

A Proposed Mechanism of Photocatalytic Oxidation of Trichloroethylene in Gas Phase

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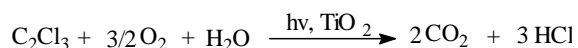
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Abstract: GC/MS has been used to identify gas phase products and intermediates formed during the gas phase photocatalytic oxidation of trichloroethylene (TCE) on TiO₂ with low BET surface area. A new byproduct, oxalyl chloride (ClCOCOCl) was detected together with other byproducts such as COCl₂, CHCl₃, DCAC and C₂HCl₅. Firstly the method of perturbation on the reaction system was conducted. Very little amount of water was carried into the feed gas and subsequent changes were observed. The discussion based on the product distribution changes led to a postulated mechanism consisting of two stages.

Keywords: Photocatalytic oxidation, trichloroethylene, product distribution.

Heterogeneous photocatalytic oxidation (PCO) using TiO₂ is attracting more and more research groups with great promise as a simple and inexpensive method to mineralize volatile organic compounds (VOCs)¹. There has been a great deal of interest in the photocatalytic oxidation of TCE due to its role as a significant environmental contaminant²⁻⁶.

In the ideal PCO reaction, TCE is completely mineralized into CO₂ and HCl:



Unfortunately the complete mineralization of TCE is often not realized as other byproducts have been identified in the reactions, for example, phosgene (COCl₂) and dichloroacetyl chloride (DCAC). However, byproducts play an important role in the study of PCO reaction. A great number of studies have proposed the mechanism of photocatalytic oxidation of TCE in gas phase by identifying the byproducts of the reaction. Many analytical methods, such as GC, GC/MS, FTIR, *in situ* Solid State NMR or trapping agents, have been used to detect the reaction intermediates.

Presently, detailed mechanism of the PCO processes at TiO₂ surface remains elusive, particularly regarding the initial steps involved in the radical reactions, which may involve one or more of the following radical species: O₂^{·-}, ·OH and Cl·. Identification of monochloroacetic acid (MCAA) as an intermediate led to the postulation that ·OH radical acted as the initiating oxidizing agent². Nimols *et al*³ observed the formation of dichloroacetyl chloride (DCAC) with high quantum rate (0.5-0.8), which resulted in the adoption of Cl· radical initiated chain reaction mechanism. Fan *et al*⁴ added isotopic

labeled water into the reaction system, but ^{18}O was not found in the products of the reaction. A mechanism involving oxygen radical was postulated to explain this outcome. Also different mechanisms have been proposed by other research groups⁵⁻⁶.

Experimental and Results

In this study, GC/MS was used to identify gas phase products and intermediates. TCE with low concentration (about 600 ppm) was degraded in a fixed-bed reactor under the illumination of UV light with the wavelength of 254 nm. Commercial titanium dioxide (mainly anatase) was reduced by $89\% \text{N}_2 + 11\% \text{H}_2$ at 673 K for 2 hours to form a catalyst with BET surface area of $6.5 \text{ m}^2/\text{g}$.

Before the PCO reaction, feed gas flowed through the reactor in dark until the concentration of TCE in the outlet gas reached a constant level. The outlet gas was carried to on-line GC with a SE-30 column and a Flame Ionization Detector for detection of intermediates, sometimes directly to GC/MS. Also Ion-selective Electrode analysis (ISE) was adopted to detect the Cl^- anion adsorbed by water. PCO reaction was carried under the same condition for several runs at room temperature, with the flow rate of feed gas ranging from 21ml/min to 120ml/min.

CO_2 , CO , HCl , COCl_2 , DCAC, CHCl_3 , C_2HCl_5 and trace ClCOCOC were identified. Chlorine also was detected by starch iodide. The product distribution changes over time after Run 10 were indicated in **Figure 1**. Normalized concentration of TCE and main byproducts was used for comparison (the concentration of C_2HCl_5 multiplied by 1/4).

Figure 1. Product Distribution over Time (Run 10)

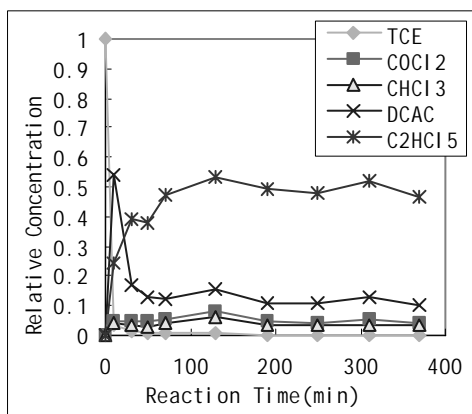
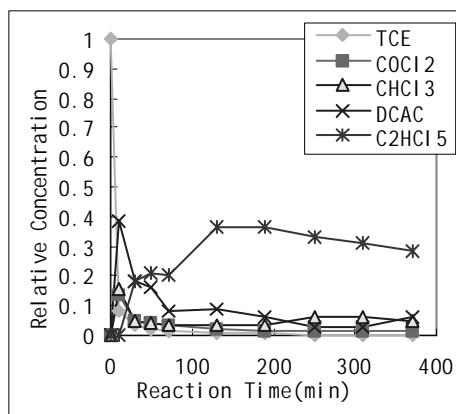


Figure 2. Product Distribution over Time after Introduction of Water (Run 12)



Within 10 minutes TCE's conversion rose to 96.7%. 40 minutes later it was above 99%. While concentration of DCAC climbed up and then decreased quickly, concentration of C_2HCl_5 went up and reached the maximum level after 130 minutes. COCl_2 and CHCl_3 existed persistently with low concentration for at least 6 hours.

Before Run 12, a method of perturbation was conducted. Very little amount of

water was carried into the system. **Figure 2** described the changes of product distribution during Run 12. In the first 10 minutes, concentration of DCAC, COCl_2 and CHCl_3 reached the maximum level. Then they declined rapidly. During this time the concentration of C_2HCl_5 remained very low. Another remarkable change was that both the maximum concentration of DCAC and of C_2HCl_5 were lower than those in **Figure 1**.

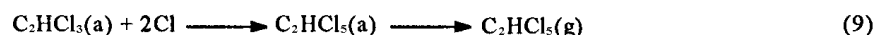
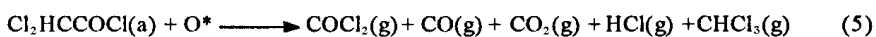
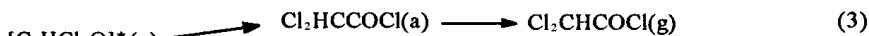
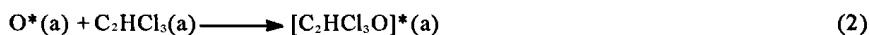
Discussion

Together with the detection of ClCOCOCl , a newly reported intermediate, the study above led to the following proposed mechanism involving oxygen and $\text{Cl}\cdot$ radical in different stages of the reaction process.

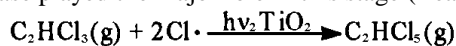
In the first stage might happen the excitation of oxygen adsorbed by the catalyst (Reaction 1, (a) means adsorbed species).



Then the reactive oxygen species (maybe O_2^- or other forms) attack the double bond of TCE, resulting in the formation of DCAC (Reaction 3, (g) means species in gas phase) or the breakage of the double bond (Reaction 4).



With the accumulation of the adsorbed products, the catalyst could adsorb less TCE (TPD experiment confirmed this opinion) and active sites for O_2 also were partly occupied. The next stage of the reaction happened mainly in the gas phase other than on the surface of the catalyst. Products formed in Reaction 6-9 were fairly the same products observed in the homogeneous gas phase PCO of TCE⁷. It was postulated that $\text{Cl}\cdot$ radical in gas phase played the major role in this stage (Reaction 10).



One source of $\text{Cl}\cdot$ radical might be the direct oxidation of Cl^- anion, which could result from the complete mineralization of TCE³.

Figure 2 confirmed the proposed mechanism above. It was concluded that water could enhance the photoadsorption of oxygen and help to scavenge the adsorbed products on the surface⁸. Difference between the product distribution changes in **Figure 1** and those in **Figure 2** could hence be reasonably explained: (i) In the first 10 minutes COCl_2 and CHCl_3 with higher concentration were observed, which were products of Reactions 1-6 involving the active oxygen species. (ii) The maximum

concentration of DCAC in **Figure 2** was lower than that in **Figure 1** due to Reaction 5 when given more amount of oxygen. (iii) The low concentration of C_2HCl_5 during the first ten minutes might attribute to the inhibition of formation of $Cl\cdot$ radical by water⁹. At the same time Chlorine in the outlet gas couldn't be detected by starch iodide. Also the mineralization rate of TCE and the concentration of Cl^- anion in the outlet gas increased remarkably.

Ten minutes later, C_2HCl_5 increased quickly although the maximum concentration was still lower than that in **Figure 1**. Chlorine also could be detected by starch iodide. These changes mean the recovery of Reaction 10, which only happened markedly after the exhaustion of water. The time when the little water was exhausted was hard to describe exactly.

Experiment using feed gas with remarkable amount of water was also carried in the same condition. The outcome was not discussed here because the mechanism with water in reaction system might be different. Anderson's work¹⁰ led to the conclusion that large BET surface area was necessary for the efficient degradation of TCE. A catalyst with surface area of $86.2m^2/g$ was adopted in our experiment. Very little amount of byproducts such as DCAC, C_2HCl_5 , $COCl_2$ and $CHCl_3$ were detected. Whether the surface area is a factor influencing the mechanism is still elusive. In the explanation of this mechanism by **Figure 2**, $\cdot OH$ radical was not mentioned as an initiating species, partly because byproducts such as monochloroacetic acid (MCAA) and dichloroacetic acid (DCAA) usually formed in the $\cdot OH$ -initiated mechanism were never detected in our experiment. But the probability still exists that $\cdot OH$ radical was involved in the reaction after the introduction of water. Further investigation is carrying on in our lab.

Acknowledgments

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