Photocatalytic oxidation of trichloroethylene in humidified atmosphere

Placidus B. Amama*, Kiminori Itoh, Masayuki Murabayashi

*Institute of Environmental Science and Technology, Yokohama National University,
79-9 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*

Abstract

Gas-phase UV-assisted catalytic oxidation of trichloroethylene (TCE) has been studied over TiO_2 glass fiber cloth (TiO_2-GFC) in a cylindrical batch reactor at different humidity levels. The apparent intermediates and products were determined by Fourier transform infrared (FTIR) spectroscopy. The effect of humidity on the photochemical oxidation reaction of TCE has also been studied in order to further elucidate the inhibitive effect of water vapor during TCE photocatalytic oxidation. After Cl atoms are generated from a possible attack of moisture-derived hydroxyl radicals on TCE, competitive adsorption between TCE and water molecules did not totally account for the reaction inhibition in humidified atmosphere. The suppression of the Cl atom-propagated chain reaction has been postulated as an additional reason for the reaction inhibition. Humidification increased the possibility of dichloroacetyl chloride (DCAC) and phosgene hydrolysis and the yield of CO_2 increased monotonically. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Trichloroethylene; Humidity; TiO_2; Advanced oxidation technique

1. Introduction

The widespread presence of volatile chlorinated organic compounds (VOCs) in the environment poses a serious environmental challenge because most of these VOCs are carcinogenic, toxic and extremely persistent in the environment. Heterogeneous photocatalysis has been demonstrated as an efficient abatement technology for the mineralization of these VOCs [1–8]. Practical photocatalytic oxidation of these undesired chlorinated organic pollutants in air usually occurs in the presence of water vapor. It is therefore necessary to elucidate its effect on photocatalytic oxidation reactions in order to enhance the application of heterogeneous photocatalysis to air treatment in habitable atmospheres.

The presence of water vapor has both inhibiting and activating capabilities on photocatalytic oxidation reactions of various VOCs. Ibusuki and Takeuchi [2] studied the oxidation of toluene on near UV-irradiated TiO_2 in the presence and absence of water at ambient temperature. They reported a remarkable oxidation rate increase between a relative humidity of 0 and 60%, an effect that may be due to an increase in the generation of hydroxyl radicals. Ollis and Peral [3] showed that the presence of 5% of water in the feed stream of 1-butanol, butyraldehyde, formaldehyde and *m*-xylene during photocatalytic oxidation influenced the reaction rates differently. Dibble and Raupp [4] investigated the intrinsic reaction rate dependence

* Corresponding author. Tel.: +81-45-339-4369;
fax: +81-45-339-4373.
E-mail address: pcd@kan.ynu.ac.jp (P.B. Amama).

of TCE photocatalytic oxidation on water vapor and showed that initial reaction rates are lowered in the presence of water vapor. They also reported that water is required to preserve photocatalytic activity and in the absence of water vapor, the photocatalytic oxidation rate of TCE is seriously retarded and total mineralization to CO_2 does not occur. Kim et al. [5] investigated the effect of water vapor on TCE photocatalytic oxidation and reported an inhibition of the reaction at high humidity using TiO_2 thin films prepared by sol–gel technique. Fu et al. [6] reported that the photocatalytic oxidation of ethylene is inhibited in the presence of water vapor.

In this study, TCE was chosen as the probe contaminant because TCE vapor is of great environmental concern, as it represents one of the most commonly detected pollutants in hazardous waste sites and landfills in many countries. The generally postulated stoichiometric chemical equation for TCE photocatalytic oxidation is given as:

$$Cl_2C{=}CHCl + \tfrac{3}{2}O_2 + H_2O \underset{h\nu\,(E>3.2\,\text{eV})}{\overset{TiO_2}{\rightarrow}} 2CO_2 + 3HCl$$

(1)
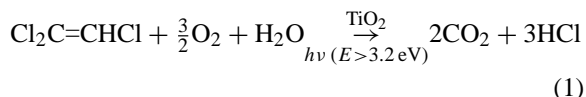
Reaction 1 underlines the importance of adsorbed water or surface-bound hydroxyl groups present on the surface of TiO_2. The complete mineralization of TCE to innocuous products (CO_2 and H_2O) is rarely achieved because of the formation of chlorinated partial oxidation products. Dichloroacetyl chloride (DCAC) and phosgene are the predominant intermediate and byproduct formed during this reaction [7,8]. These compounds are known to be highly toxic and may cause secondary pollution if complete mineralization does not occur. Thus, their fate during the photocatalytic oxidation process is of immense importance.

A gas-phase mechanism proposed by Nimlos et al. [7] for TCE photocatalytic oxidation in the presence of water vapor involves a hydroxyl radical attack on TCE molecules to form Cl atoms. These Cl atoms formed attack more TCE molecules to form intermediates and products and also forming additional Cl atoms in the process, which continue to attack TCE molecules. A large acceleration of TCE photocatalytic oxidation reaction in the repeated reaction containing products of the same reaction was observed by

Murabayashi et al. [9] and they rationalized this increase in reaction rate based on the behavior of the photochemical reaction. The chain reactions occurring on the surface of TiO_2 are considered to be responsible for the high reaction rates observed in TCE photocatalytic oxidation [8,9]. Therefore, the behavior of this reaction in humidified atmosphere is of immense significance.

In this study, the photocatalytic oxidation of TCE in gas phase at different humidity levels was carried out. We have rationalized the inhibitive effect of water vapor by taking the behavior of the photochemical reaction in humidified atmosphere into consideration. Results of the effect of water vapor on the concentrations of DCAC, phosgene and CO_2 formed during the photocatalytic oxidation reaction have been presented.

2. Experimental

2.1. Materials

Trichloroethylene (analytical grade) with stated purity of over 99% was purchased from Junsei Chemical Co. Ltd., Japan, and was used without further purification. The photocatalyst was TiO_2 coated on the surface of glass fiber cloth (TiO_2-GFC) by modified sol–gel process (dimension = 5 cm × 2.75 cm, amount of TiO_2 = 4.8 mg/cm^2). This form of photocatalyst was preferred because of its high photocatalytic activity and the ease with which it can be used in gas phase. It was kindly supplied by Nippon Muki Co. Ltd., Japan, and used as received. Ultra-high purity nitrogen gas (99.99%) used for purging FTIR was purchased from Nihon Sanso. Chlorine gas with 99% purity was purchased from Matheson Gas Products and also used as supplied. The water used in obtaining the respective humidity levels was deionized and doubly distilled by an Aquarius Automatic Water Distillation system (Advantec GSR 200).

2.2. Batch reactor and light source

The tubular batch reactor used for this investigation was specially constructed and designed for the measurement of the concentration of the reactant and product by FTIR. It consisted of a cylindrical Pyrex

glass (11 cm long and 40 mm in inner diameter) and equipped with silicon wafers at both ends to serve as IR windows. An injection port was constructed on the side of the reactor to allow the introduction of dry air and the injection of TCE and distilled water. Illumination was carried out by eight symmetrically arranged fluorescent black lights (Toshiba FL20S.BLB, 160 W output, intensity = 3.2 mW/cm^2 positioned 7 cm from the batch reactor) and emitting predominantly 320–440 nm light, which fits in the TiO$_2$ absorption spectrum. The batch reactor and fluorescent lamps were placed in a cylindrical metallic container (60 cm long and 35 cm in diameter) with fans at both ends to minimize the effect of heating caused by illumination. In all experiments, the temperature of the room was maintained at 298 K and the temperature gradient within the batch reactor was insignificant (less than $\pm 1°$C).

2.3. Procedures and analysis

The TiO$_2$-GFC was placed in the batch reactor and the atmosphere inside was replaced with dry air through the injection port and sealed with a rubber septum. The specified humidity levels were established by injecting the desired amount of deionized water through the sample port into the batch reactor using a microliter syringe. After about 15 min, a definite amount of TCE corresponding to a concentration of ca. 1410 ppmv was also injected into the batch reactor and was given time to evaporate and mix. Qualitative and quantitative analyses of TCE, DCAC, phosgene, and CO$_2$ were carried out using a high purity dry-nitrogen purged Perkin-Elmer Spectrum GX FTIR System after successive exposures of known duration to UV-illumination. The FTIR was equipped with a deuterated triglycerine sulfate (DTGS) detector. The spectra shown here were recorded by one scan at a resolution of 4 cm^{-1}, the data collection taking 8 s. The amount of TCE adsorbed was obtained by determining the average concentration of TCE in the batch reactor free of UV-illumination in the absence and presence of TiO$_2$-GFC. The difference between the two concentrations was assumed to be the amount of TCE adsorbed on TiO$_2$-GFC. The photochemical oxidation reactions were carried out under similar experimental conditions by injecting 12.28 ppmv of Cl$_2$ gas in the absence of TiO$_2$-GFC.

3. Results and discussion

3.1. Infrared spectra associated with TCE photocatalytic oxidation

The concentrations of TCE and the product species present were determined from their recorded infrared band intensities: TCE (945.6 cm^{-1}), DCAC (1076 cm^{-1}), phosgene (1783 cm^{-1}), and CO$_2$ (2346 cm^{-1}). Fig. 1 shows the comparison between the infrared spectra associated with TCE photocatalytic oxidation after 20 min at 0 and 100% relative humidity. In Fig. 1a, a typical infrared spectrum of standard TCE before photocatalytic oxidation reaction at 0 and 100% relative humidity is shown. After few minutes of illumination (<4 min of illumination for all humidity levels studied) the spectral properties of TCE disappeared. DCAC, phosgene and CO$_2$ peaks were observed. In Fig. 1b and c, the infrared spectra associated with TCE photocatalytic oxidation reactions after 20 min at 0 and 100% relative humidity are shown, respectively. The peak of CO$_2$ increased with humidity and the highest production of CO$_2$ after 20 min was observed at 100% relative humidity. The peak of DCAC was visible at the initial stage of UV-illumination (<10 min of illumination for all levels of humidity). Continued illumination led to an increase in the peak of phosgene and the disappearance of that of DCAC. The concentrations of DCAC and phosgene peaked
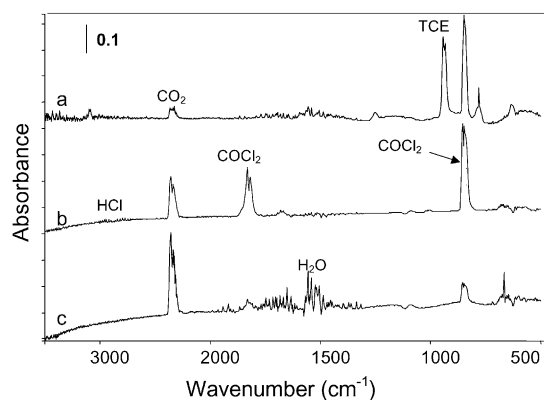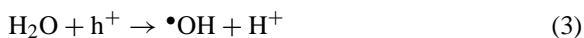

Fig. 1. Gas-phase infrared spectra associated with TCE photocatalytic oxidation reaction at 298 K: (a) before UV-illumination at 0 or 100% relative humidity; (b) after 20 min of UV-illumination at 0% relative humidity; (c) after 20 min of UV-illumination at 100% relative humidity.
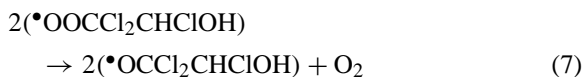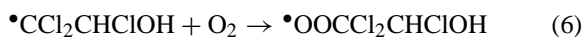
faster at lower humidity than at higher humidity. The peak of HCl became slightly visible after prolonged period (>10 min) of UV-illumination.
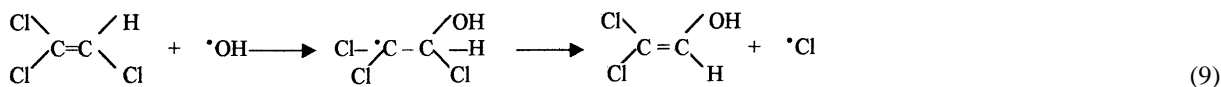
3.2. Mechanism of TCE photocatalytic oxidation

The formation of hydroxyl radicals on the surface of TiO$_2$ in the presence of water vapor due to hydrolysis has been well established [10–12]. Reactions 3 and 4 show two different reaction paths of hydroxyl radical formation after the band gap photoexcitation of TiO$_2$ with UV-light, which leads to the generation of electron–hole pairs shown in reaction 1. Reactions 3 and 4 involve the reaction of valence band holes (h$^+$) with adsorbed water molecules and hydroxyl ions present on the surface of TiO$_2$, respectively [13]:

$$TiO_2 + h\nu \rightarrow h_{vb}^+ + e_{cb}^- \tag{2}$$

$$H_2O + h^+ \rightarrow {}^\bullet OH + H^+ \tag{3}$$

$$OH^- + h^+ \rightarrow {}^\bullet OH \tag{4}$$

As proposed by Nimlos et al. [7], Cl atoms are the active species in TCE photocatalytic oxidation reaction. The Cl atoms are probably generated from a possible reaction involving an attack of moisture-derived hydroxyl radicals on TCE in a chain reaction as shown in reactions 5–8 [7]:

$$CCl_2CClH + {}^\bullet OH \rightarrow {}^\bullet CCl_2CHClOH \tag{5}$$

$${}^\bullet CCl_2CHClOH + O_2 \rightarrow {}^\bullet OOCCl_2CHClOH \tag{6}$$

$$2({}^\bullet OOCCl_2CHClOH)$$
$$\rightarrow 2({}^\bullet OCCl_2CHClOH) + O_2 \tag{7}$$

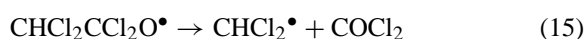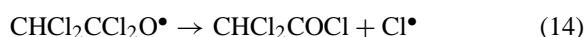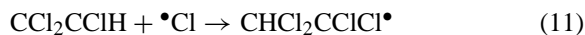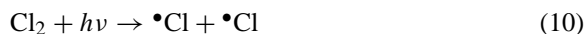$${}^\bullet OCCl_2CHClOH \rightarrow CHClOHCCl(O) + {}^\bullet Cl \tag{8}$$

It is also possible that the abstraction of Cl atom from TCE by the hydroxyl radical may have occurred according to the reaction 9.

formation of the intermediate and byproducts as shown in reactions 11–16. In the case of the photochemical reaction, Cl atoms are generated from the exposure of Cl$_2$ gas to UV-illumination as shown in reaction 10. The Cl atoms generated from this initiation step attack TCE molecules in a similar propagation step shown in reactions 11–16:

$$Cl_2 + h\nu \rightarrow {}^\bullet Cl + {}^\bullet Cl \tag{10}$$

$$CCl_2CClH + {}^\bullet Cl \rightarrow CHCl_2CClCl^\bullet \tag{11}$$

$$CHCl_2CClCl^\bullet + O_2 \rightarrow CHCl_2CCl_2OO^\bullet \tag{12}$$

$$2CHCl_2CCl_2OO^\bullet \rightarrow 2CHCl_2CCl_2O^\bullet + O_2 \tag{13}$$

$$CHCl_2CCl_2O^\bullet \rightarrow CHCl_2COCl + Cl^\bullet \tag{14}$$

$$CHCl_2CCl_2O^\bullet \rightarrow CHCl_2{}^\bullet + COCl_2 \tag{15}$$

$$CHCl_2{}^\bullet + O_2 \rightarrow CO_2 + HCl + Cl^\bullet \tag{16}$$

3.3. Inhibitive effect of water vapor

The reaction rates of photocatalytic oxidation of chlorinated hydrocarbons are far higher than the non-chlorinated hydrocarbons [8]. This is chiefly due to the fact that chlorinated hydrocarbons such as TCE are oxidized in a chain reaction propagated by Cl radicals (reactions 11–16), which progresses photochemically [7–10]. In the presence of water vapor (>25% relative humidity) the reaction rates of TCE photocatalytic oxidation reaction were greatly inhibited. The effect of humidity on TCE photocatalytic oxidation reaction is presented in Fig. 2. Previous reports [4–6,14,15] attributed this inhibitive effect of water vapor to the competitive adsorption between TCE and water vapor molecules and the blocking of active sites by hydroxyl groups accumulated on the surface of TiO$_2$. We observed that these factors were not totally responsible

$$\tag{9}$$

The Cl radical generated from the initiation step involving reactions 5–8 or reaction 9 attacks TCE and proceeds through a chain mechanism in a propagation step as proposed by Nimlos et al. [7]. This leads to the

for the reaction inhibition at high humidity because of the behavior of the photochemical reaction (Cl atom-propagated chain reaction) in humidified atmosphere.
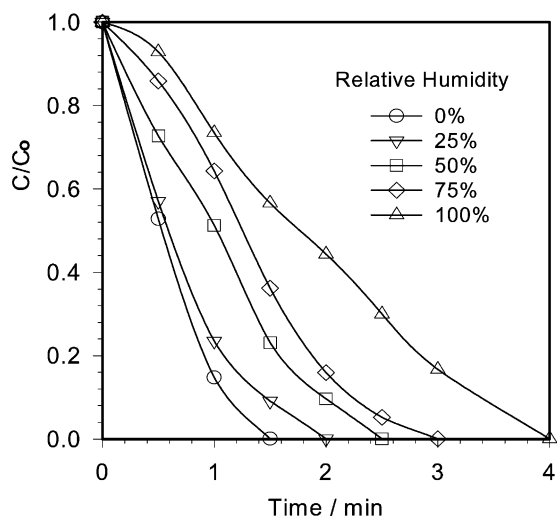
Fig. 2. Normalized concentration vs. time for TCE photocatalytic oxidation reaction at different relative humidity. TCE = 1410 ppmv, TiO$_2$-GFC = 13.75 cm^2, UV-light = 3.2 mW/cm^2, T = 298 K.

The effect of humidity on the photochemical oxidation reaction of TCE is presented in Fig. 3. This Cl atom-propagated chain reaction was greatly inhibited by water vapor. About 100% TCE conversions
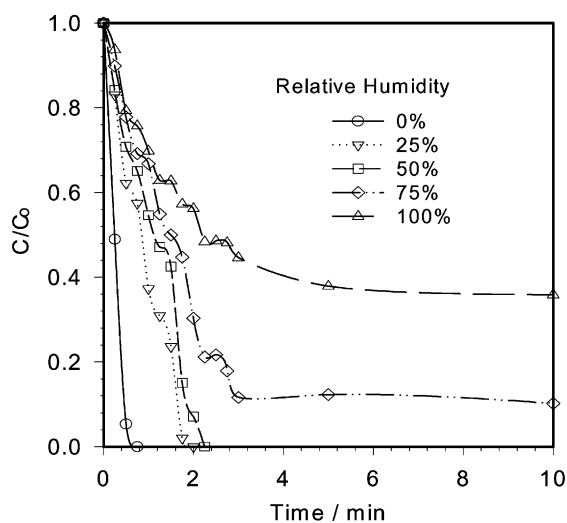
at 0% relative humidity was accomplished in 0.75 min whereas at 25 and 50% relative humidity, 100% TCE conversions were accomplished after 2 and ~2.5 min, respectively. At 75 and 100% relative humidity, 100% conversion of TCE did not take place even after 20 min. TCE conversions accomplished after 20 min at 75 and 100% relative humidity were ~88 and ~72%, respectively. This result reveals that the presence of water vapor molecules suppressed or delayed the Cl atom-propagated chain reaction that is responsible for the high reaction rates. This suppression of the photochemical reaction increased with humidity and it is capable of significantly affecting the reaction rates of the photocatalytic oxidation reaction. We postulate that this suppression is also accountable for the inhibitive effect of water vapor during TCE photocatalytic oxidation reaction at high humidity.

In Fig. 4, the effect of humidity on the initial reaction rates of the photochemical and photocatalytic oxidation reactions is presented. Although the concentrations of Cl atoms present in both reactions were not the same, the inhibition of both reactions increased with humidity and also showed similar pattern. At higher humidity (75 and 100% relative humidity), the photochemical oxidation reactions

Fig. 3. Normalized concentration vs. time for TCE photochemical oxidation reaction at different relative humidity. TCE = 1410 ppmv, Cl$_2$ = 12.28 ppmv, UV-light = 3.2 mW/cm^2, T = 298 K.
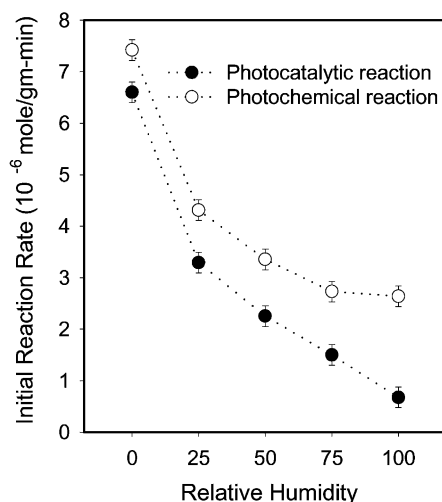

Fig. 4. Effect of humidity on the initial reaction rates of TCE photochemical and photocatalytic oxidation reactions. Same conditions as in Fig. 3.
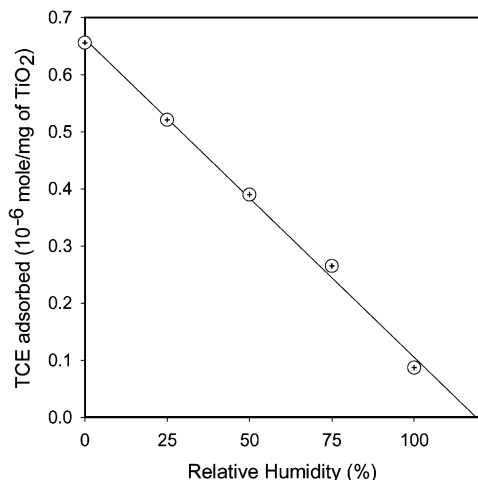
Fig. 5. Amount of TCE adsorbed as a function of humidity. Same conditions as in Fig. 3.

Fig. 6. The reaction rate of TCE photocatalytic oxidation reaction as a function of the amount of TCE adsorbed.

stopped after ∼3 min probably because the Cl atoms were completely scavenged. Also, this may have occurred because the photochemical reactions were greatly suppressed at higher humidity. Consequently, Cl atoms required to attack more TCE molecules were not readily generated from the chain reaction mechanism shown in reactions 11–16.

The effect of humidity on the adsorption of TCE on the surface of TiO_2-GFC was investigated and we found an inverse dependence of humidity on the concentration of TCE adsorbed as presented in Fig. 5. In humidified atmosphere, the adsorption of TCE on TiO_2-GFC was low suggesting the existence of a strong competitive adsorption between TCE and water molecules. The low adsorption of TCE observed at higher humidity reveals that it has a lower adsorption affinity than water and this may lower the interaction between TCE and TiO_2-GFC.

The relationship between the reaction rates (initial and average) and the humidity was investigated. As shown in Fig. 6 we observed a linear dependence of the average reaction rate (reciprocal of $t_{1/2}$ of TCE photocatalytic oxidation reaction) on the amount of TCE adsorbed while the initial reaction rate showed a non-linear dependence on the amount of TCE adsorbed. This comparison between the initial and final reaction rates is based on the hypothesis that the bulk of the reaction occurred on the surface of TiO_2-GFC.
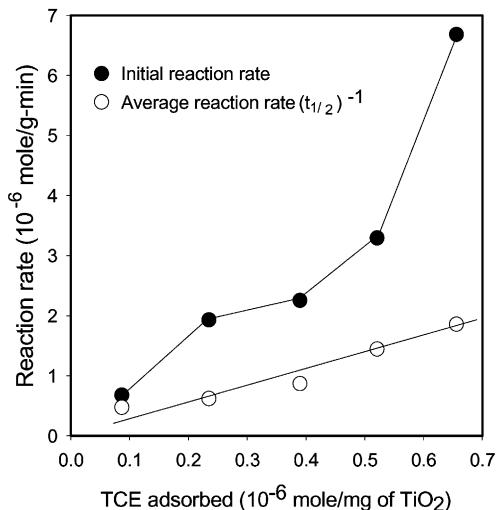
As reported by Phillips and Raupp [16], the initial process in the photocatalytic oxidation of TCE is the consumption of water molecules by the reaction. Water molecules adsorbed on the surface of TiO_2-GFC are consumed as the reaction progresses. Therefore, the initial reaction rate may reflect reactions occurring in a more humid condition. This result (Fig. 6) reveals that in the presence of substantial amount of adsorbed water molecules, the rate of the reaction is not proportional to the amount of TCE adsorbed while the reverse is the case in the absence of substantial amount of adsorbed water molecules. This deviation from linearity in the former case suggests the existence of a suppression of the photochemical reaction.

3.4. Effect of humidity on concentrations of DCAC, phosgene and CO_2

The fate of phosgene and DCAC is of immense concern even though the production of these compounds is known to be smaller in ambient concentrations when compared to the original pollutant (TCE). They are extremely toxic from a human health perspective and persistent in the environment. Some of these chlorinated partial oxidation products formed are known to be far more toxic than TCE [17]. In this particular
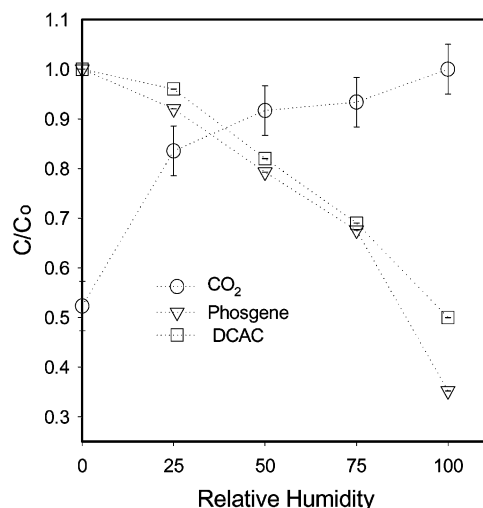
Fig. 7. Normalized photocatalytic oxidation yield of CO_2, phosgene and DCAC after 20 min of the reaction at different relative humidity. The product yields are obtained from their respective infrared band intensities.

photocatalytic oxidation reaction, the yields of DCAC, phosgene and CO_2 after 20 min of TCE photocatalytic oxidation at different humidity are based on their infrared band intensities, which have been normalized for comparison. The production of these intermediates/byproducts was greatly affected by humidification as shown in Fig. 7. As humidity increased there was a decrease in the yield of DCAC and phosgene while CO_2 yield increased monotonically. In the presence of water vapor, there is a possibility of a chemical reaction involving H_2O, phosgene and DCAC to produce CO_2 [12]. The possibility of DCAC and phosgene hydrolysis occurring may increase with humidity. Therefore, at higher humidity more phosgene and DCAC would be consumed to produce CO_2 resulting in a decrease in the production of phosgene and DCAC and an increase in CO_2 production. The production of CO_2 may follow the sequence given in reactions 17 and 18:

$$CHCl_2COCl + H_2O \rightarrow COCl_2 + CO_2 + HCl \quad (17)$$

$$COCl_2 + H_2O \rightarrow CO_2 + 2HCl \quad (18)$$
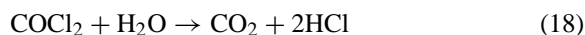
Comparatively, the low amount of CO_2 and the high amount of phosgene and DCAC produced at

lower humidity shows that complete mineralization of TCE did not occur after 20 min. This observation can be rationalized by taking into account the fact that both H_2O and O_2 are indispensable oxidants in the complete oxidation and mineralization of TCE to more environmentally benign products (CO_2 and HCl).

4. Conclusions

This study reveals that the presence of water vapor suppresses the Cl atom-propagated chain reaction which are responsible for the high reaction rates of photocatalytic oxidation of TCE and possibly other chlorinated ethenes. We propose here that both competitive adsorption and the suppression of the photochemical oxidation reaction occur simultaneously and are both responsible for the reaction inhibition observed in the presence of water vapor. As humidification increased, the concentration of CO_2 increased monotonically while DCAC and phosgene concentrations decreased.

Acknowledgements

References

[1] D.F. Ollis, H. Al-Ekabi, Photocatalytic Purification and Treatment of Water and Air, Elsevier, New York, 1993.
[2] T. Ibusuki, K. Takeuchi, Atmos. Environ. 20 (1986) 1711.
[3] J. Peral, D.F. Ollis, J. Catal. 136 (1992) 554.
[4] L.A. Dibble, G.B. Raupp, Catal. Lett. 4 (1990) 345.
[5] J. Kim, K. Itoh, M. Murabayashi, Denki Kagaku 11 (1996) 1200.
[6] X. Fu, L. Clark, W. Zeltner, M. Anderson, J. Photochem. Photobiol. A: Chem. 97 (1996) 184.
[7] M.R. Nimlos, W.A. Jacoby, D.M. Blake, T.A. Milne, Environ. Sci. Technol. 27 (1993) 732.
[8] W.A. Jacoby, D.M. Blake, R.D. Noble, C.A. Koval, J. Catal. 157 (1995) 87.
[9] M. Murabayashi, K. Itoh, K. Kawamura, in: Proceedings of the 5th International Conference on TiO2 Photocatalytic Purification and Treatment of Water and Air, Ont., Canada, 26–30 June 2000, p. 93.

[10] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.

[11] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 745.

[12] G.B. Raupp, J.A. Dumesic, J. Phys. Chem. 89 (1985) 5240.

[13] I. Izumi, W. Dunn, K. Wilbourn, F. Fan, A. Bard, J. Phys. Chem. 84 (1980) 3207.

[14] T.N. Obee, R.T. Brown, Environ. Sci. Technol. 29 (1995) 1223.

[15] K. Wang, H. Tsai, Y. Hsieh, Appl. Catal. B: Environ. 17 (1998) 313.

[16] L.A. Phillips, G.B. Raupp, J. Mol. Catal. 77 (1992) 297.

[17] W.F. Jardim, R.M. Alberici, M.M.K. Takiyama, C.P. Huang, Hazard. Ind. Wastes 26 (1994) 230.