and carbon oxides and the treatment of aqueous aldehyde solutions yields only carbon oxides [17]. This behavior is observed for nitrophenol as well.

Figure 3 presents the concentration of (*1*) nitrate and (*2*) nitrite ions as a function of the time of treatment of the nitrophenol solution. The concentration of nitrite ions initially increases after the beginning of treatment and then decreases, since nitrite rapidly disproportionates to give nitrate in an acidic medium. Assuming that the nitrate ion results from the dissociation of nitric acid, the calculation of the pH in terms of NO_3^- concentration gives values close to those obtained experimentally. Thus, pH is ~2.1 at a treatment time of 15 min. The source of nitrate ions can be both nitrophenol and nitrogen oxides and nitric acid produced in the gas phase [8]. However, the amount of decomposed nitrophenol significantly exceeds the amount of nitrate ions. Apparently, the nitrophenol groups during degradation yield nitric oxide, which is sparingly soluble in water and is released into the gas phase. A source of nitric acid is the reaction of the solution with NO_2 molecules that are formed by the discharge in air and readily converted into nitric acid, e.g. via the reaction $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$.

Although the mechanism of nitrophenol degradation by the action of electrolytic-cathode dc discharge has not been completely explored, it can be concluded that the chemical degradation is largely due to the formation of active submolecular ($^{\bullet}OH$, O, H^+, $HO_2^{\bullet}$, solvated electrons, etc.) and molecular (O_2, H_2O_2) species [19, 20]. These species have a high oxidation potential and can effectively decompose organic pollutants. A possible nitrophenol degradation scheme is as follows:

$$\begin{tikzcd}
\text{Nitrophenol} \arrow[r] & \text{Hydroxy derivatives of phenola} + NO_2^- + NO_3^- \arrow[d] & \\
& \text{Carboxylic acids} \arrow[r] \arrow[d] & \text{Aldehydes} \arrow[d] \\
& CO_2 + CO & CO_2 + CO
\end{tikzcd}$$

CONCLUSIONS

Direct-current discharge with electrolytic cathode has a high nitrophenol destruction efficiency (95%); the degradation of nitrophenol occurs at a higher rate compared to that for phenol or Sulfonol in a discharge of this type. The results can be used in the development of a plasma-chemical water decontamination technology for removal of nitrophenol.

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