

Theoretical study of dose and dose rate effect on trichloroethylene (HCIC=CCl₂) decomposition in dry and humid air under electron beam irradiation

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Abstract. Experimental data related to C₂HCl₃ (TCE) removal in dry and humid (200–1000 ppm of H₂O) air, respectively, in ambient conditions under electron beam irradiation in the dose range of 1–40 kGy has been published in the literature. Based on the experimental results a theoretical model of C₂HCl₃ decomposition was proposed for the kinetic mechanism of such process. The active radicals of Cl, O and OH play an important role in the decomposition of TCE. According to the calculations performed, the Cl⁻ dissociative electron attachment predominates in the initial stage of C₂HCl₃ decomposition. Cl radical accelerates this degradation by chain process in both humid and dry air, respectively. The OH radical produced in humid air also enhances the decomposition process of TCE.

Key words: trichloroethylene • electron beam decomposition • computer simulation

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Introduction

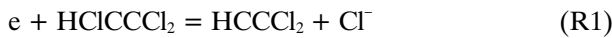
Volatile organic compounds (VOCs) which are released into atmosphere from various sources are very harmful to the environment and human health. Tetrachloroethylene (PCE) and trichloroethylene (TCE) belong to the most toxic group of VOCs and their emission are strictly regulated.

Different technologies have been studied to remove VOCs from gas phase. Electron beam (EB) treatment is one of the most promising technologies for the removal of low concentration VOCs contained in air. One of the EB technology advantages is an energy saving process [8, 9]. TCE decomposition in air by using this technology has been extensively studied [4, 12–14].

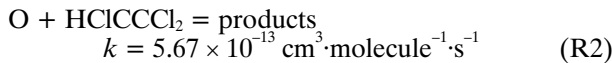
This paper is devoted to the theoretical modeling of the kinetics of HCIC=CCl₂ (TCE) decomposition during electron beam irradiation in dry and humid air, respectively. Computer calculation based on a theoretical model was performed using the published experimental results. The experimental data of HCIC=CCl₂ decomposition in dry air under the influence of electron beam were reported by Vitale *et al.* for temperature 25°C, pressure 1 atm, dose $D < 30$ kGy, dose rate ≥ 100 kGy/s [13]. Similar experiments for humid air (200–1000 ppm H₂O) were performed by Hakoda *et al.* [4] for the same temperature and pressure, dose level $D < 40$ kGy and dose rate 2.1 kGy/s. Comparing the experimental results of HCIC=CCl₂ decomposition under the influence of electron beam in dry air [13] with that in humid air [4], we find that the dose which is needed to obtain 90% of HCIC=CCl₂ decomposition in humid air is always significantly lower than that in dry air for the same level of the initial concentration of TCE. This indicates

that the dose rate may have a significant influence on trichloroethylene decomposition process. Because OH radicals are produced from water vapor in humid air, this indicates that OH radicals may also have a significant influence on trichloroethylene decomposition process.

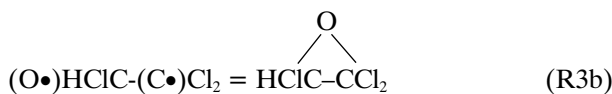
The main decomposition products of TCE are: CO, CO₂, HCl, Cl₂, COCl₂ and CHCl₂COCl, the minor decomposition product, which in the total accounts for less than 10% of the reacted carbon, is chloroform (CHCl₃). According to Vitale *et al.* [13], the decomposition process of HCIC=CCl₂ in dry air under the influence of electron beam is driven by chain reactions initiated by Cl atoms. Cl atoms are first produced in the recombination reaction between Cl⁻ ions and positive ions present in the gas mixture and then generated from some chemical chain reactions, such as reactions R6, R24a in the text. Cl⁻ ions are formed in the attachment process of the thermalized secondary electrons to TCE according to reaction R1:



The rate constant of R1 in the electron energy range 0.1 ~ 1 eV is 10⁻⁹ ~ 10⁻⁸ cm³·molecule⁻¹·s⁻¹ [12]. The secondary source of Cl radicals could be the reaction between O atoms and HCIC=CCl₂:

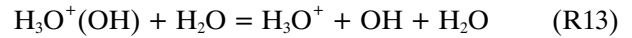
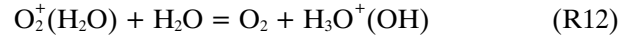
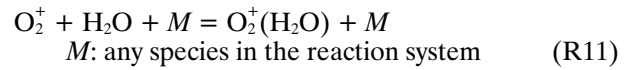


Mechanism of reaction R2 can be simplified as follows from the work of Upadhyaya *et al.* [11]. An O atom added to TCE forms a biradical (O•)HCIC-(C•)Cl₂, which will defragment (R3a) or stabilize to form epoxide (R3b) depending on the energy level. In the presence of O₂, these authors proposed that the fragmentation reaction R3a is a major reaction path because of chain reactions R4~R6.

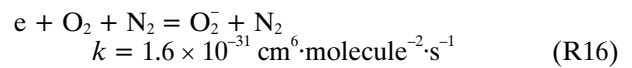
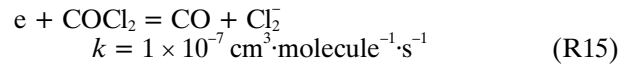
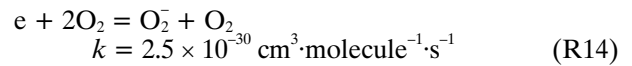


As described above, the O atom reaction with HCIC=CCl₂ is the other source of producing Cl atoms.

In humid air, the OH radicals and H₃O⁺ ions are formed with high efficiency through the rapid charge transfer reactions R7~R13:



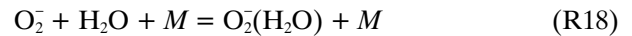
A small part of positive ions charge N₂⁺, O₂⁺ and O₂⁺(H₂O) will be transferred to HCIC=CCl₂, which leads to ion formation like HCIC=CCl₂⁺. Because of that the principal ions, which participate in recombination process with negative ions, are: H₃O⁺, NO⁺ and HCIC=CCl₂⁺. The secondary electrons, which are generated as a result of N₂ and O₂ ionization process, are being fast thermalized and react with molecules in the gas mixture mainly in reaction R1 and other reactions as follows:



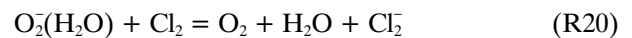
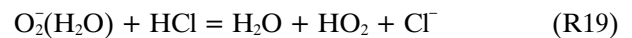
In dry air,



In humid air, O₂⁻ ions form clusters with H₂O molecules in the gas mixture investigated:



Charge is transferred to another molecule of the gas mixture, with higher electron affinity than that of oxygen. So, the main reactions of negative charge transfer from O₂⁻(H₂O) in the humid gas mixture are as follows:



The main negative ions, which participate in recombination reactions with positive ions under the experimental conditions [4], are the following ions: Cl⁻ and Cl₂⁻.

A small part of negative charge is localized in the gas mixture as NO₂⁻ (about 0.03% of the total negative ions) and NO₃⁻ (about 8.7% of the total negative ions) ions. Therefore, in the main fast ion-molecular reactions and in the recombination reactions of main negative and positive ions, such active species as Cl, OH, H, N and O will be formed with high efficiency.

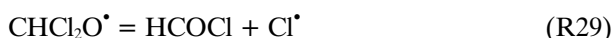
Cl radicals initiate the chain reactions of the HCIC=CCl₂ decomposition in dry and humid air, respectively (see R21~R24b).



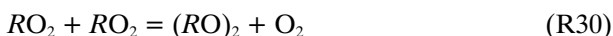


The branching ratio between reaction R24a and reaction R24b is about 10:1 based on Hasson *et al.* [5].

The mechanism of CHCl₂ radical transformation according to the model is described as follows (R25~R29):

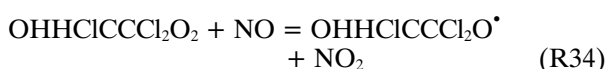


The termination reactions of chain reactions R21–R29 may be written as follows:



(Here *R* means HCl₂CCCl₂ or CHCl₂.)

The mechanism of TCE decomposition caused by OH radicals can be proposed as follows, based on publication [6]



The product of reaction R35a reacts with O₂ and forms HO₂ radicals (R36).



Nearly 40% of the HO₂ radicals react with other species to form OH radicals according to computer calculation. That leads to OH radical formation in high amounts, which additionally stimulates the TCE decomposition process by chain reactions.

In our previous work [7], the computer simulations of TCE decomposition in dry air at different initial concentration of TCE (108.1–3208.9 ppm) [13] and in humid air at an initial concentration of TCE (316 ppm) were carried out. In this work, we made computer simu-

lations of TCE decomposition under EB-irradiation in humid air at different initial concentrations of TCE. The irradiation products of TCE decomposition and the influence of water concentrations on TCE decomposition and dichloroacetyl chloride (CHCl₂COCl, DCAC) formation were also calculated. Moreover, the influence of dose rates on TCE decomposition in dry and humid air were also calculated in order to obtain better understanding of the mechanism of TCE decomposition under EB irradiation.

Modeling simulation

Theoretical model of HCIC=CCl₂ decomposition in dry and humid air under the effect of electron beam irradiation was built up based on the reaction scheme described above. The model includes five groups of reactions, such as: primary processes in N₂ and O₂ during electron beam irradiation, all main ion-molecular reactions of positive and negative charge transfer, ions recombination reactions, neutral species reactions and free radical reactions, such as: N, O, OH, H, HO₂ and Cl. A computer code Kinetic [3] and Gear method were used. The “Kinetic” code is designed for calculation the time evolution of the different main species involved in the kinetic reaction system at constant pressure and temperature. The kinetic reaction system is considered as self-contained and closed. It should obey principle of mass balance and charge balance. For “Kinetic” code applied in this work to study TCE decomposition in air under EB-irradiation, the rate of *W_j* of *j* type species generated from matrix with *k* type molecules was calculated according to Eq. (1):

$$(1) \quad W_j = \sum G_{jk} I (\rho_k/\rho)$$

where: *G_{jk}* – value of *j* type species from *k* type matrix; *I* – dose rate; *ρ_k* – gas phase density of the matrix; *ρ* – overall density of the gas phase.

The kinetic reaction system from a mathematical point of view is described by the system of ordinary differential equations (ODE). The “Kinetic” code is used Gear algorithm for numerical integration of stiff systems of ODE. 330 kinetic reactions and 80 kinds of species were included. Calculations were made in the following gas mixtures:

N₂ (80%) + O₂(20%) + TCE (*x* ppm) and
N₂(80%) + O₂ (20%) + TCE (*x* ppm) + H₂O (200–1000 ppm), respectively. The calculation input values (such as the initial concentration of O₂, N₂, TCE and H₂O, temperature, pressure, the dose rate and irradiation time) are the same as the initial conditions of the experimental work.

Results of calculation and discussion

Calculation results of HCIC=CCl₂ decomposition in dry air were reported in our previous work. Good agreement was obtained between calculation and experimental results [7].

The computer simulation of TCE decomposition and its by-products formation in humid air under elec-

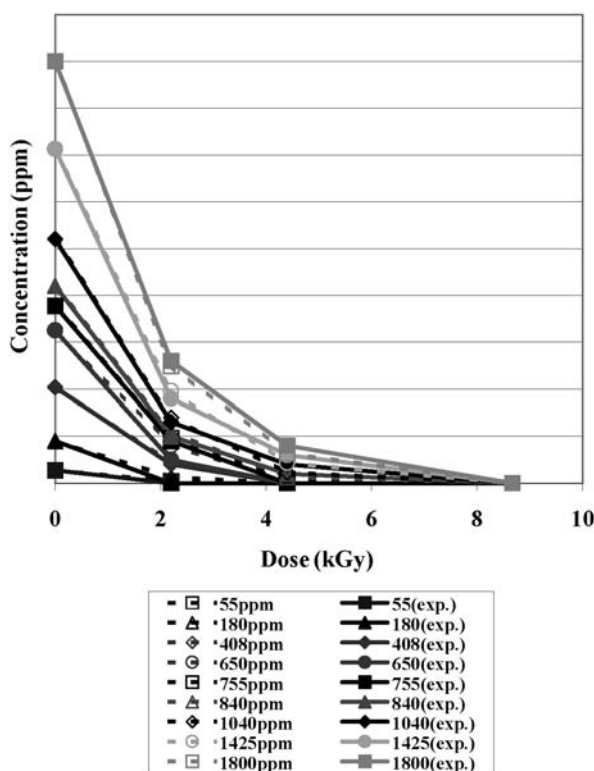


Fig. 1. Concentration of trichloroethylene vs. dose in humid air under EB-irradiation. The dashed lines and solid lines represent calculation results and experimental results [4].

tron beam irradiation was carried out, the calculation results are compared with experimental results [4] and presented in Figs. 1–3, respectively.

Figure 1 presents the TCE degradation in humid air (200 ppm H₂O) vs. dose under electron beam (EB) irradiation, the initial concentration of TCE ranges from 55 to 1800 ppm, the calculation results and experimental results are plotted in dashed lines and solid lines, respectively. 8.67 kGy dose is needed to decompose 99% TCE in humid air for an initial concentration of TCE ≤ 1800 ppm, while 25 kGy dose is needed to decompose 99% TCE in dry air for the same range of initial TCE concentration [7]. This phenomenon was observed in experiments [4, 13] and confirmed by the modeling calculation work.

For the modeling calculations, it is important to observe not only decomposition curves of TCE vs. dose, but also formation curves of its by-products under EB irradiation. Figure 2 presents the concentrations of residue TCE and products vs. dose at an initial concentration of 650 ppm TCE. Dichloroacetyl chloride (CHCl₂COCl, DCAC), carbon monoxide (CO), carbon dioxide (CO₂), phosgene (COCl₂) were identified in the experiments (solid lines in Fig. 2) by Hakoda *et al.* [4] and were predicted by the modeling simulation (dashed lines in Fig. 2). Good agreement was obtained between calculation and experimental results. Because the rate constant of reaction R24a (i.e. k_{24a}) is higher than that of reaction R24b (i.e. k_{24b}), CHCl₂COCl is the main organic product. A small amount of chloroform (CHCl₃) was identified as a minor organic product in the experiments, it is most probably formed through reaction R37,

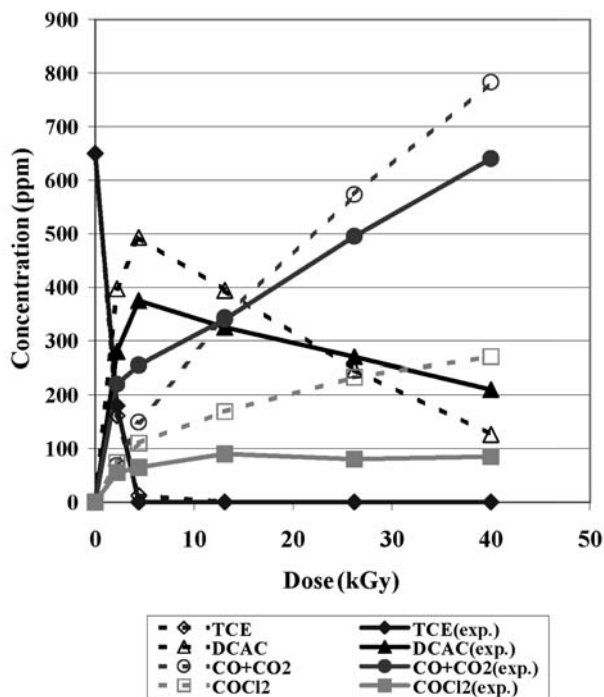


Fig. 2. Concentration of residue TCE and products vs. dose at an initial concentration of 650 ppm (the dashed lines represent results of calculation, the solid lines represent experimental data according to Hakoda *et al.* [4]).



COCl₂ and CHCl₂ formation were described in R24b.

In order to check the water concentration effect on TCE decomposition under EB-irradiation, Hakoda *et al.* investigated this problem in a series of experiments [4], and we have made a computer simulation according to their results [4]. It was found that TCE decomposition and dichloroacetyl chloride (CHCl₂COCl, DCAC) formation under EB-irradiation at an initial TCE concentration of 650 ppm are barely influenced when water concentration in the gas mixture varies from 200 to 1000 ppm (see Fig. 3).

The decomposition rate of TCE can approximately be written as

$$(2) \quad -d[\text{TCE}]/dt \approx k_1[e][\text{TCE}] + k_2[\text{O}][\text{TCE}] + k_{21}[\text{Cl}][\text{TCE}] + k_{31}[\text{OH}][\text{TCE}]$$

based on the calculation results, TCE decomposition is mainly caused by $k_{21}[\text{Cl}][\text{TCE}] + k_{31}[\text{OH}][\text{TCE}]$. The initial concentration of TCE (i.e. [TCE]) and H₂O (i.e. [H₂O]) in gas mixture determine the concentration of Cl (i.e. [Cl]) and OH radicals (i.e. [OH]) in the reaction system. When the initial concentrations of TCE and H₂O are below 1000 ppm then the rate constant of reaction R21 ($k_{21} = (8.08 \pm 0.10) \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) [1] is much larger than the rate constant of reaction R31 ($k_{31} = (2.2 \pm 0.10) \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) [2]. $k_{21}[\text{Cl}][\text{TCE}]$ plays the main role in the TCE decomposition, this is the reason why the TCE decomposition is slightly influenced at the initial TCE concentration of 650 ppm when water concentration varies from 200 to 1000 ppm. Sun *et al.* [10] made a computer simulation of 1,1-dichloroethylene (1,1-DCE) decomposition in

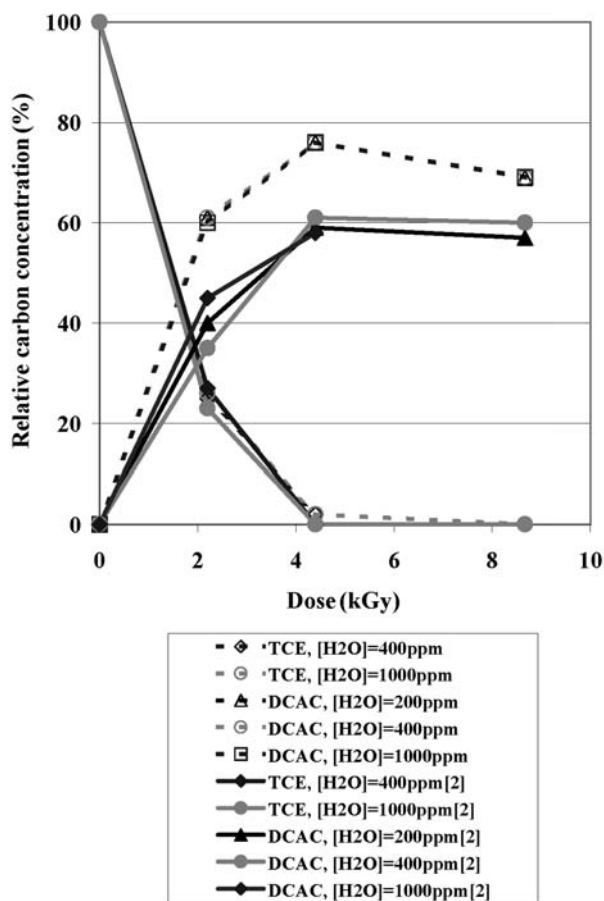


Fig. 3. The influence of water concentration (200, 400 and 1000 ppm) on the TCE decomposition and DCAC formation under EB-irradiation (the dashed lines represent results of calculation, the solid lines represent experimental data [4]).

air under EB-irradiation and found that OH radicals contributed to 1,1-DCE decomposition less than 10% when water concentration was 300 ppm. When water concentration increases to 25,000 ppm, $k_{31}[\text{OH}][\text{TCE}]$ also plays an important role in the TCE decomposition, this phenomenon was observed in the experiment by Hakoda *et al.* [4].

The experimental data provided by Hakoda *et al.* [4] reveal that in humid air (200 ppm of H₂O) and the initial HCIC=CCl₂ concentration of 50–1800 ppm, the dose level which is needed for 90% decomposition efficiency is in the range 3.6 ± 0.1 kGy (Fig. 1). According to the data obtained by Vitale *et al.* [13] for dry air, the needed dose level (> 5 kGy) is significantly higher for the same range of the initial concentration of TCE. From Fig. 3, we find that water has little influence on TCE decomposition when water concentration in the gas mixture is below 1000 ppm. What causes this effect that the dose necessary for 90% TCE removal efficiency in the study of Vitale *et al.* [13] is higher than that in Hakoda *et al.* work? By careful study, we found out that the dose rate (100 kGy/s) in Vitale *et al.* work [13] is much higher than that (2.1 kGy/s) in Hakoda *et al.* work [4]. Maybe this is the reason why the dose necessary for 90% TCE removal efficiency in Vitale *et al.* work [13] is higher than that in Hakoda *et al.* work [4]. In order to prove it, we made calculation of different dose rate influence on the TCE decomposition in dry air and in

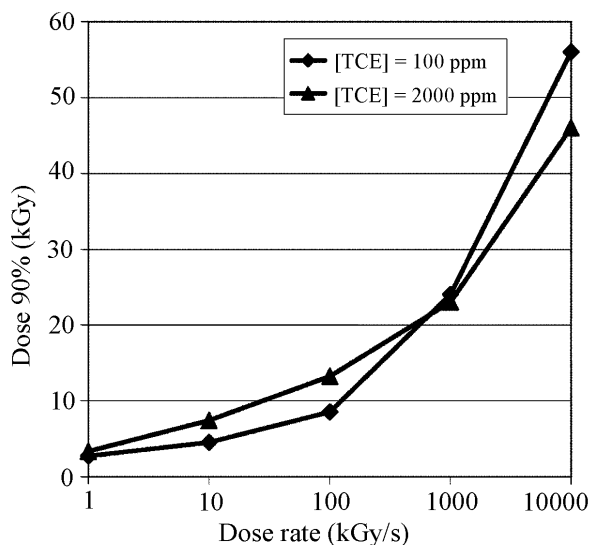


Fig. 4. Dose necessary for 90% TCE decomposition in dry air as a function of dose rate.

humid air, respectively, and the relevant results are presented in Figs. 4 and 5. It was found that the dose necessary for 90% TCE decomposition increased with increasing dose rate.

Based on our calculation results, we found that when the dose rate increases, the competition of reaction R38 against reaction R21 also increases.



thus the chain process of TCE decomposition caused by Cl radicals is slowed down. This is the reason why the dose necessary for 90% TCE decomposition in dry and humid air is higher when the dose rate is higher. The chain process of TCE decomposition slowing down with increasing dose rate was also described by Vitale *et al.* [13].

Calculation of HCIC=CCl₂ decomposition in dry air in electron beam irradiation confirms the mechanism proposed by Vitale *et al.* [13]. The decomposition

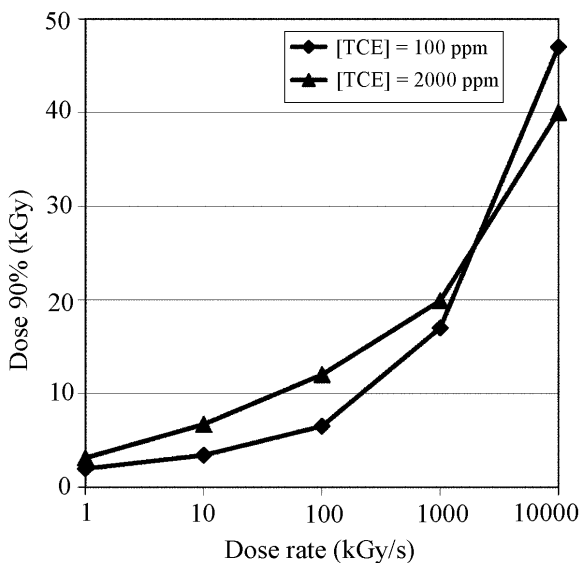


Fig. 5. Dose necessary for 90% TCE decomposition in humid air as a function of dose rate.

process is based on chain reactions initiated by Cl atoms (R21~R25). Cl atoms are generated as a result of negative Cl^- ions recombination reactions. Cl^- ions are formed in the dissociative attachment process of the thermalized secondary electrons and $\text{HCIC}=\text{CCl}_2$ molecules (R1). Part of the Cl atoms are generated from reactions initiated by oxygen atoms and $\text{HCIC}=\text{CCl}_2$.

The low dose rate, which was applied in the experiment performed by Hakoda *et al.* [4], is the reason why 90% of the $\text{HCIC}=\text{CCl}_2$ decomposition is achieved with a significantly lower dose in humid air than in dry air.

Conclusions

1. The theoretical model of the $\text{HCIC}=\text{CCl}_2$ decomposition in dry and humid air under the influence of electron beam was established.
2. The computer calculation of $\text{HCIC}=\text{CCl}_2$ decomposition was performed for the initial conditions equal to those reported in experimental works published in the literature [4, 13].
3. The experimental data and computer calculations are in best agreement when the ratio of the rate constants of reactions (R_{24a}), (R_{24b}) is chosen as $k_{24a}/k_{24b} = 10$. Such value of ratio are similar to the data devoted to the process of chlorinated chloroethylene oxidation initiated by Cl atoms presented in the literature [5].
4. Results of calculation of the $\text{HCIC}=\text{CCl}_2$ decomposition in dry air under the influence of electron beam confirm the mechanism proposed by Vitale *et al.* [13], where the decomposition process is based on chain reactions initiated by Cl atoms.
5. The mechanism of the $\text{HCIC}=\text{CCl}_2$ decomposition in humid air is similar to that in dry air, but in that case a small part of decomposition process is based on chain reactions initiated by OH radicals.
6. 90% of the decomposition efficiency was obtained with lower doses in humid air than in dry air for a similar initial concentration of $\text{HCIC}=\text{CCl}_2$ on condition that low dose rates were applied, which was proved by Hakoda *et al.* [4].

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