

Rate constants of electron-beam PAHs decomposition

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Abstract. The generalized kinetic model of the electron-beam induced processes in industrial flue gases elaborated earlier is used for the estimation of rate constants of hydroxyl-radicals interaction with high-ringed aromatic compounds. These data are received by means of the fit of the calculated PAHs concentrations to the measured ones as applied to benzo(a)anthracene, benzo(e)pyrene, benzo(a)pyrene, perylene, and dibenzo(a,h)anthracene. It is shown that the concentrations of PAHs decrease by more than an order of magnitude at the absorbed dose $D = 20$ kGy for compounds with rate constant of their interaction with OH-radical more than $10^{13} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

Key words: electron-beam flue gas treatment • PAHs decomposition • rate constants • hydroxyl radical

Introduction

The present level of utilization of organic fuels in various spheres of human activities causes considerable environment pollution by combustion products, which contain a variety of toxic admixtures such as sulphur dioxide (SO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and others. The most dangerous representatives of VOCs are polycyclic hydrocarbons (PAHs), their chlorinated and nitrated derivatives.

The use of various purification technologies for industrial treatment of flue gases makes it possible to decrease the pollutant emission. The electron-beam dry scrubbing (EBDS) process for simultaneous removal of SO_2 , NO_x , and VOCs from exhaust gases is the most intensely developed area of radiation technology application to solve environmental problems [5]. This process is based on the transformation of the main pollution species, SO_2 and NO , into corresponding acids [7]. The acids are converted into salts by the addition of neutralizing species (e.g. ammonia, NH_3), and removed from the flue gases by dry electrostatic precipitators.

The mathematical modelling of radiation-induced PAHs decomposition plays an important role in understanding process mechanisms, and allows restoring the missing kinetic information. In the present work, the generalized kinetic model of the electron-beam SO_2 , NO_x , and PAHs removal from flue gases [9] was used for the estimation of rate constants of OH-radical interaction with high-ringed aromatic compounds. These kinetic data were received on the basis of calculated concentrations fit to the measured ones [6].

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Kinetic model of radiation-induced processes in gas

The fundamental physical and chemical processes induced by electron-beam irradiation of the industrial flue gases consist of: (1) formation of active species; (2) gas-phase oxidation of SO₂ and NO in reactions with active species yielding sulphuric and nitric acids, respectively; (3) formation of the aerosol droplets upon the binary volume condensation of the sulphuric acid and water vapours; (4) liquid-phase oxidation of SO₂ in the aerosol droplets; (5) thermal SO₂-NH₃ interaction, and (6) transformation of trace PAHs impurities in reactions with active species. These processes were included in the mathematical model of simultaneous electron-beam SO₂, NO and PAHs treatment [8, 9].

The formation of active species (excited molecules, positive ions, thermalized electrons, atoms and radicals) by the action of accelerated electrons on gas macro-components (N₂, O₂, CO₂, and H₂O) on the assumption that radiation energy absorption occurs uniformly in space is described usually by means of the primary radiation yields G_{ij} , the number of intermediates X_j generated from macro-component X_i per each 100 eV of absorbed energy: $-G_{it}X_i \rightarrow \sum_j G_{ij}X_j$. The primary radiation yields G_{ij} for various pure gases are determined in radiation-chemical experiments [13].

The gas-phase chemical processes can be subdivided into charge-transfer reactions leading to the formation of comparable stable ions H₃O⁺ and transformation of negative ions followed by their recombination in the reaction with H₃O⁺, and reaction groups describing SO₂ and NO oxidation. The dominant role in this oxidation belongs to OH-radicals. Sulphuric and nitric acids formation is the result of gas-phase chemical reactions.

At the typical temperatures of the EBDS-process ($T = 60\text{--}80^\circ\text{C}$), there are realized the conditions of bulk binary condensation of water vapour and sulphuric acid. This leads to the formation of spontaneous aerosol droplets and to vapour condensation on the existing ash particles. The liquid-phase formation is accompanied with dissolution of other gaseous species, such as SO₂, NH₃, OH etc. in the aerosol droplets. The reaction of OH-radicals with dissolved SO₂ initiates a chain liquid-phase oxidation of SO₂ in droplets [9].

The interaction of PAHs molecules with OH-radicals plays a dominant initiating role in the transformation of aromatic compounds. On the stated temperature interval the corresponding reaction chain can be represented as OH-radical addition to the aromatic molecule, the formation of a bicyclic radical, and the subsequent decomposition of the aromatic ring in the interaction of the bicyclic radical with molecular oxygen and nitrogen oxide [8]. The conversion of aromatic molecules occurs in the direction of a decrease in the number of aromatic rings. The rate of this process is practically independent of temperature and is governed by the rate of the first step with rate constant k_{OH} , which depends on the type of compound. It should be noted that the presence of PAHs in the radiation zone has a negligible influence on the kinetics of SO₂ and NO oxidation since their mole fractions in gas is usually much lower. In these conditions, the concentration of active species, which are responsible for the conversion of PAHs

molecules, depends on the set gas-phase and liquid-phase chemical processes related to the oxidation of SO₂ and NO.

Results and discussion

The kinetics of aromatic hydrocarbon behaviour under irradiation was investigated at temperatures of $T \leq 80^\circ\text{C}$ where the interaction of PAHs molecules with hydroxyl radicals proceeds in accordance with the mechanism of OH-addition to aromatic ring followed by its destruction. The gas composition was typical of the electron-beam treatment of organic-fuel combustion products in the EBDS-process: N₂ = 70, O₂ = 6, H₂O = 12, CO₂ = 12 vol.%, SO₂ = 1000, NO = 300, NH₃ = 2300 ppm. The calculations were performed at pressure $p = 1$ atm, and dose rate $I = 10$ kGy·s⁻¹.

There is a moderate number of data in respect to the rate constants k_{OH} for PAHs molecules up to four-ringed [1–4, 12]. Rate constants k_{OH} for five-ringed aromatic molecules are received in the present work by means of the fit of their calculated concentrations to the measured ones on the assumption that the initial concentrations of six-ringed compounds, formation precursors of five-ringed compounds are negligible (see experimental data [6]). In this way the rate constants k_{OH} are determined for benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), perylene (Pe), and dibenzo(a,h)anthracene (dBahA), which are cited in Table 1.

Figure 1 presents the results of calculations for the dependence of some aromatic compounds normalized concentrations, x_i/x_0 on absorbed dose D , and a comparison of these results with experimental data [6] obtained at $D = 8$ kGy, and $T = 70^\circ\text{C}$. Rate constants k_{OH} for calculations were equal to 3.7×10^{13} and 1.4×10^{13} cm³·mol⁻¹·s⁻¹ for acenaphthene and

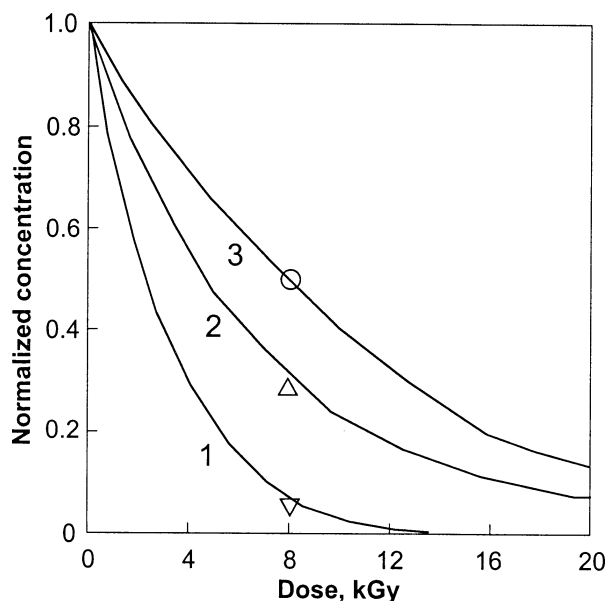


Fig. 1. Calculated (lines) and measured (points) concentrations of acenaphthene (1), naphthalene (2), and benzo(a)pyrene (3) as a function of absorbed dose at $T = 70^\circ\text{C}$. Experimental data of Chmielewski *et al.* [6].

Table 1. Estimated rate constants k_{OH} ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) and concentrations (mole fractions) for anthracene forming compounds

| Compounds | k_{OH} | $(x_{i_0})_{\text{exp}}$ | $(x_i/x_{i_0})_{\text{exp}}$ | $(x_i/x_{i_0})_{\text{calc}}$ |
|------------------------|-----------------|--------------------------|------------------------------|-------------------------------|
| Benzo(e)pyrene | 1.2E+13 | 1.0E-08 | 0.40 | 0.40 |
| Benzo(a)pyrene | 7.5E+12 | 4.4E-08 | 0.56 | 0.56 |
| Perylene | 7.1E+12 | 1.4E-08 | 0.58 | 0.58 |
| Dibenzo(a,h)anthracene | 1.4E+13 | 2.9E-09 | 0.35 | 0.35 |
| Anthracene | 4.3E+13 | 3.4E-09 | 0.36 | 0.35 |
| Benzo(a)anthracene | 1.0E+14 | 6.4E-09 | 0.26 | 0.28 |

naphthalene, respectively [4]. The rate constant $k_{\text{OH}} = 7.5 \times 10^{12} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for benzo(a)pyrene was estimated. It can be seen that under the test conditions the concentrations of PAHs decrease by more than an order of magnitude at the absorbed dose $D = 20 \text{ kGy}$ for compounds with value of k_{OH} more than $10^{13} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. Good agreement of calculated concentrations for acenaphthene and naphthalene with experimental ones allows supposing that, on the one hand, the rate constants k_{OH} used for calculations give an adequate description to the process, and, on the other hand, the formation of these compounds from higher-ringed PAHs is not important.

Real flue gases contain various PAHs kinds and differ in number of rings and in their interdependence. The interaction of OH-radicals with higher-ringed PAHs leads to their decomposition and to the formation of smaller-ringed compounds as the radiation process products. Therefore, some of these compounds may have a higher concentration after irradiation than the initial ones. In the present work, an attempt was made to include such PAHs transformation in the computation scheme, which requires special consideration for every individual compound. As an example, the radiation-induced behaviour of anthracene was considered.

The analysis of aromatic compounds, which are presented in the experimental data [6], allows supposing that the formation of anthracene (A) takes place in the reaction sequence:



followed by the destruction of anthracene molecules in the reaction with OH-radicals. The first step of this sequence, which leads to benzo(a)anthracene (BaA) formation, proceeds with the rate constants: k_{OH} for perylene and $0.4 k_{\text{OH}}$ for benzo(a)pyrene, benzo(e)pyrene, and dibenzo(a,h)anthracene in accordance with ring structure of these aromatic molecules, where k_{OH} is the rate constant of these compounds interaction with OH-radical, respectively. The second step proceeds with the rate constant $0.25 k_{\text{OH}}$. It is supposed that the other reaction products are formed in this kinetic scheme, which do not lead to anthracene formation.

The results of calculations for anthracene and benzo(a)anthracene received at the dose $D = 8 \text{ kGy}$ are shown in Table 1. Rate constant k_{OH} for anthracene was taken from the experimental data [1], where its value was measured using a refined pulsed laser photolysis/pulsed-induced fluorescence (PLP/PLIF)

technique in the temperature range between 373, and 923 K was approximated by the following modified Arrhenius equation: $k_{\text{OH}} = 4.92 \times 10^{38} T^{-8.3} \exp(-3170/T) \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. The corresponding value of benzo(a)anthracene was restored as a result of anthracene concentration fit to its experimental quantity. It can be seen from the obtained data that the applied procedure gives a wholly satisfactory description of the transformation of PAHs compounds from higher-ringed compounds to smaller-ringed ones.

It should be noted that the phase state of PAHs may be important in the context of the behaviour description of these compounds under electron-beam irradiation. The low-ringed PAHs compounds with a number of rings less than four exist almost exclusively in the vapour phase. The high-ringed aromatic hydrocarbons undergo partial absorption in the pores of soot and ash particles, which are present in combustion products. The four-ringed PAHs are distributed already uniformly between gas and particles. The percentage of five-ringed PAHs in particulate phase increase up to 70% [10]. As was demonstrated by the example of polychlorinated dioxins [11], the electron-beam decomposition of the aromatic hydrocarbons in the particulate phase was also observed, but with lower efficiency as compared with that in the gas phase. On the other hand, the reduction of the PAHs concentrations in the gas phase caused the re-establishment of the gas-particle partitioning of PAHs resulting in the reduction of the PAHs concentrations in the particulate phase. In accordance with this remark the obtained kinetic data may be regarded as average values describing the electron-beam PAHs decomposition both in gas and particulate phases.

Conclusions

1. The good agreement of calculated concentrations of acenaphthene and naphthalene with the experimental ones demonstrates that the initial OH attack on aromatic molecules is a main pathway for the removal of these compounds under irradiation conditions.
2. Calculations show that the concentrations of PAHs decrease by more than an order of magnitude at the absorbed dose $D = 20 \text{ kGy}$ for compounds with a rate constant of their interaction with OH-radical greater than $10^{13} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.
3. The available experimental data describing PAHs decomposition and mathematical models of the

EBDS-process allow determining of the missing kinetic information concerning PAHs interaction with OH-radicals.

4. There is a need to carry out additional experimental investigations that will allow making clear the mechanisms and products of PAHs decomposition.

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