

Photocatalysis of gaseous trichloroethylene (TCE) over TiO_2 : The effect of oxygen and relative humidity on the generation of dichloroacetyl chloride (DCAC) and phosgene

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Abstract

Batch photocatalytic degradation of 80 ± 2.5 ppmV trichloroethylene (TCE) was conducted to investigate the effect of the oxygen and relative humidity (RH) on the formation of the dichloroacetyl chloride (DCAC) and phosgene. Based on the simultaneous ordinary differential equations (ODEs), the reaction rate constants of TCE ($(2.31 \pm 0.28) \sim (9.41 \pm 0.63) \times 10^{-2} \text{ min}^{-1}$) are generally larger than that of DCAC ($(0.94 \pm 1.25) \sim (9.35 \pm 1.71) \times 10^{-3} \text{ min}^{-1}$) by approximate one order. The phenomenon indicates the degradation potential of TCE is superior to that of DCAC. DCAC appreciably delivers the same degradation behavior with TCE that means there exists an optimum RH and oxygen concentration for photocatalysis of TCE and DCAC. At the time the peak yield of DCAC appears, the conversion ratio based on the carbon atom from TCE to DCAC is within the range of 30–83% suggesting that the DCAC generation is significantly attributed to TCE degradation. Regarding the phosgene formation, the increasing oxygen amount leads to the inhibitory effect on the phosgene yield which fall within the range of 5–15%. The formation mechanism of phosgene was also inferred that the Cl atoms attacking the C–C bond of DCAC results to the generation of phosgene rather than directly from the TCE destruction.

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Keywords: Photocatalysis; TiO_2 ; Trichloroethylene; Dichloroacetyl chloride

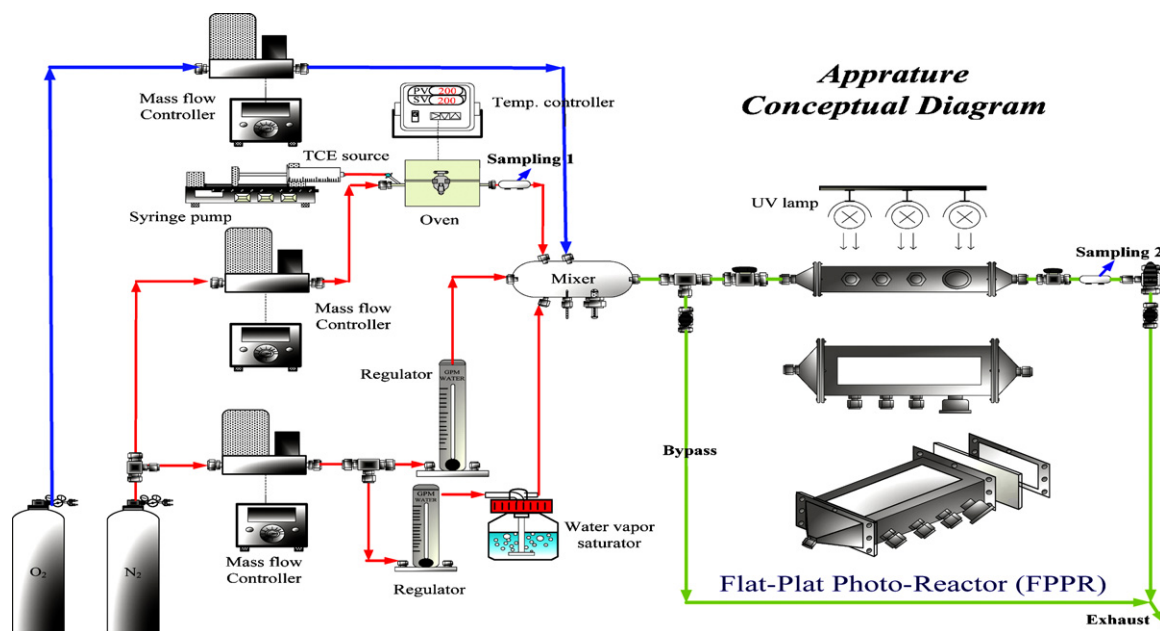
1. Introduction

In the critical problems associated with pollutant crisis, it should not overlook the fact that the chlorinated volatile organic compounds (CVOCs) are widely used in the chemical industry. Their emissions are detrimental to human through respiration and dermal absorption. Among the CVOCs, trichloroethylene (TCE) has been subjected to extent researches owing to the various utilizations, such as dry cleaning and degreasing operation as an organic solvent. Unfortunately, TCE can damage the central nervous system, skin, heart and circulatory system, or it may lead to cancer. Accordingly, it is inevitable to deal with TCE in regard to the properties of low cost and good removal efficient. The adsorption and absorption methods would produce liquid–solid phase secondary pollutants. The efficiency

of condensation and bio-filtration are limited while the capital investment and operation cost of the incineration are high despite of good pollutant decomposition efficiency [1]. Another method treating TCE is the photocatalysis based on TiO_2 , which possesses a number of advantages including stabilization, low cost, highly active feature and high performance of TCE degradation. For decades, many researches have dedicated to the TCE degradation by photocatalysis [2–8]. However, the majority of the researches engaged in the degradation performance of TCE and the distribution of its corresponding byproducts at some particular conditions [9–11]. Few researches specialized in the effect of oxygen and relative humidity (RH) on the generation of dichloroacetyl chloride (DCAC) and phosgene coupled with the corresponding mechanism. That apparently neglected the synergistic effect caused by water vapor and oxygen on the actual mechanism.

In the present research, the kinetics of TCE coupled with its predominant byproduct, DCAC, is established in the simultaneous ordinary differential equations (ODEs). Accordingly, a

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Scheme 1. The conceptual diagram of the flat-plate photoreactor (FPPR) system.

series of experiments were conducted in which we obtained the reaction rate constants for both TCE and DCAC over a range of RH and oxygen concentration. The yield of DCAC and phosgene are also investigated in the study to acknowledge DCAC and phosgene transformation as far as RH and oxygen are concerned. Coupled with the demonstrated results and literature data, the research also attempted to infer the degradation mechanism of TCE to investigate the resulting reaction pathway.

2. Experimental

The conceptual diagram of experimental apparatus in the research is shown as Scheme 1. The flat-plate-photoreactor (FPPR) was fabricated by stainless steel which was made up as flat-plate sharp with the volume of 2 L ($L=20$ cm, $W=10$ cm and $H=10$ cm), both ends of which were adhered together with two silicon wafers to avoid emission. The photocatalysts (P25 TiO_2) supported by silica board of 120 cm^2 was prepared by dip-coating method at the normalized concentration of 0.83 mg cm^{-2} . The prepared photocatalysts were subsequently deposited on the bottom of the reactor without further treatment. The liquid TCE from the syringe pump passing through the oven set at 373 K generated the gaseous TCE of $80 \pm 2.5\text{ ppmV}$ which was subsequently conducted into the reactor by nitrogen gas. The relative humidity (RH) of 10, 25, 55 and 90% corresponding to the concentration of 234, 585, 1287 and $2106\text{ }\mu\text{M}$ were established by passing nitrogen gas through a saturator containing de-ionized water. Meanwhile, oxygen of different flow rates would be injected into the reactor, constituting the concentration of 3.53, 6.48, 11.1 and 17.3 mM . Notably that all the flow into the reactor would pass through the mixer beforehand to achieve the homogeneous phase. During the reaction period, the reactor was wrapped with the heating tape maintaining at 308 K. Illumination provided by three 8 W black-light fluores-

cent lamp principally emits at 365 nm with the light intensity of $2.34 \pm 0.23\text{ mW cm}^{-2}$. Experimental methods of the investigation were carried out under a set of standard operating conditions listed in Table 1.

The concentration of TCE, DCAC and phosgene was quantified via the manual injection into the gas chromatograph (5890 II) equipped with the flame ionisation detector. In a typical experiment the GC oven was maintained at 353 K. Injector port temperature was held at 453 K and detector temperature maintained constant at 523 K. The quantitative analysis was carried out with the application of calibration curves for TCE, DCAC and phosgene. The peaks of TCE, DCAC and phosgene appear approximately at 2.5, 3.3 and 5.2 min in GC spectrum at the aforementioned conditions.

Some previous researches have proven that DCAC production is directly related to the TCE degradation which is immediately followed by the formation of phosgene and some other inorganic products, such as CO_2 , CO, HCl and Cl_2 [2,12,13]. However, the kinetics presented by the researches is oversimplified [14,15]. That means DCAC is being created and destroyed in the reacting TCE system, the rates of these reactions

Table 1
Standard operating conditions

| Experimental variable | Standard nominal value |
|---|---|
| Initial TCE concentration (ppmV) | 80 ± 2.5 |
| TiO_2 concentration (mg/cm^2) | 0.82 ± 0.03 |
| Reactor volume (L) | ~ 2 |
| Reaction temperature (K) | 308 ± 1.5 |
| Relative humidity (%) | 10–90 |
| Oxygen concentration (mM) | 0–18 |
| Incident light intensity (mW/cm^2) | 2.34 ± 0.23 |
| UV source/primary wavelength | 3 × Black light fluorescent/365 nm, 8 W |
| Solvent | Ultra pure N_2 |

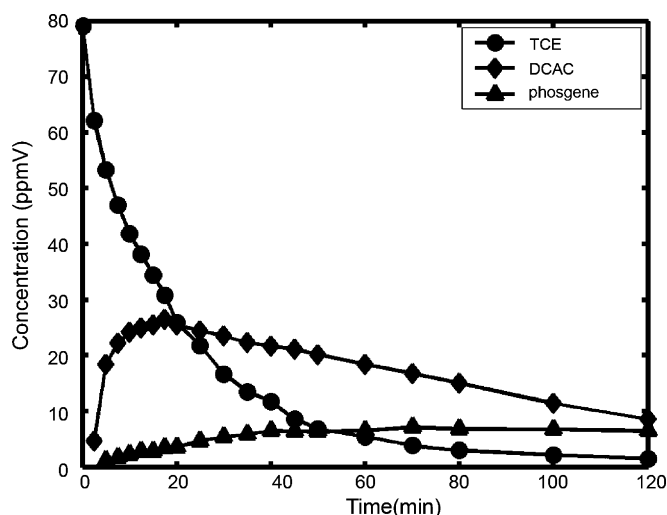


Fig. 1. The scenario of TCE, DCAC and phosgene under photocatalysis with oxygen concentration of 3.53 mM and 25% RH.

must be considered simultaneously; the effect of the presence of DCAC on the reaction rate of TCE, and vice versa. This helps to survey the degradation potential of TCE and DCAC more accurately. The reaction pathway of TCE coupled with DCAC can be described as the following channel, $\text{TCE} \rightarrow \text{DCAC} \rightarrow \text{Products}$ (phosgene, HCl, Cl_2 and CO_2). Fig. 1, a representative scenario of TCE, DCAC and phosgene also supports the proposed channel in which the formation of DCAC is followed by the degradation of TCE. Accordingly, there are two simultaneous first-order ODEs in which the dependent variables C_1 and C_2 , represent the concentrations of TCE and DCAC, respectively. k_1 and k_2 represent the reaction rate constants of TCE and DCAC, respectively. Products, such as phosgene, CO, Cl_2 , CO_2 and HCl, are unreactive in contact with the irradiated TiO_2 [16] which are beyond the consideration of the subsequent equations.

$$\frac{dC_1}{dt} = -k_1 C_1$$

$$\frac{dC_2}{dt} = -k_1 C_1 - k_2 C_2$$

The package software of Athena Workbench 8.3 based on the FORTRAN program was used to solve the simultaneous ODEs in which the Bayesian Estimation was used to find the optimum parameters with forward difference method. The parameters (k_1

Table 3
The reaction rate constants of DCAC at the varying conditions

| The reaction rate constants of DCAC (10^{-3} min^{-1}) | | | |
|--|-----------------------|-------------|-------------|
| Oxygen concentration (mM) | Relative humidity (%) | | |
| | 10 ± 5 | 25 ± 5 | 55 ± 5 |
| 0 | 6.36 ± 1.25 | 3.63 ± 1.43 | 0.94 ± 1.25 |
| 3.53 | 8.21 ± 1.41 | 5.73 ± 0.68 | 1.78 ± 1.26 |
| 6.48 | 8.27 ± 1.68 | 5.23 ± 1.50 | 1.73 ± 1.68 |
| 11.1 | 9.35 ± 1.71 | 4.89 ± 1.26 | – |
| 17.3 | – | 3.15 ± 0.96 | – |

and k_2) with 95% confidence limits were determined to have the corresponding values listed in Tables 2 and 3 and all the r^2 values were above 0.9.

3. Results and discussion

3.1. Effect of RH and oxygen on the degradation of TCE

While TCE was generated in the photoreactor, it was stable either in darkness with TiO_2 existence or free of TiO_2 under UV irradiation that the TCE degradation was less than 10% of initial concentration ($80 \pm 2.5 \text{ ppmV}$). Direct photolysis made less influence on the TCE degradation owing to the low overlap between the UV emission spectrum (the max emitting wavelength is 365 nm) and the TCE adsorption spectrum (200–230 nm) [4]. The trivial amount of TCE adsorbing on the reactor suggests the adsorption effect can be neglected during the period of interest. Based on the aforementioned results, it is reasonable to ascribe the TCE degradation to the photocatalysis over TiO_2 .

The simulated degradation rate constants of TCE (k_1) are demonstrated in Table 2. At oxygen concentration of 6.48 mM, the degradation rate constants of TCE are 9.41 ± 0.63 , 5.41 ± 0.61 and $3.80 \pm 0.28 \text{ min}^{-1}$ at RH of 10, 25 and 55%, respectively.

The value of rate constant at 10% RH is larger than that at 55% RH by a factor of 2.5. Alike trend can be observed at other oxygen concentrations. Regarding the RH effect, it is obvious that the water molecules deliver inhibitory effect on the TCE degradation, which suggests that TCE is unfavorable to occupy the active sites on the surface of TiO_2 in the presence of water vapor. The removal of physisorbed water is evidenced to be favorable

Table 2
The reaction rate constants of TCE at the varying conditions

| The reaction rate constants of TCE (10^{-2} min^{-1}) | | | | |
|---|-----------------------|-------------|-------------|-------------------|
| Oxygen concentration (mM) | Relative humidity (%) | | | |
| | 10 ± 5 | 25 ± 5 | 55 ± 5 | 90 ± 5 |
| 0 | 4.48 ± 0.14 | 3.15 ± 0.28 | 2.31 ± 0.28 | 1.34 ^a |
| 3.53 | 14.9 ± 0.56 | 7.99 ± 0.36 | 2.90 ± 1.00 | 1.10 ^a |
| 6.48 | 9.41 ± 0.63 | 5.41 ± 0.61 | 3.80 ± 0.28 | 1.69 ^a |
| 11.1 | 6.64 ± 0.40 | 5.18 ± 0.10 | 3.39 ± 0.39 | 0.91 ^a |
| 17.3 | 3.28 ± 0.74 | 3.93 ± 0.16 | – | 0.89 ^a |

^a These values are obtained by fitting TCE degradation scenario based on the pseudo-first-order equation.

to TCE degradation [8]. The aforementioned conclusion is also consistent with the previous results provided by Hedegus and Dombi [13]. Similar phenomenon was reported by Wang et al. [10] that the reaction rate decreases as the concentration of water vapor is higher than 154 μM . Comparatively,

Amama et al. [5] indicated that the photocatalysis of TCE occurring at lower humidity (<0% RH) was not greatly inhibited by water molecules. The discrepancy between the study and the results presented by Amama et al. [5] may arise from the different “normalized concentration of water vapor”, which is defined as the ratio of the concentration of water vapor to the accessible area of TiO_2 dependent on the type of the reactor. It is worthy to mention that Fan and Yates [17] proved, by the application of O-atom isotope-label, that surface adsorbed water does not involve in the TCE photo-degradation. Accordingly, the inhibitory effect on TCE degradation caused by water molecules is reasonable owing to the decreasing opportunities for TCE adsorbing on the active sites of TiO_2 surface.

It is interesting that surface adsorbed water contributes to the negative effect on the TCE degradation. Hydroxyl radical (OH^\bullet) generated from the reaction of water molecules with photo-holes was generally taken as the predominant oxidant species in the photocatalysis. However, the aforementioned results do not correspond to this mechanism suggesting that there must be other radicals to initiate the proceeding of TCE degradation. A reasonable inference that chlorine ion (Cl^-) adsorbed on the surface of TiO_2 -catalyst was oxidized directly to chlorine radical (Cl^\bullet) under UV-illumination [18,19]. The Cl^\bullet is presumed to involve in the TCE degradation as the predominant oxidant species as indicated in subsequent reaction, $\text{Cl}^- + \text{h}^+ \rightarrow \text{Cl}^\bullet$. The same concept has also been proposed by Ozaki et al. [20].

Regarding the oxygen effect on TCE degradation, the results indicate that more oxygen content do not present the anticipant phenomenon with higher degradation rate. This was contrary to the established conclusion that more oxygen content would drive the better performance or reach the plateau state for TCE degradation [13,21]. Wang et al. [21] indicated that there was no significant change on TCE degradation rate while the oxygen content was above 10% (v/v) at which the range is 0–20%. Hedegus and Dombi [13] pointed out the decomposition rate increases slightly with increasing oxygen content at which the concentration range is 0.59–42.2 mM. Such conflict may be attributed to that the “normalized oxygen concentration” in our research is larger than that in the previous researches which is defined as the ratio of oxygen concentration to the accessible area or amount of TiO_2 . Accordingly, the virtual effect of oxygen on TCE degradation is that the overload of oxygen can inhibit the photo-degradation on TCE.

3.2. Byproduct formation at different RH and oxygen concentration

Fig. 2 demonstrates the mole of DCAC and phosgene formed per mole of TCE removed at the time the peak yield of DCAC appears. Regarding oxygen effect demonstrated in Fig. 2a, about 0.2–0.55 mole of DCAC formed for every mole of TCE removed, indicated that 30–83% of the carbon in the TCE molecule was

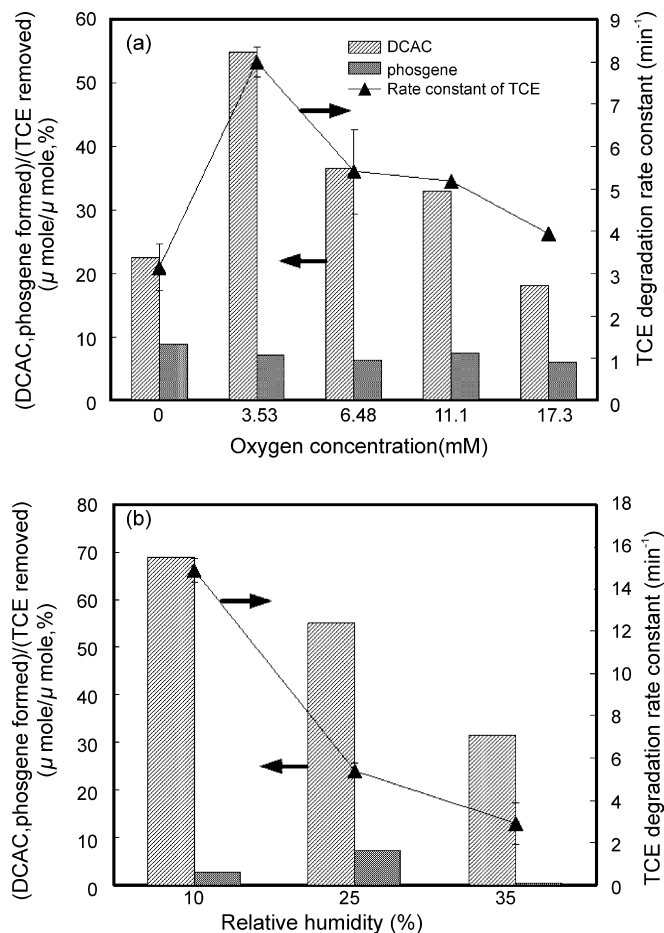


Fig. 2. (a) Effect of oxygen concentration, (b) effect of RH on the relationship between TCE degradation rate constants and formation of DCAC/phosgene at the time the peak yield of DCAC appears.

converted to DCAC. The DCAC conversion appreciably corresponds to the degradation rate of TCE suggesting that TCE degradation significantly responsible for the DCAC formation, the same phenomenon can be observed as far as RH is concerned, as indicated in Fig. 2b. Fig. 2 also demonstrates that no obvious relationship between TCE rate constant and phosgene formation. This observation indicates that the phosgene formation is attributed to the DCAC degradation rather than TCE degradation. Other products (e.g. CO , CO_2 , HCl and Cl_2) may also generate during photocatalysis, which are the possible candidate for the missing C or Cl atoms [2], were not investigated in this research.

3.3. Effect of RH and oxygen content on DCAC

Fig. 3a–c demonstrate the evolution of DCAC yield at 10, 25 and 55% RH, respectively which are normalized by initial TCE concentration so that the results from each experiment are comparable. For 10% RH condition, the peak yields of DCAC at the various oxygen concentration (Fig. 3a) fall within the range of 30–60%. The respective peak yields of DCAC for 0, 3.53, 6.48, 11.1 and 17.3 mM oxygen concentration are 45.6, 53.7, 56.9, 60.2 and 31.7%, respectively, suggesting the optimum oxygen

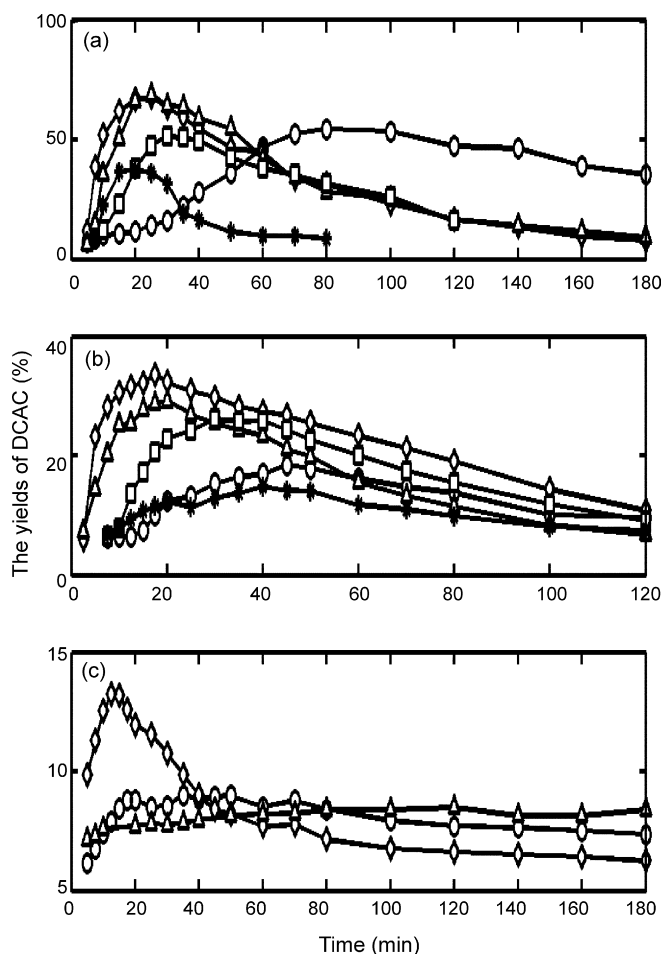


Fig. 3. Effect of oxygen on the proceeding of DCAC yield at RH of (a) 10%, (b) 25%, (c) 55% (\circ , \diamond , \triangle , \square and $*$ represent the conditions of 0, 3.53, 6.48, 11.1 and 17.3 mM O_2 , respectively).

concentration drives more yield of DCAC. The same trend can be observed at 25 and 55% RH that the corresponding peak yields of DCAC are within the range of 10–25% and 6–10%, respectively (Fig. 3b and c).

The result reflects that the yield of DCAC is corresponding to the degradation rates of TCE. The faster degradation rates of TCE, the more yields of DCAC appear, as indicated in Fig. 2. Meanwhile, Fig. 3 also demonstrates that the time when the peak yields of DCAC appear change depending on the oxygen concentration. That means the time when the peak yield of DCAC appears advance with the increasing rate constant of TCE. The results provide the solid evidence that the DCAC formation significantly attributes to TCE degradation which is consistent with the previous research [2]. In case of RH 90%, TCE degradation did not produce any detectable byproducts (detection limit: 0.1 ppm) regardless of oxygen concentration owing to its low conversion.

According to the reaction rate constants of DCAC (k_2) demonstrated in Table 3, the degradation behavior of DCAC is consistent with that of TCE. That means the degradation rate of DCAC is more rapid at lower RH than at higher RH. For the oxygen concentration of 6.48 mM, the rate constants of DCAC are $(8.27 \pm 1.68) \times 10^{-3}$, $(5.23 \pm 1.50) \times 10^{-3}$ and

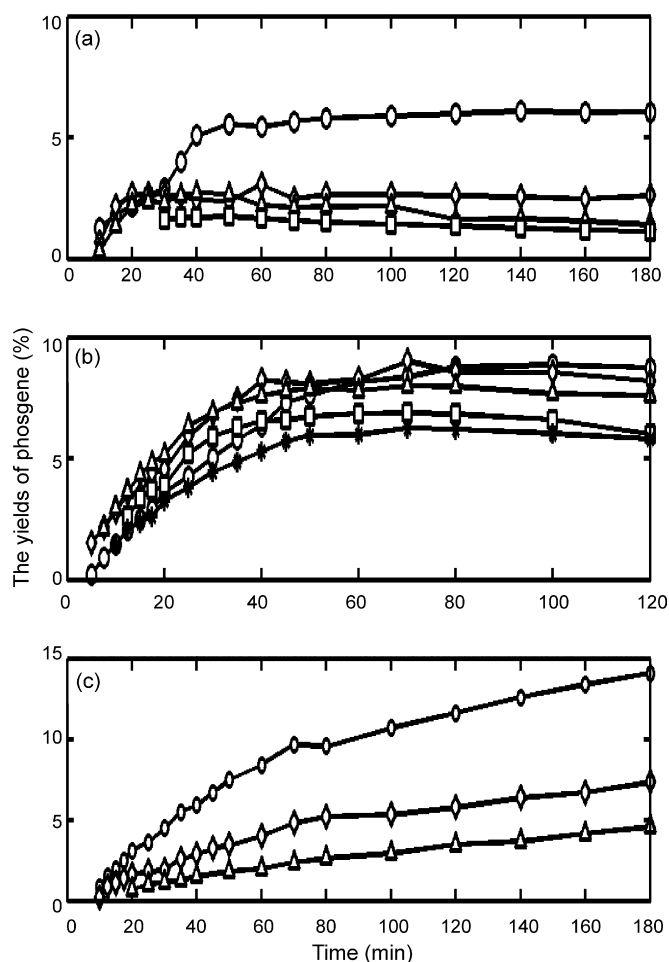


Fig. 4. Effect of oxygen on the proceeding of phosgene yield at RH of (a) 0%, (b) 25%, (c) 55% (\circ , \diamond , \triangle , \square and $*$ represent the conditions of 0, 3.53, 6.48, 11.1 and 17.3 mM O_2 , respectively).

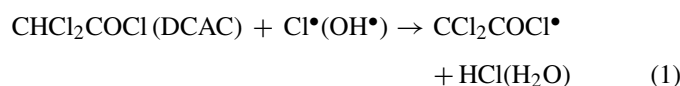
$(1.73 \pm 1.68) \times 10^{-3} \text{ min}^{-1}$ at 10, 25 and 55% RH, respectively. Meanwhile, DCAC has better degradation performance in the presence of the optimum oxygen concentration that the best reaction rate constants of DCAC are $(9.35 \pm 1.71) \times 10^{-3}$, $(5.73 \pm 0.68) \times 10^{-3}$, $(1.78 \pm 1.26) \times 10^{-3} \text{ min}^{-1}$ at 10, 25 and 55% RH, respectively. It can be concluded that the reaction rate constant of DCAC is highly relative to the RH and oxygen. Additionally, the rate constants of DCAC fail to catch up that of TCE by approximately one order. This indicates the degradation potential of DCAC is inferior to that of TCE. The phenomenon corresponds to the results presented in the previous research handled by Jacoby et al. [16], suggesting that the presence of TCE inhibits the photocatalysis of DCAC. Such behavior corresponds to the demonstrated results that TCE performs better degradation potential than DCAC even after DCAC occupy more active sites on TiO_2 surface.

3.4. Effect of RH and oxygen on phosgene

Fig. 4 presents the scenario of phosgene yield at different concentration of water vapor and oxygen. As for the RH effect, the yield of phosgene appreciably reaches a plateau more rapidly

at lower RH than at higher RH (Fig. 4). The yield of phosgene at 55% RH is still increasing within the time of interest regardless of the oxygen effect (Fig. 4c). Higher RH potentially drives phosgene gradually increase, despite the TCE degradation do not show expected performance. A reasonable inference may arise that DCAC competes more effectively with the adsorbing TCE for available surface active sites of TiO_2 [2]. Accordingly, DCAC can be gradually degraded to constitute the high yield of phosgene in the presence of RH despite the degradation potential of DCAC is inferior to TCE.

Regarding the effect of oxygen on the phosgene yield, the yield of phosgene increases with the decreasing oxygen content at either RH condition (Fig. 4). That means the phosgene tends to be produced at the oxygen-deficient conditions. It is an interesting and unexpected phenomenon discovered in this study. The result is incompatible with the mechanism demonstrated by Hedegus and Dombi [13] who indicated the generation of phosgene is owing to the consequent radical reactions initiated by the reaction of oxygen with $\text{CCl}_2\text{COCl}^\bullet$ which was firstly proposed by Nimlos et al. [2] as demonstrated in the following mechanism:



Therefore, experiments were also conducted to perform the relationship between DCAC and phosgene in which the DCAC was used as a starting material with initial concentration of 40 ± 4 ppmV at oxygen concentration of 0, 3.53, 6.48, 11.1 and 17.3 mM, respectively. The result demonstrated the yields of phosgene when DCAC reached half-life irrespective of other generated products. The yields of phosgene are 8.8 ± 0.4 , 6.7 ± 0.3 , 4.3 ± 0.5 , 2.9 ± 0.3 and $1.5 \pm 0.3\%$ at 0, 3.53, 6.48, 11.1 and 17.3 mM, respectively (Fig. 5). The phenomenon corresponds to the aforementioned results that the more oxygen content, the decreasing yields of phosgene appear while TCE is used as the starting material. This indicates that the formation of phosgene is likely relevant to the DCAC destruction rather than that of TCE. Subsequently, the authors propose a creative viewpoint relative to the TCE degradation, especially for the transformation from DCAC to phosgene, as indicated in Scheme 2 which is based on the results demonstrated herein and the literature data.

3.5. TCE degradation mechanism

Scheme 2 demonstrates the proceeding of TCE degradation which involves chain reactions initiated by the Cl atoms instead of OH radicals. Afterward, the Cl atoms is expected to react with CHClCCl_2^\bullet to form $\text{CHCl}_2\text{CCl}_2^\bullet$ [22]. $\text{CHCl}_2\text{CCl}_2^\bullet$ then combines with the charged radical-ions ($\text{O}_2^{\bullet-}$) to form $\text{CHCl}_2\text{CCl}_2\text{OO}^\bullet$ which was followed by the well-known

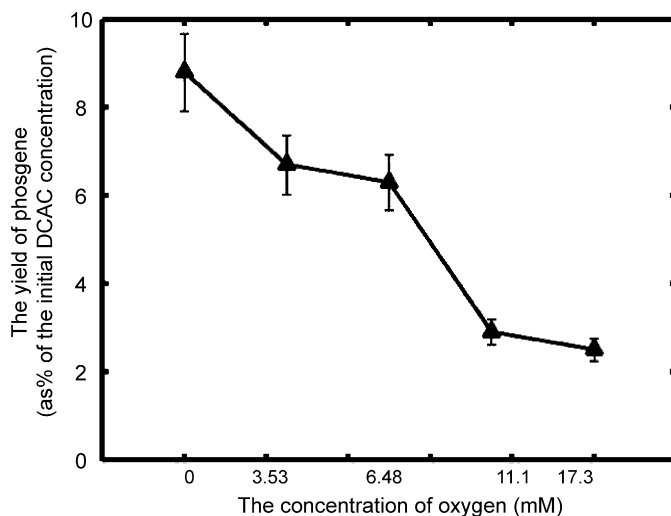
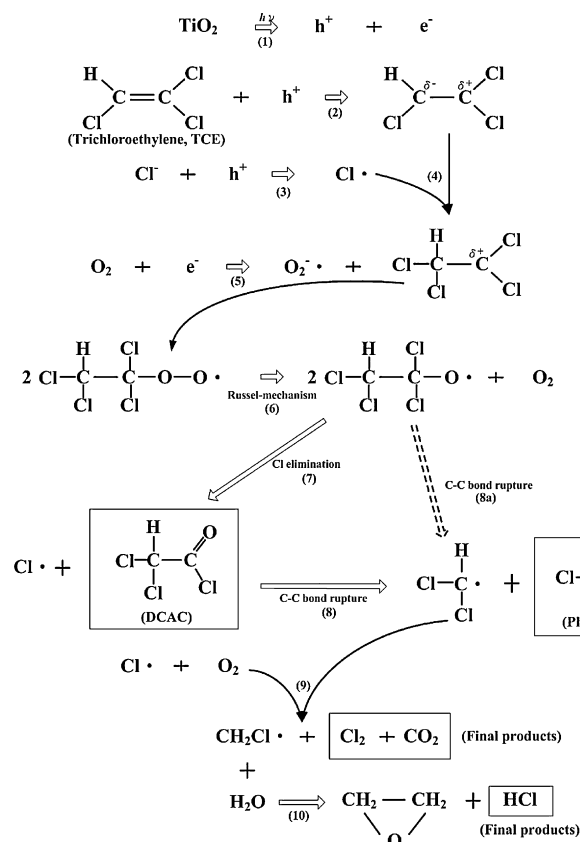


Fig. 5. Effect of oxygen on the yield of phosgene while using DCAC as the starting material at the RH of $25 \pm 2.5\%$.

Russel mechanism [13], causing the generation of the O-atom-centered radicals ($\text{CHCl}_2\text{CCl}_2\text{O}^\bullet$). The Cl-elimination of resulting $\text{CHCl}_2\text{CCl}_2\text{O}^\bullet$ leads to the formation of CHCl_2COCl (DCAC) while the C–C bond can rupture to formed phosgene (COCl_2) and dichloromethyl radicals (CHCl_2^\bullet) in which the reaction pathway are channel (7) and channel (8a), respectively [11,22,23]. Sanhueza et al. [22] also suggested that channel (7) is more favorable and chlorine radical initiated destruction of TCE



Scheme 2. Proposed mechanism of TCE degradation.

yields 90% DCAC and significantly less amounts of phosgene. However, the aforementioned pathway relative to the phosgene formation seems not to be influenced by the oxygen concentration which is not corresponding to the demonstrated results herein. The mechanism outlined in channel (8a) does not account for the formation of phosgene, it holds true that the phosgene is formed from the reaction of DCAC [2]. Therefore, the study proposes the C–C bond of the resulting DCAC is subsequently attacked by Cl atoms to form the phosgene and CHCl_2^\bullet , as indicated in channel (8). Concerning channel (8), although C–C bond energy (83 kcal/mol) is somewhat higher than that of C–Cl (81 kcal/mol) but it is feasible for the rupture of C–C on the surface of TiO_2 [23]. The CHCl_2^\bullet may proceed to further reactions with oxygen and Cl atoms to form $\text{CH}_2\text{Cl}^\bullet$, CO_2 and Cl_2 [20,23]. The retardation of the phosgene generation seems to be related to competitive reaction with Cl atoms between O_2 and DCAC. This is why the increasing oxygen amount results to the decreasing yield of phosgene concluded in this study. Channels (9) and (10) are suggestive of the immediate reaction of forming the end-products, CO_2 , Cl_2 and HCl proposed by Amama et al. [23].

4. Conclusion

The corresponding result of batch photocatalytic degradation of TCE indicates the following:

1. Regarding the photocatalysis of TCE over TiO_2 in the FPPR, there exists an optimum RH and oxygen concentration for TCE degradation. Additionally, it generates significant quantity of DCAC and phosgene.
2. The overall rate constants of TCE and DCAC fall within the range of $(2.31 \pm 0.28) \sim (9.41 \pm 0.63) \times 10^{-2} \text{ min}^{-1}$ and $(0.94 \pm 1.25) \sim (9.35 \pm 1.71) \times 10^{-3} \text{ min}^{-1}$ respectively, suggesting that the degradation potential of TCE is superior to that of DCAC.
3. The formation of DCAC is significantly attributed to the TCE degradation that the transformation ratio is approximately within the range of 30–83% at the time the peak amount of DCAC appears. The degradation behavior of DCAC is the same with that of TCE that the optimum RH and oxygen concentration provide the higher reaction rate.
4. The existence of oxygen inhibits the phosgene generation owing to the competition of the Cl atoms between DCAC and O_2 suggesting the mechanism of phosgene formation is likely from the destruction of DCAC rather than that of TCE.

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