

Decomposition of toluene in air mixtures under electron beam irradiation*

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Abstract. The model gases of toluene-air mixtures were prepared by blowing technical air into liquid toluene and then irradiated with an ILU-6 accelerator located at the Institute of Nuclear Chemistry and Technology (INCT), Poland. It was found that the decomposition efficiency of toluene increases with absorbed dose and decreases with initial concentration of toluene. At 14.5 kGy dose, the decomposition efficiencies of toluene were 50, 37 and 34.5% for the initial concentrations of toluene 32.0, 63.4 and 78.0 ppm, respectively. At 58.0 kGy dose, the decomposition efficiencies of toluene were 93.8 and 78.1%, the initial concentrations of toluene being 32.0 and 63.4 ppm, respectively. Benzaldehyde was identified as one of the by-products of toluene decomposition in an air mixture. The decomposition efficiency and by-product formation under EB irradiation were compared between toluene and 4-chlorotoluene.

Key words: toluene • 4-chlorotoluene • decomposition • electron beam

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Introduction

Emission of organic pollutants into atmosphere is very harmful to the environment and human health. Organic pollutants from off-gas must be treated before they are discharged into atmosphere. In urbanized area, volatile organic compounds (VOCs) are emitted into atmosphere mainly by anthropogenic sources. VOCs emission into atmosphere causes a serious environmental problem and is adverse to human health. It can cause ozone depletion in the stratosphere and ozone formation in the troposphere. About 40% of ozone produced photochemically might contribute to the emission of aromatics, mainly toluene [3]. Toluene concentration in waste off-gas is relatively high [15], therefore it must be treated before discharged into atmosphere.

Toluene destruction by using advanced oxidation technologies (AOTs) such as UV/ozone [9], non-thermal plasma (NTP) [1, 4], NTP combined with a catalyst [10], electron beam [5, 6] and electron beam combined with a catalyst technology [7] have been studied extensively

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in recent years. Benzaldehyde, aerosols and benzene were reported as by-products [5, 7]. Han *et al.* [5] also identified acetone, dipropyl 1,2-benzenedicarboxylic acid, nitromethane and trace amounts of hexane as by-products of decomposition of toluene.

Radical species formed from AOTs can oxidatively destroy organic pollutants present in gas phase. Electron beam (EB) technology is one of the most promising AOTs. It can simultaneously decompose multiple pollutants present in gas phase [2] at a relatively low energy consumption. In this work, we studied the efficiency of toluene decomposition vs. dose in air mixtures under electron beam irradiation and the identification of by-products. Decomposition efficiency and by-product formation under EB irradiation were compared between toluene and 4-chlorotoluene. The purpose of this work was to obtain a better insight of toluene and 4-chlorotoluene decomposition in air mixtures under EB irradiation on a lab scale in order to optimize EB operational conditions on a larger scale for aromatic organic pollutants treatment from waste off-gas in our future research.

Experimental

Preparation of a model gas of toluene-air mixtures

The setup for preparation of a model gas of toluene in air mixtures was similar to that described in our previous work [12]. Toluene model gas was prepared by bubbling synthesized air ($\geq 99.995\%$ purity; 21% O₂, N₂ as a balance gas; CO₂ ≤ 1 ppm, BOC gas company, Poland) into liquid toluene (toluene, purity $> 99.7\%$ without further purification, provided by J. K. Baker, USA). The temperature of toluene was set at 21°C with a water bath (type LW, manufactured by WSL Bytom Company, Poland). The concentration of toluene in the model gas was adjusted by controlling the flow rate of a base gas air and gas air of the same dilution by means of valves and rotameters. The model gas of toluene was injected into four connected Pyrex glass reactors by parallel connections. When concentration in glass reactors became constant, the glass reactors were sealed with stopcocks. The concentration of water in the model gas mixture was measured by a HM141-type indicator of humidity and temperature (Vaisala Company, Finland). Concentration of water in a gas mixture was 56 ppm. Experiments were carried out in ambient temperature conditions and at 1 bar atmospheric pressure.

Generation of plasma

A pulsed electron beam accelerator ILU-6 (2.0 MeV max, 20 kW max) was used to generate plasma inside glass reactors. Irradiation setup has been described previously [12]. Pyrex glass reactors were put under a scan horn of the accelerator for irradiation. The following irradiation conditions were used: 2 Hz (pulse repetition rate), 2 MeV (energy) and 60 mA (pulse current). The absorbed dose (kGy, 1 kGy = 1 kJ/kg) inside glass reactors was measured by a cellulose triacetate (CTA) film dosimeter and was recalculated based on

an empirical formula obtained between dose_(CTA) and dose_(N₂O) [11]:

$$(1) \quad \text{dose}_{(\text{N}_2\text{O})} = 2.897 * \text{dose}_{(\text{CTA})}$$

Analytical methods

Concentrations of toluene before and after irradiation in glass reactors were measured by a gas chromatograph (GC-17A, Shimadzu Corporation, Japan) equipped with a flame ionizing detector (GC-FID). A capillary column (SupercowaxTM-10, 30 m \times 0.32 mm \times 0.25 μm , Supelco Company, USA) was used. Stock solution AK-101AA-ARO (2000 $\mu\text{g}/\text{ml}$ in methanol, AccuStandard Company, USA) containing toluene was used for preparation of a calibration curve. The following conditions and parameters were applied for toluene analysis: column temperature was kept at 40°C for 1 min, then increased to 160°C at 20°C/min; flow rate of He as a carrier gas was 47 ml/min; injector temperature was 100°C and detector temperature was 250°C; injection mode was splitted (split ratio 40:1). The injection volume of toluene air mixture was 1 ml.

Organic compounds present in the reaction vessels (before and after irradiation) were adsorbed by coconut charcoal adsorbents (SKC Inc, USA) and then eluted with 5 ml of ethyl acetate (HPLC purity, provided by J. K. Baker, USA). The solid-free extract solution was obtained by using syringe filters and then its volume was decreased to approximately 0.3 ml by using a micro-extractor under continuous flow of high purity N₂ (99.995% purity, BOC gas company, Poland). A gas chromatograph equipped with a HP-5 MS column (30 m \times 0.25 mm \times 0.25 μm , Agilent technologies Incorporation, USA) coupled with the a detector (GCMS-QP 5050A, Shimadzu Corporation, Japan) was used for identification of by-products. The oven temperature was held at 40°C for 1 min, then programmed at 20°C/min to 290°C, held for 1 min. Total flow rate of a carrier gas helium was set at 15 ml/min. The injector temperature and detector temperature were set at 280°C. The injection volume of the concentrated extract solution was 1 μl with split mode (split ratio 12:1). The electron impact ionization mode of MS was applied, 70 eV energy was used.

Dose dependence of removal and decomposition efficiencies

In electron beam process, it is very important to consider energy consumption for degradation of pollutants, i.e. to answer a question how much energy (unit: kJ) is consumed/absorbed to decompose pollutants in the weight unit of the base gas.

Removal/decomposition efficiency of organic pollutants is defined as R ,

$$(2) \quad R = (C_0 - C_i)/C_0$$

where C_0 is the initial concentration of organic pollutants, unit: ppm (v/v); C_i is the concentration of organic pollutants at i kGy absorbed dose, unit: ppm (v/v).

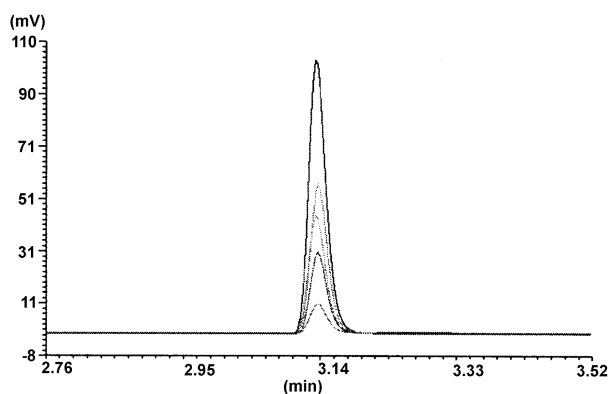


Fig. 1. Gas chromatograms of a toluene/air mixture at different doses with an initial toluene concentration of 63.4 ppm. The elution peaks of toluene recorded at different doses, downward presentation: 0, 14.5, 29.0, 43.5 and 58.0 kGy.

Results and discussion

Decomposition of toluene

Concentration of toluene in an air mixture before and after electron beam irradiation was measured by means of GC-FID.

Figure 1 shows that the decomposition efficiency of toluene increases with absorbed dose. This observation was confirmed for various initial concentrations of toluene. The respective results are presented in Fig. 2. They also indicate that the decomposition efficiency of toluene decreases with initial concentration of toluene.

Gaseous by-products

In order to obtain information of by-products produced from toluene destruction, we carried out an experiment at a high inlet concentration of toluene (151.9 ppm) and at a high absorbed dose (155.3 kGy). More than 97% toluene was decomposed. A compound eluted with a retention time 7.735 minute (see Fig. 3) was identified as benzaldehyde using Wiley library (see Fig. 4). There

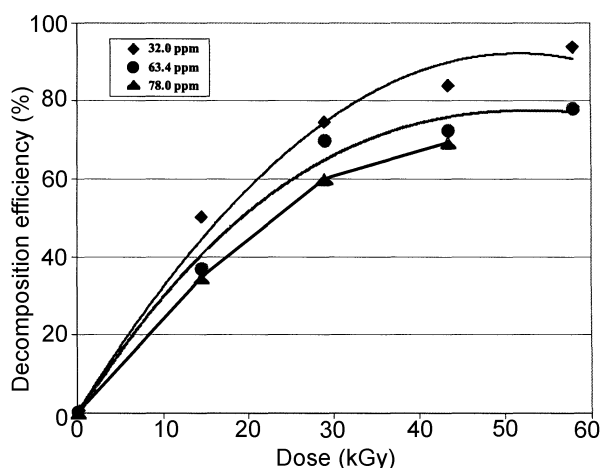


Fig. 2. Dependence of the decomposition efficiency of toluene on the dose absorbed under EB irradiation.

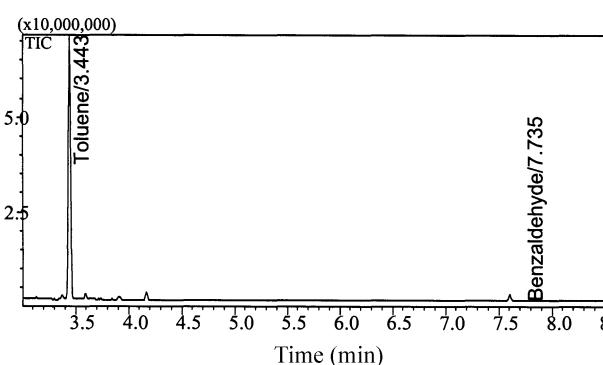


Fig. 3. A GC-MS chromatogram of a toluene/air mixture after EB-irradiation (the inlet concentration of toluene was 151.9 ppm, the dose was 155.3 kGy).

are also other by-products present, however, their identification was not attempted.

Benzaldehyde was also reported as a by-product [5, 7]. Trace amounts of acetone were also detected in accordance with an earlier work [5].

Under our experimental condition, we selected ethyl acetate as an extract solvent, its elution time from an HP-5 MS column was very close to benzene, benzene could not be detected due to MS solvent cutting time

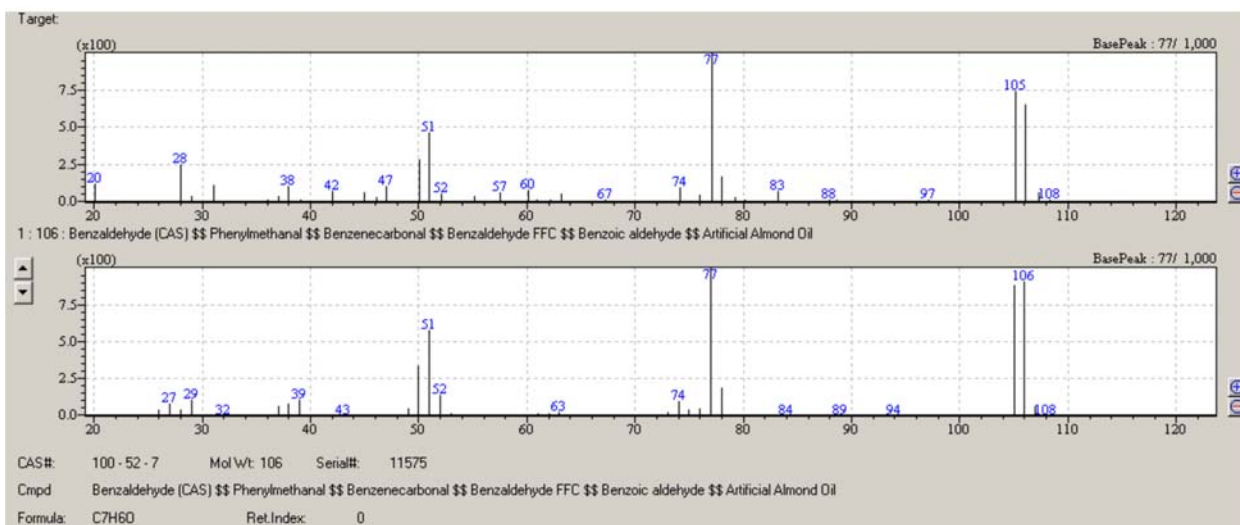


Fig. 4. Mass spectrum of the compound eluted with a retention time 7.735 min (top). Mass spectrum of benzaldehyde taken as a reference (bottom).

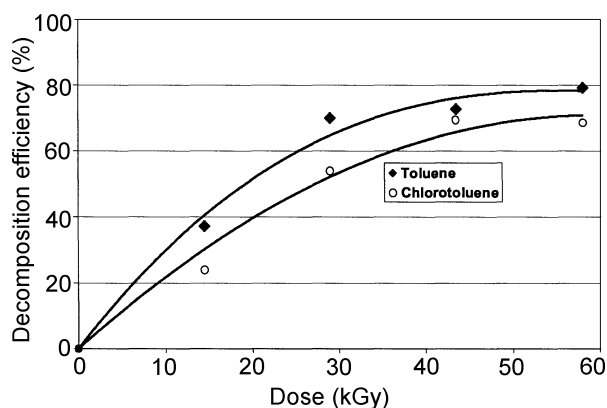


Fig. 5. Dependence of the decomposition efficiency of toluene and 4-chlorotoluene on the dose absorbed under EB irradiation (initial concentrations of toluene and 4-chlorotoluene were 63.4 ppm and 51.9 ppm, respectively).

for protection a filament of the mass detector from solvent ethyl acetate.

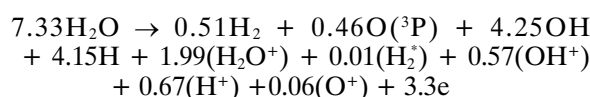
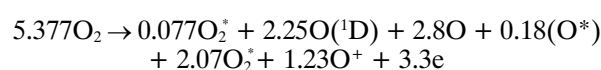
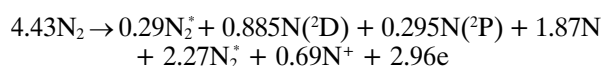
No apparent solid particle product was observed on the surface wall of the glass reactor.

Comparison of the decomposition efficiency of toluene and 4-chlorotoluene

In order to find out whether the functional group has an influence on the decomposition efficiency of aromatic compounds, we compared the decomposition of 4-chlorotoluene ($\text{ClC}_6\text{H}_4\text{CH}_3$) with that of toluene ($\text{HC}_6\text{H}_4\text{CH}_3$) in an air mixture under EB-irradiation. It was found that the decomposition efficiency of toluene is slightly higher than 4-chlorotoluene (Fig. 5). Chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$) and 4-chlorobenzaldehyde ($\text{ClC}_6\text{H}_4\text{CHO}$) were identified as by-products of 4-chlorotoluene decomposition [14]. A reaction mechanism rationalizing formation of by-products and differences in decomposition efficiency between 4-chlorotoluene and toluene will be discussed in the following chapter.

Mechanism

When energy of fast electrons is absorbed in the carrier gas, it causes ionization and excitation of nitrogen, oxygen and H_2O molecules in the carrier gas. Primary species (such as excited species, cations and radicals, etc.) and secondary electrons are formed. The secondary electrons are thermalized fast within 1 ns in air at 1 bar pressure [16]. The G -values (molecules/100 eV) of main primary species are presented as follows [8]:



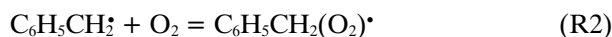
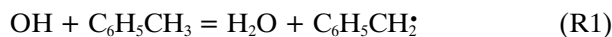
where G -values of molecules decomposed are listed

in the left side of the arrows, and G -values of species formed are listed in the right side of the arrows. 1 molecule/100 eV = 0.1037 $\mu\text{mol}\cdot\text{J}^{-1}$.

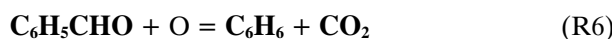
These primary species and thermalized secondary electrons formed initiate decomposition of toluene and 4-chlorotoluene. In our previous work we carried out computer simulations of the decomposition of 1,4-dichlorobenzene (1,4-DCB) present in an air mixture, by an electron beam. We showed that $\cdot\text{OH}$ -induced reactions play an important role in the decomposition of 1,4-DCB [13].

Scheme 1 illustrates 4-chlorotoluene and toluene decompositions and their by-products formations through OH radical reaction pathway. A detailed mechanism of 4-chlorotoluene decomposition under EB irradiation has been discussed [14]. The mechanism of $\cdot\text{OH}$ -induced reactions leading to decomposition of toluene is as follows.

Irradiation of a mixture of toluene and low-humidity air by an electron beam leads to the formation of $\cdot\text{OH}$ radicals. The $\cdot\text{OH}$ radicals react subsequently with toluene by hydrogen abstraction from the methyl group resulting in the formation of benzyl radicals (reaction R1). In the presence of oxygen the respective peroxy radicals derived from benzyl radicals are formed (reaction R2). The peroxy radicals undergo further recombination resulting in the formation of oxyl radicals, molecular oxygen (reaction R3a) and tetraoxide (reaction R3b). This tetraoxide intermediate can decompose according to the Russel-mechanism to benzyl alcohol, benzylaldehyde and molecular oxygen (reaction R4). $\text{C}_6\text{H}_5\text{CH}_2\text{O}\cdot$ reacts with O_2 to form benzaldehyde (R5).



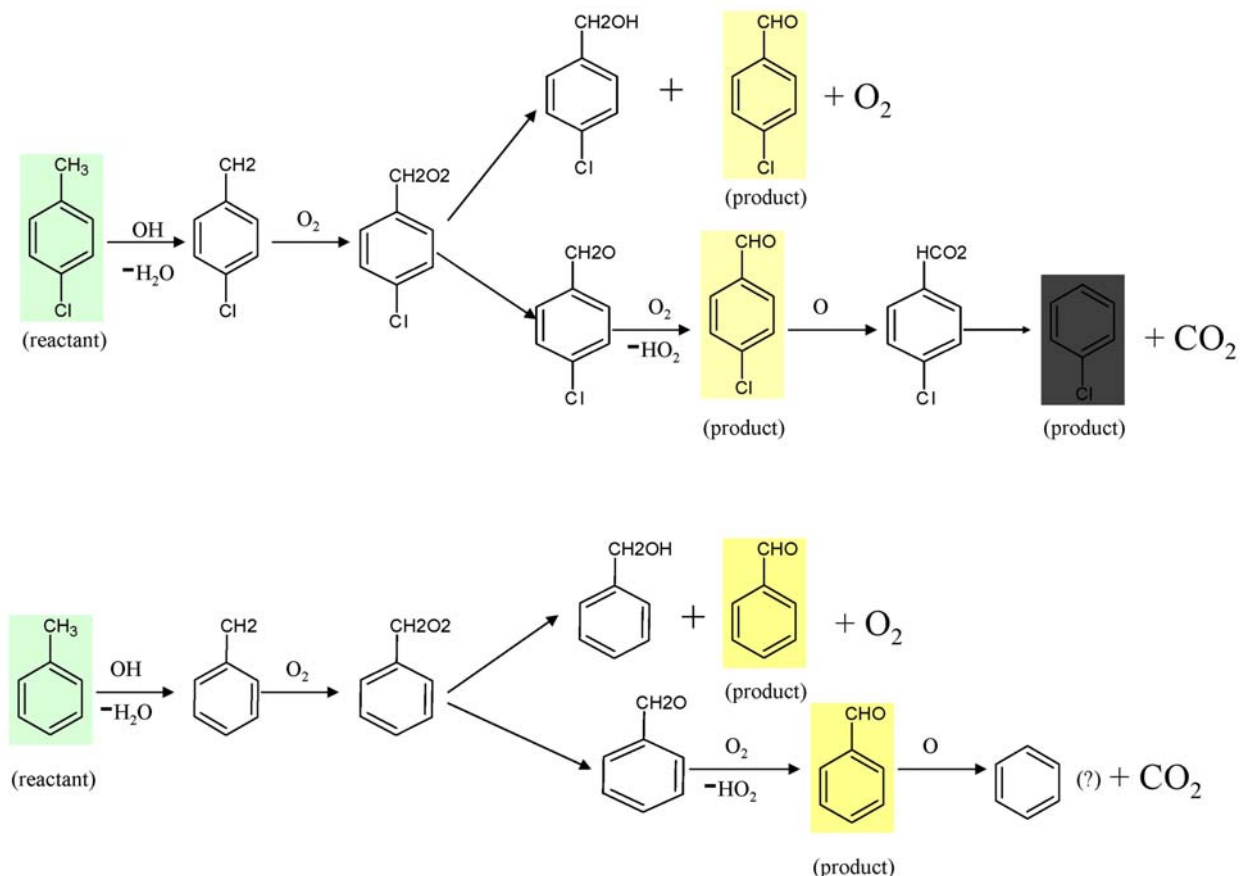
In analogy to chlorobenzaldehyde ($\text{ClC}_6\text{H}_4\text{CHO}$), benzaldehyde ($\text{HC}_6\text{H}_4\text{CHO}$) might undergo further reaction resulting in formation of benzene and CO_2 .



Since Cl is more electronegative than H, H atom abstraction from $-\text{CH}_3$ by OH radicals from toluene ($\text{HC}_6\text{H}_4\text{CH}_3$) is easier than from 4-chlorotoluene ($\text{ClC}_6\text{H}_4\text{CH}_3$), this may explain why the decomposition efficiency of toluene is slightly higher than that of 4-chlorotoluene in an air mixture under EB irradiation.

Conclusions

Toluene in an air mixture can be decomposed by using EB technology. The decomposition efficiency of toluene increases with absorbed dose, while decreases



Scheme 1. A schema of OH radical reaction pathway of 4-chlorotoluene and toluene decompositions and their by-products formation.

with initial concentration of toluene. A trace amount of benzaldehyde was identified as one of by-products of toluene decomposition in an air mixture. The decomposition efficiency of toluene in an air mixture is slightly higher than that of 4-chlorotoluene under EB irradiation. OH radicals play a main role for toluene or chlorotoluene decomposition. EB technology can be applied to remove other aromatic organic pollutants from gas phase. The applied dose depends on inlet concentration of pollutants and an emission limit of the pollutants regulated by a local government.

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