Relative reactivity of ethylene chloride derivatives with respect to plasma components of a pulsed corona discharge in air

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Abstract. The reactivity of ethylene chloride derivatives with respect to plasma components of a pulsed corona discharge in air and nitrogen was studied. Using model mixtures based on vinyl chloride, vinylidene chloride, trichlorethylene and perchloroethylene containing 250–500 ppm, relative reactivity parameters were obtained. The high reactivity of ethylene chloride derivatives has been shown. In the process of vinyl chloride removal, the reaction with ozone plays a significant role, while the high reactivity of di-, tri- and tetrachloroethylene is due to dissociative electron attachment processes.
Keywords: corona discharge, chlorinated ethylene derivatives, non-equilibrium atmospheric pressure plasma, method of competing reactions, volatile organic compounds.

1. Introduction

Ethylene chlorinated derivatives (ECDs) are volatile organic compounds (VOCs) that are widely used in various industries; are an important source of air pollution. Vinyl chloride is used as a monomer for the production of polyvinyl chloride. ECDs containing 2–4 chlorine atoms are low-toxic compounds and are widely used as effective solvents. Chlorine-containing compounds are important ecotoxicants because accumulate in the tissues of living organisms and pose a danger to the Earth's ozone layer. To purify air from VOC vapors, plasma-chemical methods using nonequilibrium plasma of electric discharges are promising [1, 2]. Similar methods are well suited for the conversion of trichlorethylene (TCE) and perchlorethylene (PCE) [3–6]. The reactivity of VOCs depends significantly on their chemical structure, so studying it within a selected functional class is of great importance. To determine the parameters of reactivity, an original method of competing reactions is being developed [7], with the help of which the relative reactivity of widely used solvents, unsaturated [8, 9] and aromatic compounds [10], and acetic esters [11]. Determining relative parameters in mixtures of components makes it possible to compensate for a number of experimental errors and, in fact, to estimate the rate constants of fast processes using the "slow" method of gas chromatography (GC). Relative reactivity parameters are useful for comparing different methods and for scaling up processes from laboratory to industrial scale.

2. Objects of study

This report presents the results of a study of the relative reactivity of ECDs, liquid under normal conditions: vinylidene chloride (VC, $CH_2=CCl_2$), TCE ($CHCl=CCl_2$), PCE ($CCl_2=CCl_2$) and gaseous vinyl chloride (ViCl, $CH_2=CHCl$). For research, components were used at a concentration of 250–500 ppm (parts per million, normalized to normal conditions), both separately and in two-component mixtures.

3. Research methodology

3.1. Experimental setup

The experimental conditions are described in detail in [12]. The source of high-voltage pulses was a generator based on SOS switching elements [13]. The discharge parameters were assessed using oscillograms made with a "Tektronix TDS-5054" oscilloscope with appropriate measuring circuits. The discharge part of the plasma-chemical reactor of a coaxial design was made of a stainless steel cylinder with an internal diameter of 110 mm, along the axis of which a steel electrode with a diameter of 0.24 mm was stretched. The length of the discharge part was 56 cm. The negative polarity

discharge had the following parameters: voltage: 100 kV; current: 25–75 A; voltage pulse duration at half maximum: 40 ns; pulse repetition rate: 10 Hz. Pulse energy E_p was measured as the average of the pulse train using an oscillogram, $E_p = \int U(t)I(t)dt$ and changed in the range of 0.03–0.14 J. Due to the electronegativity of chlorine-containing compounds, their effect on the discharge current was observed: they significantly reduced the discharge current - this effect was studied previously [14, 15]. In pure air, the discharge energy per pulse was 0.14 J

3.2. Experimental technique

The gas mixture simulating air consisted of a mixture of $N_2:O_2 = 80:20$. Appropriate amounts of liquid test substances were introduced into the mixture and the mixture was stirred with an internal fan until the composition of the impurity in the gaseous state remained constant. Next, the molar gas mixture was treated with a series of discharge pulses for 1.0 min, after which, during a pause of 5 min, the composition of the gas mixture was analyzed by GC and the ozone content was analyzed by spectrometry in the region of 255 nm. The relative error of the GC method is 3%, the error in measuring ozone content is 5%. In Fig. 1a,b are shown the concentration dependences of individual components: VC – 1, PCE – 2, TCE –3, ViCl – 4 with a concentration of 500 ppm, depending on the specific energy, E [J/dm^3] – the amount of energy put into unit volume of the gas mixture. During the experiments, the ozone concentration [O$_3$] was also measured, represented by dependencies 1.1–4.1, respectively, for the experiments in which dependencies 1–4 were obtained. For comparison, dependencies 5 show the production of ozone in clean air. In Fig. 1c shows similar dependences for a gas mixture in the form of nitrogen: VC – 1, PCE –2, TCE –3. In Fig. 2a–c are shown as an example the dependences for two-component mixtures used to determine the relative reactivity in air. In this version, VC was used as a reference. Experiments were also carried out with different ratios of initial concentrations of VC and the reference component, incl. and in a nitrogen environment.

4. Results

During the processing of ECDs mixtures in air, the formation of products (up to 5% of stoichiometry) was observed: mono- and dichloroacetic acid chloride, phosgene, etc. Similar transformations are typical for ethylene chloride derivatives [8, 16]. These are highly toxic compounds and the process of their formation will be discussed in an extended version of the manuscript.

The results characterizing the energy parameters of the processes and the factors of the relative reactivity of the components were assessed using the method of competing reactions [7]. The values of G_i [mol/100eV] – the plasma-chemical yield of impurity removal X_i, were calculated from experimental dependences, taking into account the conversion of dimensions, at a certain input energy E (1):

$$G_i \propto \frac{d[X_i]}{dE} = -k_i[X_i][R],\qquad(1)$$

where $[R]$ is the concentration of the formal reagent, which is common to all studied compounds of the selected group; k_i – constant characterizing the reactivity of a component X_i.

When the reactivity of an individual element from a group of compounds is compared, it is assumed that they react with the same formal reagent. Then the desired value of relative reactivity can be estimated by the expression (2):

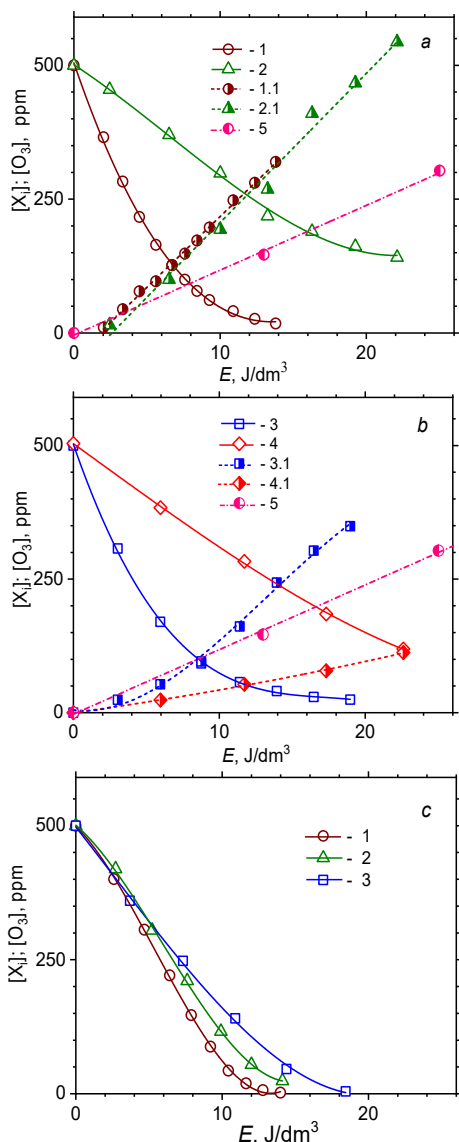$$\frac{k_i}{k_j} = \frac{G_i[X_j][R]_2}{G_j[X_i][R]_1}.\qquad(2)$$

Fig. 1. *a, b* –change in concentrations of [X_i] and [O_3] depending on the specific energy *E* in air for VC (*1*), PCE (*2*), TCE (*3*) and ViCl (*4*), O_3 in pure air (*5*). *1.1–4.1* – the corresponding concentration of ozone in air with impurities (*1–4*). *c* – similar dependences of VC (*1*), PCE (*2*), TCE (*3*) in nitrogen.
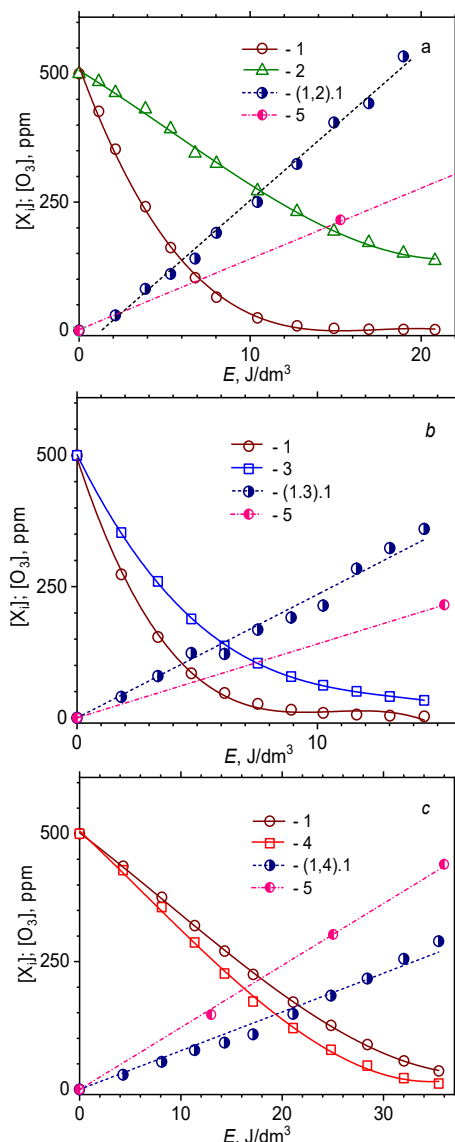
Fig. 2. Changes in the concentrations of [X_i] and [O_3] depending on the specific energy *E* for two-component mixtures in air: *a* – for VC (*1*) and PCE (*2*), *b* – for VC (*1*) and TCE (*3*) and *c* – for VC (*1*) and ViCl (*4*). Dependences (1.2).*1*–(1.4).*1* show the corresponding change in [O_3].

When conducting separate experiments for each compound, the current values of *E* will be different and for them $[R]_2 \neq [R]_1$. The consideration is also complicated by the fact that E_p also differs very much from the content of electronegative components, so the ratio of the constants will essentially be a conditional value that can serve for comparison only with many equal parameters, which is usually difficult to ensure. If we carry out an experiment with compounds simultaneously, then:

$$[R]_2 \approx [R]_1 \Rightarrow \frac{k_i}{k_j} \approx \frac{G_i[X_j]}{G_j[X_i]}. \tag{3}$$

In this case, the ratio of the constants can be calculated, assuming that we are dealing with a single formal reagent. To determine more accurate values of reactivity factors, measurements were

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carried out in two-component mixtures using expressions of type (3) from the data presented in Fig. 2, in which VC was used as a reference, for which $k_i = k_{VC}$ was taken. Factors of relative reactivity relative to it: $k_{i,VC} = k_i/k_{VC}$. The energy efficiency of the method was characterized by the value $G = \Sigma G_i$ were G_i [mol/100eV] — plasma-chemical yield of impurity removal X_i, was calculated from the slopes of experimental dependences, similar [9, 10]. Taking into account averaging, the reactivity of ethylene chloride derivatives in air: substance, $k_{i,VC}$: VC, 1.00; PCE, 0.22; TCE, 0.48; ViCl, 1.25. A similar series for nitrogen: substance, $k_{i,VC}$: VC, 1.00; PCE, 0.46; TCE, 0.59. Previously obtained values $k_{i,VC}$: VC, 1.00; PCE, 0.36; TCE, 0.68, are somewhat different from those presented here, because obtained without taking into account the peculiarities of the influence of the component content on the pulse energy [7]. It should be emphasized that the total yield of the process of removing ECs G in air and nitrogen is significant for VC, PCE and TCE and is about 30–33 mol/100 eV and 15 mol/100 mol for ViCl; which significantly exceeds those for aromatic compounds and alkyl acetates [10, 11], which indicates a principal difference in the removal mechanism. In nitrogen, these values are also significant: 20–30 mol/eV. In this case, apparently, the mechanism involving the process of dissociative electron attachment has a significant influence on the process. The behavior of vinyl chloride is somewhat different, as follows from the dependences - processes involving ozone have a significant contribution for it, while the contribution of the adhesion mechanism is reduced, this is due to the fact that the reaction rate of ViCl with O$_3$ has a constant $k = 2.46 \cdot 10^{-19} \cdot cm^3 \cdot mol^{-1} \cdot s^{-1}$ [17]. Interestingly, in the case of the conversion of ECs, the mechanism involving reactive oxygen species, as in the case of a number of other VOCs [10, 11], is not prevalent. The task of further detailed study of conversion mechanisms taking into account the found regularities is urgent.

5. Conclusions

Thus, the relative reactivity of volatile ECDs with respect to the plasma components of a pulsed corona discharge has been determined and their high reactivity has been demonstrated. The corresponding protective capabilities of the ECD when connected to the discharge circuit and the plasma-chemical outputs of the removal process are determined. The discovered regularities will be useful in the development of new plasma-chemical technologies based on the conversion of VOCs of different chemical structures.

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