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Investigation of the relative reactivity of alkyl acetate vapors with respect to the components of a pulsed discharge plasma in air

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A study was performed of the relative reactivity of vapors of a number of acetic acid esters (alkyl acetates) with respect to plasma components of a pulsed corona discharge with the voltage of 100 kV and duration of 40 ns. On model mixtures based on methyl-, ethyl-, propyl-, isopropyl-, isobutyl-, butyl-, and vinyl acetates with contents of $250-500$ ppm in air and nitrogen, the relative reactivity parameters were obtained. The reactivity of acetic acid esters increases with an increase in the hydrocarbon substituent. The high reactivity of vinyl acetate is due to the double bond reaction with ozone.

Keywords: corona discharge, acetic acid esters, alkyl acetates, vinyl acetate, non-equilibrium atmospheric-pressure plasma, air purification, volatile organic compounds.

Acetic acid esters (alkyl acetates) are volatile organic compounds (VOC) widely employed in various branches of industry as solvents and in organic synthesis. Methods are being developed, which involve the use of non-equilibrium plasma of various-type electrical discharges for air purification from VOC vapors [1–5], including vapors of ethyl acetate [5,6]. To make conclusions that allow predicting the behavior of complex compound mixtures with respect to plasma, important is to investigate the effect of the structure on reactivity of certain VOC classes. Earlier there were determined relative reactivities of general-purpose solvents [7,8], unsaturated [8] and aromatic [8,9] compounds. The use of mixtures of related-class compounds allows obtaining relative parameters of the VOC reactivity with high accuracy [7–9]. These parameters are needed for comparing alternative plasma-chemical methods based on discharges of different types.

This paper presents the results of studying relative reactivities of a number of alkyl acetates widely used as solvents, for instance, methyl acetate (AcOMe), ethyl acetate (AcOEt), propyl acetate (AcOPr), isopropyl acetate (AcOPr^i), butyl acetate (AcOBu) and isobutyl acetate (AcOBu^i). For comparison, vinyl acetate (AcOVi) was also used; this is a relatively toxic monomer used in producing polyvinyl acetate. The investigation was performed by using model mixtures. By measuring relative parameters of the mixture components, it is possible to compensate a number of errors in determining energy contributions, sampling, temperature, etc., and to obtain the relative reactivity parameters with high accuracy; therewith, the process rates may be estimated via comparison by the precise but low-rate technique of gas-liquid chromatography (GLC) [8]. In each process, the ozone content was measured, since ozone is an important product of the non-equilibrium plasma impact on oxygen-containing mixtures.

A detailed description of the experimental setup and procedure is given in [7]. The high−voltage pulse generator SM-2 was constructed based on a circuit involving SOS-switches [10]. The discharge parameters were as follows: voltage magnitude of 100 kV, current magnitude of 150 A, pulse length at half maximum of 40 ns, pulse repetition frequency of 10 Hz. The discharge system of the plasma-chemical reactor (PCR) consisted of a stainless-steel cylinder 110 mm in inner diameter and 56 cm in length. Along the cylinder axis, a potential electrode was stretched, which was made from a steel string 0.24 mm in diameter. The volume of the setupś gas system was $V = 26$ dm^3. The pulse energy was measured as an average over the pulse series by using oscillograms and appeared to be $0.10-0.18$ J (the discharge energy per pulse decreases with increasing production of ozone in the gas mixture due to its electronegative properties). The gas mixture was treated with a series of pulses during $2-5$ min, after which the gas mixture composition was analyzed by GLC during 3 min, and the ozone content was analyzed by a spectrometric method at approximately 255 nm. The GLC method error did not exceed 4%, the ozone content measurement error was not higher than 5%. As an air-simulating mixture, a commercial gas mixture „Synthetic Air" with the composition $N_2 : O_2 = 80 : 20$ (by volume) was used. Prior to starting the experiment, ozone was produced in a pure air mixture. This served as a test for stability of the experimental parameters and promoted conditioning of the PCR walls in order to minimize their influence on the process.

Fig. 1, a demonstrates the concentration dependences for the mixture of acetates, AcOMe (1), AcOEt (2),
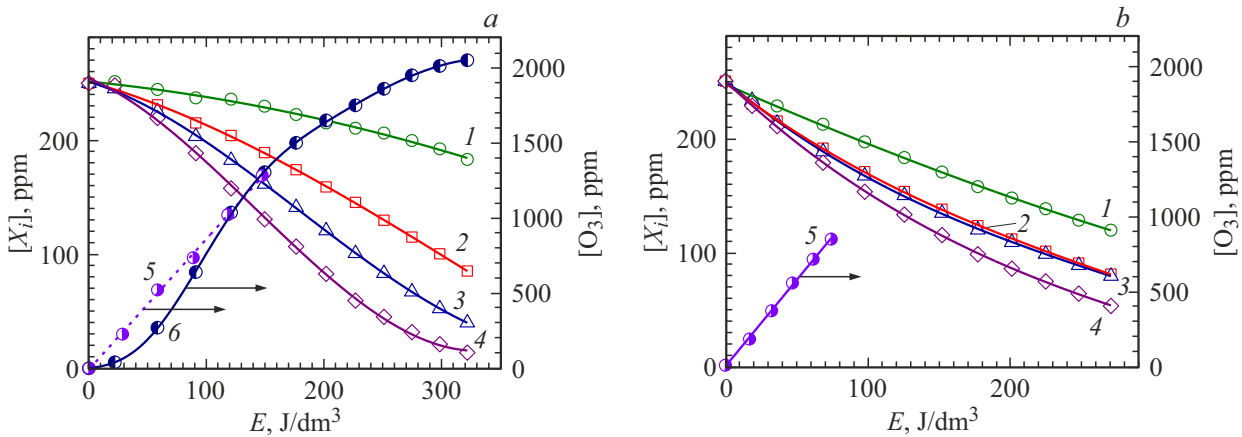
Figure 1. a — concentrations $[X_i]$ and $[O_3]$ versus specific energy E in air for AcOMe (1), AcOEt (2), AcOPr (3) and AcOBu (4), ozone in pure air (5), and ozone in air with impurities (6). b — similar dependences for nitrogen. Symbols — experiment, lines — approximation by a third-degree polynomial for impurities ($1-4$) and sixth-degree polynomial for ozone (6).

Figure 2. a — concentrations $[X_i]$ and $[O_3]$ versus specific energy E in air for AcOMe (1), AcOPr^i (2), AcOBu^i (3) and AcOBu (4), ozone in pure air (5), and ozone in air with impurities (6). b — similar dependences for nitrogen. Symbols — experiment, lines — approximation by a third-degree polynomial for impurities ($1-4$) and sixth-degree polynomial for ozone (6).
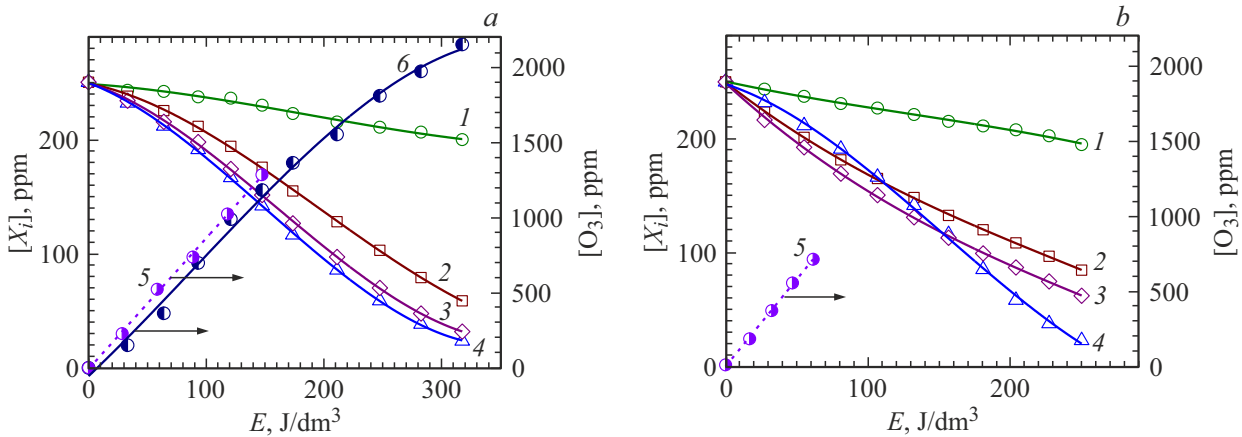
AcOPr (3), AcOBu (4), 250 ppm (parts per million) in concentration each, on specific energy E, that is, energy per unit volume of the gas mixture. In the process, the ozone concentration $[O_3]$ was also measured; it is represented by curve 6. For comparison, the ozone production in impurity-free air is shown (curve 5). Fig. 1, b presents similar dependences for a gas mixture in the form of nitrogen. In this case, the ozone content was measured, but appeared to be insignificant; therefore, the ozone production curve is not presented. To compare energy efficiencies of the processes, the dependence of the ozone production in air (curve 5) is presented for the case of the preconditioned PCR chamber. Fig. 2 presents similar E dependences for another mixture of acetates: AcOMe (1), AcOPr^i (2), AcOBu^i (3), AcOBu (4) with the concentration of 250 ppm each. The ozone concentration $[O_3]$ is represented by curve 6. For comparison, the ozone production in impurity-free air is shown (curve 5). Since ozone does not arise in

nitrogen, its production is not presented. Fig. 3, a illustrates the investigation of a mixture of acetates where one of the components was vinyl acetate, AcOVi (1), AcOEt (2), AcOPr (3), AcOBu (4) with the concentration of 250 ppm each, versus specific energy. AcOVi is a substance that is at the same time also an unsaturated compound, i.e. having an enhanced reactivity with respect to ozone, as shown earlier [8]. To reveal the ozone effect on the process of removal, AcOVi alone with concentration in air of 500 ppm was studied. Its concentration dependence on E is represented by curve 1 in Fig. 3, b; also there are shown the ozone production in pure air (curve 2) and in AcOVi-containing air (curve 3).

To describe the main regularities shown in Figs. 1−3, we calculated the values characterizing the energy parameters of the processes, as well as factors of relative reactivities of the components, by using the method of competing reactions described in detail in [8]. The data were approx-
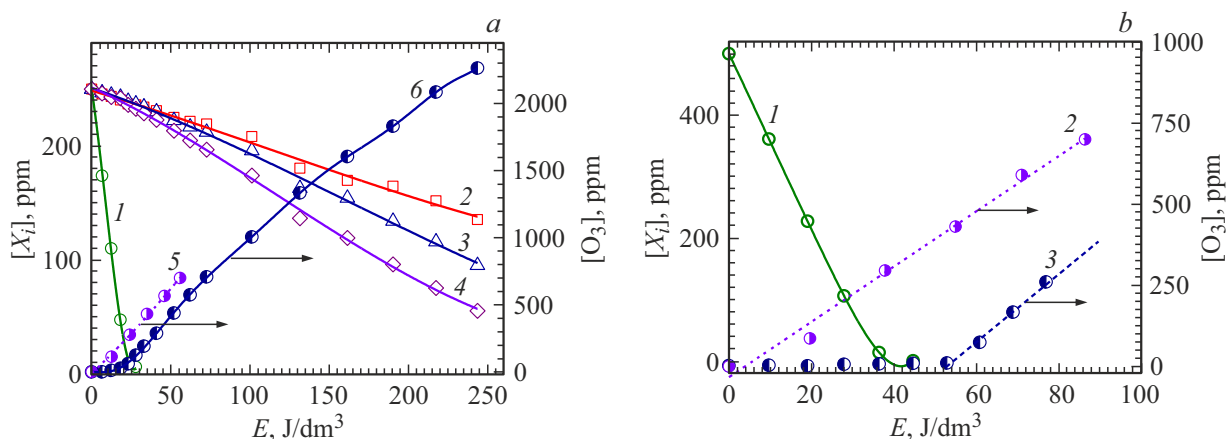
Figure 3. *a* — concentrations $[X_i]$ and $[O_3]$ versus specific energy E in air for AcOVi (*1*), AcOEt (*2*), AcOPr (*3*) and AcOBu (*4*), ozone in pure air (*5*), and ozone in air with impurities (*6*). *b* — concentrations of AcOVi (*1*), ozone in pure air (*2*) and ozone in the presence of AcOVi (*3*) versus specific energy E. Symbols — experiment.

Plasma-chemical yields and relative reactivities of the studied alkyl acetates

Source of information	Component X_i	Gas	G, mol/100 eV (100 J/dm³)				$k_{i,\mathrm{AcOBu}}$
			G_{O_3}	$G_{O_3+X_i}$	$-G_{X_i}$	$-\sum G_{X_i}$	
Fig. 1, *a*	AcOMe AcOEt AcOPr AcOBu	Air	4.85	3.31	0.073 0.200 0.301 0.410	0.984	0.130 0.415 0.671 1.000
Fig. 1, *b*	AcOMe AcOEt AcOPr AcOBu	N₂	4.95*	0.0	0.213 0.284 0.292 0.344	1.13	0.484 0.743 0.780 1.000
Fig. 2, *a*	AcOMe AcOPrⁱ AcOBuⁱ AcOBu	Air	4.85	2.35	0.069 0.263 0.340 0.366	1.04	0.162 0.710 1.116 1.000
Fig. 2, *b*	AcOMe AcOPrⁱ AcOBuⁱ AcOBu	N₂	4.95*	0.0	0.230 0.290 0.433 0.333	1.29	0.467 0.794 1.161 1.000
Fig. 3, *a*	AcOVi AcOEt AcOPr AcOBu	Air	4.80	4.30	3.21** 0.208 0.283 0.386	0.876	56** 0.457 0.653 1.000

* Obtained in the case of PCR conditioning by discharge treatment of the air mixture.
** At $E = 20$ J/dm³.

imated by third-degree polynomials. The plasma-chemical yield of impurity i removal, namely, G_{X_i} [mol/100 eV], may be calculated from the slopes of dependences given in the figures with accounting for the dimension conversion factor: $1\,\mathrm{ppm}\cdot 1\cdot \mathrm{J}^1 = 0.433$ mol/100 eV. The plasma-chemical yield of ozone is designated as G_{O_3} for pure air and $G_{O_3+X_i}$ for air containing impurity X_i. Designation G_{O_3} is used to characterize the energy efficiency of the generator with PCR [11]. G_{X_i} has a negative value,

while G_{O_3} is positive. The method energy efficiency is characterized by the sum $G = \sum G_{X_i}$. The constants characterizing the component i reactivities were calculated as $k_i = G_{X_i}/[X_i]$. To compare the reactivities, relation $k_j/k_i = G_{X_i}[X_j]/(G_{X_j}[X_i])$ was used, which was calculated in the initial region for $E = 100$ J/dm³. As a reference component, we used AcOBu for which $k_i = k_{\mathrm{AcOBu}}$ was accepted; the relative reactivity factors with respect to it were $k_{i,\mathrm{AcOBu}} = k_i/k_{\mathrm{AcOBu}}$. Generalized data are presented

in the Table. The relative reactivity is the objective of this research. With consideration to averaging, reactivity $k_{i,\mathrm{AcOBu}}$ in air is 0.15 for AcOMe , 0.44 for AcOEt, 0.66 for AcOPr, 0.70 for AcOPr$^{\mathrm{i}}$, 1.00 for AcOBu, 1.12 for AcOBu$^{\mathrm{i}}$, 56 for AcOVi. In the case of nitrogen, $k_{i,\mathrm{AcOBu}}$ is 0.47 for AcOMe, 0.74 for AcOEt, 0.78 for AcOPr, 0.79 for AcOPr$^{\mathrm{i}}$, 1.00 for AcOBu, and 1.61 for AcOBu$^{\mathrm{i}}$. Obviously, relative reactivities of acetates in the air and nitrogen plasmas are different; this may evidence for the difference between mechanisms via which active forms of nitrogen and oxygen participate in removing the acetates. What is important is that the relative reactivity of the components is constant and remains the same in mixtures of other compositions. For instance, in complex mixtures of solvents, the ratios of AcOEt and AcOBu reactivities in air are 0.43:1 [7] and 0.45:1 [8], which are very close to the obtained ratio 0.44:1 despite those components belonged to different mixtures. Emphasize that the absolute value of the acetate-removal total yield $\sum G_{X_i}$ in air is lower than that in nitrogen provided the reaction is performed in the same PCR under comparable conditions. Processes involving the nitrogen active forms, when acetates are removed with simple aliphatic substituents, are of great importance, similarly to the case of aromatic compounds [12]. This indicates that the mechanisms with participation of active oxygen forms do not prevail in this case. It is impossible to assert that organic acetates are unambiguously subject to oxidation in air under the impact of pulsed discharge plasma. This significantly contradicts a large number of publications and needs additional research. AcOVi is distinct in reactivity higher than that of the air plasma components. As shown in Fig. 3, a, the ozone production begins only after AcOVi is completely removed. Fig. 3, b presents the results of a special experiment at the initial AcOVi concentration in air of 500 ppm; the results demonstrate that, during the experiment, ozone quantitatively interacts with AcOVi, and G_{X_i} of the latter is almost the same as $G_{\mathrm{O_3}}$. The rate of the $\mathrm{AcOVi-O_3}$ reaction possesses constant $k = 2.30 \cdot 10^{18}\mathrm{cm^3 \cdot mol^{-1} \cdot s^{-1}}$ [13] and characteristic times of about a few seconds. This is caused by the presence in the substrate of a double bond with the reactivity higher than that in ozone.

Thus, relative reactivities of volatile organic acetates with respect to the plasma of pulsed corona discharge have been determined, and fundamental distinction of the vinyl acetate removal mechanism has been demonstrated. The method of competing reactions allows revealing different mechanisms for removing from air VOCs of different chemical structures by using plasma-chemical methods. The revealed regularities will be useful in developing novel plasma-chemical techniques for air purification.

Conflict of interests

The authors declare that they have no conflict of interests.

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