

Simulation of decomposition of dichloroethylenes (*trans*-DCE, *cis*-DCE, 1,1-DCE)/air under electron beam irradiation

Yongxia Sun,
Andrzej G. Chmielewski,
Sylwester Bułka,
Zbigniew Zimek,
Henrieta Nichipor

Abstract. On the basis of the experimental results, computer simulations of decomposition of dichloroethylenes for three isomers (*trans*-DCE, *cis*-DCE, 1,1-DCE) in air under electron beam were carried out. Computer code “Kinetic” and “Gear” method were used. Calculation results well agree with the experimental results. Decomposition efficiency of DCE is mainly determined by Cl^- dissociated secondary electron attachment, followed by Cl radical addition reaction with DCE.

Key words: *trans*-dichloroethylene • *cis*-dichloroethylene • 1,1-dichloroethylene • electron beam • decomposition • mechanism

Y. Sun✉

Department of Nuclear Methods in Process Engineering,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland,
Tel.: +48 22 504 1368, Fax: +48 22 504 1277,
E-mail: yongxia@ichtj.waw.pl

A. G. Chmielewski
Department of Nuclear Methods in Process Engineering,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland
and Faculty of Chemical and Process Engineering,
Warsaw University of Technology,
1 L. Waryńskiego Str., 00-645 Warsaw, Poland

Z. Zimek, S. Bułka
Department of Radiation Chemistry,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland

H. Nichipor
Institute of Radiation Physical and Chemical Problems
of the Belarussian Academy of Sciences,
Minsk-Sosny, Belarus

Received: 12 September 2006

Accepted: 16 February 2007

Introduction

Some organic compounds, which are emitted into atmosphere from various sources, are very harmful to the environment and human health. Their emission into atmosphere are strictly regulated [7, 19, 25, 26]. Removal of organic compounds from gas phase has been studied using different technologies [10, 11, 14, 17, 18, 20, 21]. Among them, electron beam is one of the promising technologies which can simultaneously remove multi-pollutants with low to medium concentrations from large flow stream industrial off-gases [6, 9]. Cold plasma is formed when primary electrons, generated from the electron beam, enter into a gas mixture containing pollutants and cause ionization and excitation of carrier gas. Secondary electrons, positive ions and excited species are formed. The secondary electrons are thermalized within nanoseconds. The thermalized secondary electrons, positive ions and excited species cause pollutant decomposition by chemical reactions.

1,1-DCE decomposition in an air mixture under electron beam (EB) irradiation was investigated experimentally [23], so were *trans*-DCE and *cis*-DCE [22, 24]. It was found that the decomposition efficiency of 1,1-DCE vs. dose is higher than that of *trans*-DCE or *cis*-DCE. Organic products of 1,1-DCE degradation in an air mixture under EB-irradiation are different from those of *trans*-DCE or *cis*-DCE. Chloroacetyl chloride (CH_2ClCOCl) was observed as a main organic by-product of 1,1-DCE degradation while no other organic compounds (except *cis*-DCE or *trans*-DCE)

were observed as by-products of *trans*-DCE or *cis*-DCE degradation under EB-irradiation by means of GC-FID analysis. 1,1-DCE, *cis*-DCE and *trans*-DCE are steric isomers with similar chemical properties. Whether their decomposition mechanism is similar or not, it is not clear to us. We developed a modeling simulation for *trans*-DCE/*cis*-DCE decomposition in an air mixture under EB-irradiation in this work, comparing it with the simulation for 1,1-DCE decomposition [15, 23] in order to obtain better understanding of the mechanism of decomposition of dichlorinated ethylene in the plasma process.

Modeling simulation

Experimental results of *trans*-DCE and *cis*-DCE decomposition in an air mixture under EB irradiation were reported in our previous work [22, 24]. Experimental works were carried out at room temperature under atmospheric conditions. Initial concentrations of *trans*-DCE were varied from 342.0 ppm to 1427.0 ppm (V/V), initial concentrations of *cis*-DCE were varied from 271.0 ppm to 1529.0 ppm (V/V). Water concentration in the gas mixture investigated was 300 ppm. A Cockcroft-Walton type electron beam accelerator (3 MeV, 25 mA max) was used for irradiation of the gas mixture contained inside a glass vessel. The absorbed dose rate inside the glass vessel was 2.083 kGy/second. The absorbed dose was adjusted by changing irradiation time of the glass vessel under electron beam. Carbon monoxide (CO), carbon dioxide (CO₂), *cis*-DCE (for *trans*-DCE decomposition) or *trans*-DCE (for *cis*-DCE decomposition) were obtained as the products, while C₂H₃Cl, CH₂CCl₂ (1,1-DCE), C₂HCl₃, C₂Cl₄ and CH₂ClCOCl were not observed in the experiments [24]. A computer simulation of *trans*-DCE or *cis*-DCE degradation in an air mixture under EB-irradiation based on the experimental results of [22–24] was built up. The calculation input values (such as: initial concentrations of O₂, N₂, H₂O and *trans*-DCE or *cis*-DCE, temperature, pressure, dose rate and irradiation time) are the same as those in experimental conditions [22, 24]. A computer code “Kinetic” [5] and “Gear” method were applied. 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 the principle of mass balance and charge balance. For “Kinetic” code applied in this work to study organic pollutant decomposition in air under EB-irradiation, the rate of W_j of j type species generated from a matrix with k type molecules was calculated according to Eq. (1):

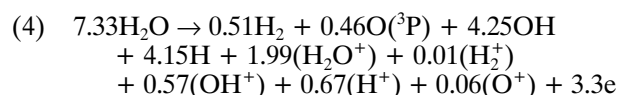
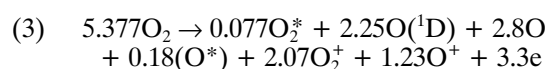
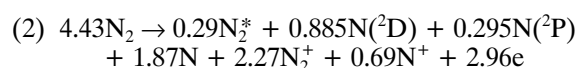
$$(1) \quad W_j = \sum G_{jk} \cdot I \cdot \rho_k / \rho$$

where: G_{jk} – value of the j type species from the 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 used a Gear algorithm for numerical integration of stiff systems of ODE. In our modeling simulation, 320 reactions involving 78 species were considered, five main groups of reactions were included, the rate constants of reactions were taken from the literature [1, 4, 13, 16]. For those kinetic reactions which are lacking literature data (unknown reactions), we proposed reaction rate constants by analogy and comparison based on the fact that the same group of chemical compounds has similar chemical properties. The proposed rate constant for those unknown reactions is expected to be one order higher or lower than its actual value. The units of rate constant in this paper are 1/s, cm³/molecule·s and cm⁶/molecule²·s for the first-, second- and third-order reactions, respectively. In this paper, we list the most important reactions which cause *trans*-DCE or *cis*-DCE decomposition in air and its by-products formation under EB-irradiation (see reactions R1–R28), compounds with bold face in these reactions are main by-products predicted by the modeling simulation. Because *trans*-DCE and *cis*-DCE are 1,2-DCEs, we built up one model to calculate these two compounds, they were distinguished from each other by *trans*-DCE or *cis*-DCE, [*trans*-DCE]⁺ or [*cis*-DCE]⁺, [*trans*-DCE][−] or [*cis*-DCE][−] in this model, respectively. For *trans*-DCE decomposition in an air mixture under EB-irradiation, the input value of initial concentration of *cis*-DCE was zero, and *vice versa*. Special attention was paid to the mass balance of chemical elements and charge balance between positive ions and negative ions.

The mechanism of *trans*-DCE and *cis*-DCE decomposition in air under EB-irradiation is described in the following way: when fast electrons from electron beams are absorbed in the carrier gas, they cause ionization and excitation process of the nitrogen, oxygen and H₂O molecules in the carrier gas. Primary species and secondary electrons are formed. The secondary electrons were fast thermalized within 1 ns in air at 1 bar pressure. The G -values (molecules/100 eV) of main primary species are simplified as follows [13]:

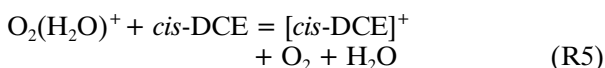
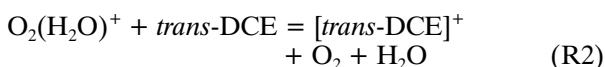


In the experimental conditions, the concentrations of N₂, O₂ and H₂O were 81%, 19%, and 300 ppm, respectively [24]. According to the concentrations and the G -values, primary species produced by N₂, O₂ and H₂O are 1600:500:1, approximately. The reasonable approximation was made and the water radiolysis was omitted in this case due to the computer software limitation. These primary species and thermalized secondary electrons formed initiate and cause decomposition of *trans*-DCE and *cis*-DCE mainly through three reaction pathways as given in reactions R1–R28.

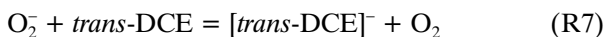
Positive charge and negative charge transfer reaction pathways

As described above, when the carrier gas air is ionized by electron beam, positive ions (such as N_2^+ , O_2^+ etc.) are formed. These positive ions transfer energy rapidly to the species with the lowest ionization potential (IP). The IP of *trans*-DCE is 9.64 ± 0.02 eV. The IP of *cis*-DCE is 9.66 ± 0.02 eV, they are smaller than the IP of N_2^+ , O_2^+ etc.

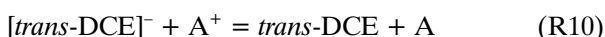
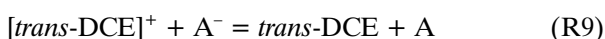
For *trans*-DCE and *cis*-DCE decomposition in air under EB-irradiation, some important positive charge transfer reactions causing *trans*-DCE and *cis*-DCE decomposition are proposed as follows (R1~R6):



Negative charge transfer reactions causing *trans*-DCE and *cis*-DCE decomposition are given below (R7~R8):



The $[\textit{trans}\text{-DCE}]^+$, $[\textit{cis}\text{-DCE}]^+$ and $[\textit{trans}\text{-DCE}]^-$, $[\textit{cis}\text{-DCE}]^-$ formed above (R1~R8) undergo neutralization through ionic recombination reactions (R9~R12)

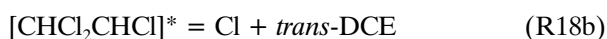
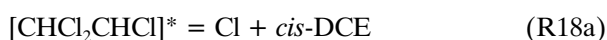
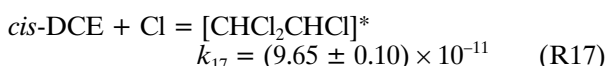
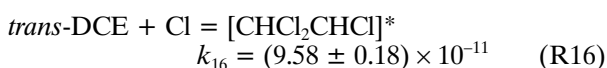
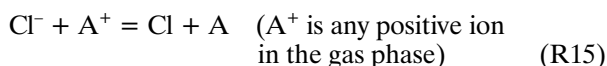
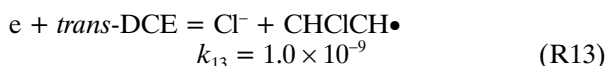


A^- , A^+ are any negative ions and positive ions in the gas phase, respectively.

Cl^- dissociation secondary electron attachment decomposition pathway

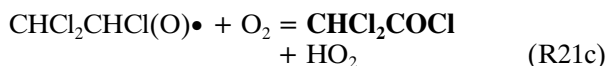
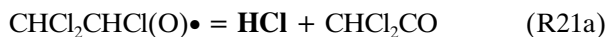
When thermalized secondary electrons attach to *trans*-DCE or *cis*-DCE, a chlorine ion (Cl^-) and $CHClCH$ radical are formed (R13, R14) [12]. The chlorinated ion undergoes neutralization by charge transfer forming a Cl atom (R15). This Cl atom adds to *trans*-DCE and *cis*-DCE producing energy-rich $[CHCl_2CHCl]^*$ radical (R16, R17) [2]. This radical by releasing a Cl atom forms *cis*-DCE, *trans*-DCE or by deactivation forms the

$CHCl_2CHCl$ radical, the branching ratios of (R18a):(R18b):(R18c) are 0.20:0.08:0.72 [2]. The relevant reactions are given as follows:



Cl^- formed in reaction R13 is the same as that formed in reaction R14, we cannot distinguish it whether it was formed in *trans*-DCE decomposition reactions with thermalized secondary electrons (R13) or *cis*-DCE decomposition reactions with thermalized secondary electrons (R14). It was treated as one species in our simulation (e.g., in reaction R15) no matter in which reaction it was formed. So, were $CHClCH\bullet$ and $[CHCl_2CHCl]^*$ etc. This is the reason why we can build one model to simulate both compounds (*trans*-DCE and *cis*-DCE) decomposition in an air mixture under EB-irradiation.

$CHCl_2CHCl\bullet$ formed in reaction R18c reacts with oxygen and goes through the peroxy radical mechanism [8].

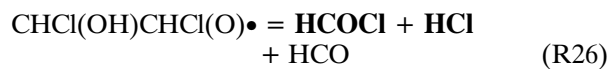
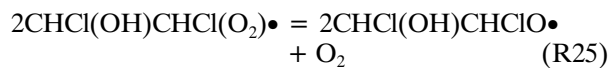
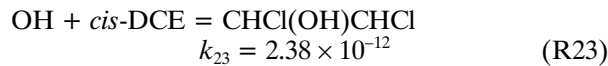
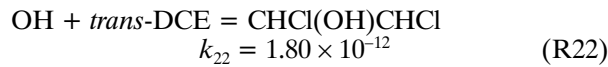


According to the work of Hasson and Smith [8], the branching ratio of reaction (R21a):(R21b):(R21c) is $(0.15 \pm 0.08):(0.77 \pm 0.08):(0.08 \pm 0.02)$. Reaction (21b) is the main channel.

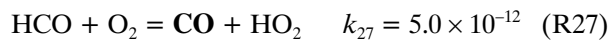
OH radicals decomposition pathway

During irradiation of low-humidity air/DCE mixtures, OH radicals are formed. The reaction of OH radicals

with chloroethylenes at room temperature, at 1 bar pressure is mainly the addition reaction (R22, R23) [3, 27]. The $\text{CHCl}(\text{OH})\text{CHCl}$ radical produced in reactions (R22, R23) may be decomposed by the reaction with oxygen molecules in the carrier gas as follows [3]:



HCO formed in reaction R26 reacts with O_2 producing CO [4],



CO reacts with OH forming CO_2 [4]



CO and CO_2 were detected as inorganic by-products in our experimental work [22, 24], they accounted for less than 10% of the total carbon.

Results of calculations and discussion

Calculation results of *trans*-DCE, *cis*-DCE degradation and their by-products formation under EB-irradiation

Computer calculations were carried out based on the model built up. The calculation results of *trans*-DCE degradation in air mixture vs. irradiation dose are presented as dashed lines in Fig. 1 and are compared with experimental results [24], which are plotted as solid lines in Fig. 1. Initial concentrations of *trans*-DCE range from 342.0 ppm to 1427.0 ppm. We find that the calculated values of *trans*-DCE concentration in an air mixture under EB-irradiation are decreased with increasing absorbed dose, this phenomenon well agrees with the experimental results. The calculated results of *trans*-DCE degradation vs. dose are a little higher than the experimental results.

Cis-DCE degradation in the air mixture vs. dose under EB-irradiation was also calculated, the results are presented as dashed lines in Fig. 2 and are compared with the experimental results (solid lines) [22]. The initial concentrations of *cis*-DCE ranged from 271.0 ppm to 1529.0 ppm. It was found that the calculated values of concentrations of *cis*-DCE in an air mixture under EB-irradiation are decreased with increasing absorbed dose, this phenomenon well agrees with the experimental results [22]. The calculated results

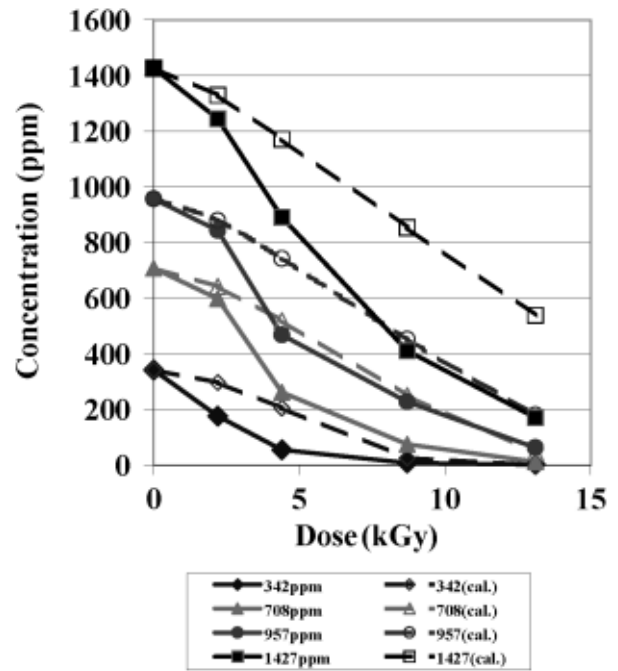


Fig. 1. Calculated and experimental results of *trans*-DCE degradation in an air mixture vs. dose under EB-irradiation. Initial concentrations of *trans*-DCE are 342, 708, 957 and 1427 ppm, respectively. Solid lines: experimental results [24]; dashed lines: calculation results.

of *cis*-DCE degradation are a little higher than the experimental results.

From the calculation results of *trans*-DCE decomposition under EB-irradiation, we notice that some active species (such as Cl, e, O_2^- , OH, O_2^+ , $\text{O}_2(\text{H}_2\text{O})^+$, N_2^+) play an important role in *trans*-DCE degradation. The relevant kinetic reactions are listed in Table 1.

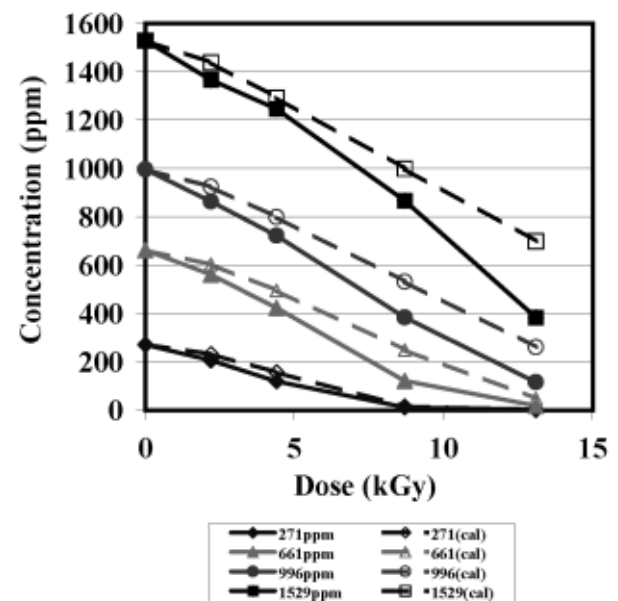


Fig. 2. Calculated and experimental results of *cis*-DCE degradation in an air mixture vs. dose under EB-irradiation. Initial concentrations of *cis*-DCE are 271, 661, 996 and 1529 ppm, respectively. Solid lines: experimental results [22]; dashed lines: calculation results.

Table 1. Kinetic reactions contribute to *trans*-DCE decomposition

Time (s)	Dose (kGy)	R16 (%)	R13 (%)	R7 (%)	R22 (%)	R1 (%)	R2 (%)	R3 (%)
0	0							
1.00E-8	2.1E-8		61.00	7.76		20.89	1.75	7.92
1.00E-7	2.1E-7		31.90	31.84		20.01	13.66	2.43
1.00E-6	2.1E-6		21.30	42.22	0.58	14.69	19.63	1.49
1.00E-5	2.1E-5	2.00	18.83	39.88	6.18	13.09	18.62	1.31
1.00E-4	2.1E-4	13.90	13.18	28.01	21.66	9.16	13.11	0.92
1.00E-3	2.1E-3	14.88	11.84	25.17	27.20	8.23	11.79	0.82
0.01	2.1E-2	14.31	11.00	23.39	31.88	7.65	10.96	0.76
0.1	0.21	18.85	8.84	18.89	37.68	6.18	8.86	0.61
0.5	1.04	39.98	6.73	14.37	26.96	4.71	6.75	0.46
1.057	2.2	57.69	4.76	10.23	18.80	3.35	4.82	0.33
2.115	4.4	78.21	3.32	7.26	13.17	2.35	3.44	0.22
4.187	8.7	78.50	2.33	5.30	9.50	1.67	2.53	0.15
6.3	13.1	82.25	1.88	4.40	7.88	1.35	2.10	0.12

Exposure to irradiation time (steady-state decomposition of *trans*-DCE with continuous irradiation) 1.057, 2.115, 4.187, 6.300 s represent 2.2, 4.4, 8.7, 13.1 kGy doses, respectively. Absorbed dose rate was 2.083 kGy/s.

The kinetic reactions listed in Table 1 were presented before (see reactions R1–R28).

From Table 1, *trans*-DCE decomposition could be described in the following three stages:

- The first stage concerns Cl dissociative thermalized secondary electron-attachment, fast charge transfer of ionized carrier gas ions and O_2^- predominant stage. In this stage, irradiation time is within 10 microseconds. This stage also exists in 1,1-DCE decomposition under EB-irradiation, the difference is that the irradiation time is within 1 microsecond [23].
- The second stage concerns 7 kinds of species (Cl , e , O_2^- , OH , O_2^+ , $O_2(H_2O)^+$, N_2^+) active stage (irradiation time is 1.0×10^{-4} – 1.0 s). Radical reactions and charge transfer reactions play almost an equal role in *trans*-DCE decomposition, this is a transition stage between the first stage and the third stage.
- The third stage concerns Cl and OH radicals prevailing stage (irradiation time is 1.0–6.3 s). Similarly to 1,1-DCE decomposition, Cl dissociative thermalized secondary electron-attachment, the kinetic reaction of Cl adding to *trans*-DCE followed by peroxy radicals reactions play a main role in *trans*-DCE decomposition. The relevant reactions are presented above (see reactions R13–R21c).

For *cis*-DCE degradation under EB-irradiation, we find that the same species (such as Cl, e , O_2^- , OH, O_2^+ , $O_2(H_2O)^+$, N_2^+) with *cis*-DCE reactions contribute to *cis*-DCE decomposition based on the calculation results, the relevant reactions are R17, R14, R8, R23, R4, R5 and R6, respectively. Similarly to *trans*-DCE decomposition under EB-irradiation, over 80% *cis*-DCE was decomposed by the reaction of Cl adding to *cis*-DCE.

In a simulation work, we need to observe not only the decomposition curves of the pollutant but also the formation curves of its by-products under EB-irradiation. Simulation results of *trans*-DCE degradation and its by-products formation are presented in Fig. 3, *cis*-DCE in Fig. 4, respectively. TC, TOP, IC in Figs. 3 and 4 are abbreviation for total carbon (TC), total

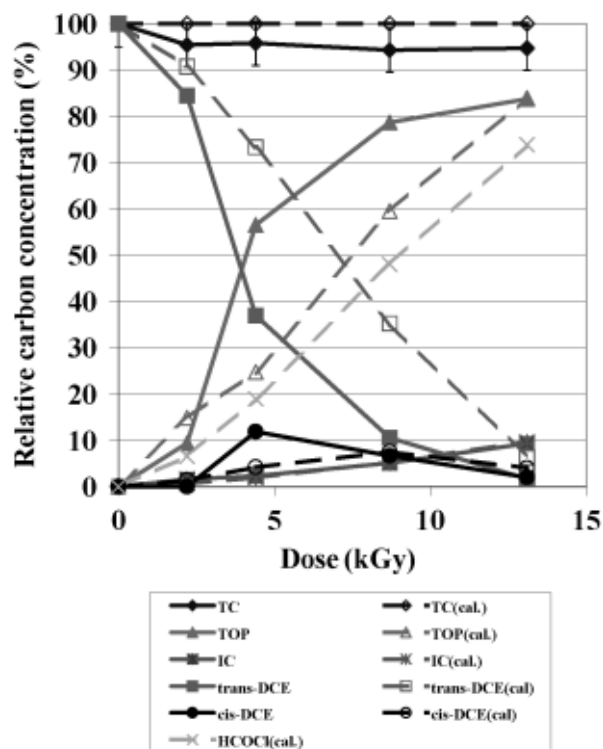


Fig. 3. Calculated and experimental results of *trans*-DCE degradation and its products formation under EB-irradiation for 708.0 ppm *trans*-DCE. Solid lines: experimental results [22]; dashed lines: calculation results.

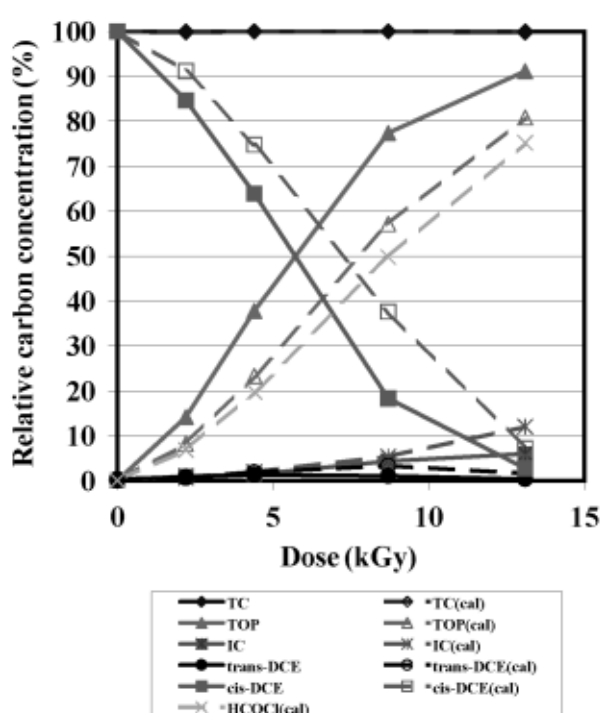


Fig. 4. Calculated and experimental results of *cis*-DCE degradation and its products formation under EB-irradiation for 661.0 ppm *cis*-DCE. Solid lines: experimental results [22]; dashed lines: calculation results.

organic products (TOP), inorganic carbon (IC) compounds (i.e. CO and CO₂), respectively. The calculation results and the experimental results [22] are plotted in dashed lines and solid lines, respectively. Formyl chloride (HCOCl), which cannot be detected by means of a GC-FID and was not found in our experiments [22], it was predicted as a main organic product following the modeling calculation results. This compound (HCOCl) was reported as a main product in Hasson and Smith's work [8] when they studied 1,2-dichloroethene (HCIC=CCIH) oxidation in oxygen initiated by chlorine atom (see reactions R16~R21 in the text).

Model discussion

For the similar range of initial concentrations of 1,1-DCE, *trans*-DCE and *cis*-DCE (904.0 ppm ~ 996.0 ppm), their decomposition curves under EB-irradiation are different based on the experimental results (Fig. 5). In order to check whether the decomposition of 1,1-DCE, *cis*-DCE and *trans*-DCE in air under EB-irradiation is mainly determined by Cl⁻ dissociative thermalized secondary electron-attachment, followed by the reaction of Cl addition to 1,1-DCE, *cis*-DCE and *trans*-DCE decomposition pathway (i.e., chain initiation reaction, such as: R29 for 1,1-DCE, R16 for *trans*-DCE and R17 for *cis*-DCE) or is determined by the chain propagation reaction (such as: R30 for 1,1-DCE decomposition under EB-irradiation, R19 for *trans*-DCE and *cis*-DCE decomposition under EB-irradiation).

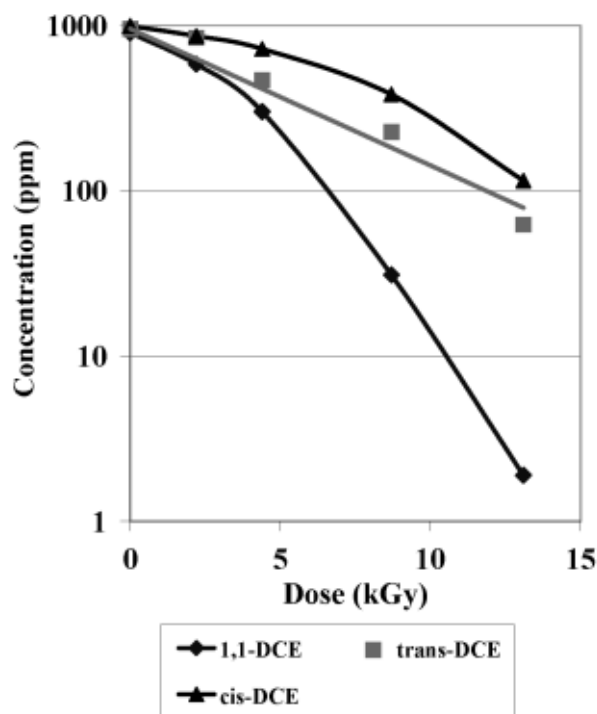
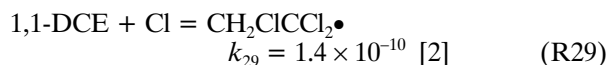


Fig. 5. Concentration of 1,1-DCE, *cis*-DCE and *trans*-DCE vs. dose under EB-irradiation.



we selected 1,1-DCE as a studied object because the main degradation products of 1,1-DCE decomposition under EB-irradiation were identified in the experiment [23]. We need not only to observe calculation results of the decomposition curves of 1,1-DCE in air under EB-irradiation, but also the formation curves of its by-products and then compare them with experimental results [23]. Mechanism of 1,1-DCE degradation and its products formation under EB-irradiation was described in details in our previous work [23] and we used the same model [23] for our calculation in this work. If 1,1-DCE decomposition is mainly determined by the chain initiation reaction (i.e., R29) not by the chain propagation reaction (R30), the reaction rate constant of R29 (k_{29}) has a large influence on the 1,1-DCE decomposition vs. dose under EB-irradiation, while the reaction rate constant of R30 (k_{30}) has little influence on the 1,1-DCE decomposition vs. dose under EB-irradiation, and *vice versa*. In order to clarify it, we change k_{29} from $1.4 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (the literature value) to $9.58 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (the assumed value, which is 0.68 times of the literature value, this value is equal to the rate constant of Cl reaction with *trans*-DCE [2]).

We found that the calculated decomposition curve of 1,1-DCE with the assumed rate constant $9.58 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ is different from the literature value (a dashed line with solid points in Fig. 6), what means the value of k_{29} has a large influence on the decomposition curve of 1,1-DCE. We may safely say that

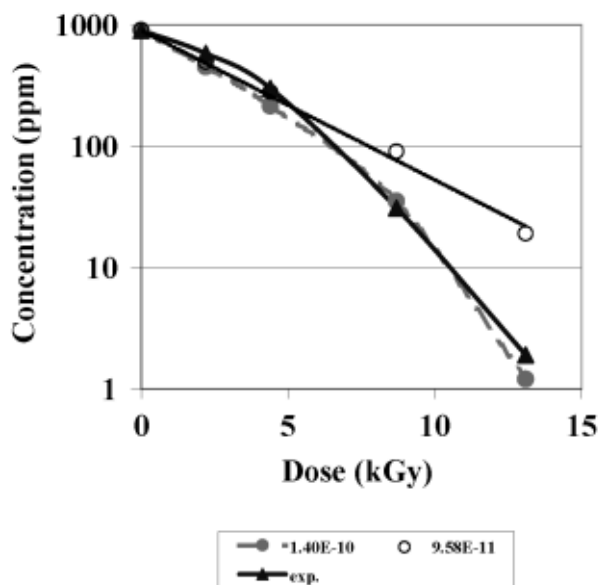


Fig. 6. Different values of k_{29} (literature value and the assumed value) influencing the calculated values of 1,1-DCE concentrations vs. dose under EB-irradiation.

1,1-DCE decomposition in air under EB-irradiation is mainly determined by the reaction of Cl^- dissociative thermalized secondary electron-attachment and the reaction of Cl addition to 1,1-DCE.

Before, during or after modeling simulation, not all reactions rate constants included in the model can be found in the literature, we have to propose rate constants for those unknown possible reactions which are lacking in literature data. We proposed rate constants of these unknown possible reactions based on the similar chemical reactions found in the literature [1, 4, 13, 16]. Whether these proposed rate constants have influence on our final calculation results or not, we made a test for 1,1-DCE decomposition (initial concentration of 1,1-DCE is 903.8 ppm) in air under EB-irradiation. We used the same model [23] for our

calculation in this work. We selected two of the important reactions (such as R29, R30) for check, changed their reaction rate constants and the calculation results are listed in Table 2. In the work of Sun *et al.* [23], we used values of $1.4 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ and $1.66 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ for k_{29} and k_{30} , respectively in our modeling simulation. k_{29} is a literature data, k_{30} is the proposed data.

If we kept k_{30} as a constant $1.66 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ and changed the value of k_{29} one order higher or one order lower than the literature data $1.4 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ to make calculations, we noticed that there were big changes in calculation values of 1,1-DCE and CH_2ClCOCl concentrations at 13.1 kGy absorbed dose. It also proves that reaction R29 plays an important role in 1,1-DCE decomposition.

There were no published data concerning reaction R30, therefore we assumed rate constant of R30 to be of 1.66×10^{-13} , based on the fact that the rate constant of CFCl_2 reaction with O_2 is 9×10^{-12} [4], the rate constant of CCl_3 reaction with O_2 is 3×10^{-12} [4], because $\text{CH}_2\text{ClCCl}_2$ is less electronegative than these two species, so the rate constant of R30 might be lower than these two species (CFCl_2 and CCl_3) reaction with O_2 .

We made calculations with different value of k_{30} and found that the different value of k_{30} (with value ranges from 1.66×10^{-11} to 1.66×10^{-15}) has little influence on our final calculation results. It also proves that 1,1-DCE decomposition is mainly determined by the chain initiation reaction (i.e., R29) not by the chain propagation reaction (R30).

Conclusions

The main results of this work can be summarized as follows:

- 1) Calculation results agree well with the experimental results published previously [22, 24]. Based on our modeling calculation results, HCOCl , which was not and cannot be detected by GC-FID in the

Table 2. Assumed rate constants influence the calculation results

1,1-DCE + Cl = $\text{CH}_2\text{ClCCl}_2 \bullet$ k_{29}	$\text{CH}_2\text{ClCCl}_2 \bullet + \text{O}_2$ = $\text{CH}_2\text{ClCCl}_2\text{O}_2 \bullet$ k_{30}	Conc. of 1,1-DCE at 13.1 kGy dose (ppm)	Conc. of CH_2ClCOCl at 13.1 kGy dose (ppm)	Remark
		1.90 (exp.)	688.7 (exp.)	experimental data [23]
1.4×10^{-10} [2]	1.66×10^{-13}	1.87 (cal.)	801.8 (cal.)	k_{29}, k_{30} used for calculation in the work of Sun <i>et al.</i> [23]
1.4×10^{-9}	1.66×10^{-13}	0 (cal.)	833.7 (cal.)	k_{29} , one order higher than 1.4×10^{-10}
1.4×10^{-11}	1.66×10^{-13}	347.3 (cal.)	418.9 (cal.)	k_{29} , one order lower than 1.4×10^{-10}
1.4×10^{-12}	1.66×10^{-13}	667.5 (cal.)	94.23 (cal.)	k_{29} , two orders lower than 1.4×10^{-10}
1.4×10^{-10}	1.66×10^{-15}	1.87 (cal.)	798.6 (cal.)	k_{30} , two orders lower than 1.66×10^{-13}
1.4×10^{-10}	1.66×10^{-11}	1.87 (cal.)	798.6 (cal.)	k_{30} , two orders higher than 1.66×10^{-13}

- experiment [22, 24], is predicted as a main organic by-product of *trans*-DCE or *cis*-DCE degradation in air under EB-irradiation. CHCl_2COCl and HCl are minor by-products.
- The geometric isomer product maximum yields calculated based on the modeling simulation are 7.47% for the formation of *cis*-DCE from *trans*-DCE degradation under EB-irradiation and 3.29% for the formation of *trans*-DCE from *cis*-DCE degradation under EB-irradiation. The corresponding geometric isomer product maximum yields measured in the experimental work [22, 24] were 11.85% and 1.03%, respectively.
 - Calculated value of the formation of inorganic carbon products ($\text{CO} + \text{CO}_2$) according to carbon balance is 9.7% at 13.1 kGy dose for 708.0 ppm *trans*-DCE decomposition under EB-irradiation based on modeling simulation, this value (9.7%) agrees well with the experimental result (9.3%) [22]. For 661.0 ppm *cis*-DCE degradation, the calculated value of the formation of inorganic carbon products ($\text{CO} + \text{CO}_2$) according to carbon balance is 12.09%, this value (12.09%) is higher than the experimental result (9.3%) [22].
 - Similarly to 1,1-DCE decomposition in the air mixture under EB-irradiation, Cl^- dissociative thermalized secondary electron-attachment reaction, fast charge transfer reactions of ionized carrier gas ions and O_2^- predominate in the initial stage of *trans*-DCE or *cis*-DCE decomposition in air under EB-irradiation. Cl radicals become significant in the later stage of EB-irradiation. The reaction pathway of Cl^- dissociative thermalized secondary electron-attachment, the kinetic reaction of Cl adding to 1,1-DCE, *trans*-DCE or *cis*-DCE followed by peroxy radicals reactions is the main path for 1,1-DCE, *trans*-DCE or *cis*-DCE decomposition in air under EB-irradiation. Rate constants of reaction of $\text{Cl}\cdot$ with 1,1-DCE, *trans*-DCE or *cis*-DCE have a big influence on the decomposition efficiency of 1,1-DCE, *trans*-DCE or *cis*-DCE. 1,1-DCE decomposition is mainly determined by the chain initiation reaction (i.e., R29) not by the chain propagation reaction (R30). The presence of OH radical increases the *trans*-DCE or *cis*-DCE decomposition efficiency.
- Acknowledgment** This work has been sponsored by scientific funds for the years 2007–2010 as an ordered research grant No. PBZ-MEiN-3/2/2006 “Engineering of processes for emission control and utilization of hazardous and greenhouse effect gases”.
- ## References
- Albritton DL (1978) Ion neutral reactions rates. *At Data Nucl Data* 22;1:1–101
 - Atkinson R (1987a) Kinetics of the gas-phase reactions of Cl atoms with chloroethenes at 298 ± 2 K and atmosphere pressure. *Int J Chem Kinet* 19:1097–1105
 - Atkinson R (1987b) A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. *Int J Chem Kinet* 19:799–828
 - Atkinson R, Baulch DL, Cox RA *et al.* (1997) Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: Supplement V. *J Phys Chem Ref Data* 26:521–1011
 - Bugaenko WL, Grichkin WL (1980) Program for modeling of chemical kinetics. Report ITEP no. 50. Institute of Theoretical and Experimental Physics, Moscow
 - Chmielewski AG, Sun Y, Licki J, Bułka S, Kubica K, Zimek Z (2003) NO_x and PAHs removal from industrial flue gas by using electron beam technology with alcohol addition. *Radiat Phys Chem* 67:555–560
 - EC (2004) The decision concerning a mechanism for monitoring community greenhouse gas emissions and for implementing the Kyoto protocol (Decision No 280/2004/EC). http://ec.europa.eu/environment/climat/greenhouse_monitoring.htm
 - Hasson AS, Smith, IWM (1999) Chlorine atom initiated oxidation of chlorinated ethenes: results for 1,1-dichloroethene ($\text{H}_2\text{C}=\text{CCl}_2$), 1,2-dichloroethene ($\text{HCIC}=\text{CClH}$), trichloroethene ($\text{HCIC}=\text{CCl}_2$), and tetrachloroethene ($\text{Cl}_2\text{C}=\text{CCl}_2$). *J Phys Chem A* 103:2031–2043
 - Hirota H, Hakoda T, Taguchi M, Takigami M, Kim H, Kojima T (2003) Application of electron beam for the reduction of PCDD/F emission from municipal solid waste incinerators. *Environ Sci Technol* 37:3164–3170
 - Jasiński M, Mizeraczyk J, Zakrzewski Z (2004) Microwave torch plasmas for decomposition of gaseous pollutants. *J Adv Oxid Tech* 7;1:51–58
 - Kim J-C (2002) Factors affecting aromatic VOC removal by electron beam treatment. *Radiat Phys Chem* 65:429–435
 - McCorkle DL, Christodoulides AA, Christophorou LG (1984) Gaseous dielectric IV. In: Christophorou LG, Pace MO (eds) *Proc of the 4th Int Symp on Gaseous Dielectrics*, April 1984, Knoxville, TN. Pergamon Press, London, pp 12–22
 - Mätzing H (1989) Chemical kinetics of flue gas cleaning by irradiation with electrons. In: Prigogine I, Rice S-A (eds) *Advances in chemical physics*. Vol. LXXX. John Wiley & Sons, Inc Press, pp 315–402
 - Mohseni M (2005) Gas phase trichloroethylene (TCE) photooxidation and by-product formation: photolysis vs. titania/silica based photocatalysis. *Chemosphere* 59:335–342
 - Nichipor H, Dashouk E, Yacko S *et al.* (2003) 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. *Nukleonika* 48:45–50
 - NIST (2000) Chemical kinetics database on the web. <http://kinetics.nist.gov/kinetics/index.jsp>
 - Peishi S, Xianwan Y, Ruohua H, Bing H, Ping Y (2004) A new approach to kinetics of purifying waste gases containing volatile organic compounds (VOC) in low concentration by using the biological method. *Journal of Cleaner Production* 12:95–100
 - Penetrante BM, Hsiao MC, Bardsley JN *et al.* (1996) Electron beam and pulsed corona processing of volatile organic compounds in gas streams. *Pure Appl Chem* 68;5:1083–1087
 - Regulation of standard emission from installation issued by Ministry of Environmental Protection (2005) *Dziennik Ustaw*, 20 Dec 2005, no 05.260, item 2181 (in Polish)
 - Santoro D, Jong V de, Louw R (2003) Hydrodehalogenation of chlorobenzene on activated carbon and activated carbon supported catalysts. *Chemosphere* 50:1255–1260
 - Shen Y-S, Ku Y (1999) Treatment of gas-phase volatile organic compounds (VOCs) by the UV/O_3 process. *Chemosphere* 38:1855–1866

22. Sun Y, Chmielewski AG (2004) 1,2-dichloroethylene decomposition in air mixture by using ionization technology. *Radiat Phys Chem* 71:433–436
23. Sun Y, Hakoda T, Chmielewski AG *et al.* (2001) Mechanism of 1,1-dichloroethylene decomposition in humid air under electron beam irradiation. *Radiat Phys Chem* 62:353–360
24. Sun Y, Hakoda T, Chmielewski AG, Hashimoto S (2003) *Trans*-1,2-dichloroethylene decomposition in low-humidity air under electron beam irradiation. *Radiat Phys Chem* 68:843–850
25. UNECE (1979) Convention on long-range transboundary air pollution. <http://www.unece.org/env/lrtap/welcome.html>
26. UNFCCC (1998) Kyoto protocol to the united nations framework convention on climate change. <http://unfccc.int/resource/docs/convkp/kpeng.pdf>
27. Zhu L, Bozzelli JW, Ho WP (1999) Reaction of OH radical with C₂H₃Cl: rate constant and reaction pathway analysis. *J Phys Chem A* 103:7800–7810