

# Photocatalytic degradation of trichloroethylene in dry and humid atmospheres: role of gas-phase reactions

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## Abstract

This study reports the role of the homogeneous photochemical oxidation (PCHO) reaction occurring in the gas-phase during heterogeneous photocatalytic degradation (PCTD) reaction of trichloroethylene (TCE) in humid and dry atmospheres. PCTD reaction was carried out in the presence of TiO<sub>2</sub> glass fiber cloth (TiO<sub>2</sub>-GFC) while chlorine radicals generated from the exposure of chlorine gas to UV-illumination induced the PCHO reaction. The reaction profiles of the PCHO and PCTD reactions monitored independently in dry and humid atmospheres by in situ FTIR spectroscopy reveal the difference between the reaction pathways of phosgene formation and DCAC oxidation. Degradation of TCE to CO<sub>2</sub> increased from 52% at 0% relative humidity (RH) to 71% at 100% RH during PCTD reactions while during PCHO reaction it decreased from 27% at 0% RH to 2% at 100% RH. Reactivity of both PCHO and PCTD reactions decreased with increasing RH. RH corresponding to ~25% RH was found to be the most favorable condition for PCTD reactions because reasonably high reactivity and mineralization of TCE can be accomplished simultaneously.

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## 1. Introduction

Environmental problems associated with volatile chlorinated organic contaminants in the atmosphere have provided the driving force for sustained fundamental and applied research in the area of environmental remediation using heterogeneous photocatalysis. Since the pioneering work of Fujishima and Honda [1], UV-assisted catalysis in the presence of TiO<sub>2</sub> has become increasingly relevant in environmental remediation because of its efficiency and potentially broad applicability [2–10]. Ultimately, the commercialization of photocatalysis, which remains a top priority among scientists in the field, would depend largely on how efficient this technology is in degrading chlorinated organic contaminants to innocuous products without the formation of undesirable chlorinated partial oxidation products.

The degradation of trichloroethylene (TCE) to CO<sub>2</sub> and HCl by photocatalytic methods has rarely been accomplished because of the formation of reaction intermediates such as DCAC, phosgene, oxalyl chloride, 1,1-dichloroethane (1,1-DCE) [11–21]. So far only few studies have reported the accomplishment of relatively high mineralization of TCE in gas–solid regime at ambient temperature. In our previous work [13], we demonstrated high mineralization of TCE (~85%) after 20 min of UV-illumination on TiO<sub>2</sub> glass fiber cloth (TiO<sub>2</sub>-GFC) pretreated with dilute HCl (~0.01N).

It is still not known whether some of the reactions that occur during TCE photocatalysis in the presence of TiO<sub>2</sub> occur in the gas-phase or on the surface of TiO<sub>2</sub> itself. The emphasis of several studies on TCE photocatalysis has been based on the reactions occurring on the surface of the photocatalyst. The photochemical oxidation (PCHO) reactions occurring in the gas-phase have not been studied extensively even though the different gas-phase products formed during PCHO may eventually be adsorbed on the surface of the photocatalyst. An understanding of gas-phase reactions

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during photocatalytic degradation (PCTD) in dry and humid atmospheres would help in the accomplishment of higher degradation of TCE. This work is aimed at elucidating the role of the PCHO reactions during photocatalysis, especially with regards to the fate of phosgene and DCAC and their eventual oxidation to  $\text{CO}_2$ . A clear comparison between the PCHO and PCTD reactions in dry and humid atmospheres has been carried out using their different reaction profiles expressed in their respective normalized concentrations.

## 2. Experimental section

Experimental data were generated in a cylindrical Pyrex-glass batch reactor of volume approximately  $110 \text{ cm}^3$ . A detailed description of the batch reactor and its operation has been described elsewhere [22]. UV-illumination was performed by eight symmetrically arranged fluorescent black lights (Toshiba FL20S.BLB, 160 W output) to obtain UV light intensity of  $3.2 \text{ mW/cm}^2$ . 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 UV-illumination. All experiments were performed at ambient temperature ( $\sim 298 \text{ K}$ ) and approximately atmospheric pressure.

Distilled deionized (DDI) water and analytical grade materials purchased from the following suppliers were used without further modification: TCE (Junsei Chemical Co. Ltd., Tokyo, Japan, 99%+), nitrogen (Nihon Sanso, Japan, 99.9%), chlorine gas (Matheson Gas Products, 99%).  $\text{TiO}_2$  coated on glass fiber cloth (named herein as  $\text{TiO}_2$ -GFC) by modified sol-gel process was generously supplied by Nippon Muki Co. Ltd., Tokyo, Japan.

$\text{TiO}_2$ -GFC (apparent size =  $5.0 \text{ cm} \times 2.75 \text{ cm}$ ,  $0.1 \text{ cm}$ ;  $4.8 \text{ g TiO}_2/\text{cm}^2$  of apparent area) 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. Relative humidity (RH) corresponding to 25, 50, 75, and 100% were established by injecting the desired amount of DDI 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 approximately 1410 ppmv was also injected into the batch reactor and was given time to vaporize and mix. PCTD and PCHO reactions were monitored in situ by FTIR spectroscopy after successive exposure of known duration to UV-illumination. The FTIR (Perkin-Elmer Spectrum GX FTIR System) which was nitrogen purged was equipped with a deuterated triglycerine sulphate (DTGS) detector and a KBr beam splitter. The PCHO reactions were carried out under similar experimental conditions by injecting 12.28 ppmv of chlorine gas in the absence of  $\text{TiO}_2$ -GFC. Chlorine atoms were generated from the exposure of chlorine gas to UV-illumination.



In addition, 1 mL of the products of the PCTD and the PCHO reactions were analyzed by GC-MS (Hewlett-Packard) in order to determine other gas-phase products that may have overlapped with known infrared peaks of phosgene and DCAC.

## 3. Results and discussion

### 3.1. Effect of humidity on the reactivity of PCTD and PCHO reactions

The effect of humidity on the reactivity (expressed in terms of half-life) of the PCHO and the PCTD reactions was studied and the result is presented in Fig. 1. The reactivity of both reactions decreased with increasing RH confirming the existence of the inhibitive effect of water vapor. A significant difference in their reactivity was observed at 0% RH than at higher RH. This may be due to the absence of the inhibitive effect of water vapor, which allows the Cl-atom promoted chain reaction to proceed without any suppression.

The process of photocatalysis begins when  $\text{TiO}_2$  is illuminated with UV-light (photons) resulting in band-gap photoexcitation and the generation of electron-hole pair. The photogenerated holes and electrons react with water molecules and oxygen molecules, respectively, to generate hydroxyl radicals [23]. Actually, the presence of water vapor is beneficial to the PCTD reaction of TCE because the hydroxyl radicals formed on the illuminated  $\text{TiO}_2$  attacks TCE to generate the active species (chlorine atoms) [11]. During the PCHO reaction chlorine atoms were generated from the photo-induced dissociation of chlorine molecule to form chlorine atoms (Eq. (1)). These chlorine atoms generated propagate the reaction mechanism according to the reaction sequence proposed by Nimlos et al. [11].

Another beneficial role that is played by OH radicals is that they are able to suppress the electron-hole recombination process because of their ability to act as hole traps [24].

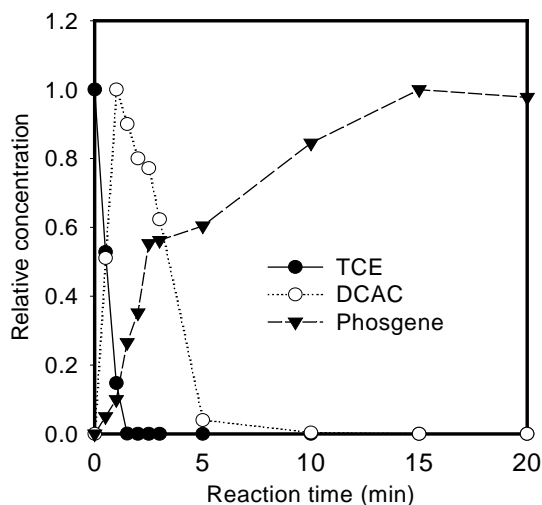


Fig. 1. Effect of RH on the reactivity of TCE PCTD and PCHO reactions.

The onset of photocatalysis involves the desorption of water molecules from the surface of  $\text{TiO}_2$ , which forms OH free radicals by capturing electron holes [11,24]. In summary, even though water molecules inhibit the PCTD reactions, it is required for the oxidation of TCE as seen in the empirical equation of TCE oxidation which involves water and oxygen as oxidants. PCTD reactions occurring at lower humidity (<50% RH) were not greatly inhibited by water vapor.

Although, other reasons [19,24–27] have been advanced to rationalize the inhibitive effect of water vapor during photocatalysis in humidified atmosphere, the suppression of the PCHO reaction by water molecules seems to be the dominant factor as reported previously [12]. This result is consistent with our earlier postulation [12] that the suppression of the PCHO reaction by water molecules is largely responsible for the decreased reactivity of the PCTD reaction shown in Fig. 1. As observed by Luo and Ollis [24], under higher concentration of water vapor, the water molecules might compete with TCE molecules on the catalyst surface sites during adsorption.

### 3.2. Reactions at low humidity

The reaction profiles of TCE, DCAC, and phosgene expressed in terms of their respective normalized absorbance during PCTD and PCHO reactions were studied at 0% RH for 20 min, Figs. 2 and 3, respectively. During PCHO reaction, the relative concentration of phosgene and DCAC peaked simultaneously and their subsequent oxidation also followed the same trend. This result shows that TCE was oxidized to DCAC and phosgene simultaneously. In contrast, during PCTD reaction, the concentration of DCAC peaked after ~2 min while that of phosgene peaked after ~15 min. Also, the relative concentration of DCAC increases with de-

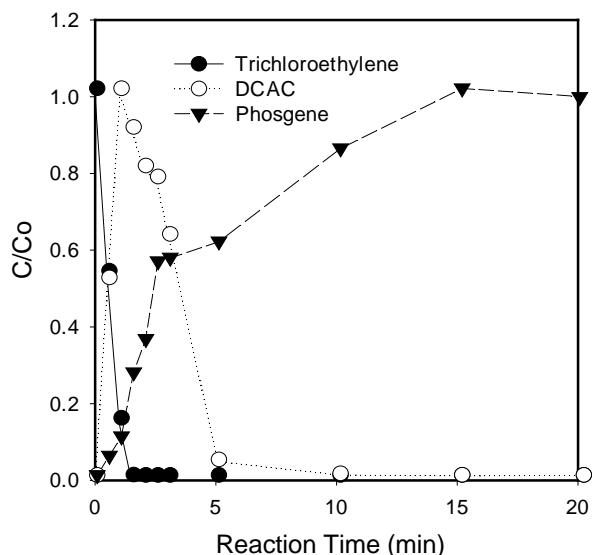


Fig. 2. The changes in the concentrations of TCE, DCAC, and phosgene during TCE PCTD reaction at 0% RH.

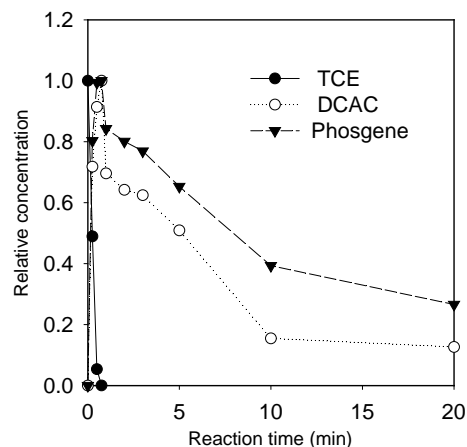


Fig. 3. The changes in the concentrations of TCE, DCAC, and phosgene during TCE PCHO reaction at 0% RH.

creasing TCE consumption confirming earlier reports that DCAC is a gas-phase intermediate [11,12,14,15,19]. These reaction profiles suggest that the predominant reaction pathway of phosgene formation during PCTD and PCHO reactions are not the same.

### 3.3. Reactions at high humidity

Figs. 4 and 5 show the reaction profiles of TCE, DCAC, and phosgene during TCE PCTD and PCHO reactions for 20 min at 100% RH, respectively. Similar trends to those observed at lower RH were observed for both reactions at this humidity except that the progress of both reactions was much slower and the PCHO reaction apparently stopped after 10 min.

Generally, a comparison of the reactions at higher and lower humidity reveals that the formation of DCAC and phosgene peaked faster at 0% RH than at 100% RH. We also observed that the oxidation of DCAC occurred after 10 min at 0% RH but at 100% RH it was greatly inhibited and only ~60% oxidation of TCE occurred after 20 min. In contrast to

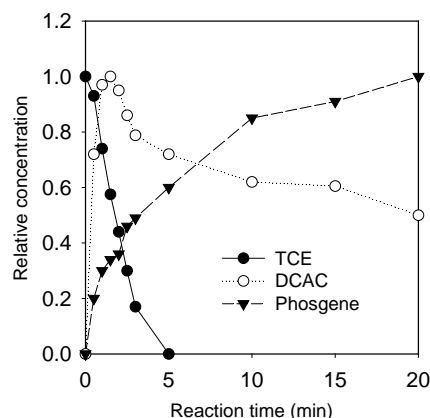


Fig. 4. The changes in the concentrations of TCE, DCAC, and phosgene during TCE PCTD reaction at 100% RH.

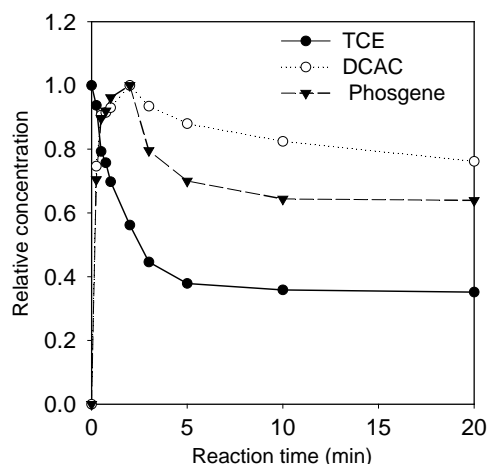
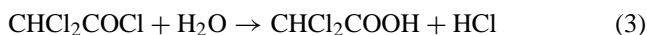
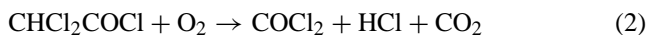


Fig. 5. The changes in the concentrations of TCE, DCAC, and phosgene during TCE PCHO reaction at 100% RH.

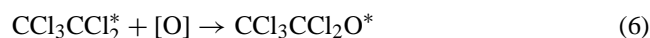
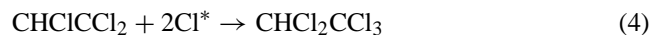
PCHO reaction, as DCAC is oxidized during PCTD reaction the yield of phosgene increases. This is an indication that reaction 2 occurs predominantly during PCTD reaction, i.e. on the surface of the photocatalyst because the C–C bond is easily cleaved.



Because both DCAC and phosgene yields peaked simultaneously and their subsequent oxidation followed the same pattern, it may also indicate that DCAC was transformed predominantly to byproducts other than phosgene during PCHO reaction. Qualitative study of the products of PCTD and PCHO reactions after 20 min by GC–MS revealed the formation of different products in the absence and presence of water vapor as shown in Table 1. Significant amount of DCAA was detected during PCHO reactions. Reaction 3 accounts for the formation of DCAA at high RH. It follows here that during PCTD reaction, DCAC predominantly undergoes hydrolysis in the gas-phase while it undergoes oxidation on the surface of the photocatalyst according to reactions 2 and 3, respectively.

### 3.4. Formation of phosgene during PCHO and PCTD reactions

The reaction profiles of PCHO and PCTD reactions suggest that the reaction pathway of phosgene formation may be different. This has been explained using reaction schemes proposed by Nimlos et al. [11] and Hung and Mariñas [20]. During PCTD reaction, the formation of phosgene was predominantly via DCAC oxidation whereas during PCHO reaction phosgene may have been formed predominantly via a different reaction pathway possibly from the dissociation of  $\text{CHCl}_2\text{CCl}_2\text{O}^*$  or  $\text{CCl}_3\text{CCl}_2\text{O}^*$ . The formation and eventual dissociation of  $\text{CHCl}_2\text{CCl}_2\text{O}^*$  and  $\text{CCl}_3\text{CCl}_2\text{O}^*$  are expressed in Ref. [11] and reactions 4–7, respectively.



Pentachloroethane, has been widely reported as one of the gas-phase products of TCE PCTD reaction. In our experiments, pentachloroethane was only detected by GC–MS during PCHO reaction at 25% RH after 20 min. The occurrence of reactions 4–7 may have been responsible for the absence of pentachloroethane at 0% RH during PCHO reaction. Its involvement in these reactions was confirmed by the presence of trichloromethyl radical, which can react with gas-phase chlorine radical to form chloroform, also detected by GC–MS for products of PCHO at 0% RH (Table 1). This observation is consistent with this reaction schemes and can, therefore, be employed in rationalizing the behavior of phosgene during TCE PCHO reaction.

The concentrations of phosgene and DCAC have not been quantified, thus, we have not determined which of them was higher in the gas-phase. Also, such a quantitative comparison would be inappropriate because chlorine gas corresponding to 12.28 ppmv was injected into the batch reactor to initiate the PCHO reaction. This may have increased the amount of the chlorinated byproducts because a correlation between the amount of chlorine gas in the gas-phase and the yield of chlorinated byproducts has been established [21].

However, it has been reported [11,19] that the concentration of DCAC formed during PCHO is greater than that of phosgene and the reverse is the case for PCTD reaction. In other words, the further oxidation of DCAC to phosgene occurred more in the presence of a photocatalyst (PCTD reaction) than in the gas-phase (PCHO reaction). This was rationalized to be due to the comparatively stronger C–C bond in comparison to the C–Cl bond. The C–C bond ruptures more easily on the surface of the photocatalyst than in the gas-phase [11]. The presence of phosgene during PCHO reaction is consistent with the results of Sanhueza et al. [28] that with all chloro olefins C=C double bond cleavage paths occur 19–31% of the time. The bond strengths of the C=C, C–C, and the C–Cl bonds are 619, 347, and 326 kJ/mol, respectively. If the cleavage of a much stronger C=C bond was observed ~30% of the time during photolysis of chloro olefins then the cleavage of the C–C bond during PCHO occurs much more than presently assumed. As observed the difference in the bond energies of the C–C and C–Cl bonds is ~21 kJ/mol, which is not significantly high.

### 3.5. Reaction intermediates and products

In our previous work [12], we reported the yields of  $\text{CO}_2$ , phosgene, and DCAC after 20 min of PCTD reaction at different RH. The formation of these compounds was greatly affected by humidification. As RH increased



Table 1

Chlorinated products detected by GC–MS during TCE PCHO and PCTD reactions after 20 min at 0 and 25% RH

Relative humidity (RH)	Main byproducts detected by GC–MS during PCHO by GC–MS during PCTO	Main byproducts detected by GC–MS during PCTO reaction
0% RH	DCAC (92), phosgene (91), DCAA (80), oxalyl chloride (83), 1,1-dichloroethane (83), carbon tetrachloride (50), chloroform (50), methylene chloride (38)	Phosgene (90), 1,1-dichloroethane (83), oxalyl chloride (74)
25% RH	DCAC (91), phosgene (79), DCAA (95), oxalyl chloride (50), 1,1-dichloroethane (64), 2,2-dichloroethanol (38), methylene chloride (46)	Oxalyl chloride (80), 1,1-dichloroethane (80), phosgene (70), ethane pentachloride (49)

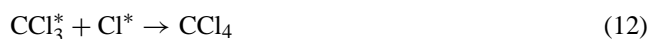
the yields of DCAC and phosgene decreased while that of CO<sub>2</sub> increased monotonically. The effect of humidity on the yields of DCAC, CO<sub>2</sub>, and phosgene during PCHO reaction after 20 min was studied (result not shown here). The effect of RH on the yield of DCAC and phosgene during PCHO reaction was similar to that observed during PCTD reactions [12]. In contrast to PCTD reaction, the yield of CO<sub>2</sub> decreases with increasing RH. The implication of this is that the further oxidation of phosgene and DCAC to CO<sub>2</sub> decreased with increasing RH. We, therefore, assume that DCAC and phosgene were actively involved in side reactions, which resulted in the formation of other chlorinated partial oxidation products as confirmed by the result of product analyses of the PCHO and PCTD reactions shown in Table 1.

The PCHO reaction of TCE at 0% RH resulted in the formation of the following by products: DCAC, phosgene, DCAA, oxalyl chloride, 1,1-dichloroethane, carbon tetrachloride, chloroform, and methylene chloride. At 25% RH, the byproducts of the reaction were similar to those detected at 0% RH except that carbon tetrachloride and chloroform were absent while 2,2-dichloroethanol was detected. The PCTD reaction at 0% RH resulted in the formation of phosgene, 1,1-DCE, and oxalyl chloride. At 25% RH, the products were essentially the same except for the presence of an additional chlorinated byproduct, ethane pentachloride. Reactions 2 and 7 account for the formation of phosgene while reaction 4 accounts for the formation of pentachloroethane. Reaction schemes were proposed in our previous work to account for the formation of recently detected byproducts, 1,1-DCE and oxalyl chloride [13]. An important observation of this reaction is its increased sensitivity to humidity.

The response value of DCAA as presented in Table 1 increased from 80 at 0% RH to 95 at 25% RH because of the reaction involving DCAC and water molecules (reaction 3). The occurrence of this reaction increases with humidity, and therefore, accounts for the increased DCAA amount. PCHO reaction at 0% RH resulted in the formation of chloroform and also carbon tetrachloride as shown in Table 1. It is possible that these compounds were also produced during PCTD reactions as reported by Hung and Mariñas [20] or even at 25% RH during PCHO but were subsequently oxidized to other compounds. The reaction scheme proposed by them [20] has been used to account for the formation of these compounds at 0% RH (reactions 8–12).



At 0% RH, the PCHO reaction progresses without any inhibition because of the non-existence of the suppression caused by water molecules at high RH. This reaction produces a high amount of chlorine atoms that continuously attack TCE molecules until they are all consumed [11]. In the presence of sufficient amount of chlorine atoms in the gas-phase, these reactive species may also get involved in side reactions with other reactive species such as dichloromethyl radical (CHCl<sub>2</sub><sup>\*</sup>) as shown in reactions 9 and 10. Subsequent decomposition of chloroform to form carbon tetrachloride by the extraction of hydrogen atom from chloroform occurs (reaction 11). The trichloromethyl radical (CCl<sub>3</sub><sup>\*</sup>) reacts with chlorine atom to form carbon tetrachloride (reaction 12). CCl<sub>3</sub><sup>\*</sup> obtained from reaction 11 can also undergo reaction 12 to form carbon tetrachloride.



FTIR studies also revealed the formation of HCl during PCHO and PCTD reactions.

### 3.6. Degradation of TCE to CO<sub>2</sub>

The complete degradation or mineralization of TCE to CO<sub>2</sub> during PCTD reaction remains the ultimate goal of the application of heterogeneous photocatalysis. Because reactions under practical conditions may be occurring at fluctuating humidity levels, it is therefore, important to understand how water vapor affects the degradation process. We have carried out a comparison of the percentage mineralization of TCE at different humidity levels during PCTD and PCHO reactions and the results are presented in Tables 2 and 3, respectively. The mineralization of TCE has been expressed in terms of a ratio, [CO<sub>2</sub>]/[TCE], representing the ratio of the

Table 2

The effect of humidity on the mineralization of TCE during PCHO reaction

RH (%)	CO <sub>2</sub> evolved (μmol)	TCE reacted (μmol)	[CO <sub>2</sub> ]/[TCE]	Mineralization (%)
0	3.55	6.6	0.50	27
25	1.67	6.6	0.25	13
50	1.14	6.6	0.17	9
75	0.68	5.8	0.12	6
100	0.16	4.8	0.03	2

Table 3  
The effect of humidity on the mineralization of TCE during PCTD reaction

RH (%)	CO <sub>2</sub> evolved (μmol)	TCE reacted (μmol)	[CO <sub>2</sub> ]/[TCE]	Mineralization (%)
0	6.87	6.6	1.04	52
25	8.89	6.6	1.35	67
50	9.10	6.6	1.37	69
75	9.21	6.6	1.39	70
100	9.40	6.6	1.42	71

concentration of CO<sub>2</sub> produced to the concentration of TCE degraded. The mineralization of TCE during the PCHO reaction was generally low (~27%) at 0% RH and decreased with increasing RH; at 100% RH only ~2% mineralization of TCE occurred. In contrast, the mineralization of TCE during the PCTD reaction was considerably high (~52%), and increased with RH. Mineralization percentage corresponding to ~70% was observed for reactions at RH > 50%. This shows that the mineralization of TCE occurs predominantly on the surface of the semiconductor and not in the gas-phase. The low mineralization of TCE observed during the PCHO reaction may be due to the low hydrolysis of phosgene and DCAC and the occurrence of several side reactions, which may have resulted to the formation of more chlorinated partial oxidation products as presented in Table 1. This was confirmed by the results of the product analysis carried out by GC–MS, which showed the presence of several chlorinated partial oxidation products after 20 min of PCHO reaction.

The mineralization of TCE observed during PCTD reactions correlates with the yield of chlorinated partial oxidation products. At higher RH, reactivity is highly reduced because of the suppression of the PCHO reaction; it would therefore, be necessary to explore ways of accomplishing the dual goals of high mineralization and high reactivity during PCTD reaction. There is a significant increase in the mineralization of TCE between 0 and 25% RH in comparison to higher RH (>50%), in which the percentage mineralization basically increases by a factor of 1. We, therefore, propose that the most favorable operating condition of TCE PCTD reaction in terms of RH is ~25% because at this humidity a reasonable compromise between reactivity and mineralization can be reached. As observed in Fig. 1, the reactivity of PCTD at 25% RH is reasonably high. Low percentage mineralization of TCE reported here may be due to the adsorption of the intermediates on the walls of the batch reactor and the short reaction time employed for this study.

#### 4. Conclusions

A comparative study of the homogeneous PCHO and the overall PCTD reactions have been performed in dry and humid conditions at 289 K. The following conclusions have been obtained.

1. The predominant reaction pathway of phosgene formation for both PCTD and PCHO reactions are different. Reaction profiles obtained from in situ FTIR spectroscopy reveal that the formation of phosgene during PCTD reaction is via DCAC oxidation while during PCHO reaction, it is formed via a different reaction pathway. We assume that it may be formed via CHCl<sub>2</sub>CCl<sub>2</sub>O\* or CCl<sub>3</sub>CCl<sub>2</sub>O\* decomposition.
2. Degradation of TCE to CO<sub>2</sub> occurs predominantly on the surface of TiO<sub>2</sub> and not in the gas-phase. While increasing humidity increases the degradation of TCE to CO<sub>2</sub> during PCTD reactions the reverse was the case for PCHO reactions. This work has shown that the optimum RH for PCTD reactions is ~25% RH because both relatively high degradation of TCE to CO<sub>2</sub> and high reactivity of PCTD reaction can be achieved simultaneously.
3. The presence of substantial amount of a recently detected chlorinated partial oxidation products (oxalyl chloride and 1,1-DCE) were confirmed during PCHO and PCTD reactions at 0 and 25% RH. These byproducts have not been quantified in the present study.

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