

**Summary of Ph.D. Thesis**

**Heterogeneous photocatalytic decomposition of  
chlorinated ethenes**

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## **1. Introduction**

Protection of the air, water resources and the soil is a complex problem, in which legislation, environmental education, the minimizing of the emission of hazardous compounds and the removal of pollution all play a determining role. Economical biological methods can often be applied in environmental protection and in cleaning and degrading procedures. However, there are numerous biologically non-degradable environmental pollutants, and some pollutants are toxic for the microorganisms applied for their destruction. On the other hand, certain technologies produce hazardous materials (e.g. trihalomethanes). The search for the solution of such problems has led to the development of efficient chemical technologies, which are energy-economic and do not produce hazardous materials. Advanced Oxidation Processes (AOPs) are widely applied to “burn” air or water contaminants at room temperature by using the oxygen of the air via the production of reactive oxygen-containing radicals. Heterogeneous photocatalysis is one kind of AOP, in which the degradation of pollutants occurs on the surface of an irradiated semiconductor. Heterogeneous photocatalytic processes have been investigated very extensively as indicated by thousands of publication during the last two decades. In spite of the large interest, however, many questions remain open, e.g. the details of chemical mechanisms and the reaction kinetic behavior of various systems. A knowledge of these problems is essential in the design and operation of cleaning technologies based on this method.

## **2. Aims**

The heterogeneous photocatalytic degradation of chlorinated organic compounds on  $\text{TiO}_2$  catalyst is the study of many research groups. In spite of very intensive research and publication activity, full details of the chemical mechanism and reaction kinetic behavior involved in these heterogeneous photocatalytic processes not available either in the gas phase or in the liquid phase. Most research has the aim of finding the optimal reaction conditions; the total decomposition of chlorinated ethenes can be attained, but the reaction mechanism remains unclear.

We have studied the effects of the concentrations of oxygen, water and substrates on the photocatalytic decompositions of perchloroethene (PCE) and trichloroethene (TCE). Consideration of the distributions of intermediates and products, the kinetic characteristics of the decomposition and the previous results allowed us to propose detailed chemical mechanisms for the catalytic transformations of TCE and PCE.

### 3. Methods

All chemicals used in the experiments were of analytical grade. Suspensions were made from titanium dioxide, as photocatalyst (Sigma Aldrich, anatase content >99%), and places it on a glass support with a surface area of 17 cm<sup>2</sup>. After drying at room temperature, the weight of the TiO<sub>2</sub> layer was 0.1 g. Pretreatment of the catalyst was carried out in the *in situ* IR reactor cell at 200 °C for 1.5 h under vacuum. This pretreatment was repeated before each measurement.

On application to a vacuum system, the previously evacuated reactor cell were filled with the PCE or TCE and oxygen and/or nitrogen and water vapor-containing gas mixtures, in pre-planned compositions. PCE and TCE (Sigma Aldrich, >99%) were used without further purification. The reactions were carried out in an *in situ* photocatalytic reactor, at atmospheric pressure and room temperature, with 1·10<sup>-4</sup>- 1·10<sup>-3</sup> M PCE or TCE in oxygen gas. In the investigation of the effect of the oxygen concentration, nitrogen was applied as diluting gas. Irradiation of the gas mixtures began 1 h after they had been transferred to the reactor. A mercury vapor lamp (Philips, 4W, type F4 T5/BLB) with maximum emission at 365 nm measured in chemical actinometry was used. The radiation intensity was about 7.2·10<sup>-9</sup> molphotons/cm<sup>2</sup>/s.

Analysis of the gas phase was performed by taking gas-phase IR spectra with a BioRad FTS60A IR spectrometer and a DTGS detector with 2 cm<sup>-1</sup> resolution; data collected over the range 400-4000 cm<sup>-1</sup> at a rate of 5 kHz. Each spectrum was recorded by averaging 64 scans. Qualitative and quantitative analyses were carried out by the measurement of absorbances and integration of the areas of peaks (calibration curves).

### 4. Results

#### 4.1. Adsorption of substrates and decomposition products on the catalyst surface

In measurements of the adsorption PCE and TCE and their degradation products, the following results were obtained.

1) The adsorption of PCE in the absence of water vapor can be characterized by a Langmuir model. In the presence of water (3.5·10<sup>-4</sup> mol/dm<sup>3</sup>) the amount of PCE adsorbed at low concentration ( $c_g < 3 \cdot 10^{-4}$  mol/dm<sup>3</sup>) was less than that measured under dry conditions, in consequence of the competitive adsorption of water and substrate. In gas mixtures containing

more PCE and water, the amount of PCE adsorbed was higher than that measured under dry conditions, because of the multilayer (BET-type) adsorption.

The adsorption of TCE under dry conditions can also be characterized by the Langmuir model. The threshold value of the amount of TCE adsorbed was about twice that measured in the case of PCE. Water vapor ( $3.5 \cdot 10^{-4}$  mol/dm<sup>3</sup>) had no influence on the amount of TCE adsorbed at its lower concentrations ( $c_g < 9 \cdot 10^{-4}$  mol/dm<sup>3</sup>), but at higher TCE concentrations water vapor enhanced the amount of TCE adsorbed.

The adsorption of trichloroacetyl chloride (TCAC) and dichloroacetyl chloride (DCAC) formed during the photocatalytic degradation of PCE and TCE was very vigorous; about 75% of the added concentration ( $1.1 \cdot 10^{-4}$  mol/dm<sup>3</sup>) was adsorbed on the catalyst surface.

The amounts of COCl<sub>2</sub> and CO<sub>2</sub> adsorbed were low; about 1-5% of the added materials were adsorbed on the catalyst surface.

#### **4.2. The photocatalytic degradation of PCE**

1) No transformation was measured in the absence of irradiated semiconductor and oxygen. The reproducibility measurement justified that the activity of the photocatalyst persist after more than 10 measurements.

TCAC was produced as intermediate, and COCl<sub>2</sub> and CO<sub>2</sub> as final products during the photocatalytic degradation of PCE. The further degradation of TCAC produced COCl<sub>2</sub> and CO<sub>2</sub>. COCl<sub>2</sub> is formed mostly in the first stage of PCE degradation (when PCE is present in the gas phase); on further irradiation (when the degradation of TCAC is significant), its production rate is lower. The rate of production of CO<sub>2</sub> is monotonous. The degradation of PCE begins with an induction period. The adsorption processes do not have a significant influence on the induction period.

2) The rate of degradation of PCE and the rate of accumulation of products were practically independent of the initial concentration of PCE after the induction period. The concentrations of TCAC and COCl<sub>2</sub> formed increased on increase of the initial concentration of PCE; the amount of CO<sub>2</sub> was enhanced only slightly in this stage of PCE decomposition.

The rate of degradation of PCE increased with increasing initial oxygen concentration up to a certain level (up to the oxygen concentration in air). The decomposition rates of the investigated substrate were practically the same in pure oxygen and in air. This finding is of importance in environmental applications.

3) The addition of water vapor to the initial gas mixture decreased the rate of degradation of PCE. There was a good correlation between the amount of PCE adsorbed and the rate of

degradation of PCE in the presence of water vapor. On increase of the concentration of water in the gas phase, the measured amounts of TCAC and  $\text{COCl}_2$  in the gas phase decreased, because of their hydrolysis. In the presence of a very high concentration of water ( $7.1 \cdot 10^{-4} \text{ mol/dm}^3$ ) trichloroacetic acid (TCAA) was formed, in the same concentration as the TCAC formed in the gas mixtures under dry conditions.

### 4.3. The photocatalytic degradation of TCE

1) The rate of degradation of TCE and the rate of accumulation of products were practically independent of the initial concentration of TCE after the induction period. The concentrations of DCAC and  $\text{COCl}_2$  formed increased on increase of the initial concentration of TCE; the amount of  $\text{CO}_2$  was enhanced only slightly in this stage of TCE decomposition.

2) The initial concentration of TCE had no significant effect on its degradation rate and has no effect on the rate of accumulation of DCAC,  $\text{COCl}_2$  and CO.

Elevation of the oxygen concentration up to  $c=7.58 \cdot 10^{-3} \text{ mol/dm}^3$  increased the rate of degradation of TCE. The rate of decomposition of TCE was almost same in air and in pure oxygen. At lower oxygen concentrations, small amounts of  $\text{C}_2\text{HCl}_5$  and  $\text{CHCl}_3$  was detected. The relative amounts of oxygen-containing products decreased on decrease of the initial oxygen content in the gas mixture. Addition of water vapor had no significant effect on the rate of degradation of TCE. In gas mixtures containing water vapor, the amounts of DCAC and  $\text{COCl}_2$  formed were lower, because of their hydrolysis.

### 4.4. Proposed reaction mechanism

It was established that the intermediates TCAC and DCAC initiate the degradation of PCE or TCE. Based on the results mentioned above, previous results and chemical evidence, reaction mechanisms are proposed for the decompositions of PCE (Fig. 1) and TCE (Fig. 2). The main features of the proposed reaction mechanisms are as follows:

1) Direct charge transfer occurs on the surface of the semiconductor from the photogenerated electrons and holes to the adsorbed molecules (PCE/TCE and oxygen). The radical-ions formed in these charge-transfer steps react with each other, followed by rearrangement of the molecules, on addition of the oxygen molecule, and intermediates and products are formed by

decomposition of the oxygen-containing radicals. The intermediates TCAC or DCAC produced participate in the degradation chain, and accelerate the decomposition of PCE or TCE.

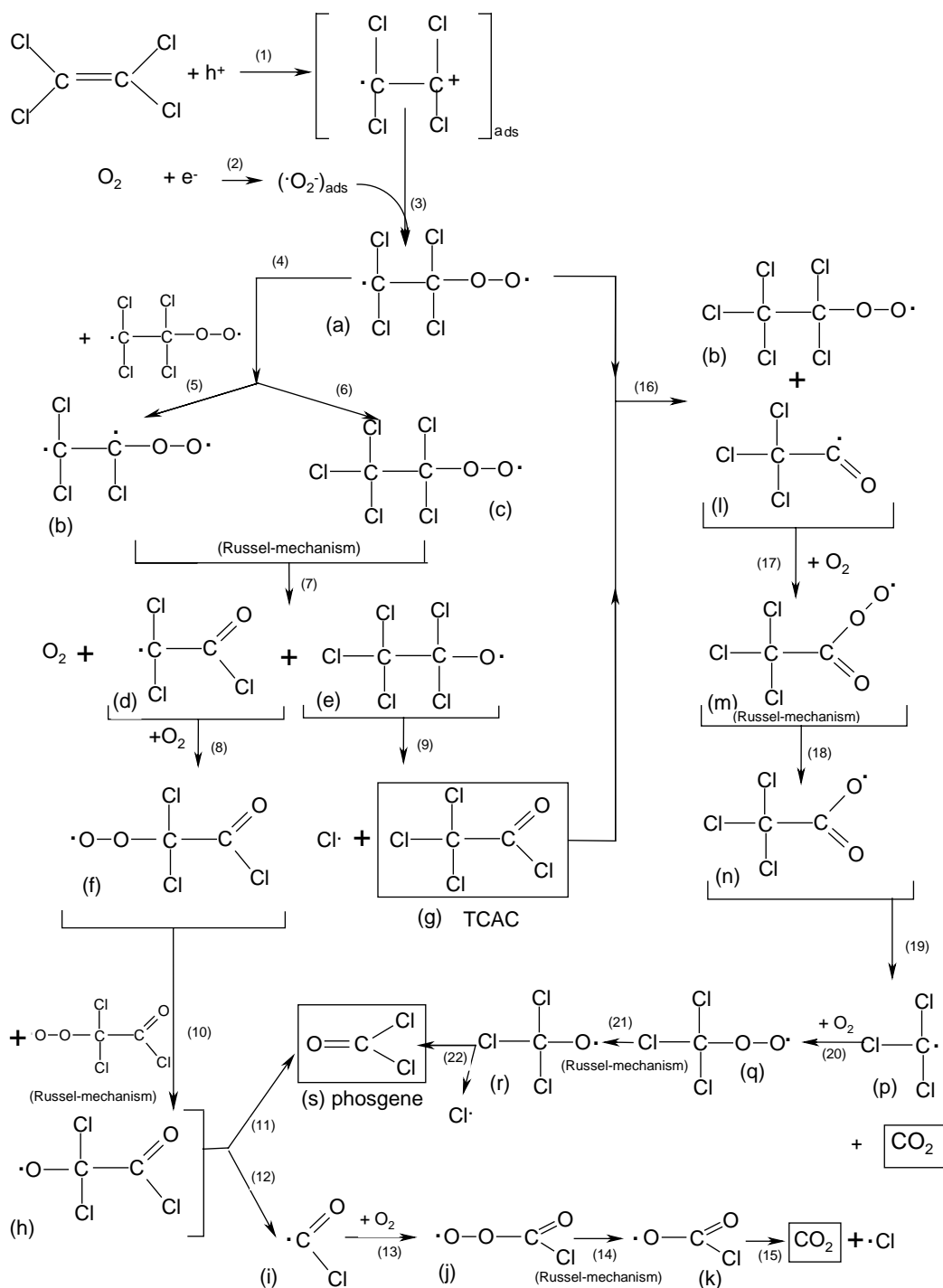


Fig. 1. Proposed reaction mechanism for degradation of PCE

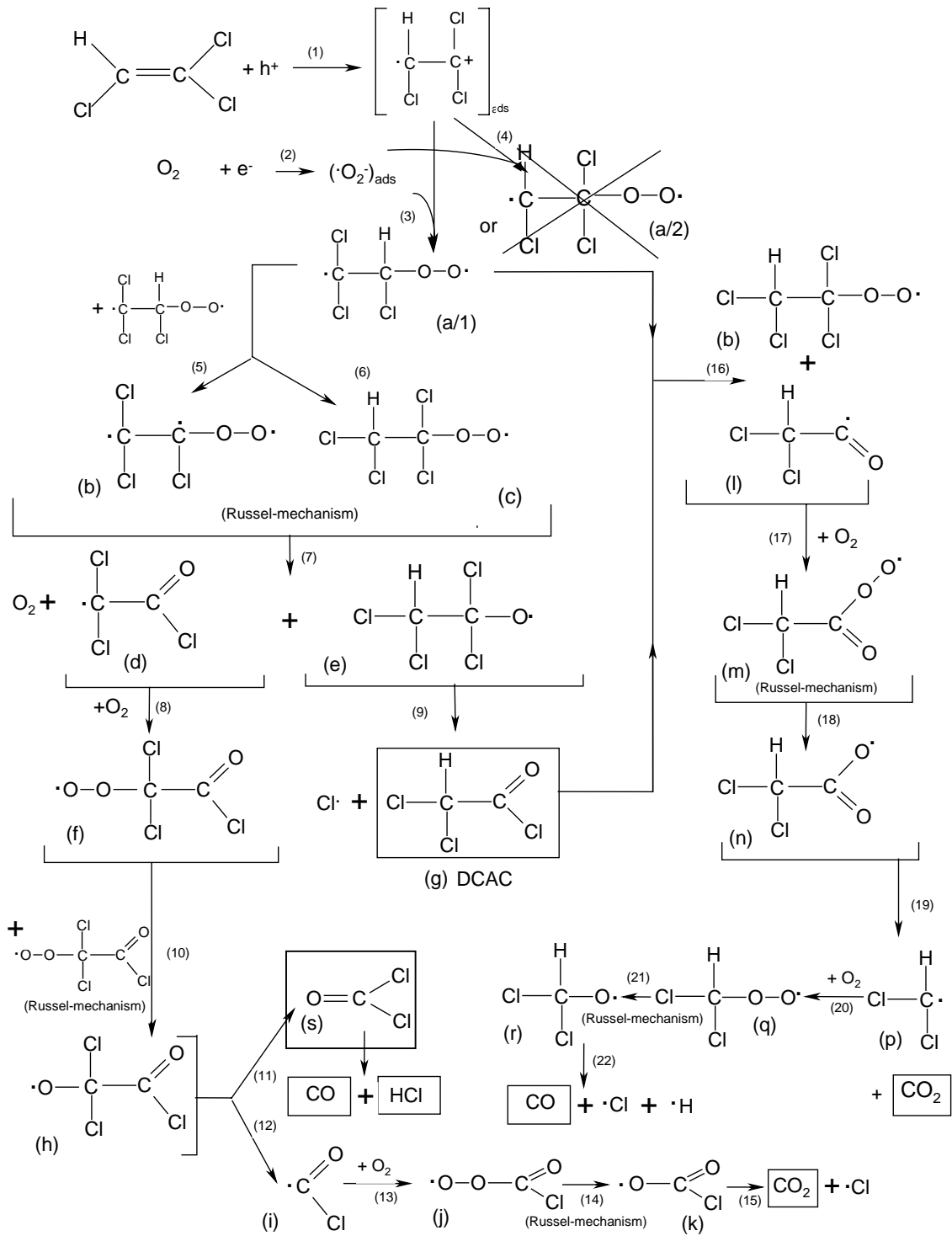


Fig. 2. Proposed reaction mechanism for degradation of TCE

2) The differences between the two reaction mechanisms are caused by the special behavior of the superoxy radical-ion, formed in the combinations (reactions 3 and 4) of the species formed in hole (1) and electron (2) trapping; in this way H-containing radicals are formed, which can yield CO via dichloromethoxy radical formation.

## 5. Publications

### Papers

1) **Márta Hegedűs**, András Dombi, Imre Kiricsi

Photocatalytic decomposition of tetrachloroethylene in the gas phase with titanium dioxide as catalyst

*React. Kinet. Catal. Lett.*, 74 (2001) 209

2) **M. Hegedűs**, A. Dombi

*Heterogeneous photocatalytic decomposition of chlorinated ethenes as indoor air pollutants*

Proceedings of International Conference on Ozone. Ozone: a Clean Source for Activated-Oxygen Oxidations and Disinfections. Wasser Berlin 2003, pp 369-381

7-11 April 2003, Berlin, Germany

3) **Márta Hegedűs**, András Dombi

Comparative study of heterogeneous photocatalytic decomposition of tetrachloroethene and trichloroethene in the gas phase

*Applied Catalysis A, General*, 271 (2004) 177

4) **Márta Hegedűs**, András Dombi

Gas-phase heterogeneous photocatalytic oxidation of chlorinated ethenes over titanium dioxide: perchloroethene

*Applied Catalysis B, Environmental*, 53 (2004) 141

5) **Márta Hegedűs**, András Dombi

Gas-phase heterogeneous photocatalytic oxidation of chlorinated ethenes over titanium dioxide: trichloroethene

*Applied Catalysis B, Environmental*, (submitted for publication)

### Presentations at conferences

1) **M. Hegedűs**, Z. A. Fekete, I. Hannus, A. Dombi

*Decomposition of halogenated hydrocarbons in gas-phase heterogeneous photocatalysis*

5th Pannonian International Symposium on Catalysis, Kazimierz Dolny, Poland, 2000



2) **Hegedűs M., Kónya Z.,** Dombi A. Hannus I., Kiricsi I.

*Heterogén fotokatalitikus reakciók az atmoszférában (Heterogeneous photocatalytic reactions in the atmosphere)*

V. Magyar Aeroszol Konferencia, Szeged, 2000.

3) **Hegedűs M.,** Dombi A.

*Tetraklór-etilén gázfázisú lebontása heterogén fotokatalízissel (Decomposition of tetrachlorethene by application of heterogeneous photocatalysis)*

VII. Nemzetközi Környezetvédelmi Szakmai Diákkonferencia, Mezőtúr, 2001

4) **Hegedűs M.,** Dombi A.

*Gázfázisú szennyezők lebontása heterogén fotokatalízissel (Decomposition of gaseous air pollutants by application of heterogeneous photocatalysis)*

XXIV. Kémiai Előadói Napok, Szeged, 2001

5) **M. Hegedűs,** A. Dombi

*Decomposition of halogenated hydrocarbons in gas phase over TiO<sub>2</sub> photocatalyst*

ISIRR 2002, Novi Sad, Yugoslavia, 2002

6) **M. Hegedűs,** A. Dombi

*Decomposition of chlorinated organic compounds in the air using titanium dioxide as photocatalyst*

CERECO 2003 – The 4th International Conference on Carpathian Euroregion Ecology, Miskolc-Tapolca, 2003

7) **M. Hegedűs,** I. Ilisz, A. Dombi

*Study of the photocatalytic decomposition of perchloro- and trichloroethenes in gas phase*

3rd European Meeting on Solar Photocatalysis: Environmental Applications (SPEA3), Barcelona, Spain, 2004.