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Mechanism of Phenol Degradation Processes Induced by Direct-Current Atmospheric-Pressure Discharge in Air

E. S. Bobkova, A. V. Sungurova, and V. V. Rybkin

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 January 17, 2013; in final form, March 4, 2013

Abstract—The phenol degradation kinetics and the buildup kinetics of the products hydroxyphenols, nitrophenols, carboxylic acids, and formaldehyde in electrolytic-cathode direct-current discharge have been studied, as well as the formation of nitric acid. On the basis of the results, a scheme of the processes has been proposed; calculations according to this scheme describe well the experimental data on the degradation kinetics of phenol and the formation/decay kinetics of its transformation products.

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There is currently increasing interest in processes of severe oxidation of water for destruction of toxic substances. The conventional methods based on membrane technologies, adsorption, chlorination, and ozonation are expensive and often ineffective. Therefore, intensive research into the use of highenergy chemistry methods, in particular, gas discharge techniques for this purpose is in progress [1]. Examples of relevant pilot units have been reported in [2].

Phenol is a widespread pollutant. It has teratogenic and carcinogenic activity. For this reason, its decomposition induced by various types of discharge, such as pulsed positive corona [3], dielectric-barrier discharge (DBR) [4], contact glow discharge electrolysis [5], and gliding arc [6], has been widely studied. In all the studies reported to date, the phenol degradation kinetics was investigated and no data on the product buildup kinetics were obtained available. Only some qualitative measurements were made. In [7], we showed that the decomposition of phenol under these conditions yields carboxylic acids and aldehydes as some of the products, wherein the aldehydes are formed from the acids. However, calculations showed that these products are insufficient for the carbon balance. Optimization of the overall process and its management require knowledge of the reaction mechanism involving the formation and decay of other products. Thus, the aim of this work was to obtain such data using electrolytic-cathode DC discharge.

The experimental setup is described in [8]. Atmospheric-pressure dc discharge in air was excited by applying a constant voltage across the metal anode and the surface of the solution. The anode–electrolyte surface distance was 4 mm. The discharge current was 40 mA. A phenol solution in distilled water with a concentration of 0.53 mmol/L was used. After the discharge treatment of the solution over a certain time, the concentrations of phenol and its degradation products were determined. A fresh portion batch of the solution was used for each time. The electrolyte volume was 80 mL.

The concentration of phenol was measured by the fluorescence technique (Flyuorat-02 fluorimeter). Phenol was extracted with butyl acetate followed by re-extraction into water and the subsequent acidification of the resulting solution. For the photometric determination of hydroxylated phenol derivatives, their reaction with 4-aminoantipyrine in the presence of potassium hexacyanoferrate in an alkaline medium (pH 10) was employed followed by measuring adsorption at a wavelength of 540 nm (Hitachi U-2001 spec-



Fig. 1. Dependence of the concentration of (1) hydroxylated phenol derivatives and (2) phenol on the treatment time. The symbols and curves refer to the experimental and calculated data, respectively.



Fig. 2. Dependence of the (1) concentration of nitrate ions and (2) pH on the treatment time The symbols and curves refer to the experimental and calculated data, respectively.

trophotometer). A procedure for determination of nitrates was based on their reaction with sodium salicylate in the presence of sulfuric acid yielding a salt of nitrosalicylic acid, which absorbs light at a wavelength of 400 nm. The nitrophenol concentration was found by measuring the absorbance of the solution at a wavelength of 350 nm. The qualitative composition of active species in the gas phase was determined from the discharge emission spectrum, which was recorded in digital form with an Avaspec-2048 universal monochromator (600 lines/mm grating) in the wavelength range of 200–900 nm.

The measurements showed that the discharge treatment of the phenol solution led to the degradation of phenol (Fig. 1), the formation of carboxylic acids and aldehydes [9], and a decrease in the pH of the solution (Fig. 2). Acid concentrations were too small to be responsible for the pH lowering observed; moreover, the acids disappeared with a treatment time of ~40 min, while the pH of the solution continued to increase slowly. In addition, in the range of 5-15 min, the solution took a yellowish color, which disappeared over time. Yellowing of the solution was also mentioned by Tomizawa and Tezuka [5]. They attributed this phenomenon to the formation of hydroxyphenols. It is known that solutions of hydroxyphenols are col-



Fig. 3. Dependence of the nitrophenol concentration on the treatment time. The symbols and curves refer to the experimental and calculated data, respectively.

orless. Spectrophotometric analysis showed that the compounds in question are *ortho*- and *para*-nitrophenols, which gave the characteristic color. The time dependence of the *o*- and p-C₆H₅NO₃ concentration measured was nonmonotonic, reaching a maximum of 0.1 mmol/L (Fig. 3). Nitrophenols can be formed by the reaction of phenol with nitric acid. This is evidenced by the fact that the buildup of nitrate ions NO₃ takes place in the solution along with a decrease in pH (Fig. 2). The source of nitric acid can be nitrogen oxides that are produced in the gas phase and dissolve in water. Indeed, the discharge emission spectrum dis-

played strong γ -bands of NO molecules in the UV

Along with the aforementioned products, hydroxylated phenol derivatives were detected in the solution; the kinetics of their concentration changes are shown in Fig. 1. Calculations showed that all the phenol degradation products according to their concentrations measured make up 80% of carbon contained initially in the solution. The missing carbon is possibly due to the formation of CO_2 molecules in the gas phase. In particular, the formation of CO_2 was observed during the oxygen DBR treatment of a phenol solution [8]. Thus, the process of phenol degradation can be in general represented as follows:



region.

To describe the kinetics of the reactions, we used their set presented in the table. The choice of reactions (1)-(20) and their rate constants was substantiated in [7, 9] when we simulated the hydrogen peroxide for-

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Phenol transformation reactions

No.	Reaction	$\log K$
1	$H_2O \rightarrow H' + OH$	-5.4
2	$H_2O \rightarrow H^+ + OH^+ + e_{solv}$	-5.4
3	$e_{SOLV} + H_2O_2 \rightarrow OH^{\cdot} + OH^{-}$	10.5
4	$H' + H_2O \rightarrow OH + H_2$	10.5
5	\cdot OH + H ₂ O ₂ \rightarrow HO [•] ₂ + H ₂ O	7.8
6	$OH + H_2 \rightarrow H' + H_2O$	8.1
7	$OH + O_2 \rightarrow O_2 + OH^-$	10
8	$OH + OH \rightarrow H_2O_2$	11.2
9	$\rm H^+ + OH^- \rightarrow H_2O$	11.5
10	$\mathrm{H}_{2}\mathrm{O} + \mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{H}_{2}$	-6.5
11	$OH + H_2O_2 \rightarrow O_2 + H_2O$	7.8
12	$CH_2O + HO_2^{\bullet} \rightarrow HCO + H_2O_2$	1.2
13	$\text{HCO} + \text{HO}_2^{\bullet} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	10.9
14	$CH_2O \rightarrow CH_2O_G$	-3.5
15	$\mathrm{CH}_{2}\mathrm{O} + \mathrm{OH}^{\bullet} \rightarrow \mathrm{CO}_{2} + \mathrm{H}_{2} + ^{\bullet}\mathrm{H}$	7.3
16	$CO_2 \rightarrow CO_{2G}$	1.8
17	$CO_2 + H_2O \rightarrow H_2CO_3$	1.0
18	acids $\rightarrow CH_2O + H_2O$	6.3
19	acids $\rightarrow CO_2 + H_2O$	2.0
20	Phenol + OH \rightarrow acids	6.9
21	$NO_g \rightarrow NO$	1.31×10^{-8}
22	$NO + HO_2 \rightarrow HNO_3$	11.1
23	Phenol + $OH^{\bullet} \rightarrow hydroxyphenols$	6.5
24	hydroxyphenols \rightarrow acids	-4.1
25	Phenol + HNO ₃ \rightarrow nitrophenol + OH \cdot	9.1
26	nitrophenol + OH \rightarrow acids + HNO ₃	7.0

Note: $\log K$ is the decimal logarithm of rate constant in L mol⁻¹ s⁻¹, L² mol⁻² s⁻¹, or s⁻¹; the subscript g refers to the gas phase; e_{solv} is the solvated electron. * The rate of the reaction in mol L⁻¹ s⁻¹.

mation and phenol degradation processes resulting in carboxylic acids and aldehydes. The rate constant for reaction (22) was taken as given in [10]. The rate constants of the other reactions were varied during the calculation so as to describe the experimentally observed kinetics. In the same way, the rate of reaction (21) was adjusted. Estimates by the flux density $j_{NO} = 0.25 \times N_{NO} \times V_T (N_{NO} \text{ is the number density of NO molecules}, V_T = \sqrt{\frac{8kT}{\pi M}}$ is the thermal velocity, and T = 1500 K [11]) showed that an NO number concentration of

 $\sim 9 \times 10^{12}$ cm⁻³ in the gas phase is required to ensure this reaction rate. We are unaware of any experimental measurement of NO concentration for these conditions. For low-pressure (100 Pa) air plasma at a current of 80 mA in a tube of 1.5 cm radius, the NO concentration was 2×10^{14} cm⁻³ [12].

The system of rate equations relevant to the table was solved by the fifth-order Gear method with 1% accuracy. The calculation results given in Figs. 1-3 are in good agreement with the experimental data, thereby suggesting that the suggested reaction scheme is quite likely.

In summary, the degradation of phenol and the formation/decay processes of its principal destruction products have been investigated. A kinetic reaction scheme that satisfactorily describes the experimental data has been proposed.

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