



# The reaction pathway for the heterogeneous photocatalysis of trichloroethylene in gas phase

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## Abstract

Trichloroethylene (TCE) has been widely used in industry. It is considered a hazardous and carcinogenic air pollutant. In this investigation, TCE photocatalytic reactions were performed in a packed bed reactor configured as a continuous flow reactor and a FT-IR sample cell used as a batch reactor to determine the intermediates under irradiation by 365 nm UV light. In this study, the intermediates detected during these reactions were phosgene, dichloroacetyl chloride (DCAC), chloroform, hexachloroethane, alcohols, esters, aldehydes, carbon monoxide, and carbon dioxide. The possible reaction mechanisms began with the Cl<sup>-</sup> subtraction. The Cl radicals then interacted with TCE to form various intermediates and products. © 2002 Elsevier Science B.V. All rights reserved

*Keywords:* Titanium dioxide; Trichloroethylene; Photocatalysis; Pathway

## 1. Introduction

In recent years, volatile organic compound (VOC) emissions have had a dramatic hazardous impact upon public health. Many countries have implemented emission controls on these compounds. The most common VOCs are produced by solvents used for chemical processing, printing, food, lacquer, and wire insulation industries [1]. Among these compounds,

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chlorinated hydrocarbons have been determined as harmful and carcinogenic substances. Because of their toxicity and biodegradation resistance, the emission of these compounds is an important environmental issue. Traditional treatments for VOCs include incineration, catalytic oxidation, absorption, adsorption, condensation and bio-filtration. These methods are not entirely satisfactory. For instance, incineration has good decomposition efficiency but requires high capital and operation cost [1]. Condensation and bio-filtration have limited capacity for efficient treatment. Absorption and adsorption processes produce secondary liquid or solid phase pollutants.

Recently, the use of  $\text{TiO}_2$  as light excitation source for heterogeneous photocatalysis to oxidize refractory organic compounds has received considerable attention. The advantages of gaseous heterogeneous photocatalytic reactions over liquid phase reactions are as follows: (1) the diffusion in the gas phase is favored; (2) OH radical scavengers (such as alkalinity) do not interfere; (3) electron scavengers (such as  $\text{O}_2$ ) are rarely limiting; (4) photons absorbed by the solvent (water) are low [2].

Several researchers have applied the photocatalytic technique to oxidize chlorinated hydrocarbons. Dibble [3] studied the effect of moisture on the photocatalytic reaction of trichloroethylene (TCE). The TCE reaction rate was faster in a stream without moisture than a stream with moisture, but did not last long. This indicated that the moisture was an essential component for photocatalytic reactions although it hampered the reaction. Larson and Falconer [4] proposed that the chloride ions and other intermediates accumulated on the  $\text{TiO}_2$  surface reduced the activity of catalysts. The presence of water molecules could remove these species to reactivate the catalysts. Kutsuna et al. [5] used a  $\text{TiO}_2$  coated cylindrical reactor for the decomposition of TCE. This process involved a two-stage decomposition reaction. First, the trichloroethylene transformed into dichloroethylene and the dichloroethylene decomposed into  $\text{CO}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$ . Jardim et al. [2] used fixed bed and fluidized bed reactors to decompose TCE. With 20%  $\text{O}_2$ , the products detected by the GC-MS were phosgene, chloroform, carbon tetrachloride, dichloroacetyl chloride (DCAC), dichloroacetic acid and pentachloroethane. Without oxygen, the products detected were pentachloroethane, 1-pentachloropropene, 1,1,3,4-tetrachloro-1,3-butadiene. Wang et al. [6] used a packed bed reactor for the photocatalytic reaction of TCE. The results showed that there was competitive adsorption for TCE and water on the  $\text{TiO}_2$  surface. The kinetics satisfied the bimolecular Langmuir-Hinshelwood model form. Luo and Ollis [7] studied the photocatalysis of a toluene and trichloroethylene mixture. When the concentration of toluene was larger than  $90 \text{ mg/m}^3$ , the addition of TCE would promote the degradation of toluene, and there was no influence when the concentration of added TCE was greater than  $90 \text{ mg/m}^3$ . Hung and Marinas [8,9] studied the intermediates in TCE photocatalysis. They determined trace amounts of chloroform, carbon tetrachloride, 1,2-dichloroethylene, tetrachloroethylene, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane and hexachloroethane by GC-MS.

Many studies have applied FT-IR, molecular beam mass and GC-MS to detect the products of the TCE photocatalysis. This investigation applied FT-IR and NMR to analyze the reaction products and compared those with the reported data shown in the literature. Finally, a reaction pathway for the photocatalytic decomposition of trichloroethylene was proposed.



light intensity. The reactor outflow tubing was inserted into a volumetric flask filled with tetrahydrofuran (THF) to absorb the evolved gas for 6 h. After completion, the solution was vacuum-concentrated at 60 °C until the concentrated solution volume did not change, and then evacuated for 4 h. A portion of the concentrated solution was analyzed by FT-IR (Perkin Elmer Paragon 500). The other portion was analyzed using  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Varian Germini 300).

### 2.3. The batch experiment

The batch reactor was a FT-IR gas sample cell (1.9 cm i.d.  $\times$  10 cm L) filled with reaction gas with KBr windows on both ends. The procedure for preparing the catalyst was similar to the continuous flow reactor but without dipping in a  $\text{TiO}_2$  suspension. The sample cell was washed inside with a suspension of 5% (w/v)  $\text{TiO}_2$ , and the procedures expressed above were repeated. During the reaction, this sample cell was placed into the FT-IR spectrometer sample chamber for in situ infrared analysis, and the UV light tube was placed on the open end of the sample chamber. A black cloth covered the entire sample chamber to avoid interference from outside light. To obtain a significant signal from the FT-IR, the TCE concentration was increased to  $4.94 \mu\text{g}/\text{m}^3$ , and the oxygen content 20% (v/v), moisture 0.27% (v/v), and  $0.31 \text{ mW}/\text{cm}^2$  light intensity were performed in the batch experiment.

## 3. Results and discussion

The TCE IR spectrum in the FT-IR gas sample cell is shown in Fig. 2. The IR bands at 3832, 3740 and  $1695 \text{ cm}^{-1}$  are characteristic of the vibrational modes of water molecules.

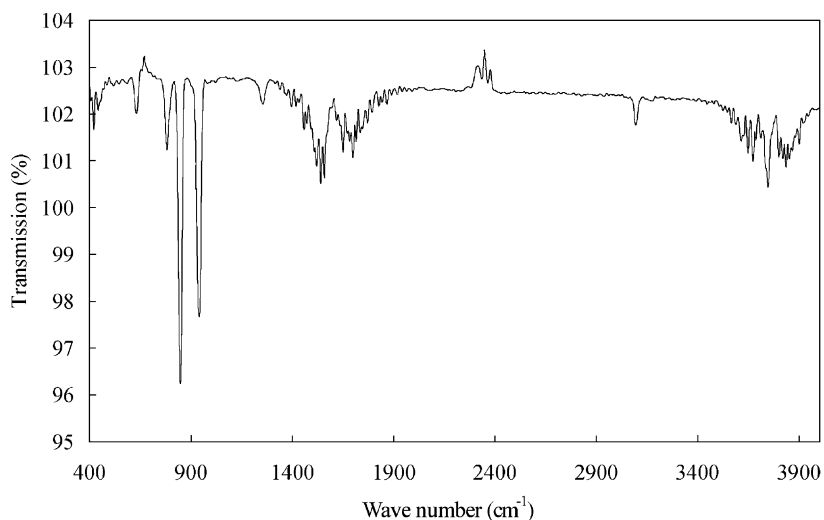


Fig. 2. FT-IR spectrum of TCE (TCE =  $4.94 \mu\text{g}/\text{m}^3$ , humidity = 0.27%,  $\text{O}_2$  = 20%).

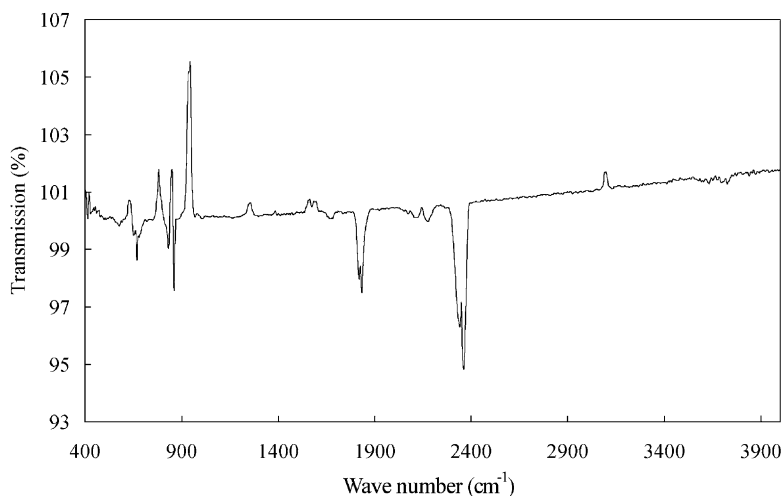


Fig. 3. UV irradiated FT-IR spectrum normalized with Fig. 2 (TCE =  $4.94 \mu\text{g}/\text{m}^3$ , humidity = 0.27%,  $\text{O}_2$  = 20%, UV =  $0.31 \text{ mW}/\text{cm}^2$ ).

Additional bands at  $3090, 1540, 1250, 940, 847, 780, 632$  and  $450 \text{ cm}^{-1}$  are characteristic of the TCE vibrational modes of TCE. This mixture was irradiated as a batch operation with a  $0.31 \text{ mW}/\text{cm}^2$  light intensity for 5 min. The FT-IR spectrum after normalization with Fig. 2 is shown in Fig. 3. The upward peaks at  $3090, 1580, 1540, 1250, 945, 933, 849, 784, 632$  and  $430 \text{ cm}^{-1}$  indicated a decrease in the TCE species after reaction. The downward peaks at  $3854, 3786, 2361, 2338, 2175, 2114, 1832, 1820, 1683, 860, 832, 666$  and  $575 \text{ cm}^{-1}$  indicated that a new species was produced after the reaction. The IR bands at  $3854, 3786$ , and  $1683 \text{ cm}^{-1}$  were due to the OH vibration of water molecules and indicated the release of water at the initial stage. Additional products were identified by matching almost signals with the reference spectra [10–12] as shown in Table 1. These products were carbon dioxide, carbon monoxide, DCAC and phosgene.

Fig. 4 shows the FT-IR spectrum of the concentrated sample from the effluent gas of the continuous flow reactor. Comparison with the reference THF IR spectrum [12], the appearance of  $2954, 2877, 1443, 1380, 1066$  and  $921 \text{ cm}^{-1}$  bands indicated the presence of residual THF in the sample. The additional peaks could not be clearly classified due to the complexity. It only assigned to OH stretch ( $3381 \text{ cm}^{-1}$ ) and C–O stretch ( $1344, 1032 \text{ cm}^{-1}$ )

Table 1  
Reaction products of the batch irradiated experiment from FT-IR

Compound	Wave number ( $\text{cm}^{-1}$ )
$\text{CO}_2$	2361, 2338
CO	2338, 2175, 2114
$\text{CHCl}_2\text{COCl}$	1820, 575
$\text{COCl}_2$	1832, 860, 832, 666

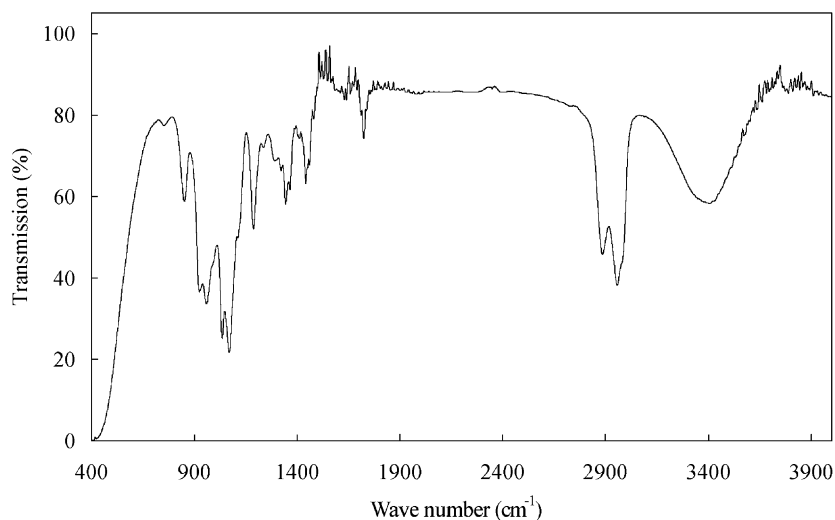


Fig. 4. FT-IR spectrum from concentrated sample (TCE =  $1.54 \mu\text{g}/\text{m}^3$ , humidity = 0.27%,  $\text{O}_2$  = 20%, flow rate = 300 ml/min, UV =  $0.45 \text{ mW}/\text{cm}^2$ ).

of alcohols, C=O stretch ( $1721 \text{ cm}^{-1}$ ) and C–O stretch ( $1290, 1184 \text{ cm}^{-1}$ ) of esters [13].  $^1\text{H}$  and  $^{13}\text{C}$  NMR also confirmed the presence of residual THF with  $^1\text{H}$  chemical shifts at 1.8 and 3.8 ppm and  $^{13}\text{C}$  chemical shifts at 27.6 and 67.5 ppm [14]. Comparison between the sample and the reference compound NMR spectra could not clearly identify all reaction species due to the complexity of the spectrum. Only  $^1\text{H}$  chemical shift was found at 7.2 ppm and  $^{13}\text{C}$  chemical shift at 77.0 ppm that corresponded to  $\text{CHCl}_3$  [14]. The  $^{13}\text{C}$  chemical shifts at 77.0 and 106.2 ppm corresponded to  $\text{C}_2\text{Cl}_6$  [14]. The rest of the peaks was not identified by splitting of signal and coupling constant. These chemicals were systematically characterized using the bonding chemical shift [15], including alcohols, esters and aldehydes (Table 2).

Table 2  
Reaction products of the continued irradiated experiment from NMR

Compound	Chemical shift for $^1\text{H}$ (ppm)	Chemical shift for $^{13}\text{C}$ (ppm)
Tetrahydrofuran	1.8, 3.8	27.6, 67.5
Chloroform	7.2	77.0
Hexachloroethane		77.0, 106.2
Alcohols	1.9 (RO–H) 3.9 (H–COH) 5.0 (RO–H)	67, 77 (C–O)
Esters	2.2 (H–C–COOR) 3.9 (RCOO–C–H)	67, 77 (C–O) 178 (C=O)
Aldehydes	2.5 (H–C–C=O) 9.7 (RCHO)	220 (C=O)

Table 3  
The products for the photocatalytic reaction of TCE in literature

Authors	Analytic equipment	Products
Nimlos et al. [16]	FT-IR, molecular beam mass	C <sub>2</sub> HOCl <sub>3</sub> , COCl <sub>2</sub>
Jacoby et al. [11]	FT-IR	C <sub>2</sub> HOCl <sub>3</sub> , COCl <sub>2</sub> , CO, HCl, CO <sub>2</sub>
Berman and Dong [17]	GC-ECD	COCl <sub>2</sub> , HCl, CO, CO <sub>2</sub> (have proceeded the analysis of CCl <sub>4</sub> , CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , CH <sub>3</sub> Cl, C <sub>2</sub> HCl <sub>5</sub> , C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub> , but not found)
Raupp and Junio [18]	FT-IR	Aldehydic or carboxylic hydrocarbon
Kutsuna et al. [5]	GC-MS	CHCl <sub>3</sub> , COCl <sub>2</sub> , CO, CO <sub>2</sub>
Jardim et al. [2]	GC-MS	20% O <sub>2</sub> : COCl <sub>2</sub> , CHCl <sub>3</sub> , CCl <sub>4</sub> , C <sub>2</sub> HOCl <sub>3</sub> , CHCl <sub>2</sub> COOH, C <sub>2</sub> HCl <sub>5</sub> No O <sub>2</sub> : C <sub>2</sub> HCl <sub>5</sub> , C <sub>3</sub> HCl <sub>5</sub> , C <sub>4</sub> H <sub>2</sub> Cl <sub>4</sub>
Hung and Marinas [8]	GC-MS	CHCl <sub>3</sub> , CCl <sub>4</sub> , C <sub>2</sub> Cl <sub>4</sub> , C <sub>2</sub> HCl <sub>5</sub> , C <sub>2</sub> Cl <sub>6</sub> , HCl, Cl <sub>2</sub>
Hung and Marinas [9]	GC-MS	The same as above

From the FT-IR and NMR results, the products detected in this investigation were carbon dioxide, carbon monoxide, DCAC, phosgene, chloroform, hexachloroethane, alcohols, esters and aldehydes. By comparing these results with those reported in the literature (Table 3), alcohols and esters were not mentioned before. Nimlos et al. [19] studied the heterogeneous photocatalytic reaction of ethanol in the gas phase. They proposed the reaction pathway to be: alcohols → aldehydes → carboxylic acids. Aldehydes were the intermediate in the photocatalytic decomposition of TCE by Dibble [3] as also observed in this study. Chloro-organic acid was one of the intermediates detected by Jardim et al. [2]. In addition, from the viewpoint of alcohols production in organic chemistry [20], the chloroalkanes can react with hydroxyl ions to form alcohols. Thus, a similar pathway as proposed by Nimlos et al. [19] might proceed the alcohol photocatalytic reaction. Since such intermediates as aldehydes and carboxylic acids were present, the esterification reaction could proceed to form esters. The other intermediates such as carbon tetrachloride, pentachloroethane, and 1-pentachloropropene shown in Table 3 were not identified in this study. This might be due to the decomposition or condensation of these compounds in the tubing before analysis. In addition, the intermediates identified in the literature varied significantly according to different experimental conditions or analytic methods. It is noted that in this study, the effluent gas was absorbed by the absorbent for 6 h. Therefore, significant amounts might have been collected resulting in the detecting some byproducts.

The IR spectra of UV-irradiated TCE at different reaction times in the bath experiment are shown in Fig. 5. The stretching vibration bands of C–Cl at 940, 632 and 430 cm<sup>-1</sup> disappeared after 5 min, indicating that the dechlorination of TCE occurred at the initial stage of reaction. The IR intensity of DCAC increased at first but gradually diminished. While, phosgene increased with the decreasing of DCAC. It indicated that DCAC could be further decomposed in the photocatalytic reaction, and then formed phosgene. Moreover, CO<sub>2</sub> constantly increased throughout the reaction because it was the final product.

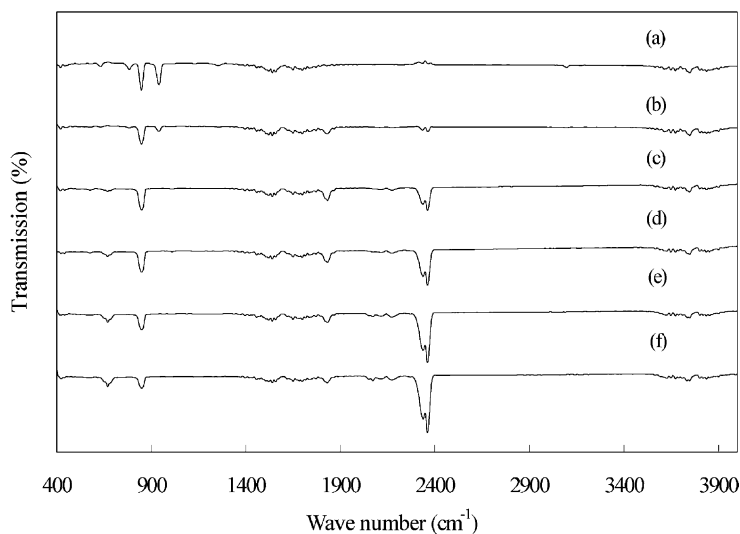
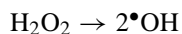
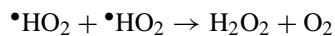
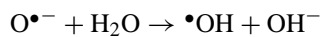
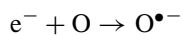
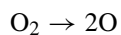
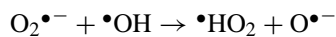
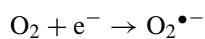
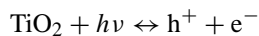


Fig. 5. FT-IR spectra of TCE at different reaction times: (a) 0 min (b) 1 min (c) 5 min (d) 10 min (e) 30 min (f) 50 min (TCE = 4.94  $\mu\text{g}/\text{m}^3$ , humidity = 0.27%,  $\text{O}_2$  = 20%, UV = 0.31  $\text{mW}/\text{cm}^2$ ).

### 3.1. Reaction pathway

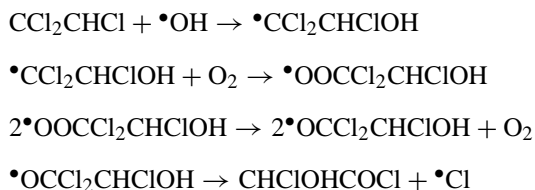
The heterogeneous photocatalytic reactions were initiated by photon irradiation as follows [21]:



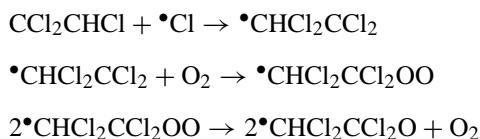
When the  $\text{TiO}_2$  surface was irradiated by photons, electron–hole pairs were produced by the excitation, which in turn led to subsequent reactions producing hydroxyl, hydroperoxyl, and oxygen radicals to react with the reactants.



Kleindienst et al. [22] studied the homogeneous reaction of TCE with OH radicals with the following mechanism:



Sanhueza et al. [23] studied the homogeneous reaction of vinyl chloride with  $\text{Cl}_2$ , which formed  $\bullet\text{Cl}$  to initiate reaction and proposed the reaction mechanism as follows:

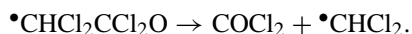


The attack on the C–H bond in TCE by  $\bullet\text{Cl}$  produced an alkyl radical, which formed a peroxy radical upon reaction with  $\text{O}_2$ . The peroxy radical reacted with another peroxy radical to produce an alkoxy radical. After the formation of the alkoxy radical, two steps were possible:

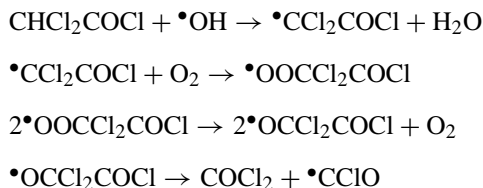
- loss of  $\bullet\text{Cl}$  to form DCAC:



- rupture of the C–C bond in the alkoxy radical to form  $\text{COCl}_2$  and dichloromethyl radical:



Since products such as DCAC and phosgene were also detected in this investigation, as well as the species change as in Fig. 5, a similar mechanism for the heterogeneous photocatalytic reaction might exist. That is,  $\bullet\text{OH}$  produced in the photocatalytic reaction reacted with TCE to form  $\bullet\text{Cl}$ , and then produced DCAC or phosgene. Nimlos et al. [16] also proposed the formation of phosgene from the DCAC photocatalytic reaction:

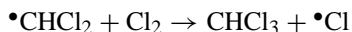


$\text{COCl}_2$  could then be further decomposed to form CO and  $\text{Cl}_2$ .

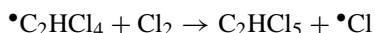
Sanhueza et al. [23] reported that TCE was converted into DCAC about 90% of the time. While in Jacoby et al.'s [11] finding for the photocatalytic reaction of DCAC and TCE, the ratio of  $\text{COCl}_2/\text{CO}$  was about two. Jacoby et al. [11], thus, concluded that another reaction path besides the formation of DCAC could exist. From the results of this study,  $\text{CHCl}_3$ ,

$C_2Cl_6$ , alcohols, esters and aldehydes were also found in addition to DCAC and phosgene. Therefore, there should be other reaction paths.

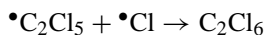
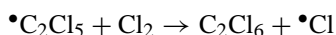
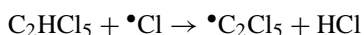
Huybrechts and Meyers [24] studied the homogeneous photoreaction of TCE with  $Cl_2$ . The  $\bullet CHCl_2$  produced from the alkoxy radicals as proposed by Sanhueza et al. [23] might react with chlorine molecules to form  $CHCl_3$ :



moreover,  $C_2HCl_5$  was formed by alkyl radicals and  $Cl_2$ :

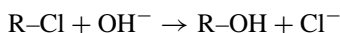


In addition, Huybrechts et al. [25] investigated the homogeneous photo-reaction of pentachloroethane, and indicated that the formation of  $\bullet C_2Cl_5$  by  $C_2HCl_5$  led to the production of  $C_2Cl_6$ :

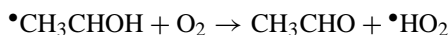
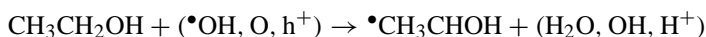


Although pentachloroethane was not identified in this study, several researchers claimed to have identified this compound [2,8,9]. The mechanism proposed by Huybrechts et al. [25] in the homogeneous reaction might be appropriate for this investigation. The formation of alkoxy and alkyl radicals during the production of DCAC and phosgene would proceed the chlorination reaction with Cl to form chloroalkanes.

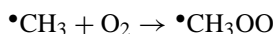
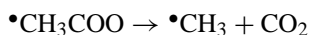
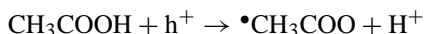
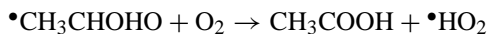
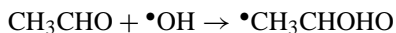
The formation of alcohols could be derived from the hydrolysis of the chloroalkanes produced above [20]:

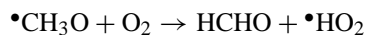
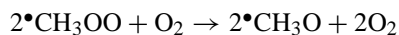


Nimlos et al. [19] studied the heterogeneous photocatalytic reaction of ethanol in the gas phase and proposed the following mechanism:



Ethanol reacted with an OH radical or electron-hole to form an ethanol free radical. The free radical then reacted with  $O_2$  to form acetaldehyde. Further, acetaldehyde reacted with  $\bullet OH$  and  $O_2$  to form acetic acid. The acetic acid then reacted with an electron-hole to form a methyl radical, which finally oxidized to form formaldehyde:





Through similar acetaldehyde reactions, formaldehyde was transformed into formic acid and finally mineralized into  $\text{CO}_2$ . In addition, small amounts of esters might be formed by the esterification reaction between the alcohols and carboxylic acids [13].

The primary mechanisms in heterogeneous photocatalytic reactions were the reactions between the reactants and free radicals. To sum up the mechanisms of the homogeneous and heterogeneous reactions mentioned above, the proposed pathways for heterogeneous photocatalysis of TCE in the gas phase are shown in Fig. 6. The initial TCE reaction

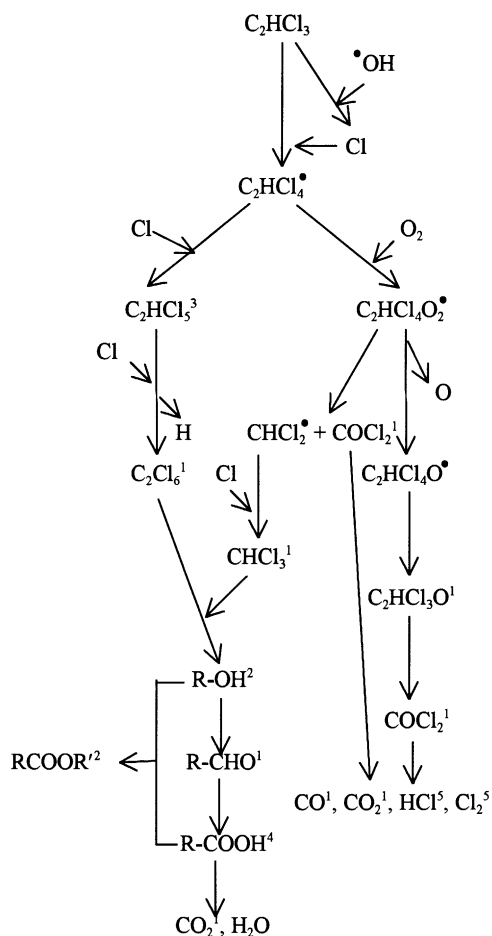


Fig. 6. The proposed pathway for the heterogeneous photocatalysis of TCE in the operation conditions of this investigation (1: detected in this investigation and literature, 2: new product detected in this investigation, 3: quoted from [2,8,9], 4: quoted from [2], 5: quoted from [8,9]).

with  $\bullet\text{OH}$  leads to the dechlorination reaction that forms  $\bullet\text{Cl}$ . The chlorine radicals further reacts with TCE to form alkyl radicals. The reaction might then proceed into two possible directions. (1) *Oxidation*: oxygen and OH radicals might participate in reactions to convert TCE into DCAC with phosgene as the major path. (2) *Chlorination*: alkyl radicals react with chlorine to form chloroalkanes. The chloroalkanes could then be hydrolyzed to form alcohols and produce the aldehydes, carboxylic acids, and esters.

#### 4. Conclusions

Through the monitoring of the reaction products, some products such as alcohols and esters that had not been mentioned in the literature were identified. Other products, including dichloroacetyl chloride, phosgene, chloroform, hexachloroethane, aldehydes, carbon monoxide and carbon dioxide were also identified as also reported in the literature.

Based on literature information, the possible reaction mechanisms for heterogeneous photocatalytic oxidation of TCE may involve a series of reactions with initial dechlorination. The major path leads to the formation of dichloroacetyl chloride and phosgene along with small portions of chlorination to form chloroalkanes. The chloroalkanes are further transformed into alcohols, aldehydes, carboxylic acids, and esters.

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