

The kinetics of 1,1-dichloroethene ($\text{CCl}_2=\text{CH}_2$) and trichloroethene ($\text{HCIC}=\text{CCl}_2$) decomposition in dry and humid air under the influence of electron beam

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Abstract New experimental data related to the removal of $\text{C}_2\text{H}_2\text{Cl}_2$ and C_2HCl_3 in dry and humid (300 ppm of H_2O) air at atmospheric pressure and a temperature of 25°C under the influence of electron beam in the dose range $1 < D < 100$ kGy are published. Taking into account these experimental data, theoretical models of the decomposition of both compounds and computer simulations were performed by the present authors to find the kinetics of such processes. The influence of active atoms Cl, O and OH radicals on the VOC degradation process has been established. The theoretical model of $\text{C}_2\text{H}_2\text{Cl}_2$ degradation under the influence of electron beam in dry and humid air describes the $\text{C}_2\text{H}_2\text{Cl}_2$ decay and formation of the main products like Cl_2 , COCl_2 , CO, CO_2 , HCl, HCOCl and $\text{C}_2\text{H}_2\text{Cl}_2\text{O}$. The results of calculation of the kinetics of $\text{C}_2\text{H}_2\text{Cl}_2$ decomposition were compared with data obtained experimentally for the $\text{C}_2\text{H}_2\text{Cl}_2$ concentration range 321–2213 ppm. It was established that the relation between the rate constants of intermediate product decomposition: $\text{C}_2\text{H}_2\text{Cl}_3\text{O} \Rightarrow \text{C}_2\text{H}_2\text{Cl}_2\text{O} + \text{Cl}$ (k_1), $\text{C}_2\text{H}_2\text{Cl}_3\text{O} \Rightarrow \text{COCl}_2 + \text{CH}_2\text{C}_2$ (k_2) should be $k_1/k_2 = 40$. The theoretical model of C_2HCl_3 degradation under the influence of electron beam in dry and humid air describes the C_2HCl_3 decay and formation of the main products like Cl_2 , COCl_2 , CO, CO_2 , HCl, HCOCl and $\text{C}_2\text{HCl}_3\text{O}$. A detailed comparison of experimental and theoretical data for the C_2HCl_3 concentration 108–3206 ppm shows that the relation between the rate constants of intermediate product decomposition: $\text{C}_2\text{HCl}_4\text{O} \Rightarrow \text{C}_2\text{HCl}_3\text{O} + \text{Cl}$ (k_3), $\text{C}_2\text{HCl}_4\text{O} \Rightarrow \text{COCl}_2 + \text{CHCl}_2$ (k_4) should be $k_3/k_4 = 40$. The theoretical model of C_2HCl_3 degradation under the influence of electron beam in dry and humid air describes the C_2HCl_3 decay and formation of the main products like Cl_2 , COCl_2 , CO, CO_2 , HCl, HCOCl and $\text{C}_2\text{HCl}_3\text{O}$. A detailed comparison of experimental and theoretical data for the C_2HCl_3 concentration 108–3206 ppm shows that the relation between the rate constants of intermediate product decomposition: $\text{C}_2\text{HCl}_4\text{O} \Rightarrow \text{C}_2\text{HCl}_3\text{O} + \text{Cl}$ (k_3), $\text{C}_2\text{HCl}_4\text{O} \Rightarrow \text{COCl}_2 + \text{CHCl}_2$ (k_4) should be $k_3/k_4 = 10$. It was also found that O_2^+ ions have been formed in a gas mixture as a result of charge transfer process from N_2^+ ions, partly in excited form, which may lead to charge transfer to C_2HCl_3 and degradation of those particles. According to performed calculation, it can be stated that in humid air (300 ppm of H_2O) VOC degradation is occurring mainly due to a chain reaction stimulated by Cl atoms, but also OH radicals are playing an important role. In the described gas mixture, the OH radicals are formed in the following reactions: $\text{O}_2^+ + \text{H}_2\text{O} + \text{M} \Rightarrow (\text{O}_2^+)\text{H}_2\text{O} + \text{M}$, $\text{O}_2^+(\text{H}_2\text{O}) + \text{H}_2\text{O} \Rightarrow \text{O}_2 + (\text{H}_3\text{O}^+)\text{OH}$, $(\text{H}_3\text{O}^+)\text{OH} + \text{H}_2\text{O} \Rightarrow \text{H}_3\text{O}^+ + \text{OH} + \text{H}_2\text{O}$. VOC degradation process under the influence of electron beam is more effective in humid air than in dry air for the same initial VOC concentration level. This conclusion is also supported by experimental data.

Key words 1,1-dichloroethene • trichloroethene • electron beam decomposition • theoretical model • kinetics calculation

Introduction

This paper is devoted to studies of the kinetics of theoretical modelling of the decomposition of chloroethylenes under the influence of electron beam in dry and humid air. The computer calculations based on theoretical models were performed according to experimental results described in the literature. The experimental data of $\text{H}_2\text{C}=\text{CCl}_2$ and $\text{HCIC}=\text{CCl}_2$ decomposition in dry air under the influence of electron beam were published by Vitale *et al.* for a temperature of 25°C , pressure 1 atm and dose range < 100 kGy [13] and $D < 30$ kGy [15]. Similar experiments for humid air (300 ppm H_2O) were performed by Hakoda *et al.* [3, 4] and Sun *et al.* [10] for the same temperature and pressure and dose level $D < 13$ kGy. The experimental results of $\text{H}_2\text{C}=\text{CCl}_2$ and $\text{HCIC}=\text{CCl}_2$ decomposition under the influence of electron beam in dry and humid air are presented in Figs. 1–4.

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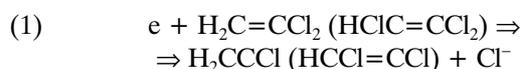
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Received: 22 February 2002, Accepted: 13 December 2002

As it can be seen in these Figures, the dose needed to obtain 90% of $\text{H}_2\text{C}=\text{CCl}_2$ and $\text{HCIC}=\text{CCl}_2$ decomposition in humid air for the same level of their initial concentration is always significantly lower than that in dry air. This indicates that OH radicals may have a significant influence on the decomposition process of chloroethylenes.

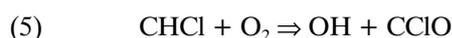
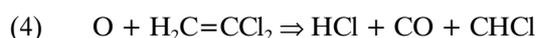
The main decomposition products are: CO , CO_2 , HCl , Cl_2 , COCl_2 , CH_2ClCOCl and CHCl_2COCl for $\text{H}_2\text{C}=\text{CCl}_2$ and $\text{HCIC}=\text{CCl}_2$, respectively. According to Vitale *et al.* [13, 14], the decomposition process of chlorinated ethylenes in dry air under the influence of electron beam is driven by a chain reaction initiated by Cl atoms. The presence of Cl atoms resulted from a recombination process between Cl^- ions and positive ions present in a gas mixture. The Cl^- ions are formed in the attachment process of thermalized electrons, which were generated in the gas mixture during ionization caused by electron beam, to molecules of chlorinated ethylenes according to reaction (1).



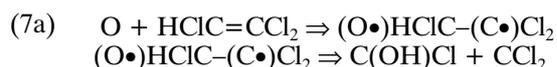
The rate constant of reaction (1) depends on the energy of thermalized electrons. For instance, when the electron energy range is 0.1–1 eV, the rate constant is in the range $10^{-10} \sim 10^{-9} \text{ cm}^3/\text{s}$ for $\text{CH}_2=\text{CCl}_2$ and $10^{-9} \sim 10^{-8} \text{ cm}^3/\text{s}$ for $\text{HCIC}=\text{CCl}_2$, respectively [14]. The secondary source of Cl atoms can be produced between O atoms and chlorinated ethylenes in the following reactions:



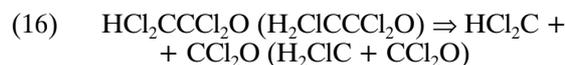
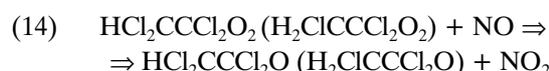
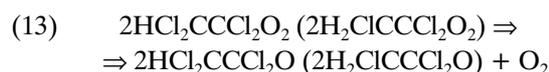
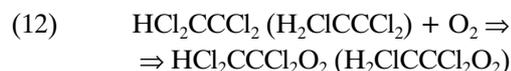
The following mechanism for reaction (2) was suggested by Sanhueza *et al.* [8]:



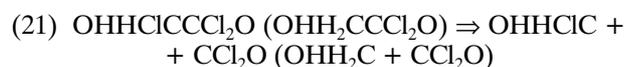
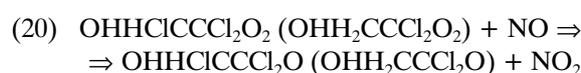
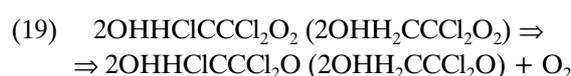
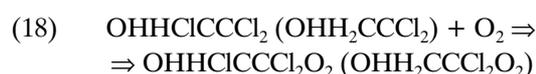
Mechanism of reaction (3) is simplified as follows from Ref. [12]. O atoms were added to trichloroethylen to form biradical $(\text{O}\bullet)\text{HCIC}-(\text{C}\bullet)\text{Cl}_2$, which will defragment (7a) or stabilize to form epoxide (7b), according to energy level. In the presence of O_2 , the present authors propose that defragmental reaction (7a) will be the major reaction because of chain reactions (8), (9), (10).



As described above, the reaction of O atoms with chloroethylenes is an other source of Cl atoms. The Cl atoms initiate the chain reaction of the decomposition of chlorinated ethylenes in dry air. Here should be mentioned that the Cl atoms add to the less chlorinated carbon [5].

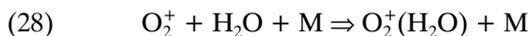
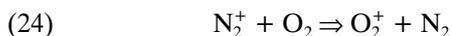


In humid air the decomposition mechanism of chlorinated ethylenes is composed of reactions (1)–(16) and the reactions based on the presence of OH radicals. The results published in the literature by Zhu *et al.* [16] indicate that the decomposition mechanism of chlorinated ethylenes caused by OH radicals can be as follows:

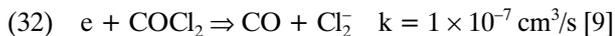


Reactions (21)–(23) products formed during the decomposition process stimulate the HO_2 radical formation. Nearly 40% of the HO_2 radicals reacts within the gas mixture and form OH radicals according to computer calculation. This leads to the OH radical formation in higher amount which additionally stimulate the chlorinated ethylene decomposition process. The Cl atoms, which are formed according to reaction (22), support chain reactions (11)–(16) of the decomposition of chlorinated ethylenes.

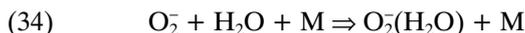
In humid air, the OH radicals and H₃O⁺ ions are formed with a high efficiency through rapid charge transferring reactions:



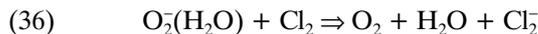
A small part of charge of the positive ions N₂⁺ O₂⁺ O₂⁺(H₂O) will be transferred to chloroethylene molecules leading to ion formation like HCIC=CCl₂⁺ and H₂C=CCl₂⁺. Because of this, the principal ions, which participate in the recombination process with negative ions, will be as follows: H₃O⁺, NO⁺, HCIC=CCl₂⁺ and H₂C=CCl₂⁺. The electrons, which are generated as a result of N₂ and O₂ ionization process, are being thermalized and react with the molecules in the gas mixture mainly in reaction (1) and other reactions as follows:



O₂⁻ ions form a cluster with H₂O molecules in the investigated gas mixture:



The main reaction of negative charge transfer from O₂⁻(H₂O) in the gas mixture will be as follows:



The main negative ions which participate in the recombination process with positive ions in experimental conditions described by Hakoda *et al.* [3, 4] and Sun *et al.* [10] are the Cl⁻ and Cl₂⁻ ions.

A small part of the negative charge is localized in the gas mixture as NO₂⁻ and NO₃⁻ ions. Therefore, in the main fast ion-molecular reactions of the charge transfer and in the recombination processes of the main negative and positive ions, such active particles as Cl, OH, H (adequately HO₂: H + O₂ ⇒ HO₂), N and O will be formed with high efficiency.

Based on these described above the theoretical models of decomposition of H₂C=CCl₂ and HCIC=CCl₂ in dry and humid air under the influence of electron beam have been established. The model includes five reaction groups, such as: primary processes in N₂ and O₂ under the influence of electron beam, all the main ion-molecular reactions of positive and negative charge transfer, ion recombination reactions, neutral particles chemistry: N, O, OH, H, HO₂, Cl in the following gas mixtures N₂ + O₂ + X ppm (X means H₂C=CCl₂, HCIC=CCl₂) and N₂ + O₂ + X ppm (X means H₂C=CCl₂, HCIC=CCl₂) + 300 ppm H₂O.

The kinetic study has been performed using the Kinetic program and the Gear method [1]. The calculations were done applying up to 330 chemical reactions with up to 80 particles.

Results of calculations and discussion

Calculation results of the chloroethylene (H₂C=CCl₂, HCIC=CCl₂) decomposition process are shown in Figs. 1–4 as solid curves. Experimental data [3, 4, 10, 13, 15] are shown as dashed line. Input values are the same as the initial conditions of the experimental work.

Figures 1 and 2 illustrate good agreement between the calculated and experimental results, which were obtained for dry air in the full range of initial concentration

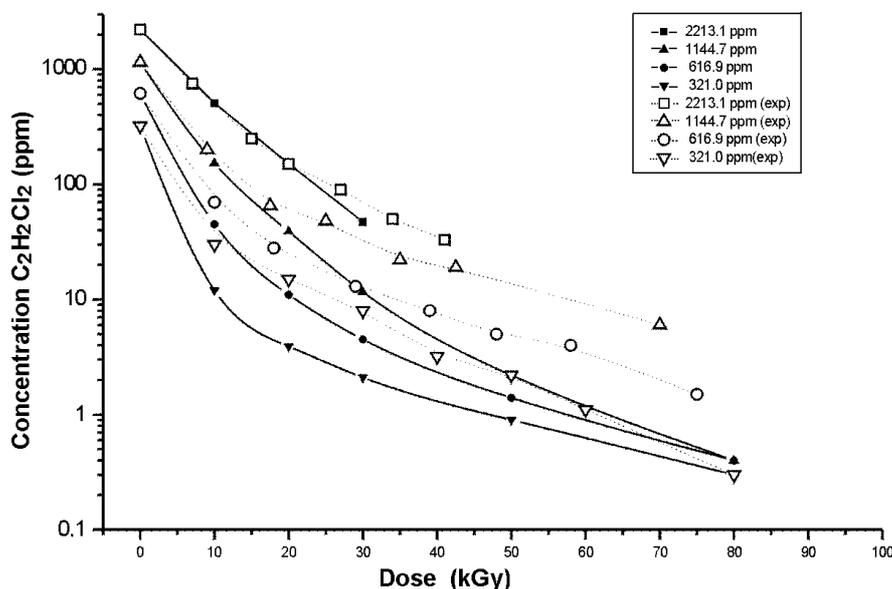


Fig. 1. Concentration of 1,1-dichloroethene vs. electron beam dose deposited in dry air for different VOC's initial concentration levels. The solid curves represent results of the calculated and experimental data according to Vitale *et al.* [13].

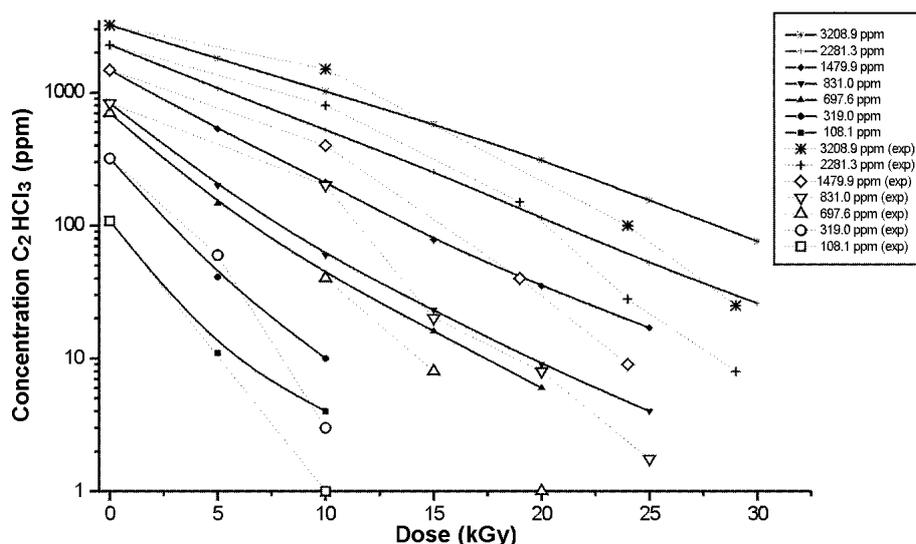


Fig. 2. Concentration of trichloroethylene vs. electron beam dose deposited in dry air for different VOC's initial concentration levels. The solid curves represent results of the calculated and experimental data according to Vitale *et al.* [15].

321–2213 ppm for $\text{H}_2\text{C}=\text{CCl}_2$ and 108–3209 ppm for $\text{HCIC}=\text{CCl}_2$, respectively. The calculations were performed with a certain rate constant of reaction (1):

$$\begin{aligned} k_1(\text{H}_2\text{C}=\text{CCl}_2) &= 10^{-9} \text{ cm}^3/\text{s} \\ k_1(\text{HCIC}=\text{CCl}_2) &= 7 \times 10^{-9} \text{ cm}^3/\text{s} \end{aligned}$$

The calculation results, compatible with experimental data, were obtained when the relation between the rate constants of reactions (15) and (16) were as follows:

$$\begin{aligned} k_{15}/k_{16}(\text{H}_2\text{C}=\text{CCl}_2) &= 40 \\ k_{15}/k_{16}(\text{HCIC}=\text{CCl}_2) &= 10 \end{aligned}$$

Similar relations were found by experimental data [5], which describe the chloroethylene oxidation process ($\text{H}_2\text{C}=\text{CCl}_2$; $\text{HCIC}=\text{CCl}_2$) initiated by Cl atoms:

$$\begin{aligned} k_{15}/k_{16}(\text{H}_2\text{C}=\text{CCl}_2) &= 49 \\ k_{15}/k_{16}(\text{HCIC}=\text{CCl}_2) &= 10 \end{aligned}$$

Preliminary calculations for $\text{HCIC}=\text{CCl}_2$ revealed that the obtained results for the dose range 20–30 kGy and high

initial concentrations are significantly higher than the experimental data. A modification to the model has been introduced. When the charge is transferred from the N_2^+ ions to the oxygen molecules the ions O_2^+ in excited state are formed. The oxygen ions in excited state can react according to the formula:



Such a formula has been proposed in accordance with the literature data [11]. The above reaction is concurrent to the reaction:



With the rate constant $10^{-14} \text{ cm}^3/\text{s}$ of the above reaction, the results of calculation for a dose of $\leq 30 \text{ kGy}$ are in good agreement with experimental data. In contrast to that, for calculation related to $\text{H}_2\text{C}=\text{CCl}_2$ and a dose range of $50 < D < 100 \text{ kGy}$ the relation between the calculated and experimental data are not so close. This depends on selection of the rate constant of reaction (1).

Figures 3 and 4 illustrate the good agreement between

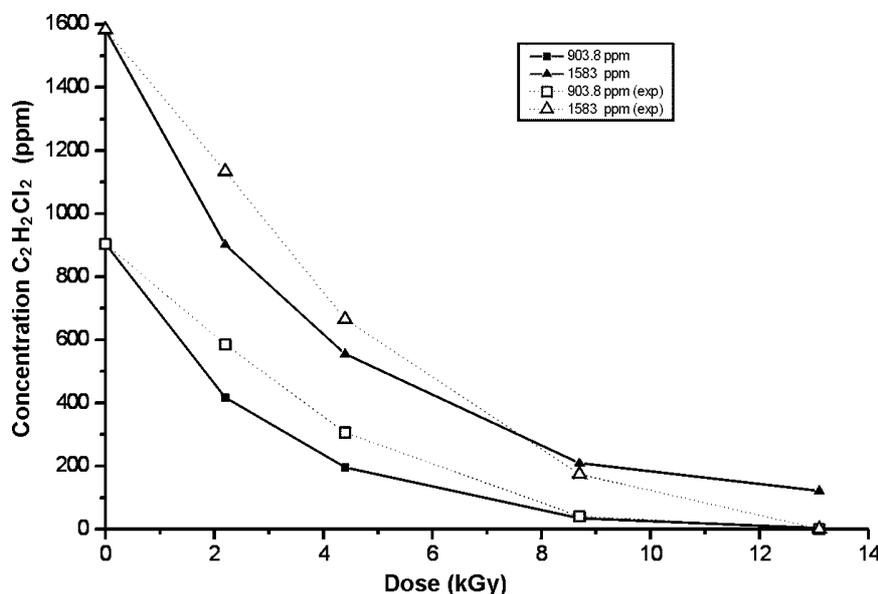


Fig. 3. Concentration of 1,1-dichloroethene vs. electron beam dose deposited in humid air for different VOC's initial concentration levels. The solid curves represent results of the calculated and experimental data according to Sun *et al.* [10].

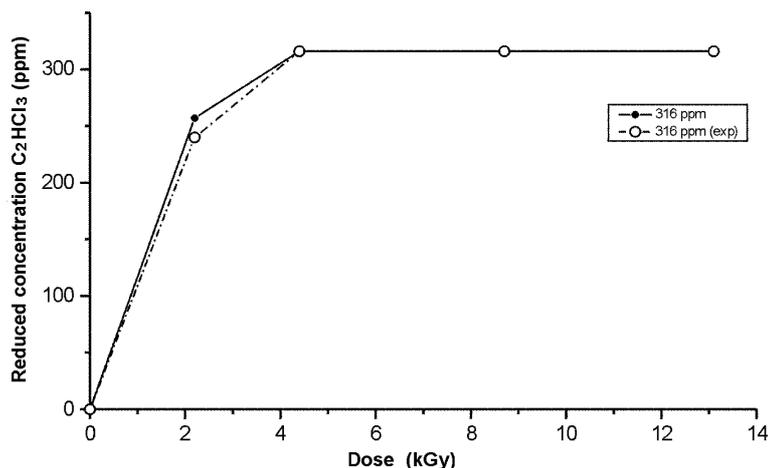


Fig. 4. Reduced concentration of trichloroethylene vs. electron beam dose deposited in humid air. The solid curves represent results of the calculated and experimental data according to Hakoda *et al.* [3].

the calculated and experimental data provided by Hakoda *et al.* [3, 4] and Sun *et al.* [10] for the full range of concentration 904–1583 ppm of $\text{H}_2\text{C}=\text{CCl}_2$ and 316 ppm of $\text{HCIC}=\text{CCl}_2$ in the case of gas mixture containing 300 ppm of H_2O . The results of calculations have been obtained for $\text{H}_2\text{C}=\text{CCl}_2$ assuming that:

$$k_{21}/k_{22}(\text{H}_2\text{C}=\text{CCl}_2) = 2$$

Taking into account that for $\text{HCIC}=\text{CCl}_2$ the relation between the rate constants of reactions (21)–(23) are as follows: $k_{23} \gg k_{21} + k_{22}$.

In both cases, the relation of H_3O^+ and recombination of Cl_2^- ions follows the formula:



The results of calculation reveal that for dose $D < 2.2$ kGy the total CO and CO_2 concentration, in respect to $\text{HCIC}=\text{CCl}_2$, can be evaluated as $\text{DC}_{\text{CO}+\text{CO}_2}/\text{DC}_{\text{C}_2\text{HCl}_3} < 11\%$. The total concentration of the organic gas products (OGP), in respect to $\text{HCIC}=\text{CCl}_2$, is equal to $\text{DC}_{\text{OGP}}/\text{DC}_{\text{C}_2\text{HCl}_3} \approx 99\%$. Both values are close to the experimental data, described by Hakoda *et al.* [3, 4] and Sun *et al.* [10], amounting to 9.4% and 92%, respectively.

The results of calculation reveal that for the dose $D < 2.2$ kGy the total CO and CO_2 concentration, in respect to $\text{H}_2\text{C}=\text{CCl}_2$, can be evaluated as $\text{DC}_{\text{CO}+\text{CO}_2}/\text{DC}_{\text{C}_2\text{H}_2\text{Cl}_2} < 5\%$. The total concentration of the organic products, in respect to $\text{H}_2\text{C}=\text{CCl}_2$, is equal to $\text{DC}_{\text{OGP}}/\text{DC}_{\text{C}_2\text{H}_2\text{Cl}_2} \approx 100\%$. Both values are close to the experimental data, described by Hakoda *et al.* [3, 4] and Sun *et al.* [10], amounting to $\leq 4\%$ and $\leq 100\%$, respectively.

The calculation results of the decomposition of both chloroethenes in dry air under the influence of electron beam confirmed the mechanism proposed by Koch *et al.* [6] and Vitale *et al.* [13]. The decomposition process is based on the chain reactions initiated by Cl atoms, which are generated in at the initial stage as a result of recombination reactions of negative Cl^- ions. The Cl^- ions are formed in the dissociative attachment process of thermalized electrons to chloroethylene molecules. Part of the Cl atoms is generated as a result of reactions initiated by oxygen atoms and chloroethylene molecules.

The calculation results of ethene decomposition performed in humid air (dry air + 300 ppm H_2O) showed

that the mechanism of chloroethylene decomposition in humid air is similar to that in dry air, but in additional significant part of chloroethylenes is decomposed in the chain reaction initiated by OH radicals. OH radicals are formed partly from ion-molecular reactions and partly are generated in reactions initiated by oxygen atoms with chloroethylene molecules indicated by a respective reaction number. That is the reason why 90% of the decomposition of chloroethylenes is achieved with a significantly lower dose in humid air than in dry air.

Conclusions

1. Theoretical models of the decomposition of chloroethylenes in dry and humid air under the influence of electron beam were established.
2. Computer calculations of the chloroethylene decomposition were performed in initial conditions equal to those reported in the literature.
3. The experimental data and computer calculations are in the best agreement when the relation between the rate constants for reactions (15), (16) are as follows: $k_{15}/k_{16}(\text{H}_2\text{C}=\text{CCl}_2) = 40$; $k_{15}/k_{16}(\text{HCIC}=\text{CCl}_2) = 10$. Such relations are similar to the data devoted to the oxidation process of chlorinated chloroethylenes initiated by Cl atoms as presented in the literature [5].
4. Calculations results of the decomposition of both chloroethylenes in dry air under the influence of electron beam confirmed the mechanism proposed by Vitale *et al.* [13], where the decomposition process is based on the chain reaction initiated by Cl atoms.
5. The decomposition mechanism of chloroethylenes in humid air is similar to that in dry air, but in that case a significant part of decomposition process is based on the chain reaction initiated by OH radicals.
6. That is the reason why 90% of the chloroethylene decomposition efficiency is obtained with a lower dose in humid air than in dry air for a similar initial concentration of chloroethylenes.

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