Photocatalytic degradation of chlorinated propenes using TiO_2

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Abstract

The photocatalytic degradation of chlorinated propenes using TiO_2 was investigated by FTIR spectroscopy. The chlorinated propenes were degraded to HCl, CO_2, CO, H_2O, and HCOOH during UV irradiation. During the degradation of 3-chloro-1-propene, the concentrations of CO_2, CO, and HCOOH increased just after starting the irradiation. The onset of the HCl formation was delayed. On the other hand, the onset of the HCOOH formation was delayed during the degradation of 1-chloro-1-propene. During the degradation of 2-chloro-1-propene, the rate of the HCOOH production was slower than that during the degradation of 3-chloro-1-propene although the HCl production was not delayed. These results indicated that HCOOH was produced by the degradation of the double-bonded carbon bonding to two H atoms during the initial stage. The chlorinated compounds were preferentially produced from the double-bonded carbon bonding to the Cl atom and rapidly degraded to HCl, CO_2, and CO during the initial stage. The residual part was degraded in the latter steps. Furthermore, it is suggested that the Cl atom on one of the double-bonded C atoms of the propenes was transferred to the other C atom before the degradation. Consequently, the double-bonded carbon bonding to two H atoms in 2-chloro-1-propene was chlorinated, then degraded to HCl, CO_2, and CO during the initial stage.

Keywords: Titanium dioxide, Photocatalysis, Chlorinated propene, Chlorinated butene, Degradation

INTRODUCTION

Groundwater and soil pollution due to trichloroethylene (TCE) are serious problems because TCE has been used as an effective organic solvent or a cleaning reagent and inappropriately treated in many locations all over the world. Photolysis is one of the effective purification methods to alleviate such pollution. However, this method produces some harmful intermediate compounds, such as dichloroacetylchloride (DCAC) and phosgene ($COCl_2$), during its degradation process [1,2]. Although $COCl_2$ is degraded to HCl and CO_2 in the presence of water during the photoreaction process, further light irradiation is required for the degradation of DCAC. It is very important to perform the complete purification of such pollutants without producing harmful compounds. The photocatalytic degradation of TCE and the other chlorinated olefins using TiO_2 during low-energy irradiation is also a more efficient purification method of these pollutants [1,2]. However, this procedure also produces intermediate chlorinated compounds, such as DCAC and $COCl_2$ [1−24]. Many researchers have suggested the relevant adsorption and degradation mechanisms based on a physicochemical analysis. They reported that the degradation of TCE proceeded by active species, such as the hydroxyl radical, chlorine radicals [3,5−7,10−17], and adsorbed oxygen species [8,9]. Although it is well known that DCAC is degraded on TiO_2 to produce $COCl_2$, CO_2, and HCl during the photocatalytic process, the details of its degradation mechanism including the adsorption form of such chemicals have not yet been totally clarified. It is important for developing the preparation of photocatalysts and control of the photocatalytic reaction to elucidate the relationship between the adsorption form of the species and the reactivity. There are some studies that have reported the adsorption form of the intermediate species,

such as DCAC and $COCl_2$, by FTIR or solid-state NMR analysis [8−10,21−26].

It was suggested that chlorinated ethenes bond to the oxygen molecules adsorbed on TiO_2, on which the degradation of the double-bonded carbons bonding to two Cl atoms produced $COCl_2$ during the photocatalytic reaction [20]. The suggested degradation process of TCE is shown in Figure 1. The DCAC production from TCE indicated that a Cl atom on one of the double-bonded C atoms was transferred to the other C atom before the degradation. These mechanisms were presumed from the photocatalytic degradation products of some chlorinated ethenes and the reaction of the adsorbed $^{18}O_2$ [18,19,27,28].

In this study, compared to the degradation process of chlorinated ethenes, the photocatalytic reaction of chlorinated propenes and a chlorinated butene on TiO_2 was investigated by a simple analysis method, FTIR spectroscopy, in order to understand the important degradation processes of chlorinated olefins. The influence of the molecular structure on the reaction process was discussed in order to confirm the previously suggested adsorption and degradation mechanisms of such compounds [20].

EXPERIMENTAL

Materials

Titanium tetraisopropoxide, ethanol, and nitric acid, (Wako, S grade or reagent grade) were used without further purification. Water was ion-exchanged and distilled. The chlorinated propenes (1-chloro-1-propene, 2-chloro-1-propene, and 3-chloro-1-propene) and 3-chloro-1-butene (Tokyo Kasei, reagent grade) and the dry air gas (Okaya Sanso, ca. nitrogen 79 % + oxygen 21 %) were used without further purification.

Preparation of Photocatalysts

The sol–gel reaction system was prepared in a nitrogen atmosphere by mixing 6.35 cm^3 of titanium tetraisopropoxide, 33.10 cm^3 of ethanol, 0.41 cm^3 of water, and 0.14 cm^3 of concentrated nitric acid as the catalyst of the sol–gel reaction. The sol–gel reaction system was thoroughly stirred during the reagent addition and for additional 10 min at room temperature. Glass wool was washed with ethanol and then dried. The dipping wool was withdrawn vertically from the sol–gel reaction system in a vial at the speed of 10 mm min^{-1} under nitrogen gas at ambient temperature. Finally, the wool was kept at ambient temperature for 1 day, heated at 773K for 1 h in air and then cut into 3 cm lengths. The crystalline phase of the TiO_2 film on glass was determined using an X-ray diffractometer (Rigaku RINT-2200V).

Photocatalytic Degradation of Chlorinated Propenes

The glass wool coated with TiO_2 was placed in an infrared cell filled with dried air. The infrared cell consisted of a cylinder made of Pyrex glass and two plates of KBr single crystals as the infrared windows, which are sealed by Teflon O-rings. Each sample gas for the degradation experiment was generated from a Permeater (GASTEC Co., PD-1B) by using the dry air. The gases passed through the cell for 1 h at 12 dm^3 h^{-1}, and then valves of the cell were closed. The degradation reactions for the chlorinated propenes were carried out in the cell by near-UV light irradiation from a 4-W black light bulb (Toshiba FL4BLB) at ambient temperature. The gas phase IR spectra were observed using a Shimadzu FTIR-8300 as a function of time. We can assume that the chemical species present in the reaction cell are in equilibrium between the gas phase and on the TiO_2 surface. Therefore, the decomposed species on the TiO_2 surface appears in the

FTIR spectra. The changes in the concentrations of the species in the gas phase were estimated from the absorbance and molar absorption coefficient values at their main peak wave numbers. The flakes of the TiO_2 used for the photocatalytic degradation were pressed in KBr pellets and their IR spectra were obtained using the FTIR spectrophotometer.

RESULTS AND DISCUSSION

Reaction analysis of chlorinated propene

The XRD pattern of the TiO_2 film on glass has peaks at 25.3°, 36.9°, 37.8°, 38.6°, and 48.1° assigned to the anatase-type crystal structure as shown in Figure 2.

Figure 3 shows the FTIR spectra of the 3-chloro-1-propene gas phase before and after the UV irradiation for 30−400 min. Before the irradiation, peaks were observed at 3100 and 2970 cm^{-1} assigned to the C−H anti-symmetric and symmetric stretching, respectively, at 1680 cm^{-1} assigned to the C=C stretching, at 1421 and 935 cm^{-1} assigned to the $C-H_2$ bending, at 1259 cm^{-1} assigned to the C−H bending, and at 757 cm^{-1} assigned to the C−Cl stretching vibrations. The peak intensities assigned to 3-chloro-1-propene decreased with an increase in the irradiation time. The peaks increased in their intensities at 3037−2723 cm^{-1} assigned to HCl, at 2398−2280 cm^{-1} assigned to CO_2, and at 2231−2066 cm^{-1} assigned to CO. Additionally, the peak intensities at 1750 and 1105 cm^{-1} assigned to the C=O and C−O stretching of HCOOH, respectively, increased with time. Weak peaks were observed at 3900−3500 and 1700−1500 cm^{-1} assigned to the O−H stretching and bending of H_2O, respectively, at the final stage.

The species adsorbed on the TiO_2 surface were also observed as a function of time by

FTIR spectroscopy. Figure 4 shows the FTIR spectra of the TiO_2 sample used for the photocatalytic degradation of 3-chloro-1-propene before and after the UV irradiation for 60−400 min. The differences between each spectrum and the initial spectrum were also shown. All the spectra have a peak at around 1630 cm^{-1} due to the H_2O adsorbed on the TiO_2 surface. The intensity of the broad band at 1800−1300 cm^{-1} increased with time. The differential spectra indicated an increase in the peak intensities at around 1570 and 1350 cm^{-1} assigned to the COO^- antisymmetric and symmetric stretching of $HCOO^-$, respectively [29,30]. This result indicated that the HCOOH produced by the degradation of 3-chloro-1-propene was strongly adsorbed on the TiO_2 surface and formed $HCOO^-$ due to the strong interaction between the carboxylate group and the surface Ti species. The peak intensities at around 1720 cm^{-1} due to the C=O stretching of HCOOH, as well as at around 1630 cm^{-1} due to the adsorbed H_2O, also increased with time. This result indicated that the $HCOO^-$ adsorbed on the TiO_2 surface was hydrolyzed and formed the HCOOH weakly adsorbed on the surface.

Figure 5 shows the changes in the concentrations of 3-chloro-1-propene and its degradation products, HCl, CO_2, CO, H_2O, and HCOOH, in the gas phase and the absorbance increase for $HCOO^-$ and H_2O adsorbed on the TiO_2 sample with the irradiation time. The concentrations of CO_2, CO, and HCOOH increased just after starting the irradiation. On the other hand, the onset of the HCl formation was delayed. A small amount of H_2O was observed in the gas phase because the produced H_2O was mainly adsorbed on the TiO_2 surface. The absorbance for the $HCOO^-$ adsorbed on the TiO_2 sample increased with the increase in the concentration HCOOH in the gas phase. The absorbance for the adsorbed H_2O also increased with that of the adsorbed $HCOO^-$. Figures 6 and 7 show the changes in the concentrations of 1-chloro-1-propene and

2-chloro-1-propene, respectively, and their degradation products, HCl, CO_2, CO, H_2O, and HCOOH, in the gas phase and the absorbance increase for $HCOO^-$ and H_2O adsorbed on the TiO_2 sample with the irradiation time. During the degradation of 1-chloro-1-propene, the onset of the HCOOH concentration was delayed compared to those of the other products. It is presumed that HCOOH is produced from the degradation of the double-bonded carbon bonding to two H atoms during the initial stage of the degradation of 3-chloro-1-propene. No double-bonded carbon of 1-chloro-1-propene bonds to two H atoms. The chlorinated compounds were preferentially produced from the double-bonded carbon bonding to the Cl atom and rapidly degraded to HCl, CO_2, and CO. During the degradation of 2-chloro-1-propene, the rate of the HCOOH production was slower than that during the degradation of 3-chloro-1-propene although it has the double-bonded carbon bonding to two H atoms. It is suggested that the Cl atom on one of the double-bonded C atoms of the propenes was transferred to the other double-bonded C atom before the degradation, similarly to the TCE degradation as shown in Figure 1. In a previous report, the $COCl_2$ was readily produced by the photocatalytic degradation of 1,1-dichloroethylene, TCE, and tetrachloroethylene because the two Cl atoms are bonded to one of the double-bonded carbons [20]. During the initial stage of the degradation of 1-chloro-1-propene and 2-chloro-1-propene, the chloroformic acid (ClCOOH) or formyl chloride (ClCHO) can be produced from the double-bonded carbon bonding to the Cl atom and rapidly degraded to HCl and CO_2 or CO [31]. On the other hand, 3-chloro-1-propene cannot produce HCl during the initial stage. During the degradation of each propenes, the absorbance for the $HCOO^-$ adsorbed on the TiO_2 sample increased with the increase in the concentration HCOOH in the gas phase. The absorbance for the adsorbed H_2O also increased with that of the adsorbed $HCOO^-$.

The photocatalytic degradation of 3-chloro-1-butene was also investigated in order to confirm the production process of HCOOH as shown in Figure 8. The degradation of 3-chloro-1-butene also produced HCOOH from just after the irradiation because one of its double-bonded carbons bonds to two H atoms.

Degradation mechanism of chlorinated propenes on TiO_2 surface

It was previously reported that the TiO_2 adsorbing oxygen molecules and chlorinated ethenes formed the charge transfer species ($[Ti^{3+}-O^{-}]^*$) with these molecules by light irradiation, and caused the photocatalytic reaction [20,27,28]. The degradation process of TCE was suggested as shown in Figure 1. HCl, CO_2, and CO are produced via DCAC and $COCl_2$ during the TCE degradation process. $COCl_2$ was presumed to be produced from the double-bonded carbon bonding to two Cl atoms in TCE. The DCAC production from TCE indicated that a Cl atom on one of the double-bonded C atoms was transferred to the other C atom before the degradation.

The suggested mechanism of the chlorinated propenes is shown in Figure 9. Oxygen molecules were adsorbed on the TiO_2 surface. The chlorinated propenes are also adsorbed on the TiO_2 surface that had adsorbed the oxygen. The double bond is weakened by bonding to the oxygen atoms. HCOOH was produced by the degradation of the double-bonded carbon bonding to two H atoms during the initial stage. On the other hand, ClCOOH was preferentially produced from the double-bonded carbon bonding to the Cl atom and rapidly degraded to HCl, CO_2, and CO during the initial stage. The Cl atom bonding to the double-bonded C atom was transferred to the other C atom during the UV irradiation as observed during the photocatalytic degradation of TCE on the TiO_2. After the production of HCOOH or ClCOOH, the residual part is adsorbed on the oxygen

atoms adsorbed on the TiO_2 surface in steps. HCOOH or ClCOOH as well as HCl, CO_2, and CO are also produced during the reaction steps. During the 3-chloro-1-propene degradation, the HCl production was delayed because the chlorinated residuals were degraded in the latter steps. On the other hand, HCOOH was produced in the latter steps during the 1-chloro-1-propene degradation.

Table 1 shows the quasi-first-order rate constants of the photocatalytic degradation of the chlorinated propenes and 3-chloro-1-butene. The degradation of 2-chloro-1-propene and 1-chloro-1-propene was faster than that of 3-chloro-1-propene. The degradation of 3-chloro-1-butene was the slowest. The constants indicated the reactivity of the Cl atom of each compound. The double-bonded carbon bonding to the Cl atom was rapidly degraded because it was activated by the oxygen atom. This phenomenon induced a fast HCl production. The Cl atom bonded to the single-bonded C atom reacted in the latter step, thus delaying the HCl production.

Some carbonyl compounds as the intermediate products were adsorbed on the TiO_2 surface during the photocatalytic degradation of TCE [8−10,21−26]. In the present case, a number of intermediate products was adsorbed on the TiO_2 surface because the concentrations of the detected products were lower than those expected from the initial concentration of the substances. $HCOO^-$ and H_2O were observed on the TiO_2 surface as the main products as shown in Figure 4.

CONCLUSIONS

The important processes of the photocatalytic degradation reaction of chlorinated propenes and a chlorinated butane on TiO_2 were investigated by FTIR spectroscopy compared to that of TCE. The influence of the molecular structure on the reaction

process was discussed in order to understand the main degradation mechanism of such compounds. The chlorinated propenes were degraded to HCl, CO_2, CO, H_2O, and HCOOH during the UV irradiation. During the degradation of 3-chloro-1-propene, the concentrations of CO_2, CO, and HCOOH increased just after starting the irradiation. The onset of the HCl formation was delayed. On the other hand, the onset of the HCOOH formation was delayed during the degradation of 1-chloro-1-propene. During the degradation of 2-chloro-1-propene, the rate of the HCOOH production was slower than that during the degradation of 3-chloro-1-propene although the HCl production was not delayed. These results indicated that HCOOH was produced from the degradation of the double-bonded carbons bonding to two H atoms during the initial stage after the substrate was adsorbed on the oxygen atoms already adsorbed on the TiO_2 surface. This is similar to the TCE degradation, in which $COCl_2$ was produced from the degradation of the double-bonded carbons bonding to two Cl atoms. The chlorinated compounds, such as ClCOOH, were preferentially produced from the double-bonded carbon bonding to the Cl atom and rapidly degraded to HCl, CO_2, and CO during the initial stage. After the production of HCOOH or ClCOOH, the residual part was adsorbed on the oxygen atoms already adsorbed on TiO_2 surface, and then degraded in steps. HCOOH or ClCOOH as well as HCl, CO_2, and CO are also produced during the latter steps. Furthermore, it is suggested that the Cl atom on one of the double-bonded C atoms of the propenes was transferred to the other C atom before the degradation as observed during the TCE degradation. Consequently, the double-bonded carbon bonding to two H atoms in 2-chloro-1-propene was chlorinated, and then degraded to HCl, CO_2, and CO during the initial stage.

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Table 1 Quasi-first order rate constants of the photocatalytic degradation of chlorinated propenes (1-chloro-1-propene, 2-chloro-1-propene, and 3-chloro-1-propene) and 3-chloro-1-butene.

Compound	Rate constant / min^{-1}
1-chloro-1-propene	7.2×10^{-3}
2-chloro-1-propene	8.0×10^{-3}
3-chloro-1-propene	5.2×10^{-3}
3-chloro-1-butene	9.5×10^{-4}

Figure captions

Figure 1 Degradation process of trichloroethylene.

Figure 2 XRD pattern of the TiO_2 sample.

Figure 3 Change in FTIR spectrum of 3-chloro-1-propene in gas phase during the photocatalytic degradation. The spectra observed (1) before and after (2) 30-min, (3) 60-min, (4) 120-min, and (5) 400-min UV irradiation.

Figure 4 Change in (a) FTIR spectrum of the TiO_2 sample used for the photocatalytic degradation of 3-chloro-1-propene and (b) differences between each spectrum and the initial spectrum. The spectra observed (1) before and after (2) 60-min, (3) 120-min, (4) 210-min, and (5) 400-min UV irradiation.

Figure 5 Time course of (a) concentrations of 3-chloro-1-propene (3CP) and each product in gas phase during the photocatalytic degradation and (b) absorbance increase for $HCOO^-$ and H_2O adsorbed on the TiO_2 sample.

Figure 6 Time course of (a) concentrations of 1-chloro-1-propene (1CP) and each product in gas phase during the photocatalytic degradation and (b) absorbance increase for $HCOO^-$ and H_2O adsorbed on the TiO_2 sample.

Figure 7 Time course of (a) concentrations of 2-chloro-1-propene (2CP) and each

product in gas phase during the photocatalytic degradation and (b) absorbance increase for $HCOO^-$ and H_2O adsorbed on the TiO_2 sample.

Figure 8 Time course of (a) concentrations of 3-chloro-1-butene (3CB) and each product in gas phase during the photocatalytic degradation and (b) absorbance increase for $HCOO^-$ and H_2O adsorbed on the TiO_2 sample.

Figure 9 Degradation process of chlorinated propenes.

Figure 1

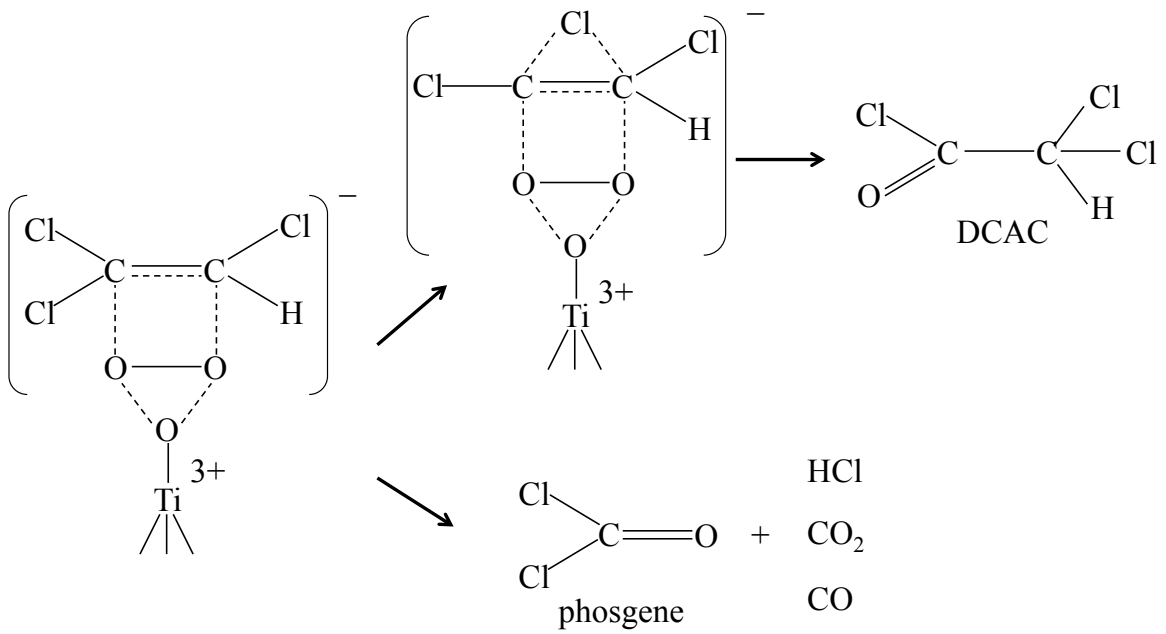
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Figure 2

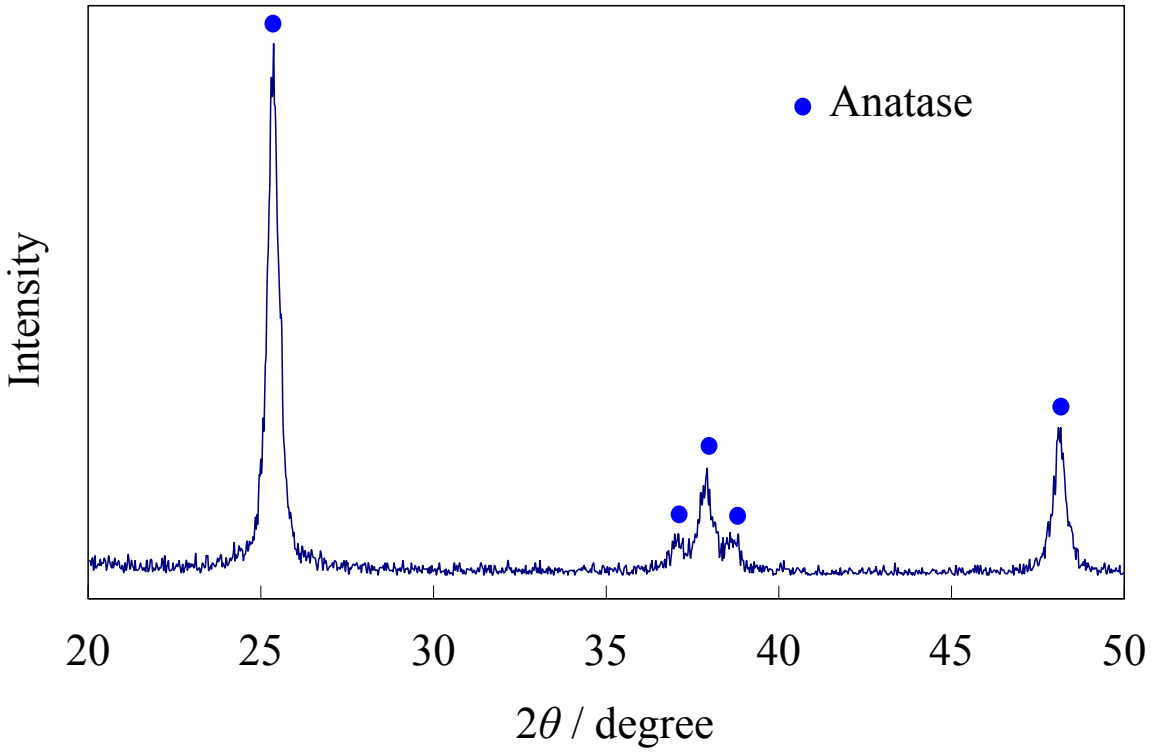
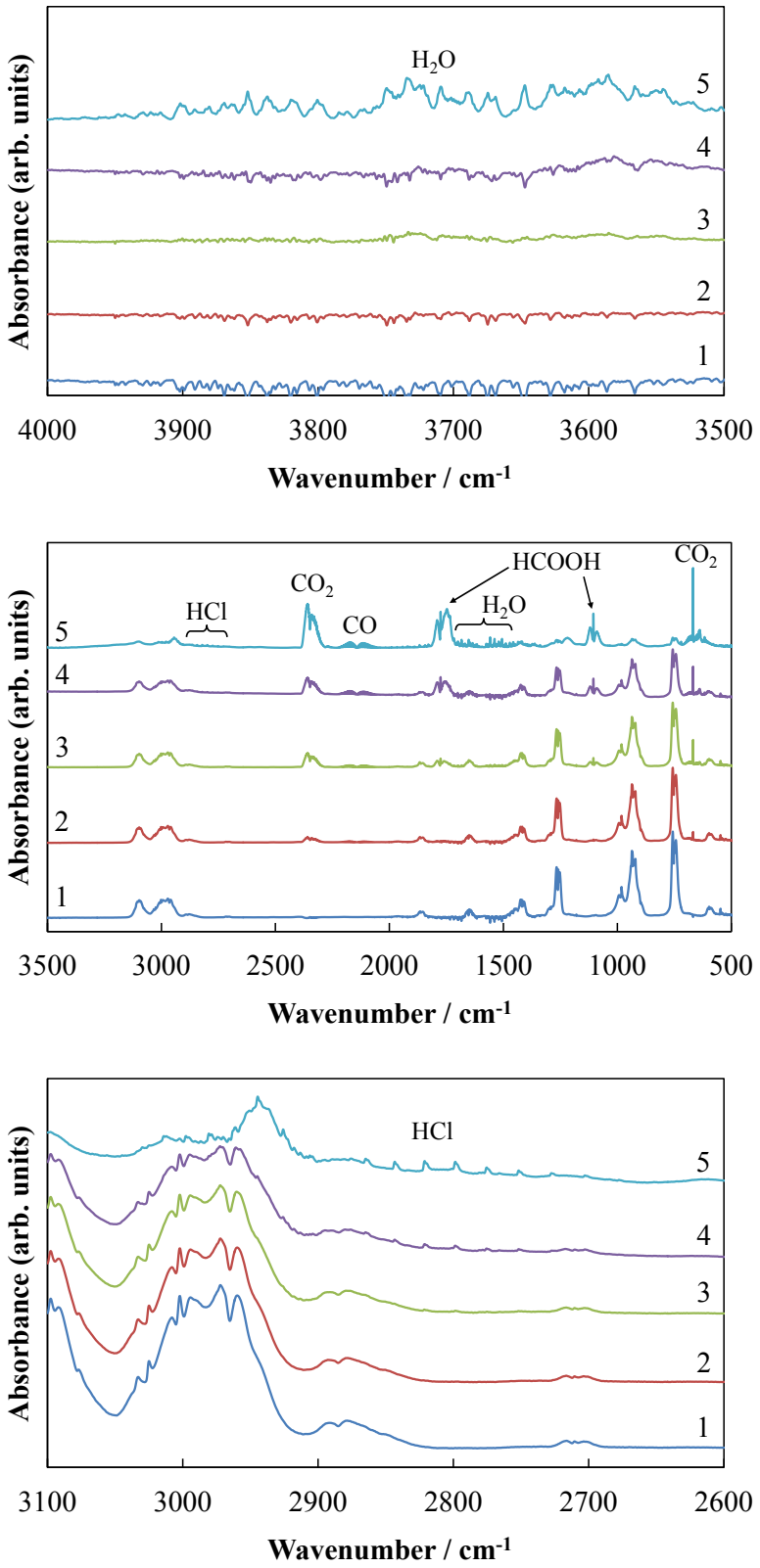


Figure 3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CO2
CO
HCOOH
H2O
CO2
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4
3
2
1
Absorbance (arb. units)
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3000
2500
2000
1500
1000
500
Wavenumber / cm-1
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5
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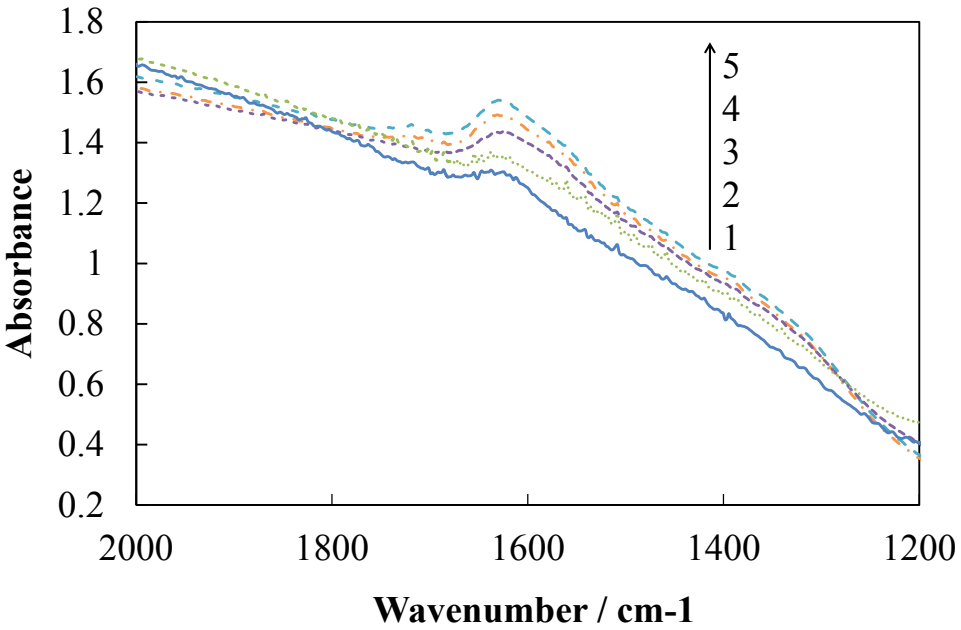
Wavenumber / cm-1

Figure 4

(a)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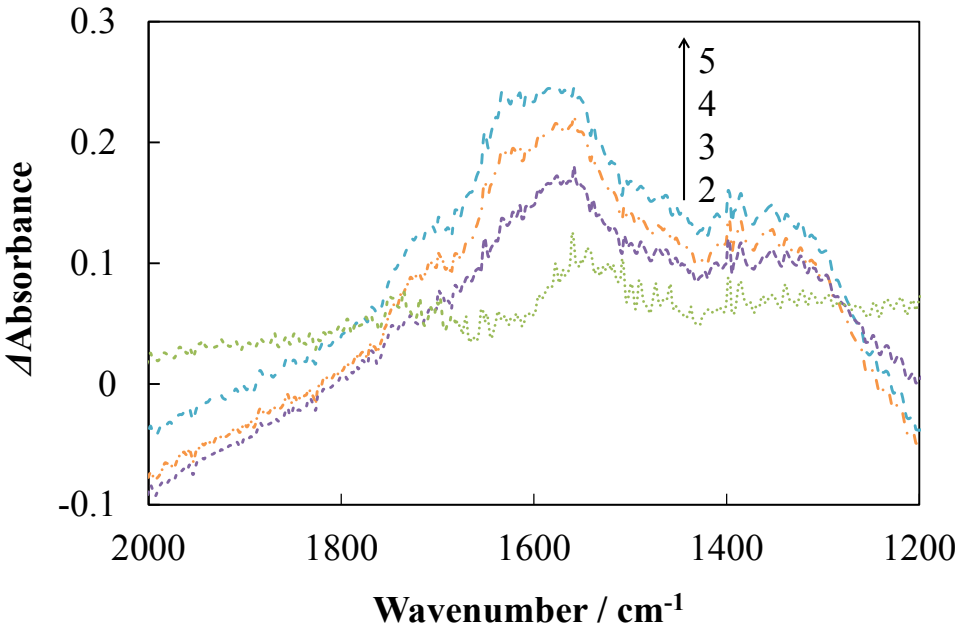
(b)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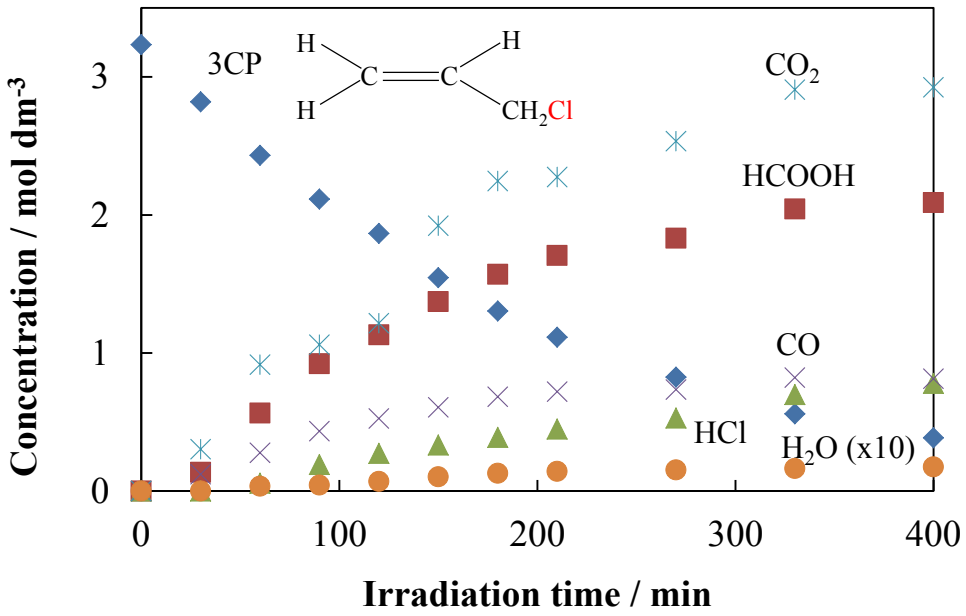
2

Figure 5

(a)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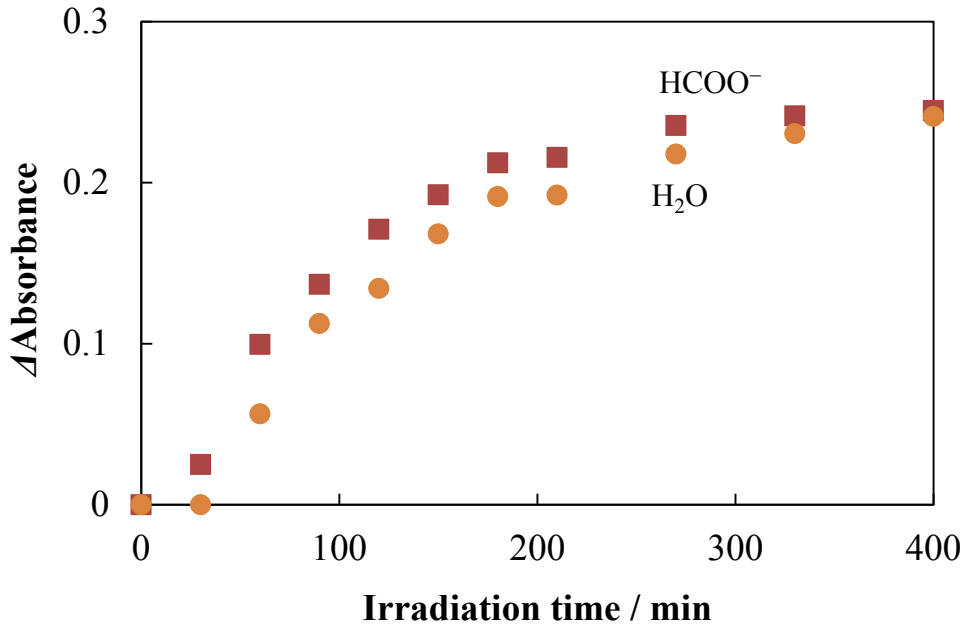
3
0
100
200
300
400
Irradiation time / min

(b)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H2O
ΔAbsorbance
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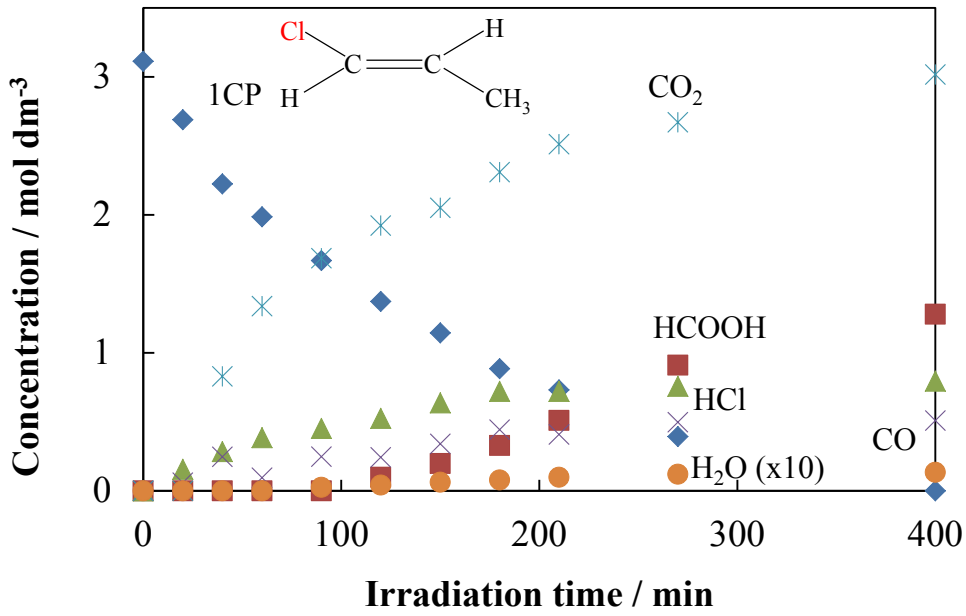
0.2
0.3
0
100
200
300
400
Irradiation time / min

Figure 6

(a)


Concentration / mol dm-3
Irradiation time / min
1CP
Cl
H
C
C
H
H
CH3
CO2
HCOOH
HCl
CO
H2O (x10)
0
1
2
3
0
100
200
300
400

(b)

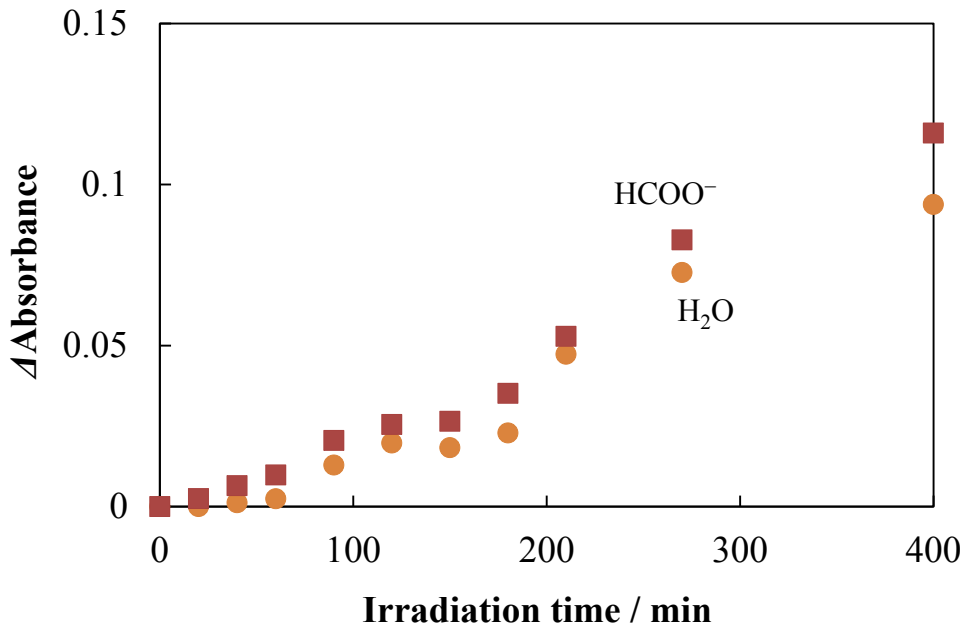
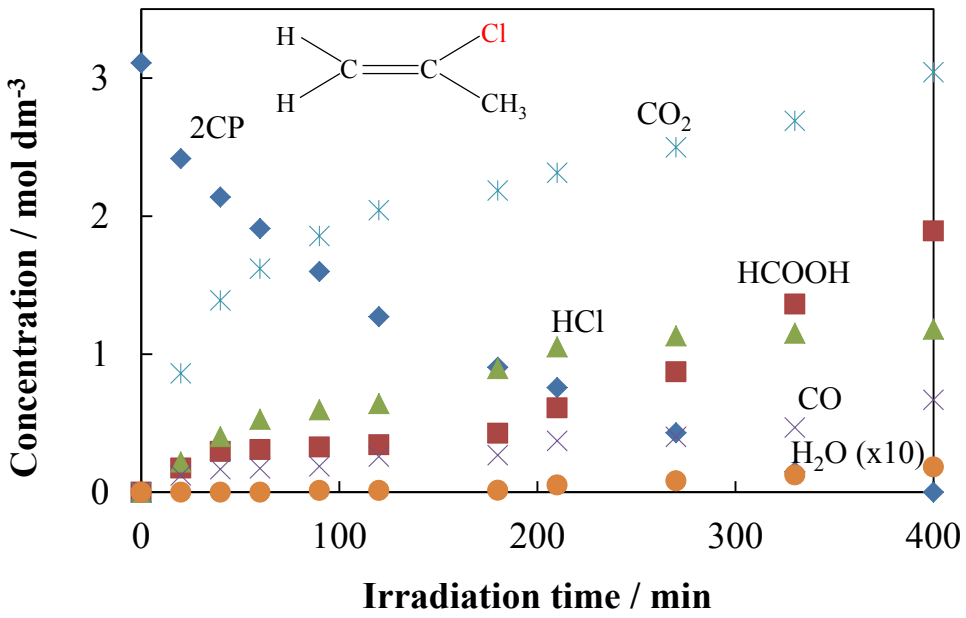

ΔAbsorbance
Irradiation time / min
HCOO−
H2O
0
0.05
0.1
0.15
0
100
200
300
400

Figure 7

(a)


Concentration / mol dm-3
Irradiation time / min
2CP
CO2
HCOOH
HCl
CO
H2O (x10)
H
H
C
C
Cl
CH3
0
1
2
3
0
100
200
300
400

(b)

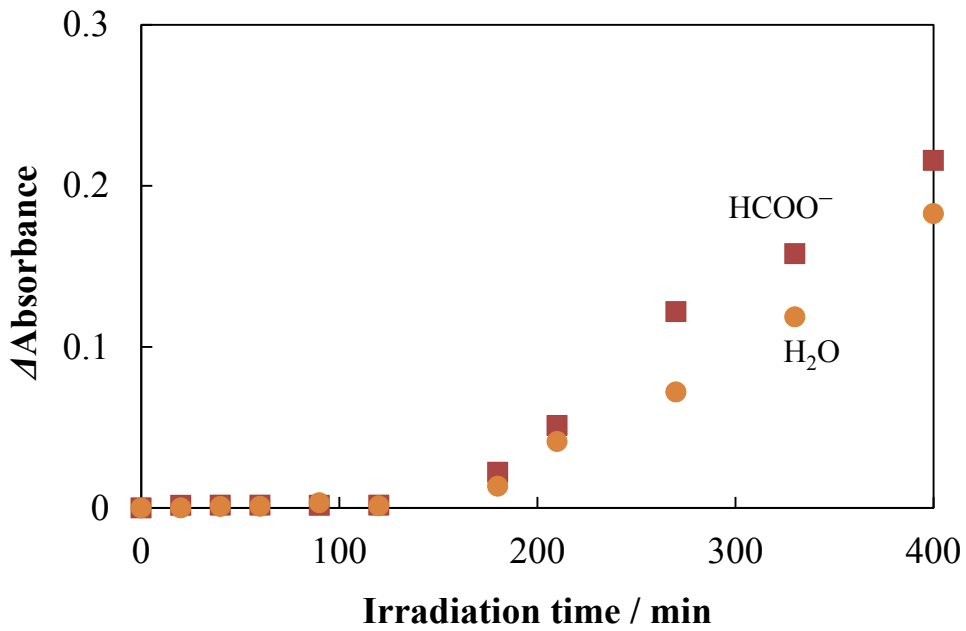
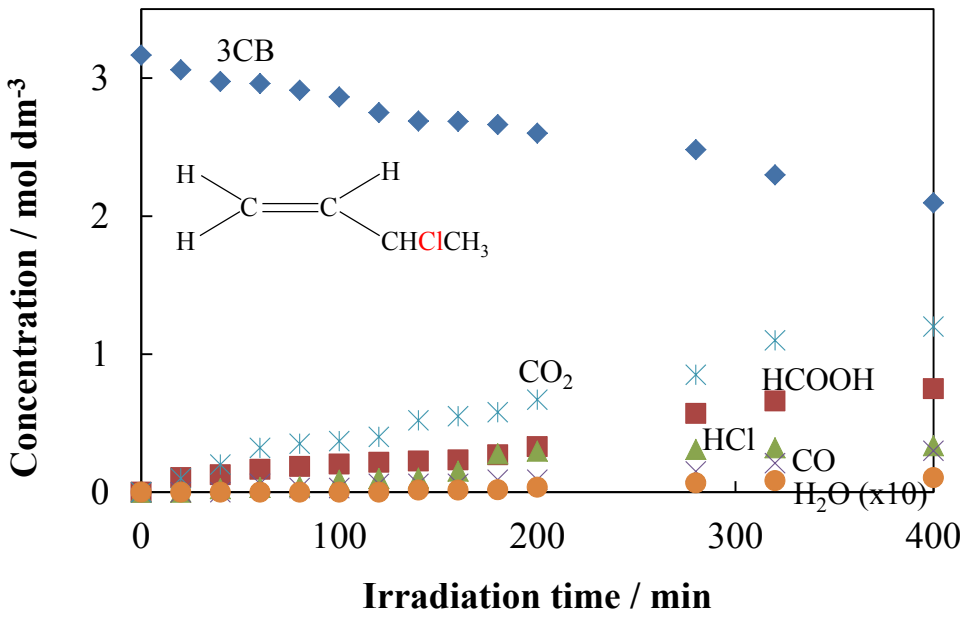

ΔAbsorbance
Irradiation time / min
HCOO−
H2O
0
0.1
0.2
0.3
0
100
200
300
400

Figure 8

(a)


3CB
H
H
C
C
H
CHClCH3
CO2
HCOOH
HCl
CO
H2O (x10)
Concentration / mol dm-3
Irradiation time / min
0
1
2
3
0
100
200
300
400

(b)

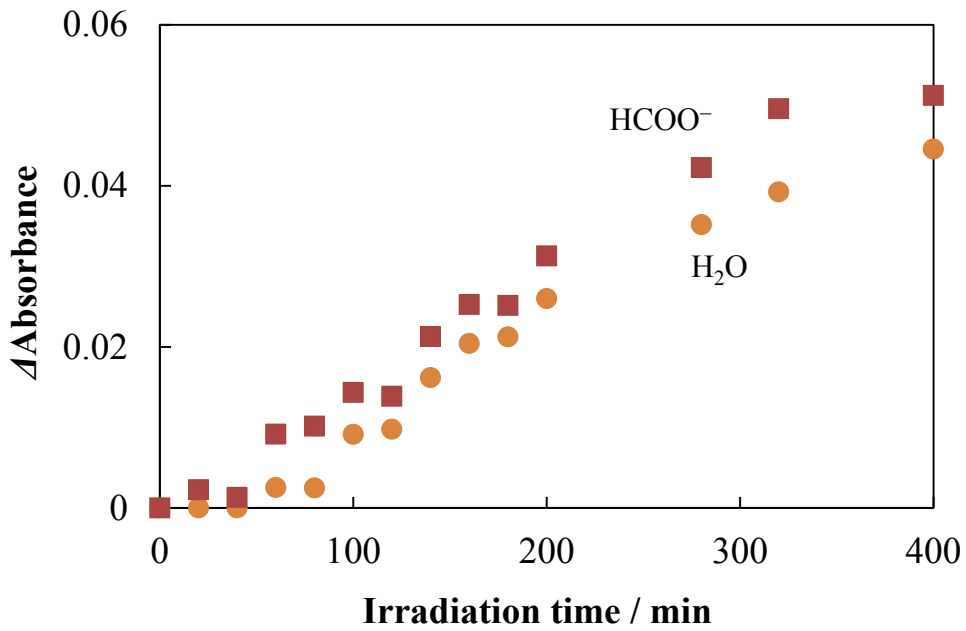
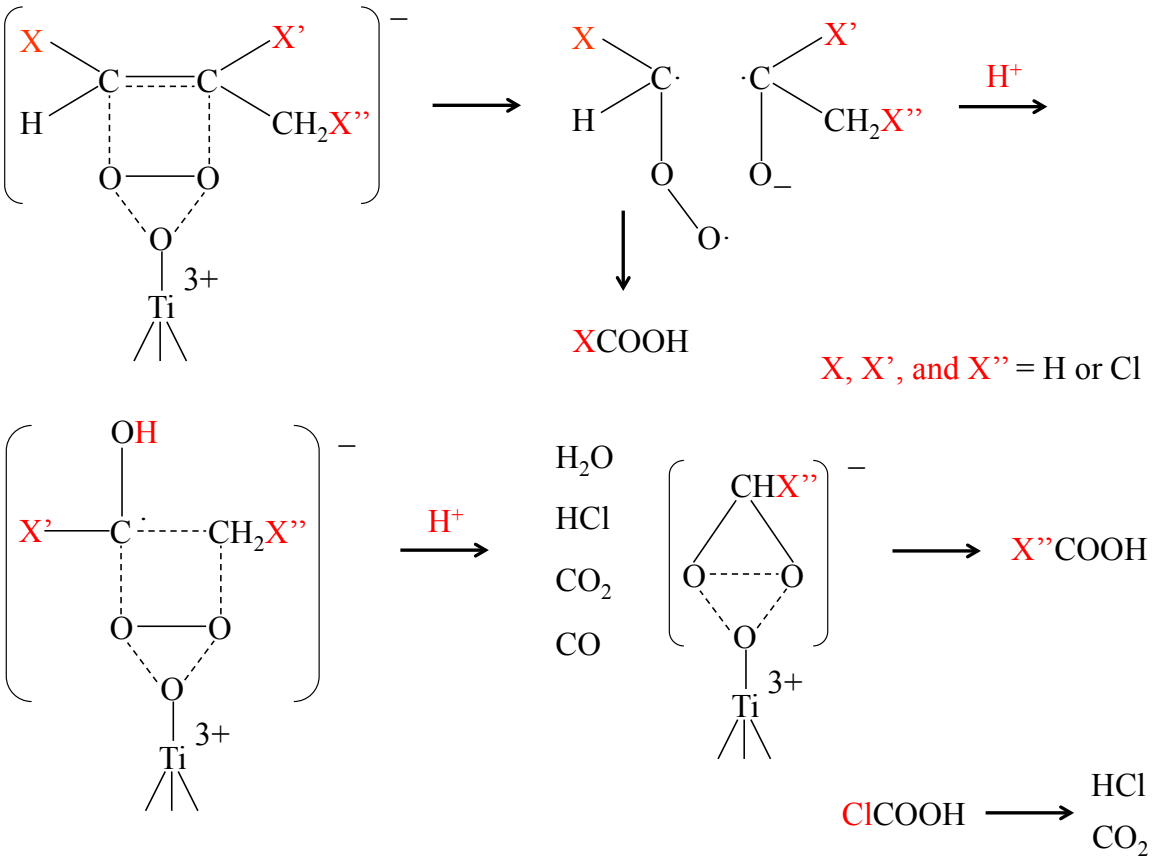

HCOO−
H2O
ΔAbsorbance
Irradiation time / min
0
0.02
0.04
0.06
0
100
200
300
400

Figure 9


X
X'
H
CH2X''
3+
Ti
H+
XCOOH
X, X', and X'' = H or Cl
OH
X'
CH2X''
H2O
HCl
CO2
CO
CHX''
X''COOH
ClCOOH
HCl
CO2