TRANS-1,2-DICHLOROETHYLENE DECOMPOSITION IN HUMID AIR UNDER GAMMA-RAY IRRADIATION

Yong-Xia Sun *, A.G.Chmielewski ,

Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland
*corresponding author:
yongxia@orange.ichtj.waw.pl
Fax: +48-22-811 1917

Abstract

Decomposition of trans-1,2-dichloroethylene(trans-DCE) in humid air under gamma-ray irradiation has been investigated. Inorganic and organic products were analyzed by a TOC analyzer and a Gas-Chromatography. G-values and energy consumption of decompositions of trans-DCE have been obtained. Irradiation dose rate influence on the trans-DCE degradation and its products formation has been studied and mechanism of trans-DCE degradation has been proposed in this work.

Introduction

Chloroethylenes, which are emitted into atmosphere from various industrial processes, are very harmful to the environment and human health.

Chloroethylenes degradation have been studied extensively in recent years by using different technologies. Electron beam (EB) treatment seems to be a promising technology for removal of low concentration chloroethylenes contained in air . Sun et al.(1) studied 1,1-dichloroethylene(1,1-DCE) decomposition in humid air mixture and Won et al.(2) studied chloroethylenes/air mixture(mainly trichloethylene) decomposition in flow system by this technology. In order to achieve better understanding of trans- -dichloroethylene's degradation by using ionization radiation technology, gamma ray irradiation was applied. In our present work, we studied trans-DCE decomposition and its products distribution under gamma-ray irradiation, moreover irradiation dose rate influence on the trans-DCE degradation and its products formation were investigated, energy consumption was considered and mechanism of decomposition of trans-DCE was proposed. Based on the authors knowledge, there is little work reported trans-DCE degradation in air mixture under gamma-ray irradiation.

Methods

The method of preparation trans-1,2-dichloroethylene (trans-DCE) model gas and irradiation conditions were described in details previously (3). In brief, trans-DCE model gas was prepared by bubbling technical air (carbon dioxide is below 1ppm) into liquid trans- DCE (trans-DCE. Purity >98.0%, from Tokyo Kasei Kogyo Co. Ltd. , pure liquid trans-1,2-DCE without further purification). A water bath was used to control temperature of liquid trans-DCE. The saturated gas was diluted by the same technical air in a gas mixer and introduced into the five connected Pyrex glass vessels. The concentration of trans-DCE in the model gas was adjusted by controlling the flow rates of the substrate saturated gas and the dilution gas using rotameters as well as by controlling the temperature of water bath. When concentration of last glass vessel became constant, the glass vessels were sealed with the stopcocks. Four Pyrex glass vessels were used for irradiation; one was used as reference gas to detect the initial concentration of trans-DCE model gas mixture. The water concentrations in the model gas mixture were estimated about 300 ppm.

A plate type Co-60 with the capacity of 65,811Ci was used for gamma ray irradiation. The distance of the glass vessel reactor from the Co-60 source was 30cm. The absorbed dose in the glass vessel reactor was measured by a CTA film dosimeter (FTR-125, Fuji Photo Film Co.) and the dose rate was evaluated to be 3.79kGy/hr..

The concentration of the produced organic compounds was measured by a gas chromatography (GC-8A. Shimadzu Seisakusho Ltd.) with a flame ionizing detector(GC-FID) and a packed

column(BX-20 100/120, 2mm i.d.× 3m, GL Science Inc.). The concentrations of total carbon (TC) and inorganic carbon (IC) were measured by a TOC–analyzer with an infrared detector. (TOC-10B, Shimadzu Seisakusho Ltd).

The experiments were carried out at ambient condition(1 atmosphere and 298 K). Carbon monoxide (CO), carbon dioxide (CO_2) , and cis-DCE were obtained as products while vinyl chloride (C_2H_3Cl), 1,1-dichloroethylene , thichloroethylene (C_2HCl_3), tetrachloroethylene (C_2Cl_4) $CH_2ClCOCl$ were not observed.

Results and discussion

1 Trans-DCE degradation efficiency vs. dose in gamma-ray irradiation

Trans-DCE degradation efficiency vs. dose under gamma-ray irradiation was shown in Table1. It was found that 99.85% trans-DCE decomposed at 7.58kGy, 99.76%, 98.43% trans-DCE decomposed at 11.37kGy for initial concentration of trans-DCE 316ppm, 684ppm and 963ppm, respectively. For higher initial concentration of trans-DCE, 89.18% and 85.32% trans-DCE were decomposed at 15.16kGy absorbed dose for initial concentration trans-DCE 1433ppm, 2188 ppm respectively.

Table 1: Trans-DCE degradation efficiency vs. dose in gamma-ray irradiation

Dose(kGy)	316ppm	684ppm	963ppm	1433ppm	2188ppm
0	316,3	684	962,7	1433	2188
3,79	51,14	244,6	413,1	1080	1955,7
7,58	0,45	45,4	170,1	442,5	999,8
11,37	0	1,61	15,1	286,7	748,5
15,16		0,53	0,78	155,1	321,2

2 G-values of decomposition of trans-DCE

FromTable 1, G-values of decomposition of trans-DCE under gamma-ray irradiation was calculated and result is shown in Table 2. It has been found that G-values of trans-DCE are very large and markedly depend on initial concentration. For example, G-values of trans-DCE are 14 at 316ppm and 53 at 2188ppm. G-value vs. initial concentration of trans-DCE under gamma-ray irradiation could be mathematically fitted by equation 1:

G-value = 19.989 $\ln(C_0)$-101.67 (1)

Where: G-value: molecules/100eV;

C_0: initial concentration of trans-DCE, 316ppm $\leq C_0 \leq$ 2188ppm.

This phenomenon indicates that trans-DCE decomposition partly proceeds by chain reactions.

Table 2 G-values of decomposition of trans-DCE

Conc.(ppm)	316	684	963	1433	2188
G-Value(molecules/100eV)	13,96	28,22	35,03	43,78	52,51

3 Degradation products distribution

Degradation of trans-DCE products under gamma-ray irradiation were analyzed by the GC-FID and the TOC analyzer. It was found that carbon monoxide (CO), carbon dioxide (CO_2) , and cis-dichloroethylene were obtained as products while vinyl chloride (C_2H_3Cl), thichloroethylen (C_2HCl_3), tetrachloroethylene (C_2Cl_4), chloroacetyl chloride ($CH_2ClCOCl$) were not observed. Table 3. shows TOP formation decreasing and IC formation increasing at various absorbed dose for different initial concentration of trans-DCE. Inorganic carbon (IC) formation is linear increased with the dose increasing except for 316ppm trans-DCE at 15.16 kGy absorbed dose. IC concentration is 17.2%, 12.8% , 9.8% and 7.2% for 316ppm, 684ppm, 963ppm and 1433ppm trans-DCE at 15.16kGy , respectively. Other organic compounds are formed but were not identified by this work.

Table 3. TOP formation decreasing and IC formation increasing at various absorbed dose for different initial concentration of trans-DCE

DCE(ppm)	TOP			IC		
	7.58kGy	11.37kGy	15.16kGy	7.58kGy	11.37kGy	15.16kGy
316ppm	89.36%	83.8%	82.8%	10.3%	16.2%	17.2%
	Δ(TOP)	- 5.56%	- 1.0%	Δ(IC)	+ 5.9%	+ 1.0%
684ppm		90.16%	87.12%		9.6%	12.8%
	Δ(TOP)		- 3.04%	Δ(IC)		+ 3.2%
1433ppm		90.32%	90.12%		8.1%	9.8%
	Δ(TOP)		- 0.2%	Δ(IC)		+ 1.7%

4. Irradiation dose rate influence on the trans-DCE degradation and products formation.

In order to get information of dose rate influence on the trans-DCE decomposition and its product formation, trans-DCE was irradiated by different dose rate under gamma-ray irradiation. The results were shown in Table 4.

Different dose rates were obtained by changing the distance of the glass vessel reactors from the Co-60 source. Total absorbed dose was 3.3kGy. The experimental results were shown inTable 4. It is found that trans-DCE decomposition and its products formation have no change between 0.87 kGy/hr and 6.13 kGy/hr dose range. TC is almost 100 in this dose rate range that means no aerosol products are formed. When absorbed dose rate increase to 13.1 kGy/hr, trans-DCE decomposition efficiency is increased and aerosol products are formed. Organic products in gas-phase (TOP) are almost equal at all absorbed dose rate(0.87~13.1kGy).

Table 4. Irradiation dose rate influence on the trans-DCE degradation and products formation

Dose rate(kGy/hr)	TC	IC	trans-DCE	TOP
0,87	100	2,7	80,23	17,07
1,75	99,2	1,4	80,48	17,32
3,49	98,5	1,5	83,54	13,46
6,13	100	1,8	79,38	18,82
13,1	79,2	5,8	55,85	17,55

5. Reaction mechanism

It is well known that there is no difference in the chemical effects on materials between eb and gamma-ray irradiation. Mechanism of 1,1-DCE decomposition and its product formation has been described in details previously(1) for eb irradiation. Mechanism of trans-DCE decomposition in gamma-ray irradiation is similar to that of 1,1-DCE. Trans-DCE decomposition was mainly caused by thermal electrons(e_{th}), Cl, and OH radicals. Here are listed most important reactions involving in trans-DCE decomposition.

Conclusions

The main results of this study are summarized as follows:

1) It has been found that 99.85% trans-DCE decomposed at 7.58kGy, 99.76%, 98.43% trans-DCE decomposed at 11.37kGy for initial concentration of trans-DCE 316ppm, 684ppm and 963ppm, respectively. For higher initial concentration of trans-DCE, 89.18% and 85.32% trans-DCE were decomposed at 15.16kGy absorbed dose for initial concentration trans-DCE 1433ppm, 2188 ppm respectively. G-values of trans-DCE are very large and markedly increase with initial concentration increasing. It indicates that trans-DCE decomposition involves chain reactions.
2) HCOCl is the possible main organic product and cis-DCE is a minor organic product. Cis-DCE's formation reached to 7.65%, 12.38%, 11.77% for 316ppm, 684ppm and 963ppm trans-DCE at 3.79kGy and 13.3% for 1433ppm at 7.58kGy. CH_2=CHCl, CH_2=CCl_2, CHCl=CCl_2, CCl_2=CCl_2, $CH_2ClCOCl$ were not found as other organic products in this work. Inorganic carbon (IC) formation is linear increased with the dose increasing except for 316ppm trans-DCE at 15.16 kGy absorbed dose. IC concentration is 17.2%, 12.8% , 9.8% and 7.2% for 316ppm, 684ppm, 963ppm and 1433ppm trans-DCE at 15.16kGy , respectively.
3) Irradiation dose rate influence on the trans-DCE degradation and its products formation have been studied. It is found that trans-DCE decomposition and its products formation have no change between 0.87 kGy/hr and 6.13 kGy/hr irradiation dose rate range.
4) Mechanism of trans-DCE decomposition under gamma-ray irradiation is clarified. Cl^- Dissociative electron attachment reactions mainly contribute to trans-DCE decomposition while OH radicals existing increase trans-DCE decomposition efficiency.

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