Light-triggered oxy-chlorination of cyclohexane by metal chlorides

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ABSTRACT

This paper discloses that visible light can trigger efficiently the oxy-chlorination of cyclohexane by some metal chlorides at ambient temperature under N_2 atmosphere. Among the metal chlorides examined, only a few metal chlorides with easily changeable valence such as $VOCl_3$, $CuCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$ were found to be efficient chlorinating agents for this photoreaction in acetonitrile or acetone, providing mono- and di-chlorinated cyclohexane as main products, with concomitant formation of a small amount of cyclohexene, cyclohexanol and cyclohexanone. $CuCl_2 \cdot 2H_2O$ was the most active chlorinating agent for this photoreaction, but provided an appreciable amount of the non-chlorinated products. $FeCl_3 \cdot 6H_2O$ possessed the best selectivity for the chlorinated products. In addition, it was found that a suitable amount of concentrated HCl was capable of realizing the visible light-driven $CuCl_2 \cdot 2H_2O$ or the UV-driven $FeCl_3 \cdot 6H_2O$ to catalyze photo-oxy-chlorination of cyclohexane under air, providing a high chlorination efficiency (turnover number (TON), 2.46 for $CuCl_2 \cdot 2H_2O$ and 4.66 for $FeCl_3 \cdot 6H_2O$). This is likely because the HCl can itself be used as a chlorinating agent; on the other hand, it also efficiently promotes the photoredox cycling of $CuCl_2$ or $FeCl_3$, as supported by UV–vis spectra. Based on these findings, a free radical mechanism for the present photo-oxy-chlorination system was proposed.

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1. Introduction

Oxy-chlorination of cyclohexane by the chloride-containing agents continues to be an important and challenging process, because chlorocyclohexane, one of the main products of this reaction, is a key intermediate in the production of a pharmaceutical trihexyphenidyl hydrochloride [1,2], a pesticide tricyclic tin hydroxide [3], an anti-scorching agent for rubber N-(cyclohexylthio)phthalimide [4,5] and a fine chemical cyclohexylamine [6]. Usually, the following three methods are used for the large-scale synthesis of chlorocyclohexane: (i) substitution of cyclohexanol by hydrogen chloride [7]; (ii) addition of cyclohexene by hydrogen chloride [8] and (iii) chlorination of cyclohexane by chlorine [9]. The substitution and addition methods have advantages of using simple and facile operation conditions and providing excellent chlorocyclohexane selectivity, but the high cost of raw materials makes these two methods uncompetitive. The chlorination route has the advantage of using cheap raw materials and providing high conversion efficiency, but it needs to use toxic, corrosive, and hazardous molecular chlorine as a chlorinating agent, which can lead to the corrosion of reaction equipment and the production of various environmental contaminants.

Various new halogenation approaches using halogen-containing compounds have been explored to replace the traditional halogenation by molecular halogen [10–18]. For example, some chloride salts [19] and a transition–metal complex $[Fe^{II}(TPA)Cl_2]$ (TPA = Tris(2-pyridylmethyl) amine) [20,21], respectively using peracetic acid and *tert*-butyl hydroperoxide (TBHP) as a terminal oxidant, can be used to efficiently convert cyclohexane to chlorocyclohexane. In addition, iodobenzene dichloride ($PhICl_2$) sometimes serves as an efficient chlorinating agent [14,22,23]. Upon light irradiation, $PhICl_2$ can efficiently chlorinate cyclohexane and toluene [22]. The chlorination chemistry described above is stoichiometric with respect to the chloride-containing compounds and/or the terminal oxidants; further adding an excess amount of the oxidant easily leads to substrate oxygenation instead of chlorination. Donald and co-workers [24] have reported that some iron complexes such as $Fe^{II}(OPPh_3)_4^{2+}$, $Fe^{II}(bpy)_2^{2+}$, $Fe^{II}(OH_2)_6^{2+}$, and $Fe^{III}Cl_3$ can catalytically activate 1:1 H_2O_2/HCl combinations for the efficient chlorination of cyclohexane. However, this catalytic chlorination process needs to use the costly catalyst and consume a mass of H_2O_2 to achieve an efficient conversion of cyclohexane.

It is well known that photoexcited iron or copper chloride complexes are able to induce hydrocarbon oxygenation under aerobic

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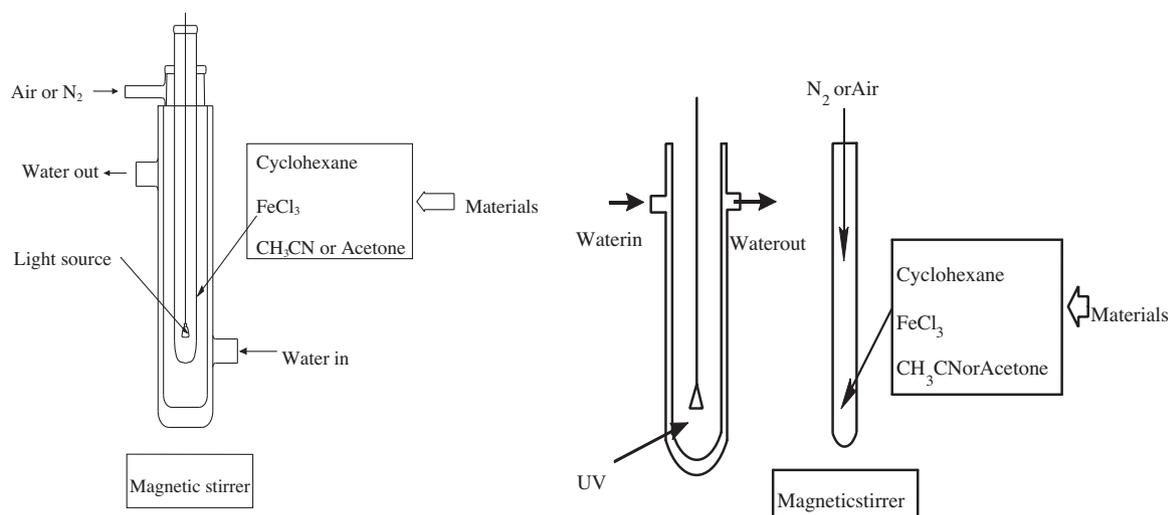*E-mail address:* fzhhnu@tom.com (Z. Fu).

Fig. 1. Self-assembled visible light reactor (left) and UV light reactor (right) used in this study.

conditions [25–28]. Notably, small amounts of chlorination were described in the original reports [27,28]. Maldotti et al. [29] have also reported that the stoichiometric chlorination of cycloalkanes with iron chloride heterogenized with amberlite was carried out efficiently under light irradiation. More recently, in the development of metal chlorides-catalyzed cyclohexane oxygenation by molecular oxygen under visible light irradiation, we also found that the photo-assisted oxy-chlorination of cyclohexane easily occurred when $FeCl_3$ was used [30]. However, the efficiency of photochlorination of cyclohexane by metal chloride is unsatisfactory at present, and to the best of our knowledge, a photocatalyzed chlorination process has not been achieved so far. Herein, we report initial results obtained using the visible light-driven oxy-chlorination of cyclohexane with various metal chlorides and the iron chloride or copper chloride-catalyzed oxy-chlorination of cyclohexane with HCl under UV or visible light irradiation and air atmosphere.

2. Experimental

2.1. Materials and apparatus

Materials and reagents used in this study were cyclohexane, n-hexanol, acetonitrile (CH_3CN), acetone (CH_3COCH_3), ethyl acetate, N,N-dimethyl amide (DMF) iron chloride ($FeCl_3 \cdot 6H_2O$), copper(II) chloride ($CuCl_2 \cdot 2H_2O$) and other metal chlorides, all of which were of analytical grade. Distilled water was used throughout this experiment.

2.2. UV–vis spectrophotometer

The liquid UV–vis spectra of samples were recorded from 200 to 800 nm on a UV-2450 spectrophotometer (Shimadzu, Japan).

2.3. Procedure of photo-oxy-chlorination of cyclohexane

Light-driven oxy-chlorination of cyclohexane with metal chloride was performed in a self-assembled photo-reactor equipped with a water-cooled condenser (see Fig. 1 left), and a 35 W tungsten-bromine lamp equipped with an UV light filter was immersed in the acetonitrile or acetone (5 mL) solution containing cyclohexane (1 mmol) and metal chloride (0.1–3.0 mmol). The reaction mixture was stirred magnetically under an N_2 or air atmosphere (1 atm) and sustained visible light irradiation, and the temperature of the reaction solution increased to 35 °C because of

the heating effect of light irradiation. Additionally, in the experiments of UV-driven oxy-chlorination of cyclohexane with $FeCl_3$, the above-mentioned reaction mixture was irradiated continuously by a 300 W high-pressure mercury lamp from its side face at 35 °C (see Fig. 1 right). After the desired irradiation time had elapsed, a small portion of the reaction mixture (0.5 mL) was sampled from the reactor, and the products were quantitatively analyzed on an Agilent 6890N gas chromatograph (GC) with a SE-54 quartz capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID) using n-hexanol as an internal standard. Both the injector and detector temperature were 250 °C, and the column temperature was 80 °C. The isolated products were satisfactorily identified by comparing the MS spectra with those of the authentic samples. Each experiment was repeated in duplicate, the data deviation between two parallel experiments was lower than *ca.* 5%.

3. Results and discussion

3.1. Characterization results

UV–vis spectra of various metal chlorides in acetonitrile (CH_3CN) are presented in Fig. 2. These metal chlorides generally showed two kinds of characteristic bands: some very weak d–d bands assigned to metal ions in a low energy region (500–800 nm) and some charge transfer (CT) bands between metal ions and ligands in a high energy region (200–500 nm) [31]. Among these CT bands, the CT band at 200–300 nm is probably assigned to the $M^{n+}O^{2-} \rightarrow M^{(n-1)+}O^-$ transition of $M^{n+} \cdot H_2O$ [32]. The CT bands with λ_{max} higher than 300 nm likely originate from the $M^{n+}Cl^- \rightarrow M^{(n-1)+}Cl$ transition of MCl_n molecules. It was further seen from Fig. 2 that $CuCl_2 \cdot 2H_2O$ and $VOCl_3$ possessed a CT absorption band near 460 and 400 nm in CH_3CN, respectively, and the CT absorption band centered around 360 nm in $FeCl_3 \cdot 6H_2O$ presented an absorption edge prolonged to the visible region of 380–500 nm. This is likely because the coordination effect of CH_3CN as electron-accepting molecule with MCl_n leads to red shift of the $M^{n+}Cl^- \rightarrow M^{(n-1)+}Cl$ transition to a visible region, as previously reported by some literature [30,33]. Other metal chlorides containing metal cations of low oxidizability, such as $ZnCl_2$, $CoCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $SnCl_4 \cdot 5H_2O$ and $NiCl_2 \cdot 6H_2O$, had hardly any response to the visible light of this region in CH_3CN, as a consequence of their $M^{n+}Cl^- \rightarrow M^{(n-1)+}Cl$ transition needing a higher energy.

The effect of solvent on the absorption capacity of metal chlorides in the visible region was further checked using $FeCl_3 \cdot 6H_2O$
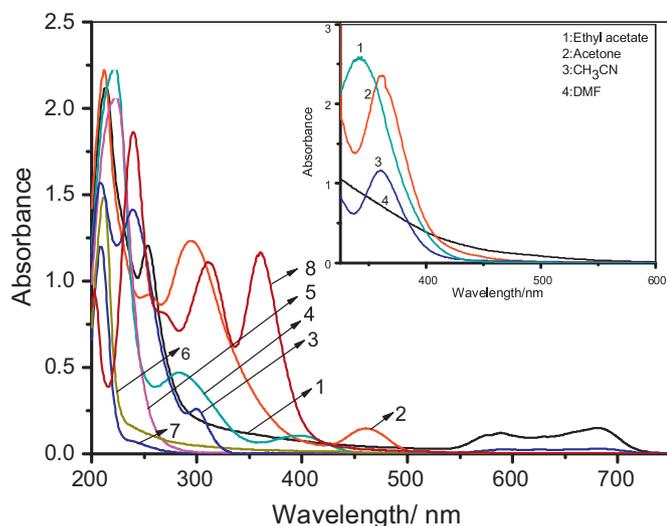
Fig. 2. The UV–vis spectra of various metal chlorides in acetonitrile solvent (4.0×10^{-4} M, 1: $CoCl_2 \cdot 6H_2O$; 2: $CuCl_2 \cdot 2H_2O$; 3: $ZnCl_2$; 4: $VOCl_3$; 5: $SnCl_4 \cdot 5H_2O$; 6: $MnCl_2 \cdot 4H_2O$; 7: $NiCl_2 \cdot 6H_2O$; 8: $FeCl_3 \cdot 6H_2O$). Inset is the UV–vis spectra of $FeCl_3 \cdot 6H_2O$ in different solvents (4.0×10^{-4} M).

as a representative. As shown in the inset of Fig. 2, the visible absorption edge of $FeCl_3 \cdot 6H_2O$ was influenced obviously by solvent. In comparison with CH_3CN, ethyl acetate, and especially acetone gave a stronger and wider absorption edge, while dimethylamide (DMF) gave a weaker but much wider absorption edge. The solvent-mediated effect on the visible absorption edge of $FeCl_3 \cdot 6H_2O$ probably originates from their coordination interaction with $FeCl_3 \cdot 6H_2O$.

3.2. Photo-oxy-chlorination results

3.2.1. Photo-oxy-chlorination performance of various metal chlorides

Table 1 lists data for the visible light-triggered oxy-chlorination of cyclohexane with some metal chlorides (1 equiv.) in CH_3CN at 35 °C under an N_2 atmosphere. Entries 1–5 illustrate that $MnCl_2 \cdot 4H_2O$, $ZnCl_2$, $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ with a negative standard redox potential (SRP) and $SnCl_4 \cdot 2H_2O$ with a positive SRP were nearly invalid for this chlorination, providing less than 2% of cyclohexane conversion in CH_3CN solvent. This is likely due to these metal chlorides having no response to visible light. A few metal chlorides such as $VOCl_3$, $FeCl_3 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ with a positive SRP, which can respond to visible light, were found to be efficient chlorination agents to this photoreaction, affording mono- and di-chlorinated cyclohexane as major reaction products, with concomitant formation of a small quantity of cyclohexanol, cyclohexanone and cyclohexene (see entries 6–8). Among them, $CuCl_2 \cdot 2H_2O$ showed the best photoreaction effect, providing about 66.6% of cyclohexane conversion with a relatively low selectivity for the chlorinated products (72.3%) after 8 h of visible light irradiation (see entry 7). $FeCl_3 \cdot 6H_2O$ exhibited a good reactivity and provided an excellent selectivity for the chlorinated products (entry 8). Entry 9 shows that the oxy-chlorination of cyclohexane with $FeCl_3 \cdot 6H_2O$ did not occur in the absence of visible light, indicating that the present oxy-chlorination is indeed triggered by visible light.

The influence of solvent on the photo-oxy-chlorination was further examined by using 2 equiv. of $FeCl_3 \cdot 6H_2O$ as an example and the results are shown in Table 1. Among the solvents examined, acetone ($\varepsilon = 20.7$) and CH_3CN ($\varepsilon = 37.5$) with a moderate and strong polarity, respectively, were found to be the best two media for

this reaction, providing a moderate cyclohexane conversion (43.9 and 46.9%) with a good selectivity for chlorocyclohexane (91.0 and 81.8%, see entries 10–11). Notably, this photochlorination did not easily occur in another DMF medium of strong polarity ($\varepsilon = 36.7$, entry 12), which is likely due to the capture effect of DMF on the free radicals produced in the photoreaction [34]. Ethyl acetate with a weak polarity ($\varepsilon = 6.0$) also provided a low chlorinated efficiency for the present photoreaction (see entries 13) owe to itself transformation to acetic acid, which has been confirmed by use of GC-MS measurement. The formation of acetic acid should originate from ethyl acetate hydrolysis.
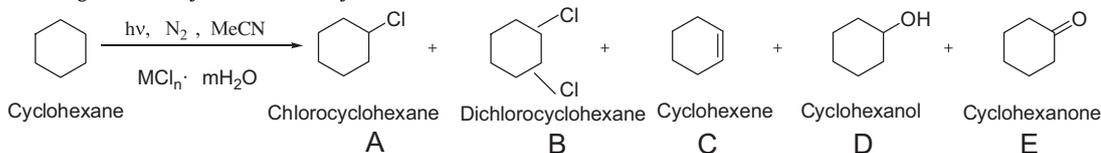
3.2.2. Effect of various parameters

In the following experiments, the influence of the amount of chlorinating agent $FeCl_3 \cdot 6H_2O$ and irradiation time on the photo-oxy-chlorination of cyclohexane was checked by using CH_3CN or acetone as a medium. As shown in Fig. 3A, when the photoreaction was carried out in CH_3CN, an increase in the amount of $FeCl_3 \cdot 6H_2O$ from 0.5 to 2 mmol resulted in the continuous and considerable increase of cyclohexane conversion from 27.7 to 46.9% and the gradual decrease of chlorocyclohexane selectivity from 90.4 to 81.8%, with a concomitant increase in dichloro-cyclohexane selectivity from 8.3 to 16.7%. After that, the conversion and selectivity for the chlorinated products were hardly influenced by the amount of $FeCl_3 \cdot 6H_2O$. The effect of the amount of $FeCl_3 \cdot 6H_2O$ on cyclohexane conversion in acetone was very similar to that in CH_3CN (Fig. 3B vs. Fig. 3A), but the selectivity for chlorocyclohexane was hardly influenced by the amount of $FeCl_3 \cdot 6H_2O$. This illustrates that a further photo-oxy-chlorination of chlorocyclohexane can be restrained efficiently in acetone.

Fig. 4A shows that when the irradiation time was between 2 and 12 h, the curve of cyclohexane conversion in CH_3CN climbed sharply with irradiation time; after 12 h, it climbed slowly and eventually achieved ca. 58.8% at 16 h. The selectivity for chlorocyclohexane continuously decreased with time, with a concomitant increase in dichlorocyclohexane selectivity, while the selectivity for cyclohexene was hardly influenced by the time. Fig. 4B shows that cyclohexane conversion in acetone continuously increased with irradiation time and eventually achieved ca. 60.1% after 16 h. The effect of irradiation time on the selectivity for various products in acetone was very similar to that in CH_3CN.

3.2.3. Photocatalyzed oxy-chlorination of cyclohexane

In order to realize a catalysis cycling of the present photo-oxy-chlorination, we tried to use concentrated HCl as a chlorinating agent for the $FeCl_3$ or $CuCl_2$-photocatalyzed cyclohexane oxy-chlorination under visible irradiation and the results are listed in Table 2A. Entry 1 shows that when a mixture of $FeCl_3 \cdot 6H_2O$ (0.1 mmol) and cyclohexane (1 mmol) in CH_3CN (5 mL) was irradiated by 35 W halogen lamp for 12 h under N_2 atmosphere, the obtained cyclohexane conversion (15.7%) was higher than the stoichiometric amount of $FeCl_3 \cdot 6H_2O$ (10%), and a small amount of the oxygenated products cyclohexanol and cyclohexanone was also found in addition to the main product chlorocyclohexane. This implies that the present reaction possesses some photocatalytic cycling character. When the photoreaction described above was carried out under air atmosphere (see entry 2), the conversion and the selectivity for the oxygenated products were ca. 21.7 and 36.9%, respectively, being obviously higher than both those obtained under N_2 atmosphere. This is mainly due to a contribution to the $FeCl_3$-photocatalyzed oxygenation of cyclohexane by molecular oxygen. Adding 0.1 mL of concentrated HCl to the above-mentioned photoreaction system was invalid to the improved cyclohexane conversion under N_2 atmosphere (entry 3), and contrarily resulted in the decreased cyclohexane conversion under air atmosphere (entry 4). Moreover, its introduction

Table 1
Visible light-driven oxy-chlorination of cyclohexane with various metal chlorides.[a]

Cyclohexane → hν, N₂, MeCN, MClₙ· mH₂O →
Chlorocyclohexane **A** + Dichlorocyclohexane **B** + Cyclohexene **C** + Cyclohexanol **D** + Cyclohexanone **E**

Entry	Metal chloride	Conv. (%)	Selectivity of products[b] (%)					SRP[c] (V)
			A	B	C	D	E	
1	MnCl₂·4H₂O	0.0	–	–	–	–	–	$E(Mn^{2+}/Mn) = -1.19$
2	ZnCl₂	0.0	–	–	–	–	–	$E(Zn^{2+}/Zn) = -0.76$
3	CoCl₂·6H₂O	0.0	–	–	–	–	–	$E(Co^{2+}/Co) = -0.28$
4	NiCl₂·6H₂O	2.0	–	–	–	51.2	48.8	$E(Ni^{2+}/Ni) = -0.26$
5	SnCl₄·5H₂O	0.0	–	–	–	–	–	$E(Sn^{4+}/Sn^{2+}) = 0.15$
6	VOCl₃	30.8	48.4	11.9	10.4	23.5	5.7	$E(VO^{3+}/VO^{2+}) = 0.99$
7	CuCl₂·2H₂O	66.6	54.0	18.3	12.0	12.4	3.3	$E(Cu^{2+}/Cu^+) = 0.15$
8	FeCl₃·6H₂O	36.9	87.0	11.5	1.5	–	–	$E(Fe^{3+}/Fe^{2+}) = 0.77$
9[d]		0.0	–	–	–	–	–	
10[e]		46.9	81.8	16.7	1.5	–	–	
11[e,f]		43.9	91.0	7.8	1.2	–	–	
12[e,g]		2.5	100	–	–	–	–	
13[e,h]		4.2	100	–	–	–	–	

[a] Cyclohexane (1 mmol), metal chloride (1 mmol), solvent, CH₃CN (5 mL), N₂ (1 atm), temperature (308 K), time (8 h), using 35 W halogen lamp as a light source.

[b] A = chlorocyclohexane, B = dichlorocyclohexane, C = cyclohexene, D = cyclohexanol, E = cyclohexanone. The selectivity for these products was directly calculated based on their yields.

[c] Standard redox potential in aqueous solution.

[d] Without light irradiation.

[e] Using 2 mmol of FeCl₃·6H₂O.

[f] Solvent, acetone (5 mL).

[g] Solvent, DMF(5 mL).

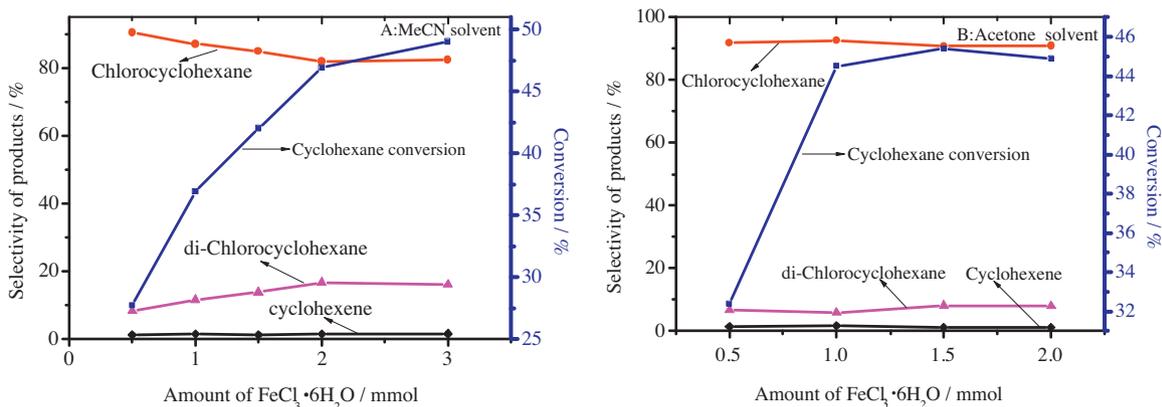[h] Solvent, ethyl acetate (5 mL).

Fig. 3. Effect of FeCl₃·6H₂O amount on the photo-oxy-chlorination of cyclohexane (1 mmol) in CH₃CN or acetone under N₂ (irradiation time, 8 h).
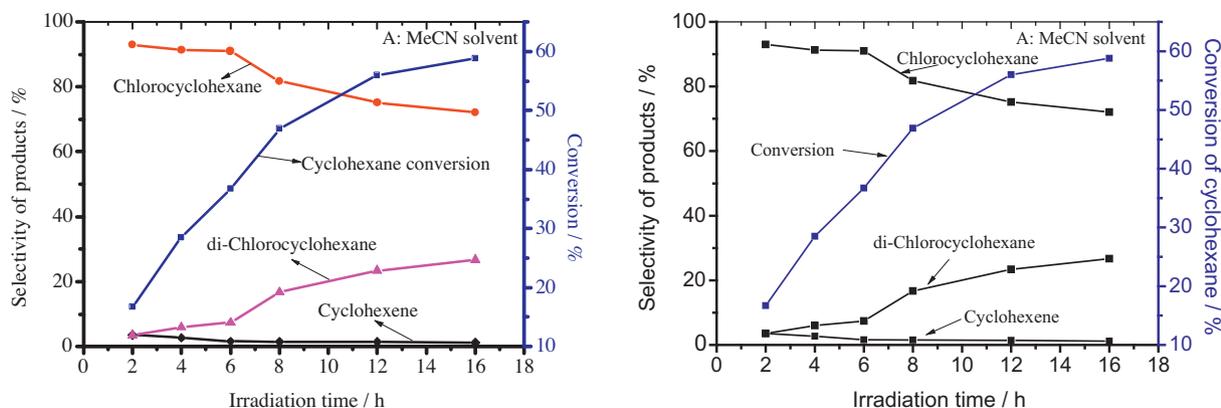

Fig. 4. Effect of irradiation time on the photo-oxy-chlorination of cyclohexane (1 mmol) with FeCl₃·6H₂O(2 mmol) in CH₃CN or acetone (5 mL) under N₂.

Table 2A
Effect of the additive concentrated HCl on the photocatalyzed oxychlorination of cyclohexane under visible light irradiation.[a]

Entry	Catalyst	HCl (mL)	Atmos.	Conv. (mol%)	TON[b]	Selectivity of products (%)				
						A	B	C	D	E
1	$FeCl_3$	–	N_2	15.7	1.37	87.0	–	1.3	8.6	3.1
2		–	Air	21.7	1.37	63.1	–	–	15.8	21.1
3		0.1	N_2	16.7	0.84	50.5	–	–	5.3	44.2
4		0.1	Air	17.6	0.58	32.9	–	–	8.3	58.8
5	$CuCl_2$	–	N_2	17.6	0.77	43.8	–	5.1	38.7	12.4
6		–	Air	19.2	0.80	41.6	–	–	35.2	19.2
7		0.1	N_2	18.3	1.24	68.0	–	4.9	23.1	4.0
8		0.1	Air	41.7	2.46	51.7	3.6	5.4	18.3	21.0
9		0.2	Air	42.6	2.47	58.0	–	2.8	21.8	17.4
10		0.3	Air	41.0	2.26	55.1	–	2.8	25.3	16.8

[a] Cyclohexane (1.0 mmol), $FeCl_3 \cdot 6H_2O$ (0.1 mmol), CH_3CN (5 mL), temperature (308 K), time (12 h), using 35 W halogen lamp, N_2 or Air pressure, 1 atom. The calculation of product selectivity saw the annotation b in Table 1.

[b] Turnover number (TON) based on the chlorinated products = (chlorocyclohexane (mmol) + 2dichlorocyclohexane (mmol))/$FeCl_3 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$ (0.1 mmol).

Table 2B
Effect of adding concentrated HCl on the $FeCl_3 \cdot 6H_2O$-photocatalyzed oxychlorination of cyclohexane under UV light irradiation.[a]

Entry	HCl (mL)	Atmos.	Conv. (mol%)	TON	Selectivity of products (%)				
					A	B	C	D	E
11	–	N_2	15.0	1.17	78.3	–	1.2	17.7	2.8
12	–	Air	21.5	1.90	88.4	–	3.4	8.2	–
13	0.1	N_2	28.5	3.05	75.8	15.6	4.6	3.8	–
14	0.1	Air	45.6	4.66	67.4	17.4	5.2	9.0	–
15	0.2	Air	37.6	3.80	76.1	12.5	4.9	5.7	0.8
16[b]	0.1	N_2	7.1	–	55.6	–	2.7	41.7	–

[a] Using 300 W high-pressure mercury lamp, other conditions were the same with those of Table 2A. The calculation of product selectivity saw the annotation b in Table 1.

[b] Without $FeCl_3 \cdot 6H_2O$.

significantly decreased the photo-chlorinated efficiency (turnover number (TON) based on the chlorinated products, entries 3 *vs.* 1, TON, 0.84 *vs.* 1.37; entries 4 *vs.* 2, TOF, 0.58 *vs.* 1.37), being due to an obvious increase of cyclohexanone selectivity. In comparison with the $FeCl_3 \cdot 6H_2O$, the $CuCl_2 \cdot 2H_2O$ showed a slightly higher activity, but an obviously lower chlorination selectivity for the photo-oxy-chlorination of cyclohexane under visible light irradiation and N_2 atmosphere (see entry 5). When the $CuCl_2 \cdot 2H_2O$-catalyzed this photoreaction was carried out under air atmosphere (see entry 6), the conversion and the selectivity for the oxygenated products were *ca.* 19.2 and 54.4%, respectively, being slightly higher than both those obtained under N_2 atmosphere. The reason that the $CuCl_2$-catalyzed photoreaction of cyclohexane is not obviously improved under air atmosphere is because the formation of the precipitate $Cu_2(OH)_3Cl$ in the photocatalysis process can hamper the photo-catalysis cycling of $CuCl_2$ [30]. When the concentrated HCl (0.1 mL) was added to the $CuCl_2$-mediated photoreaction system under N_2 atmosphere, the conversion hardly increased, but the photo-chlorinated selectivity was obviously improved (entry 7). Entry 8 shows that the additive HCl could significantly promote the $CuCl_2$-catalyzed photoreaction of cylcohexane under air atmosphere, providing *ca.* 41.7% of conversion with a much higher photo-chlorination efficiency than that without the additive HCl (see entries 8 and 6, TON, 2.46 *vs.* 0.8). This favorable effect of HCl is likely due to the following two reasons: (i) the HCl itself is an efficient chlorinating agent for the $CuCl_2$-catalyzed photo-chlorination; and (ii) it participates in the photoredox cycling of $CuCl_2$, as previously reported by us [30]. Entries 9–10 show that an attempt to further increase the HCl amount (0.2–0.3 mL) was hardly invalid in improving the conversion and the photo-chlorinated efficiency, this is likely because the use of an excess amount of concentrated HCl can lead to the decreased solubility of cyclohexane in CH_3CN.

Table 2B lists the data for the $FeCl_3$-mediated cyclohexane photoreaction under UV irradiation. Entries 11 and 12 illustrate that

the photo-chlorinated efficiency driven by UV light under N_2 (TON, 1.17) was slightly lower than that triggered by visible light (1.37), but the contrary result was observed under air atmosphere (TON, 1.90 *vs.* 1.37). Entry 13 shows that adding 0.1 mL of concentrated HCl to the reaction system obviously promoted this UV-driven photocatalytic reaction under N_2, providing a much higher TON (3.05) compared to the case without the additive HCl (TON, 1.17). This promoted effect also became more noticeable under air, which can provide *ca.* 4.66 of TON (entry 14). Further increasing the concentrated HCl to 0.2 mL, however, resulted in the decreased TON (3.80, entry 15). Entry 16 shows that a photoreaction of the concentrated HCl itself with cyclohexane also occurred under UV light irradiation, but its photo-chlorinated efficiency was very low (7.1% of conversion). This indicates that the improved effect of HCl on the UV-driven photo-oxy-chlorination does not mainly originate from its own photo-chlorination.

In order to explore the reason that the additive HCl is capable of promoting the $FeCl_3$-photocatalyzed oxy-chlorination of cyclohexane under UV light but is not under visible light, we measured the UV–vis absorption spectra of $FeCl_3$ in the present photoreaction media and system and the results are shown in Figs. 5 and 6, respectively. It is seen from Fig. 5 that the existence of concentrated HCl obviously increased the four UV absorption bands of $FeCl_3$ in CH_3CN, but decreased the absorption capacity of $FeCl_3$ in a visible light of 400–500 nm (see inset in Fig. 5). Fig. 6 further illustrates that the characteristic absorption bands of $FeCl_3$ in the presence of HCl under air were still well preserved after 2 h of UV light irradiation (curves 3 *vs.* 1) and only slightly weakened after 2 h of visible light irradiation (curves 2 *vs.* 1), but significantly decreased in the absence of HCl under the same photoirradiation conditions (curves 5–6 *vs.* 4). We propose from these findings that the HCl may participate in the photoredox cycling of $FeCl_3$ whether visible or UV light is used, but its hypochromic effect on the absorption of $FeCl_3$ in the visible region likely offsets its contribution to the photocatalytic cycling, which can lead it to hardly improving
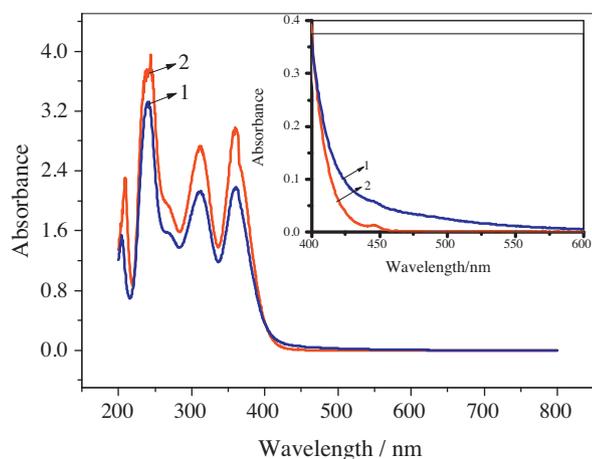
Fig. 5. UV–vis spectra of $FeCl_3 \cdot 6H_2O$ (4×10^{-4} M, 1: in CH_3CN (5 mL); 2: in CH_3CN (4.9 mL) and concentrated HCl (0.1 mL)). Inset is the amplified absorption edge of $FeCl_3 \cdot 6H_2O$ in a visible region.

the visible light-driven photocatalysis reaction. Evidently, the doubling effects of HCl on the improved UV absorption and promoted photoredox cycling of $FeCl_3$ should be the two main reasons that can lead it to obviously improving the UV-driven photocatalysis oxy-chlorination.

3.3. Photoreaction mechanism

Based on the results presented here, as well as those in previous studies [26–30], it is apparent that the stoichiometric oxy-chlorination of metal chlorides with cyclohexane under
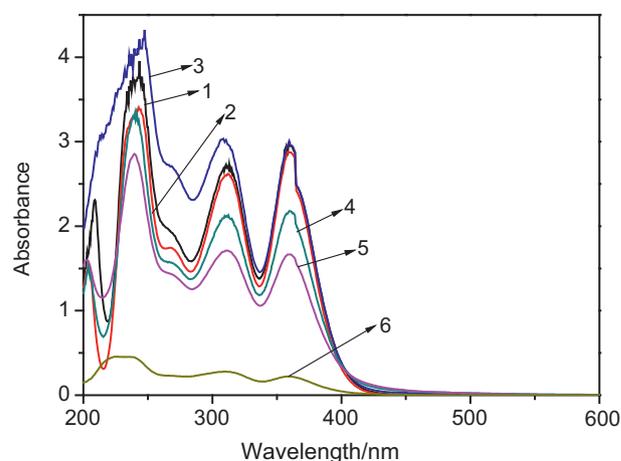
**Fig. 6.** UV–vis spectra of the $FeCl_3 \cdot 6H_2O$ (0.1 mmol) photocatalyzed cyclohexane (1 mmol) reaction system in CH_3CN (5 mL) under air. (The system was diluted to the concentration of $FeCl_3 \cdot 6H_2O$ for 4×10^{-4} M with CH_3CN before measurement). 1: The system with the concentrated HCl (0.1 ml); 2: after 2 h of using a visible light to irradiate the 1; 3: after 2 h of using an UV light to irradiate the 1; 4: The system without the concentrated HCl; 5: 2 h of using a visible light to irradiate the 4; 6: after 2 h of using an UV light to irradiate the 4.)

visible light is better explained according to the following reaction pathways (using $FeCl_3 \cdot 6H_2O$-photoreaction system as an example, see Scheme 1). Firstly, the visible light-driven electron-transfer process between metal and Cl^- ions can lead to the oxidation of Cl^- ions to Cl atoms and the reduction of Fe(III) to Fe(II) ions (Eq. (1)). The obtained radical species Cl atom may then abstract one H atom from cyclohexane to form a cyclohexyl radical (Eq. (2)), which would be followed by combination of another Cl atom to the
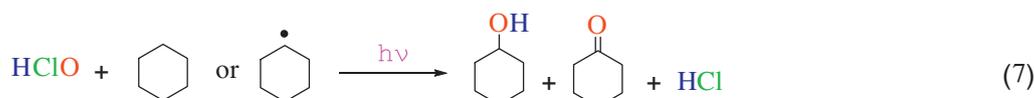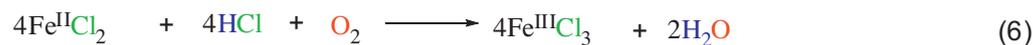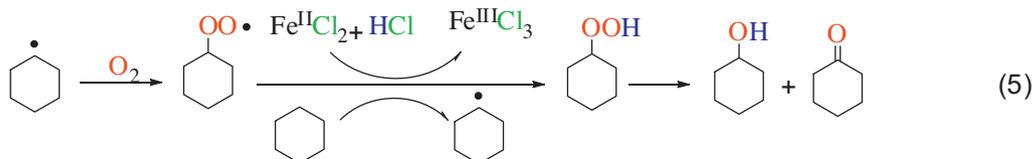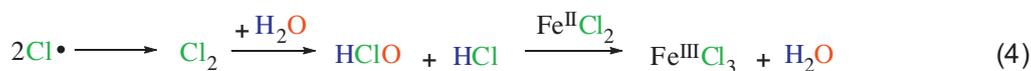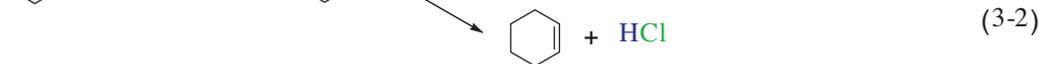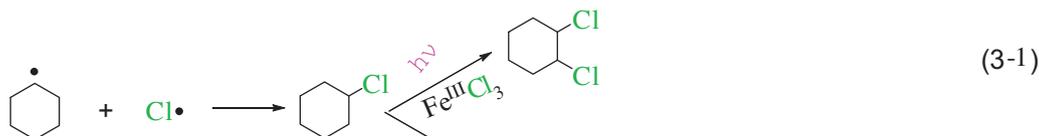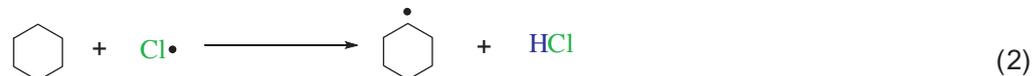
Scheme 1. Proposed photo-oxy-chlorination and photocatalytic oxy-chlorination mechanism.

cyclohexyl radical to form a chlorocyclohexane. The latter is further chlorinated to form a dichloro- cyclohexane through the three steps described above (Eq. (3-1)). The formation of cyclohexene, as reported previously by our groups [30], should be due to the further transformation of chlorocyclohexane *via* a complex and an unverified photoreaction pathway (Eq. (3-2)). The following three pathways are likely responsible for the $FeCl_3 \cdot 6H_2O$-photocatalyzed oxy-chlorination. The first pathway is that the molecular chlorine generated by the combination of two Cl atoms reacts with water to form a HClO and a HCl, then the $Fe^{II}Cl_2$ generated from the photoreduction of $Fe^{III}Cl_3$, with the help of HCl, is easily oxidized by the HClO to regenerate the original $Fe^{III}Cl_3$ (Eq. (4)). Maldotti et al. [29] have reported that $Fe^{III}Cl_3$ immobilized on Amberlite ($Amb^+/FeCl_4^-$) can efficiently achieve the photo-oxy-chlorination of cyclohexane, and its reduced form ($Amb^+/FeCl_3^-$) is easily oxidized to regenerate the starting $Amb^+/FeCl_4^-$ by addition of ClO^- at the end of the photochemical experiment. It is evident that the regenerated experiment reported by Maldotti et al. provides a direct proof for the first pathway. The second pathway is that the cyclohexyl radical combines with the O_2 in air to form a cyclohexyl peroxy radical ($CyOO^\bullet$). The latter, as proposed by Takaki et al. [28] and our groups [30] in the $CuCl_2$-photocatalyzed cyclohexane oxidation under O_2 atmosphere, is likely converted to a cyclohexyl hydroperoxide ($CyOOH$) through the following two routes (Eq. (5)): (i) The $CyOO^\bullet$ may oxidize the $Fe^{II}Cl_2$ to form a $CyOOH$ and the starting $Fe^{III}Cl_3$ in the participation of HCl, and (ii) it may abstract one H atom of cyclohexane to yield a $CyOOH$ and another cyclohexyl radical. Finally, the $CyOOH$ can be converted to form the corresponding alcohol and ketone (Eq. (5)). The third pathway is that the $Fe^{II}Cl_2$ is directly oxidized to the starting $Fe^{III}Cl_3$ by O_2 in the presence of HCl (Eq. (6)).

The proposed three catalysis pathways may explain the experimental results in Tables 2A and 2B. Evidently, the photocatalytic cycling of $Fe^{III}Cl_3$ under N_2 atmosphere is only realized *via* the first pathway described above, and the formation of cyclohexanol and cyclohexanone is undoubtedly due to the photooxidation of cyclohexane and cyclohexyl radical by HClO, respectively, as shown in Eq. (7). The photocatalytic cycling of $Fe^{III}Cl_3$ under air atmosphere can be achieved *via* the three pathways described above. Based on the fact that the selectivity for the oxygenated products in the UV-driven $FeCl_3$ photocatalysis system under air does not increase obviously compared to that under N_2, we propose that the third pathway likely plays a dominant role in the photocatalytic cycling of $Fe^{III}Cl_3$ under air. The proposed mechanism shown in Scheme 1 may explain the difference among the photo-chlorination performance of other metal salts. It is evident that Eq. (1) hardly occurs upon the metal chlorides of containing metal cations of low oxidizability such as $MnCl_2$, $ZnCl_2$, $CoCl_2 \cdot 6H_2O$ and $NiCl_2$ (see their standard redox potential listed Table 1). $SnCl_4 \cdot 5H_2O$ with a similar redox potential to $CuCl_2 \cdot 2H_2O$ does not show any photo-chlorinated activity, which is likely due to its weak absorption to visible light and strong hydrolysis in CH_3CN containing water. Only high-valence metal-containing chlorides that are hardly hydrolyzed, easily absorb UV or visible light and realize the redox cycle (such as $VOCl_3$, $CuCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$) can serve as a good photo-chlorinating agent or catalyst, as supported by the above characterization and reaction results.

4. Conclusion

In summary, we have developed the use of light-driven oxy-chlorination of cyclohexane with metal chlorides and the $FeCl_3$-/$CuCl_2$-photocatalyzed oxy-chlorination of cyclohexane with concentrated HCl under UV–vis light irradiation and air atmosphere. The present photo-oxy-chlorination system has the

following advantages: (i) using cheap metal chlorides $CuCl_2$ and especially $FeCl_3$ as an efficient chlorinating agent or a photocatalyst; (ii) utilization of more accessible visible light and more-cost effective acetonitrile or acetone as solvent; and (iii) a highly chlorinated selectivity. It is anticipated that this photo-reaction or catalysis system can be applied in the oxy-chlorination of other organic compounds.

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