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Investigation of the relative reactivity of aromatic compounds in air under the action of pulsed discharge plasma

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Based on the method of competing reactions, a method for determining the relative reactivity of aromatic vapors in relation to the plasma components of a pulsed corona discharge is developed. The parameters of the relative reactivity of aromatic compounds in the air and nitrogen stream were obtained using model mixtures based on benzene, toluene, and xylene with a content of 250−500 ppm. The effect of water vapor on the process is shown. The obtained data will be useful for optimizing the processes of plasma-chemical air purification from the vapors of toxic aromatic compounds.

Keywords: Corona discharge, aromatic compounds, non-equilibrium atmospheric pressure plasma, air purification, volatile organic compounds, BTEX.

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Aromatic organic compounds are volatile organic compounds (VOCs) that are important toxic components of ventilation emissions of industrial facilities. Methods for removing VOCs from the air with the use of non-equilibrium plasma of electric discharges of various types are currently being developed [1–6]. A considerable part of these studies are focused on toluene, which is one of the most widespread aromatic compounds from the BTEX (benzene, toluene, ethylbenzene, xylene) series produced in the coke-processing industry [7–10]. The diversity of methods and data presentation techniques makes it hard to compare the reported results. This is due to the lack of a unified approach to the selection of parameters characterizing the process efficiency. We have demonstrated that the use of model mixtures of compounds allows one to determine relative reactivity parameters of VOCs with a high accuracy [11,12]. The efficiency of utilization of the discharge energy is characterized by the plasma-chemical yield of the formal reagent. These parameters may be the quantities needed to compare alternative methods and scale processes.

In the present study, we report the results of examination of the relative reactivity of common aromatic compounds (benzene, toluene, and *o*-xylene) with respect to the components of plasma generated in air by a pulsed corona discharge. Components were studied both separately and in combination. Under otherwise equal conditions, compounds compete with plasma components for reacting; this makes it possible to determine the reactivity parameter accurately and estimate the rate of fast processes using the gas–liquid chromatography technique [13].

The experimental procedure and setup were discussed in detail in [11,13]. The analytical treatments are similar to those applied in [13]. A high-voltage pulse generator was constructed using SOS switches [14]. The discharge parameters were as follows: a voltage amplitude of 100 kV, a current amplitude of 490 A, a half-height pulse duration of 20 ns, and a pulse repetition rate of 10 Hz. The discharge part of a plasma-chemical reactor was a stainless-steel cylinder with an inner diameter of 85 mm and a length of 56 cm. A potential electrode made of steel wire 0.24 mm in diameter was stretched along the cylinder axis. The volume of the gas system of the setup was $V = 26$ l. The pulse energy was averaged over a series of pulses and fell within the 0.55−0.65 J range. The experiment involved discharge treatment (2−5 min) and analysis of the ozone and VOCs content (3 min). A commercially available „synthetic arr“ gaseous mixture with a composition of [N_2]:[O_2]=80:20 (by volume) was used as a model of air.

Figure 1, *a* presents the variation of concentrations of aromatic components (benzene (*1*), toluene (*2*), and *o*-xylene (*3*)), which had an initial concentration of 500 ppm each, with specific energy E expressed in J/l (i.e., with the amount of energy supplied to a unit volume of the gaseous mixture). Experiments were performed separately for each component. Ozone concentration [O_3] was also measured in each case; the corresponding dependences for the ozone concentration are denoted as *4.1–4.3*. The yield of ozone in clean air is presented for comparison (*5*). It is evident that aromatic compounds feature different reactivities with respect to plasma components. In accordance with the procedure outlined in [13], all components were introduced simultaneously into the mixture to determine the relative reactivity values. Figure 1, *b* shows the dependences for concentrations of aromatic compounds with all of them being present simultaneously in the mixture in an initial concentration of 500 ppm each, while Fig. 2, *a* presents similar dependences corresponding to an initial component

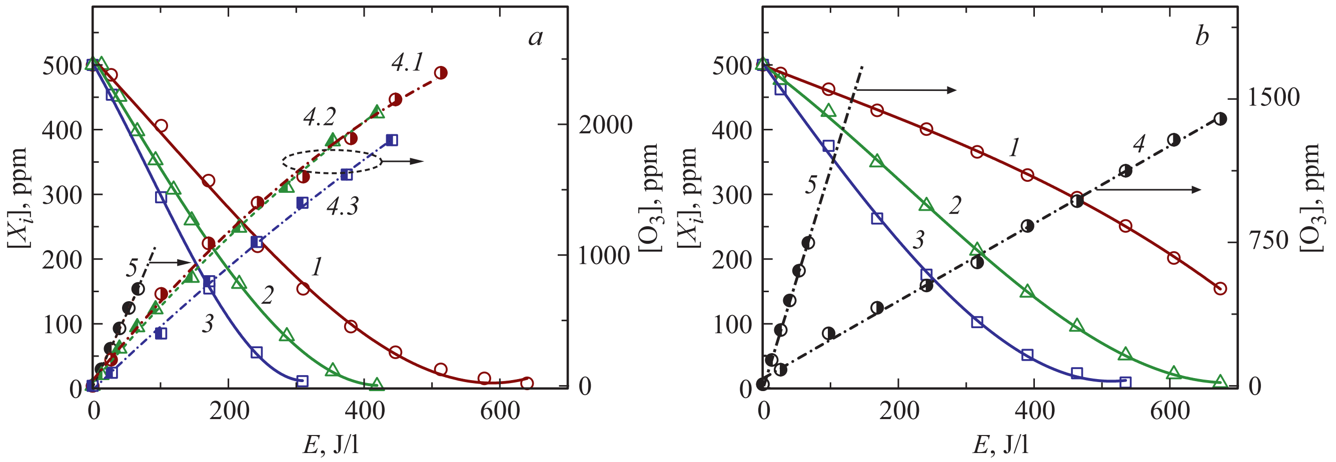

Figure 1. *a* — Variation of $[X_i]$ and $[O_3]$ concentrations with specific energy E in air for benzene (*1*), toluene (*2*), *o*-xylene (*3*), ozone with benzene present (*4.1*), ozone with toluene present (*4.2*), ozone with *o*-xylene present (*4.3*), and ozone in clean air (*5*). *b* — Variation of $[X_i]$ and $[O_3]$ concentrations with specific energy E in air with all components being present simultaneously (in an initial concentration of 500 ppm each) for benzene (*1*), toluene (*2*), *o*-xylene (*3*), ozone (*4*), and ozone in clean air (*5*). Symbols denote experimental data, while curves represent the result of a second-order polynomial approximation.

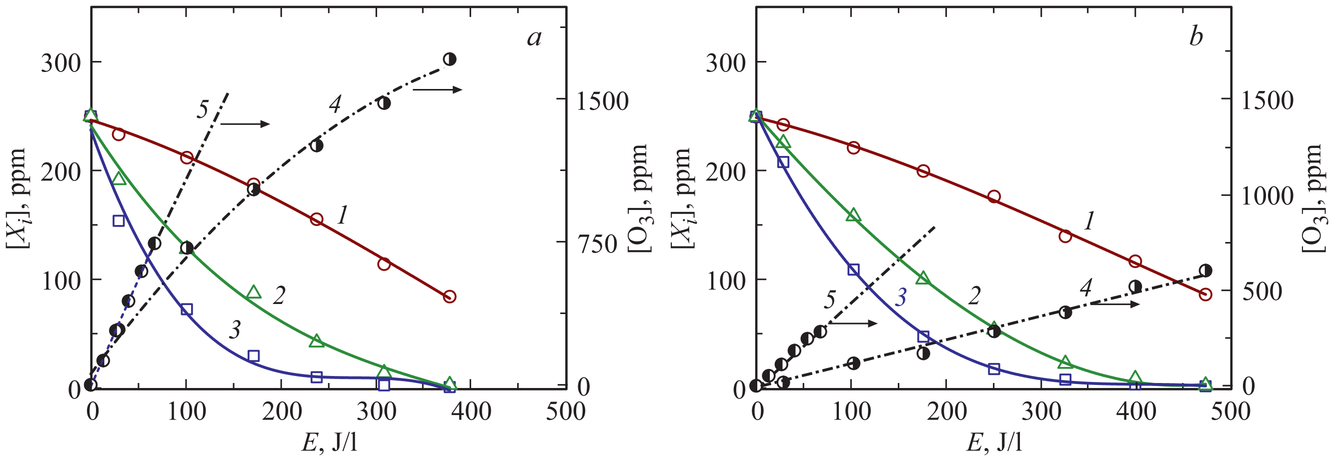

Figure 2. *a* — Variation of $[X_i]$ and $[O_3]$ concentrations with specific energy E in air with all components being present simultaneously (in an initial concentration of 250 ppm each) for benzene (*1*), toluene (*2*), *o*-xylene (*3*), ozone (*4*), and ozone in clean air (*5*). *b* — The same, but with an addition of 2 vol.% of H_2O vapor. Symbols denote experimental data, while curves represent the result of a second-order polynomial approximation.

concentration of 250 ppm. An experiment (Fig. 2, *b*) with 2 vol.% of H_2O added to the mixture and the other conditions being equal to those in Fig. 2, *a* was performed in order to investigate the influence of water vapor. Figure 3 presents the results of an experiment with nitrogen being the major component of the gas mixture.

The values characterizing the energy parameters of processes and the factors of reactivity of components were calculated to reveal the key trends presented in Figs. 1–3. Data were approximated with second-order polynomials (curves). The slopes of dependences may be used to calculate plasma-chemical yield G_i of a certain process (in units of mol/100 eV) with account for the coefficient of conversion of dimensions in the figures: $1\,\text{ppm} \cdot \text{l} \cdot \text{J}^{-1} = 0.433\,\text{mol/100 eV}$. The ozone yield is denoted as G_{O_3} for air and as $G_{O_3} + X_i$ for air containing impurities X_i. Accordingly, the process of removal of impurities is characterized by a negative G_i value, while G_{O_3} is positive. The energy efficiency of the method is quantified by cumulative value $G = \sum G_i$. The constants characterizing the reactivity of components i were calculated as $k_i = G_i/[X_i]$. Expression $k_j/k_i = G_j/[X_j]/(G_i/[X_i])$ was used to compare the reactivities of two components; calculations were performed in the initial region with $E = 100$ J/l. Being the most widespread and the best-investigated VOC, toluene ($k_i = k_{tol}$) was used as a reference component, and relative relativity factors with respect to it were calculated as $k_{i,tol} = k_i/k_{tol}$. The values of all the mentioned quantities

Plasma-chemical yields and relative reactivity of aromatic compounds

Data source	Component X_i	$[X_0]$, ppm	Gas	G, mol/100 eV				k_i	$k_{i,tol}$
				G_{O_3}		$-G_i$	$-\sum G_i$		
				Air	Air $+X_i$				
Fig. 1, *a*	Benzene	500	Air	4.85	2.65	0.51	0.51	3.0	0.6
	Toluene	500		4.85	2.65	0.73	0.73	5.0	1.0
	Xylene	500		4.85	2.16	0.91	0.91	7.0	1.4
Fig. 1, *b*	Benzene	500	Air	4.85	0.81	0.18	1.17	0.88	0.44
	Toluene	500				0.39		2.16	1.00
	Xylene	500				0.60		3.86	1.78
Fig. 2, *a*	Benzene	250	Air	4.85	2.35	0.16	0.98	1.78	0.26
	Toluene	250				0.38		6.7	1.00
	Xylene	250				0.44		14.3	2.13
Fig. 2, *b*	Benzene	250	Air $+2$ vol.% H_2O	1.89	0.56	0.13	0.94	1.31	0.26
	Toluene	250				0.36		5.25	1.00
	Xylene	250				0.45		9.3	1.77
Fig. 3	Benzene	250	N_2	–	–	0.20	0.98	2.26	0.45
	Toluene	250		–	–	0.36		4.92	1.00
	Xylene	250		–	–	0.43		6.77	2.13

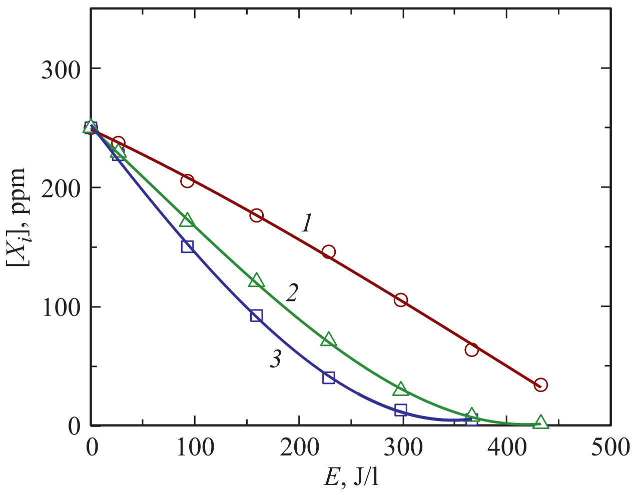

Figure 3. Variation of $[X_i]$ concentrations with specific energy E in nitrogen with all components being present simultaneously for benzene (*1*), toluene (*2*), and *o*-xylene (*3*). Symbols denote experimental data, while curves represent the result of a second-order polynomial approximation.

are listed in the table. When components are isolated (Fig. 1, *a*), the process of removal of each impurity competes only with the process of deactivation of reactive plasma particles. This is evidenced by a certain equalization of the values of relative reactivity (see the last column). When all components are present simultaneously in the mixture, they compete with each other, and the relative reactivities of toluene, benzene, xylene are related as 0.44:1.0:1.78. Following a two-fold reduction in the concentration of components to 250 ppm, the relative reactivity of xylene increases with respect to that of benzene: the corresponding ratio is 0.26:1.0:2.13. The apparent deviation from the law of mass action allows one to identify the operation of different mechanisms of removal of mixture components. Ozone yield G_{O_3} in air without impurities may be used to characterize quantitatively the efficiency of a specific experimental setup and to optimize its electrophysical parameters. Tabulated data suggest that the amount of ozone decreases by 2.5–4 molecules following the removal of a single aromatic compound molecule. This ratio is significantly higher than the one corresponding to unsaturated compounds, where the ratio is near-stoichiometric [15,16]. The ozone yield decreases considerably after the introduction of water vapor, but the energy efficiency of impurity removal changes only slightly, and the relative reactivity remains approximately the same. These data suggest that processes involving reactive oxygen species are of secondary importance in the removal of aromatic compounds. The results of examination of processes in nitrogen-based mixtures confirm this: the relative reactivity and the overall plasma-chemical yield both change only marginally. Thus, in agreement with the data from [10], the reactivity of aromatic compounds with respect to plasma components increases with the number of methyl groups. Reiterating the conclusions made in [8], we found that the processes involving reactive nitrogen species are essential to the removal of aromatic compounds.

The discussed method of application of VOC mixtures provides an opportunity to estimate rapidly the relative reactivities of volatile aromatic compounds and may serve as a means for identifying different mechanisms of plasma-chemical removal of VOCs of various chemical structures.

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Conflict of interest

The authors declare that they have no conflict of interest.

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