Investigation of the relative reactivity of volatile organic compounds in the air plasma of a pulsed corona discharge by the method of competing reactions

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Abstract. A method for determining the relative reactivity of volatile organic compounds (VOCs) with respect to the air plasma of a pulsed corona discharge is proposed. It is based on the use of specially selected mixtures of organic compounds. The approach is based on the method of competing reactions: all components of the mixture are in equal conditions, so the relative reactivity can be determined with high accuracy using the gas chromatography. The parameters of scaling processes are proposed – plasma chemical yield, relative reactivity, formal reagent as a set of plasma components. In this paper, using the example of a number of VOCs, we demonstrate the extended capabilities of the method using a special technique for processing experimental data. More accurate data on the relative reactivity of a number of VOCs of wide application have been obtained. It is proposed to use the energy yield of ozone as a criterion for the energy efficiency of a plasma chemical installation.

1. Introduction

Volatile organic compounds (VOCs) accompany ventilation emissions of industrial enterprises [1, 2]. One of the most effective methods of air purification from them are plasma-chemical and plasma-catalytic methods based on the treatment of air flows with non-equilibrium plasma created by electric discharges of various types [3-10]. Despite a significant number of studies, there is a certain problem of comparing the results of different authors – the comparison criteria and energy efficiency parameters for scaling processes from laboratory to industrial are not clearly formulated. We have proposed a method based on the use of model mixtures [4, 5]. Using a mixture of components under equal conditions, it is possible to compare their reactivity and make relative measurements with high accuracy. A similar method is used to calculate reaction constants and is known as the method of competing reaction. The advantage of the method in the application of the study of the decomposition of VOCs by plasma-chemical methods is the possibility of using an accurate method of gas-liquid chromatography (GC). In this paper, using the example of a number of VOCs, the extended capabilities of the method with the use of a special method for processing experimental data are demonstrated. Refined data on the relative reactivity of a number of widely used VOCs were obtained.

2. Formal description of VOC removal processes by plasma chemical methods

The main processes of impurity removal can be represented using the method of formal kinetics [11-13] using a system of equations:
Analysis

\[
\begin{align*}
\frac{d[X_i]}{dt} &= -k_i [X_i][R], \\
\frac{d[R]}{dr} &= k_R - \sum_{i=1}^{N} k_i [X_i][R] - k_d [R],
\end{align*}
\]

(1)

where \([X_i]\) is the concentration of the \(i\)-th impurity, \([R]\) is the concentration of the formal reagent \(R\) as a set of active plasma components, \(k_i\) is the rate constants of the corresponding processes, \(N\) is the number of impurities, \(k_R\) is the operating time constant \(R\), \(k_d\) is the decontamination constant \(R\).

![Figure 1](image1.png)

**Figure 1.** Dependences of the concentrations of impurities \([X_i]\) at \([X_i]_0 = 100\%\) on time in comparative units for one series at \([R]_0 = 50\%\): (a) – for each impurity separately; (b) – with the combined presence of impurities. \(k_i\): \(k_1 = 3:1.5:1.0\) for \(i = 1, 2, 3\), respectively. 1: \(X_1\), \(k_1 = 0.002\); 2: \(X_2\), \(k_2 = 0.001\); 3: \(X_3\), \(k_3 = 0.00067\).

The analysis of expression (1) allows us to identify a number of features that must be taken into account when modeling air purification processes by plasma chemical methods. In installations where a plasma chemical reactor (PCR) of a fixed volume is used for research, it is possible to determine the concentrations of components with high accuracy. To do this, the gas test mixture of a certain volume is processed by a series of electric discharge pulses, followed by a procedure for analyzing the composition of the gas mixture using an accurate GC method. It is obvious that the GC method cannot determine the concentrations of components in real time, this imposes certain requirements for conducting experiments. So, figure 1 (a) shows the solution of system (1) at \(k_d = 0\) (we neglect the deactivation processes), from which it is noticeable as components \(X_i\) with the ratio of the values of the velocity constants correlated as \(k_i\): \(k_2: k_3 = 3:1.5:1.0\) at a separate content, they react with 0.5 equivalents of the formal reagent \(R\). By the time of the analysis (usually after 3 minutes or more) all the components have time to react and reach the same concentration, and it is not possible to find out the real reactivity of each of the components. When all the components are present together, as shown in figure 2 (b), the concentrations of the components reach stationary values, from which the relative reactivity of each of the components can be determined. The concentration of the formal reagent cannot be calculated accurately under real conditions, since the constants \(k_R\) and \(k_d\) in equation (1) are not known. Based on the concentrations measured after each series, if the \(k_i\) are within the same order of magnitude, the ratio of concentrations can be calculated with acceptable accuracy (see figure 1 (b)) using a formula similar to that used in [14-17]:

\[
\frac{k_j}{k_i} = \frac{\Delta[X_j]}{\Delta[X_j]} \left(\frac{[X_j]_0 + [X_j]}{[X_j]_0 + [X_j]}\right).
\]

(2)
The calculation of the ratio of the values of the velocity constants $k_j/k_i$ is the basis of the method of competing reactions. Obviously, if we know the $k_i$ of one of the substances in the mixture, the parameters of the remaining components can be obtained from the obtained stationary concentrations, even if the processes proceed at a high speed. Stationary concentrations can be measured by an accurate, but slow method of GC. Expression (2) has an acceptable accuracy (~5%) for most applications in the range of values $[X_i]_0 < [X_i] < 0.5 [X_i]_0$; for wider ranges, the nonlinearity of the dependence $[X_i](t)$ must be taken into account. The concentration dependences for the full range of concentration changes, similar to those shown in figure 1, under the condition of continuous operation of $R$, as shown in figures 2 (a) and (b). It is necessary to pay attention to the characteristic concave of the graphs of components 2 and 3 and the convexity of graph 1 – this is a characteristic sign that the components being removed share one formal reagent, compete for interaction with it and are essentially removed by one prevailing mechanism.

![Figure 2](image-url)

**Figure 2.** Dependences of impurity concentrations $[X_i]$ on time for the full range of concentration changes, with continuous operation of the reagent $R$, the conditions are similar to figure 1. (a) – for each impurity separately; (b) – with the combined presence of impurities.

3. **Experimental setup**

Installation is similar to the one described in [15]. It consists of a plasma chemical reactor with a total gas volume of 26 dm\(^3\). The discharge part consists of a cylinder with a diameter of 85 mm and a length of 56 cm, along the axis of which a potential electrode from a guitar string with a diameter of 0.24 mm is stretched. The PCR was powered by two different generators built on the principle of SOS switching [18]. The installations parameters are shown in table 1.

| Parameter                              | Experimental setup | Installation 1 | Installation 2 |
|----------------------------------------|--------------------|----------------|----------------|
| High-voltage generator                 | SM-4               | SM-2           |
| Pulse duration (FWHH) (ns)             | 20                 | 45             |
| Voltage (amplitude) (kV)               | 105                | 62             |
| Current (amplitude) (A)                | 540 (300)\(^a\)   | 65             |
| Pulse energy (J)                       | 0.5–0.7 (0.3–0.4)\(^a\) | 0.08–0.15    |
| Pulse repetition rate (Hz)             | 10                 | 10             |

\(^a\) – when adding 0.1 vol.% CCl\(_4\).

Earlier [19] it was concluded that the energy efficiency of ozone production can be a criterion for the effectiveness of the installation as a PCR for the implementation of plasma chemical processes. Figure 3 shows the production of ozone at two different setups presented in table 1. As can be seen
from the figure, the *Installation 2* has a lower productivity, but a higher energy efficiency of ozone production (and, as a result, the efficiency of plasma chemical transformations).

![Figure 3. Dependence of [O₃] on E: 1 – on Installation 2; 2 – on Installation 1.](image)

4. Results and discussion

The main components of air are nitrogen, oxygen and water vapor. Electrical discharges of any kind lead to the formation of highly active atomic oxygen in the air, which, in turn, interacts with molecular oxygen to form ozone. To identify the role of processes involving oxygen and its forms, experiments are usually conducted to remove VOCs in gas mixtures with different N₂:O₂ ratios, with or without the addition of water vapor. Using the method of competing reactions, standard mixtures that were studied earlier [14-17]. It is a mixture of solvents of general use [16], a mixture of aromatic compounds and unsaturated compounds with an expanded composition [20]. It is interesting to know how much information obtained at different times can be compared and how much the ratio of the relative reactivity of components in mixtures with different composition of mixtures is observed in experiments.

Taking into account the specifics of the experiments, instead of the expression (1), a system of equations of the material and energy balance can be used, similar to the one used in [15, 17], while all the characteristic features of the observed dependencies are preserved, but the parameters have a physical meaning tied to the energy of the processes:

$$\begin{align*}
\frac{d[X_i]}{dE} &= -k_i [X_i] [R], \\
\frac{d[R]}{dE} &= G_R - \sum_{i=1}^{N} k_i [X_i] [R] - k_d [R],
\end{align*}$$

where $k_i$ have a different dimensionality (in contrast to (1)) and characterize the so-called characteristic energy, $G_R$ is the plasma chemical yield of the reagent $R$, $E$ is the specific energy, i.e. the energy injected in a unit volume of gas. The ratio of the values $k_i/k_i$ is identical to that obtained from (1) and also characterizes the component relative reactivity. $G_R$ characterizes the energy efficiency of the installation as a generator of reagent $R$, $k_d$ characterizes the processes leading to unproductive consumption of reagent $R$ on the walls of the reactor and due to side processes, including reactions of by-products of transformation. Due to these processes, it is difficult to calculate the exact current value of $R$ and the values of $k_i$, but the ratio $k_i/k_i$ can be calculated with high accuracy. $d[X_i]/dE$ – in equation (3), this is nothing else than $G_i [\text{mol} / 100 \text{ eV}]$ – the plasma chemical yield of the removal of component $i$, with the corresponding recalculation of the dimensions shown in the figures 4 and 5: 1 ppm-l/J = 0.433 mol/100. This visual parameter is widely used in plasma chemistry and characterizes the parameters of processes for calculating energy costs. The energy efficiency of the method is characterized by the total value $G = \Sigma G_i$.  

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The experimental dependences were satisfactorily approximated by a polynomial of the 2nd degree $P_i(E)$, as shown below in the graphs of experimental dependences by lines in figures 4 and 5: the value of the ratio of constants is calculated:

$$[X_i](E) = a_i + b_i E + c_i E^2,$$

$$G_i(E) = P_i(E) = b_i + 2c_i E,$$

$$k_{i,\text{tol}} = \frac{P_i'(E)P_i(E) - (b_i + 2c_i E)(a_i + b_i E + c_i E^2)}{(b_i + 2c_i E)(a_i + b_i E + c_i E^2)}.$$

4.1. Vapors of commonly used solvents
A model mixture based on solvent vapors was proposed earlier [14-16]. In our opinion, it is important to use the same mixtures in different methods of processing experimental data for comparing methods. A mixture of compounds was used for the study: hexane (C₆H₁₄), benzene (C₆H₆), toluene (C₆H₅CH₃), ethyl acetate (CH₃COOC₂H₅), butyl acetate (CH₃COOC₄H₉), and acetone (CH₃COCH₃). These compounds are widely used as solvents for paints and organic synthesis. The experiments were carried out on the Installation 1 (see the parameters in table 1). Below are the results of experiments for a mixture of components with a content of 250 ppm each in pure dry nitrogen (figure 4 (a)), in nitrogen with the addition of 10% O₂ (figure 4 (b)), in nitrogen with the addition of 20% O₂ (figure 4 (c)). The next mixture was also tested with the addition of 2% water vapor (figure 4 (d)). To clarify the role of electronegative additives (according to [21, 22]), the results of experiments with the addition of 0.1% CCl₄ are also presented (figure 4 (e)). Toluene was used as a comparison component, as the most common and studied VOCs, for which $k_i = k_{i,\text{tol}}$ and the factors of relative reactivity relative to it $k_{i,\text{tol}} = k_i/k_{i,\text{tol}}$ were calculated. All the results are summarized in table 2.

**Table 2.** The dependences of $k_{i,\text{tol}}$ for a mixture of components in different conditions.

| i   | Component $X_i$ (at 250 ppm) | $k_{i,\text{tol}}$ (at $E = 100$ J/l) for a gas mixture: |
|-----|-----------------------------|----------------------------------------------------------|
|     |                             | $N_2$ | $N_2 + 10\%$ O₂ | $N_2 + 20\%$ O₂ | N₂⁺20% O₂ +2% H₂O | N₂⁺20% O₂ +0.1% CCl₄ |
| 1   | CH₃COCH₃                    | 0.48  | 0.22            | 0.15            | 0.08            | 0.1              |
| 2   | C₆H₆                        | 0.63  | 0.40            | 0.34            | 0.32            | 0.33             |
| 3   | CH₃COOC₂H₅                  | 0.51  | 0.34            | 0.32            | 0.33            | 0.36             |
| 4   | CH₃COOC₄H₉                  | 0.78  | 0.34            | 0.77            | 0.83            | 1.12             |
| 5   | C₆H₁₄                       | 0.66  | 0.84            | 0.91            | 1.03            | 1.65             |
| 6   | C₆H₅CH₃                     | 1.00  | 1.00            | 1.00            | 1.00            | 1.00             |
| $-G$ | $E = 100$ J/l              | 0.92  | 0.68            | 0.76            | 0.85            | 1.52             |
|     | (mol/100eV)                 | 0.83  | 0.64            | 0.72            | 0.77            | 1.12             |

It can be seen that aromatic compounds (C₆H₄ and C₆H₅CH₃) are removed better in nitrogen than in air, this indicates that active forms of nitrogen participate in their removal, which is in good agreement with [23]. Adding 0.1% CCl₄ increases energy efficiency of the process, similar to [21, 22], while significantly increasing the efficiency of removing C₆H₁₄, the appearance of an additional mechanism for removing it.

4.2. Aromatic compound vapors
Aromatic compounds are products of coke chemical production. The BTEX mixture (Benzene, Toluene, Ethylbenzene, Xylene) is a standard for toxicity assessment and is an undivided product of coke chemical industries. They are used as highly effective solvents, in organic synthesis, etc. They
have increased toxicity. Various methods of air purification from vapors of aromatic compounds using discharge plasma are presented in [23-26]. We studied a mixture of benzene (C₆H₆), toluene (C₆H₅CH₃), ethylbenzene (C₆H₅C₂H₅) and o-xylene (o-C₆H₄(CH₃)₂). The experiments were carried out on the Installation 2 (see the parameters in table 1). Figure 5 (a) shows the concentration dependencies, the data of the dependencies are presented in table 3.

![Figure 4](image_url)

**Figure 4.** Dependences [Xᵢ] on E for gas mixtures: (a) – N₂; (b) – N₂ + 10% O₂; (c) – N₂ + 20% O₂; (d) – N₂ + 20% O₂ + 2% H₂O; (e) – N₂ + 20% O₂ + 0.1% CCl₄. Markers are an experiment, lines are an approximation by a polynomial of the 2nd degree. 1: X₁ = CH₃COCH₃; 2: X₂ = C₆H₆; 3: X₃ = CH₃COOC₆H₄; 4: X₄ = CH₃COOC₆H₉; 5: X₅ = C₆H₁₄; 6: X₆ = C₆H₅CH₃.

It should be noted that the ratio of the reactivity of benzene and toluene kᵢ,tol = 0.36 for benzene in this mixture is very close to what is presented in table 2: kᵢ,tol = 0.34 and 0.32 [16], which indicates a good applicability of the method of competing reactions for predicting the results of various experiments.

4.3. Unsaturated aromatic compounds
Unsaturated compounds are highly toxic ones which are used as monomers for the production of plastics. In many cases, a mixture of monomers is used for the production of plastics, so our research has additional significance. A triple mixture was used: methyl methacrylate (MMA, CH$_2$=C(CH$_3$)COOCH$_3$), styrene (C$_6$H$_5$CH=CH$_2$) and $\alpha$-methylstyrene (C$_6$H$_5$C(CH$_3$)=CH$_2$). As a comparison component, styrene was used, as the most common and studied unsaturated oil, for which $k_i = k_{st}$ and the factors of relative reactivity relative to it $k_{i,st} = k_i/k_{st}$ were calculated. Figure 5 shows the concentration dependencies, the data of the dependencies are presented in table 4.

### Table 3. Dependences of $k_{i,\text{tot}}$ for a mixture of components in different conditions.

| Parameter | $E$ (J/l) | Component $X_i$, ([$X_i$]$_0$ = 250 ppm). $i$ |
|-----------|-----------|------------------------------------------|
| $k_{i,\text{tot}}$ | 100 | 0.36 | 1.00 | 1.21 | 1.96 |
| 200 | 0.29 | 1.00 | 1.18 | 1.96 |
| $-G$ (mol/100eV) | 100 | 1.08 | | |
| 200 | 1.27 | | | |

**Figure 5.** The dependences of [$X_i$] on $E$ in N$_2$ + 20% O$_2$. Markers are an experiment, lines are an approximation by a polynomial of the 2nd degree. (a): 1: $X_1 = $C$_6$H$_6$; 2: $X_2 = $C$_6$H$_5$CH$_3$; 3: $X_3 = $C$_6$H$_5$C$_2$H$_5$; 4: $X_4 = \alpha$-C$_6$H$_5$(CH$_3$)$_2$. (b): 1: $X_1 = $CH$_2$=C(CH$_3$)COOCH$_3$; 2: $X_2 = $C$_6$H$_5$CH=CH$_2$; 3: $X_3 = $C$_6$H$_5$C(CH$_3$)=CH$_2$.

As it has shown [14, 20], the method of competing reactions can be used to determine the relative reactivity of unsaturated compounds with respect to plasma components. By making combinations of two or more compounds, you can calculate the parameters of one compound relative to the other, so it is important to calculate relative values. The results are shown in the table 4. Styrene is selected as the standard. Which is close for the data [20, 22]. But in this case, $\alpha$-methylstyrene is removed better in a triple mixture. This may mean that it is deleted by several mechanisms.

### 5. Conclusion

The possibilities of the method of competing reactions for determining the relative reactivity of vapors of known commonly used and aromatic solvents with respect to the plasma of a pulsed discharge are demonstrated. The method used allows us to obtain a larger amount of information for one experiment, which allows us to significantly increase the efficiency of research on the development of promising air purification technologies using gas discharge plasma. The parameters of the relative
reactivity can be useful for the development of plasma technologies for air purification based on electric discharges of various types.

Table 4. The dependences of $k_{i,at}$ for a mixture of components in different conditions.

| Parameter | $E$ (J/l) | Component $X_i$ ($[X_i]_0 = 250$ ppm), $t$ |
|-----------|-----------|-----------------------------------|
|           |           | 1 | 2 | 3 |
|           |           | CH$_2$=C(CH$_3$)COOCH$_3$ | C$_3$H$_6$CH=CH$_2$ | C$_3$H$_6$C(CH$_3$)=CH$_2$ |
| $k_{i,at}$ | 100       | 0.46 | 1.00 | 1.85 |
|           | 200       | 0.56 | 1.00 | 1.57 |
| $-G$ (mol/100eV) | 100 | | 6.17 | |
|           | 200       | | 6.15 | |

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