



## 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<sub>2</sub> atmosphere. Among the metal chlorides examined, only a few metal chlorides with easily changeable valence such as VOCl<sub>3</sub>, CuCl<sub>2</sub>·2H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O 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<sub>2</sub>·2H<sub>2</sub>O was the most active chlorinating agent for this photoreaction, but provided an appreciable amount of the non-chlorinated products. FeCl<sub>3</sub>·6H<sub>2</sub>O 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<sub>2</sub>·2H<sub>2</sub>O or the UV-driven FeCl<sub>3</sub>·6H<sub>2</sub>O to catalyze photo-oxy-chlorination of cyclohexane under air, providing a high chlorination efficiency (turnover number (TON), 2.46 for CuCl<sub>2</sub>·2H<sub>2</sub>O and 4.66 for FeCl<sub>3</sub>·6H<sub>2</sub>O). 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<sub>2</sub> or FeCl<sub>3</sub>, 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<sup>II</sup>(TPA)Cl<sub>2</sub>](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<sub>2</sub>) sometimes serves as an efficient chlorinating agent [14,22,23]. Upon light irradiation, PhICl<sub>2</sub> 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<sup>II</sup>(OPPh<sub>3</sub>)<sub>4</sub><sup>2+</sup>, Fe<sup>II</sup>(bpy)<sub>2</sub><sup>2+</sup>, Fe<sup>II</sup>(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup>, and Fe<sup>III</sup>Cl<sub>3</sub> can catalytically activate 1:1 H<sub>2</sub>O<sub>2</sub>/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<sub>2</sub>O<sub>2</sub> 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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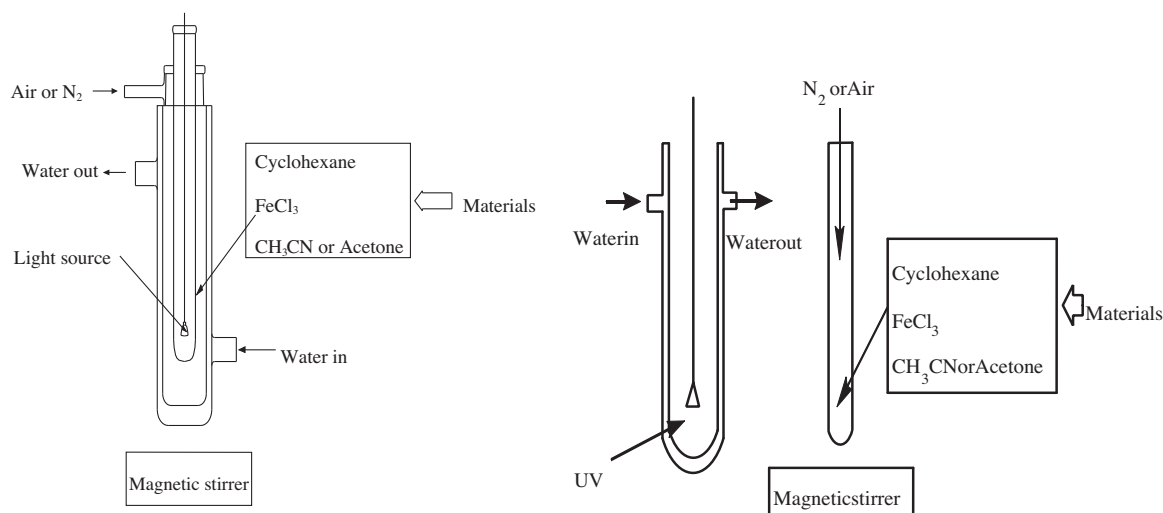


Fig. 1. Self-assembled visible light reactor (left) and UV light reactor (right) used in this study.

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  $\text{FeCl}_3$  was used [30]. However, the efficiency of photo-chlorination 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 ( $\text{CH}_3\text{CN}$ ), acetone ( $\text{CH}_3\text{COCH}_3$ ), ethyl acetate, *N,N*-dimethyl amide (DMF) iron chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), copper(II) chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) 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  $\text{N}_2$  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  $\text{FeCl}_3$ , 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  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ ) 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 ( $\text{CH}_3\text{CN}$ ) 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  $\text{M}^{n+}\text{O}^{2-} \rightarrow \text{M}^{(n-1)+}\text{O}^-$  transition of  $\text{M}^{n+} \cdot \text{H}_2\text{O}$  [32]. The CT bands with  $\lambda_{\text{max}}$  higher than 300 nm likely originate from the  $\text{M}^{n+}\text{Cl}^- \rightarrow \text{M}^{(n-1)+}\text{Cl}$  transition of  $\text{MCl}_n$  molecules. It was further seen from Fig. 2 that  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{VOCl}_3$  possessed a CT absorption band near 460 and 400 nm in  $\text{CH}_3\text{CN}$ , respectively, and the CT absorption band centered around 360 nm in  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  presented an absorption edge prolonged to the visible region of 380–500 nm. This is likely because the coordination effect of  $\text{CH}_3\text{CN}$  as electron-accepting molecule with  $\text{MCl}_n$  leads to red shift of the  $\text{M}^{n+}\text{Cl}^- \rightarrow \text{M}^{(n-1)+}\text{Cl}$  transition to a visible region, as previously reported by some literature [30,33]. Other metal chlorides containing metal cations of low oxidizability, such as  $\text{ZnCl}_2$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , had hardly any response to the visible light of this region in  $\text{CH}_3\text{CN}$ , as a consequence of their  $\text{M}^{n+}\text{Cl}^- \rightarrow \text{M}^{(n-1)+}\text{Cl}$  transition needing a higher energy.

The effect of solvent on the absorption capacity of metal chlorides in the visible region was further checked using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

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