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 H₂C=CCl₂ and HCIC=CCl₂ 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 \cite{13} and D < 30 kGy \cite{15}. Similar experiments for humid air (300 ppm H₂O) were performed by Hakoda et al. \cite{3,4} and Sun et al. \cite{10} for the same temperature and pressure and dose level D < 13 kGy. The experimental results of H₂C=CCl₂ and HCIC=CCl₂ decomposition under the influence of electron beam in dry and humid air are presented in Figs. 1–4.

The kinetics of 1,1-dichloroethene (CCl₂=CH₂) and trichloroethene (HClC=CCl₂) decomposition in dry and humid air under the influence of electron beam

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As it can be seen in these Figures, the dose needed to obtain 90% of H$_2$C=CCl$_2$ and HClIC=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$_2$ClCOCI and CHClClCOCl for H$_2$C=CCl$_2$ and HClIC=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).

(1)  e + H$_2$C=CCl$_2$ ($\text{HClIC=CCl}_2$) $\Rightarrow$ H$_2$CCCl ($\text{HClIC=CCl}_2$) + Cl$^-$

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 $10^{-10}$ – $10^{-5}$ cm$^3$/s for CH$_2$=CCl$_2$ and $10^{-5}$ – $10^{-8}$ cm$^3$/s for HClIC=CCl$_2$, respectively [14]. The secondary source of Cl atoms can be produced between O atoms and chlorinated ethylenes in the following reactions:

(2)  O + H$_2$C=CCl$_2$ $\Rightarrow$ products;  k = 9.8 x $10^{-13}$ cm$^3$/s

(3)  O + HClIC=CCl$_2$ $\Rightarrow$ products;  k = 5.67 x $10^{-13}$ cm$^3$/s

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

(4)  O + H$_2$C=CCl$_2$ $\Rightarrow$ HCl + CO + CHCl

(5)  CHCl + O$_2$ $\Rightarrow$ OH + CCIO

(6)  CCIO $\Rightarrow$ CO + Cl

Mechanism of reaction (3) is simplified as follows from Ref. [12]. O atoms were added to trichloroethylene to form biradical (O•)HClIC=(C•)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).

(7a)  O + HClIC=CCl$_2$ $\Rightarrow$ (O•)HClIC=(C•)Cl$_2$

(7b)  (O•)HClIC=(C•)Cl$_2$ $\Rightarrow$ HClIC=CCl$_2$

(8)  O$_2$ + ClCl $\Rightarrow$ ClO + CCIO

(9)  CCIO $\Rightarrow$ CO + Cl

(10)  COHCl + Cl $\Rightarrow$ HCl + CCIO

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].

(11)  Cl + HClICCl$_2$ (H$_2$CCCl$_2$) $\Rightarrow$ HClICCl$_2$ (H$_2$CCCl$_2$)

(12)  HClICCl$_2$ (H$_2$CCCl$_2$) + O$_2$ $\Rightarrow$ HClICCl$_2$ (H$_2$CCCl$_2$) + O$_2$

(13)  2HClICCl$_2$ (2H$_2$CCCl$_2$) + O$_2$ $\Rightarrow$ 2HClICCl$_2$ (2H$_2$CCCl$_2$) + O$_2$

(14)  HClICCl$_2$ (H$_2$CCCl$_2$) + NO $\Rightarrow$ HClICCl$_2$ (H$_2$CCCl$_2$) + NO$_2$

(15)  HClICCl$_2$ (H$_2$CCCl$_2$) $\Rightarrow$ HClICCl$_2$ (H$_2$CCCl$_2$) + Cl

(16)  HClICCl$_2$ (H$_2$CCCl$_2$) $\Rightarrow$ HClICCl$_2$ (H$_2$CCCl$_2$) + Cl

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:

(17)  HClICCl$_2$ (H$_2$CCCl$_2$) + OH $\Rightarrow$ OHHCICCl$_2$ (OHH$_2$CCCl$_2$

(18)  OHHCICCl$_2$ (OHH$_2$CCCl$_2$) + O$_2$ $\Rightarrow$ OHHCICCl$_2$ (OHH$_2$CCCl$_2$)

(19)  2OHHCICCl$_2$ (OHH$_2$CCCl$_2$) $\Rightarrow$ 2OHHCICCl$_2$ (OHH$_2$CCCl$_2$) + O$_2$

(20)  OHHCICCl$_2$ (OHH$_2$CCCl$_2$) + NO $\Rightarrow$ OHHCICCl$_2$ (OHH$_2$CCCl$_2$) + NO$_2$

(21)  OHHCICCl$_2$ (OHH$_2$CCCl$_2$) + NO $\Rightarrow$ OHHCICCl$_2$ (OHH$_2$CCCl$_2$) + NO$_2$

(22)  OHHCICCl$_2$ (OHH$_2$CCCl$_2$) $\Rightarrow$ OHHCICCl$_2$ (OHH$_2$CCCl$_2$) + Cl

(23)  OHHCICCl$_2$ (OHH$_2$CCCl$_2$) $\Rightarrow$ OHHCICCl$_2$ (OHH$_2$CCCl$_2$) + HCl

Reactions (21)–(23) products formed during the decomposition process stimulate the HO$_2$ radical formation. Nearly 40% of the HO$_2$ radicals react 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 H$_3$O$^+$ ions are formed with a high efficiency through rapid charge transferring reactions:

(24)  \[ \text{N}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}_2 \]

(25)  \[ \text{N}^+ + \text{O}_2 \rightarrow \text{O} + \text{NO}^+ \]

(26)  \[ \text{N}^+ + \text{O}_2 \rightarrow \text{N} + \text{O}_2^+ \]

(27)  \[ \text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N} \]

(28)  \[ \text{O}_2^+ + \text{H}_2\text{O} + \text{M} \rightarrow \text{O}_2^+(\text{H}_2\text{O}) + \text{M} \]

(29)  \[ \text{O}_2^+(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_3\text{O}^+(\text{OH}) \]

(30)  \[ \text{H}_3\text{O}^+(\text{OH}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{OH} + \text{H}_2\text{O} \]

A small part of charge of the positive ions N$_2^+$ O$_2^+$ O$_2^+(\text{H}_2\text{O})$ will be transferred to chloroethylene molecules leading to ion formation like HCl=CCl$_2^+$ and H$_2$C=CCl$_2^+$. Because of this, the principal ions, which participate in the recombination process with negative ions, will be as follows: H$_2$O$^+$, NO$^+$, HCl=CCl$_2^+$ and H$_2$C=CCl$_2^+$. The electrons, which are generated as a result of N$_2$ and O$_2$ ionization process, are being thermalized and react with the molecules in the gas mixture mainly in reaction (1) and other reactions as follows:

(31)  \[ \text{e} + 2\text{O}_2 \rightarrow \text{O}_2^+ + \text{O}_2 \quad \text{k} = 2.5 \times 10^{-30} \text{cm}^3/\text{s} \quad [2, 7] \]

(32)  \[ \text{e} + \text{COCl}_2 \rightarrow \text{CO} + \text{Cl}_2 \quad \text{k} = 1 \times 10^{-7} \text{cm}^3/\text{s} \quad [9] \]

(33)  \[ \text{e} + \text{O}_2 + \text{N}_2 \rightarrow \text{O}_2^+ + \text{N}_2 \quad \text{k} = 1.6 \times 10^{-31} \text{cm}^3/\text{s} \quad [2, 7] \]

O$_2^+$ ions form a cluster with H$_2$O molecules in the investigated gas mixture:

(34)  \[ \text{O}_2^+ + \text{H}_2\text{O} + \text{M} \rightarrow \text{O}_2(\text{H}_2\text{O}) + \text{M} \]

The main reaction of negative charge transfer from O$_2^+$ (H$_2$O) in the gas mixture will be as follows:

(35)  \[ \text{O}_2(\text{H}_2\text{O}) + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{HO}_2 + \text{Cl}^- \]

(36)  \[ \text{O}_2(\text{H}_2\text{O}) + \text{Cl}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{Cl}_2^- \]

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 Cl$_2^-$ ions.

A small part of the negative charge is localized in the gas mixture as NO$_2^-$ and NO$_3^-$ ions. Therefore, in the 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 HO$_2$: H + O$_2$ → HO$_2$), N and O will be formed with high efficiency.

Based on these described above the theoretical models of decomposition of H$_2$C=CCl$_2$ and HCIC=CCl$_2$ 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 N$_2$ and O$_2$ 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, HO$_2$, Cl in the following gas mixtures N$_2$ + O$_2$ + X ppm (X means H$_2$C=CCl$_2$, HCIC=CCl$_2$) and N$_2$ + O$_2$ + X ppm (X means H$_2$C=CCl$_2$, HCIC=CCl$_2$) + 300 ppm H$_2$O.

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 (H$_2$C=CCl$_2$, HCIC=CCl$_2$) 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].](image-url)
321–2213 ppm for H₂C=CCl₂ and 108–3209 ppm for HClC=CCl₂, respectively. The calculations were performed with a certain rate constant of reaction (1):

\[ k_1 (\text{H}_2\text{C}=\text{CCl}_2) = 10^{-9} \text{ cm}^3/\text{s} \]
\[ k_1 (\text{HClC}=\text{CCl}_2) = 7 \times 10^{-9} \text{ cm}^3/\text{s} \]

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

\[ \frac{k_{15}}{k_{16}} (\text{H}_2\text{C}=\text{CCl}_2) = 40 \]
\[ \frac{k_{15}}{k_{16}} (\text{HClC}=\text{CCl}_2) = 10 \]

Similar relations were found by experimental data [5], which describe the chloroethene oxidation process (H₂C=CCl₂; HClC=CCl₂) initiated by Cl atoms:

\[ \frac{k_{15}}{k_{16}} (\text{H}_2\text{C}=\text{CCl}_2) = 49 \]
\[ \frac{k_{15}}{k_{16}} (\text{HClC}=\text{CCl}_2) = 10 \]

Preliminary calculations for HClC=CCl₂ 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 N₂⁺ ions to the oxygen molecules the ions O₂⁺ in excited state are formed. The oxygen ions in excited state can react according to the formula:

\[ [\text{O}_2^+]^* + \text{C}_2\text{HCl}_3 \Rightarrow \text{O}_2 + \text{C}_2\text{HCl}_2^* + \text{Cl} \]  

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

\[ [\text{O}_2^+]^* + \text{M} \Rightarrow \text{O}_2^* + \text{M} \]

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 H₂C=CCl₂ 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. 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].](image)

![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].](image)
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 H₂C=CCl₂ and 316 ppm of HClC=CCl₂ in the case of gas mixture containing 300 ppm of H₂O. The results of calculations have been obtained for H₂C=CCl₂ assuming that:

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

Taking into account that for HClC=CCl₂ 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 \( \text{H}_3\text{O}^+ \) and recombination of Cl⁻ ions follows the formula:

\[ \text{(39)} \quad \text{H}_3\text{O}^+ + \text{Cl}^- \rightarrow \text{H}^+ + \text{H}_2\text{O} + 2\text{Cl} \]

The results of calculation reveal that for dose \( D < 2.2 \) kGy the total CO and CO₂ concentration, in respect to HClC=CCl₂, can be evaluated as \( D\text{CO} + D\text{CO}_2 / D\text{CCl}_2 < 11\% \). The total concentration of the organic gas products (OGP), in respect to HClC=CCl₂, is equal to \( D\text{OGP} / D\text{CCl}_2 ≈ 99\% \). 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 CO₂ concentration, in respect to H₂C=CCl₂, can be evaluated as \( D\text{CO} + D\text{CO}_2 / D\text{CCl}_2 < 5\% \). The total concentration of the organic products, in respect to H₂C=CCl₂, is equal to \( D\text{OGP} / D\text{CCl}_2 = 100\% \). Both values are close to the experimental data, described by Hakoda et al. [3, 4] and Sun et al. [10], amounting to ≤ 4% and ≤ 100%, respectively.

The calculation results of the decomposition of both chloroethylenes 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 H₂O) 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: \( k_{15}/k_{16}(\text{H}_2\text{C}=\text{CCl}_2) = 40; k_{15}/k_{16}(\text{HClC}=\text{CCl}_2) = 10 \). 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.

References