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Chlorine-Radical-Mediated Photocatalytic Activation of C−H Bonds with Visible Light**

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The selective activation and transformation of C(sp^3)−H bonds in alkanes to produce higher-value products is of great importance in both fundamental and applied chemistry.[1] Since these bonds are both thermodynamically strong and kinetically inert, conventional catalytic strategies for the activation step require the use of toxic, aggressive, and expensive reagents under rather stringent conditions.[2] Heterogeneous semiconductor photocatalysis is considered to be a promising alternative for the activation of C−H bonds under mild conditions.[3] The use of cheap and abundant molecular oxygen as the oxidant and light as the driving force makes such processes especially appealing for green chemical reactions for industrial applications. However, most photocatalytic reactions require high-energy ultraviolet radiation and show extremely low visible-light activity.[4] Therefore, the development of an environmentally friendly and highly efficient photocatalytic system that can transform inert alkanes into functionalized products under visible light is significant and highly desirable.

Although the C(sp^3)−H bonds in alkanes are strong and difficult to cleave directly, they react readily with extremely reactive species, such as free radicals.[5] For example, the aggressive hydroxyl radical usually generated in photocatalysis has been the typical initiator of C−H cleavage, but mineralizes nearly all organic compounds owing to its poor selectivity. The chlorine radical, which shows similar hydrogen-abstraction behavior, was reported by the Ollis research group to enhance activity in the photocatalytic degradation of gaseous contaminants under UV irradiation, although no direct evidence for its formation was provided.[6] However, the idea of chlorine-assisted photocatalysis has not drawn much attention, since its practical application has been restricted to the photodegradation of gas-phase trace pollutants by irradiation with UV light. Recently, our research group found that TiO_2-based photocatalysts with chlorine chemisorbed on their surface showed a remarkable improvement in photocatalytic activity in the degradation of gaseous organic substrates under irradiation with visible light.[7] This finding makes photocatalytic reactions more practical owing the availability of endlessly renewable solar energy. Most interestingly, the behavior of these chlorinated TiO_2-based photocatalysts in the degradation of aromatic alkanes depended on whether UV or visible light was used. Under UV irradiation, both high conversion and extensive mineralization of toluene were observed, whereas under irradiation with visible light, high conversion and rather low mineralization were observed. In the latter case, the low mineralization suggested that toluene had been transformed into oxygenated products other than CO_2. This result led us to reason that this chlorine-radical-mediated strategy might be more promising for the selective transformation of alkanes: a widely sought yet elusive process in organic synthesis.

Herein, we report the application of surface-chlorinated $BiOBr/TiO_2$ (CBT) for the selective activation of C(sp^3)−H bonds in alkanes under irradiation with visible light. The generation of chlorine radicals and their pivotal role in these heterogeneous photocatalytic processes were revealed for the first time. The use of a cheap, environmentally friendly inorganic semiconductor photocatalyst and solar energy make this method more green and sustainable than conventional C−H bond-activation strategies.

The oxygenation of hydrocarbons was initially carried out in benzotrifluoride (Btf) over $BiOBr/TiO_2$ (BT) under irradiation with visible light ($\lambda > 420$ nm) with a moderate light intensity of 250 mW cm^{-2} (see Table S1 in the Supporting Information). Although it occurred with almost 100% selectivity for the formation of the corresponding aldehyde or ketone, the conversion of toluene and cyclohexane was low (ca. 1%), since the photocatalytic activation of C−H bonds by semiconductors usually shows extremely low activity under visible-light irradiation. Surprisingly, when CBT was used as the photocatalyst under similar conditions, a significantly improved conversion ratio was observed. The conversion of toluene and cyclohexane reached 18.5 and 11.8%, respectively, which was about 18 and 13 times that observed for toluene and cyclohexane over BT. Meanwhile, the chlorinated system maintained good selectivity for conversion into benzaldehyde (80.2%) and cyclohexanone (95.2%). The CBT catalyst was also active for the transformation of other hydrocarbons, with 55.0% conversion of ethylbenzene and 33.3% conversion of *p*-xylene. In all cases, no chlorinated products were detected by GC.

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Inspired by these initial promising results, we further investigated the photocatalytic oxygenation of hydrocarbons over CBT in the absence of an organic solvent, since solvent-free conditions are environmentally friendly and more practical for the separation of the desired products (Table 1). Like in Btf, the catalyst CBT also showed highly improved performance under solvent-free conditions with respect to that of BT for the oxidation of pure hydrocarbons. Upon irradiation for 4 h, the conversion of toluene over CBT reached 1.0%, which was about 8.3 times that observed for the reaction over BT (Table 1, entries 1 and 2). The amount of benzaldehyde produced in 4 h was 85.1 μmol per milliliter, which corresponds to a high selectivity of 90.6% and a high turnover number (TON) of 20.9. In the case of cyclohexane, the conversion observed over CBT was 15.7 times more than that over BT, whereas the selectivity for the formation of cyclohexanone was still high at 82.8% (Table 1, entries 3 and 4). When the reaction was scaled up by a factor of 5, toluene and cyclohexane were also converted into benzaldehyde and cyclohexanone in high yield (423.0 and 151.0 μmol, respectively; Table 1, entries 5 and 6). Both the yield per gram of the photocatalyst and the reaction rate for the oxidation of toluene and cyclohexane with excitation by visible light ($\lambda >$ 420 nm) are superior to those observed with previously reported photocatalytic systems.[4f–i] CBT also showed significantly improved activity for the conversion of ethylbenzene and *p*-xylene into their oxygenated products (Table 1, entries 8 and 10). Although the conversion over CBT in the absence of a solvent seems lower than that in Btf, the absolute yield of the corresponding aldehyde or ketone and the TON are far greater.

Table 1: Photocatalytic oxygenation of several typical hydrocarbons over chlorinated (CBT) and nonchlorinated (BT) BiOBr/TiO_2 catalysts under irradiation with visible light and solvent-free conditions.[a]

Entry	Substrate	Cat.	Yield[b] [μmol]	Conv. [%]	Sel. [%]	TON
1	toluene	BT	9.8	0.12	86.7	–
2	toluene	CBT	85.1	1.00	90.6	20.9
3	cyclohexane	BT	2.6	0.03	100	–
4	cyclohexane	CBT	36.0	0.47	82.8	9.7
5[c]	toluene	CBT	423.0	1.03	87.4	21.5
6[c]	cyclohexane	CBT	151.0	0.40	81.3	8.3
7	ethylbenzene	BT	36.7	0.48	93.8	–
8	ethylbenzene	CBT	133.7	1.90	86.2	34.5
9	*p*-xylene	BT	34.3	0.38	96.1	–
10	*p*-xylene	CBT	109.1	1.32	91.6	26.4
11[d]	toluene	CBT	158.8	1.80	94.0	37.4
12[d]	cyclohexane	CBT	68.3	0.85	87.0	17.5
13[d]	ethylbenzene	CBT	284.4	3.60	96.7	65.3
14[d]	*p*-xylene	CBT	183.3	2.23	90.6	44.9
15[e]	toluene	CBT	151.0	1.86	86.2	38.9
16[e]	cyclohexane	CBT	53.0	0.68	83.6	14.1
17[e]	ethylbenzene	CBT	305.1	4.28	87.4	77.5
18[e]	*p*-xylene	CBT	221.0	2.83	86.2	56.8

[a] General reaction conditions: photocatalyst (20 mg), substrate (1 mL), room temperature, O_2 atmosphere (0.1 MPa), visible-light irradiation ($420 < \lambda < 780$ nm), light intensity: 250 mW cm^{-2}, irradiation time: 4 h. [b] Yield of benzaldehyde, cyclohexanone, acetophenone, or *p*-tolualdehyde. [c] The reaction was carried out on a larger scale (toluene: 5 mL, photocatalyst: 100 mg). [d] The reaction was carried out with an irradiation time of 12 h. [e] The reaction was carried out with a light intensity of 450 mW cm^{-2}.

We also explored the effects of different variables on the activity over CBT. In all cases, no chlorinated products were detected. An increase in the reaction time from 4 to 12 h led to high conversion of the substrates as well as good selectivity for the formation of the corresponding aldehyde or ketone (Table 1, entries 11 and 12). When we increased the light intensity from 250 to 450 mW cm^{-2} to increase the number of incident photons, the conversion of all substrates increased; however, the selectivity for the formation of the corresponding aldehyde or ketone decreased slightly (Table 1, entries 15 and 16). The CBT chlorine content was also found to play a critical role in the selective transformation of toluene and cyclohexane. The use of CBT catalysts obtained by treating BT with higher concentrations of HCl led to the oxygenated products in higher yields (Figure 1 a; see also Table S1). The dependence of the activity on the intensity and wavelength of the incident light indicates that the transformation of hydrocarbons over CBT is typically photocatalytic (Figure 1 b). The estimated apparent quantum efficiency (AQE) for the transformation of hydrocarbons into oxygenated products reached 15.3 and 6.7% (at $\lambda = (430 \pm 25)$ nm) for toluene and cyclohexane, respectively (see Figure S1 in the Supporting Information). Although CBT can only absorb light with a wavelength lower than 550 nm, it still catalyzed the formation of benzaldehyde from toluene (2 mL) in satisfying yield (251.9 μmol) with high selectivity (83.1%) under natural solar radiation with a low intensity of 80 mW cm^{-2} (see Table S2). All of these results indicate that the oxygenation of

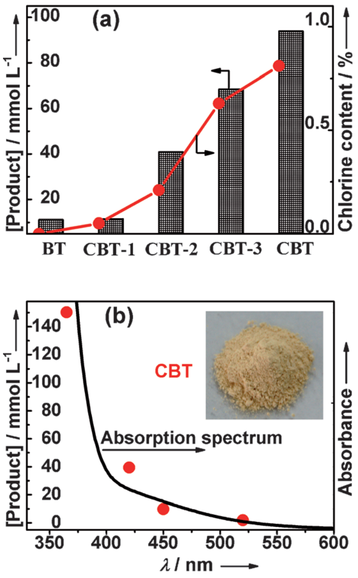


Figure 1. Influence of a) the chlorine content in the photocatalyst and b) the wavelength of the incident light on the yield of oxygenated products derived from the photocatalyzed conversion of toluene. The results in (b) were obtained with the catalyst CBT, a photograph of which is shown.

hydrocarbons over irradiated CBT is controllable, chemically productive, and even practically applicable (see Table S3).

In a control reaction over HF-treated BT, almost no improvement in activity was observed for the oxygenation of toluene with respect to the equivalent reaction over BT (see Table S1). This result ruled out the possible contribution of the introduced Brønsted acid to the enhanced activity[8] and together with the dependence of the activity on the chlorine content suggested that chlorine was involved in the oxygenation process over CBT. The electron spin resonance (ESR) spectrum of irradiated CBT (in the absence of O_2) in the presence of *N-tert*-butyl-α-phenylnitrone (PBN) as a trapping agent showed a large double-quartet splitting corresponding to the Cl-PBN$^\bullet$ adduct[9] and thus confirmed the formation of chlorine radicals during the selective oxidation of hydrocarbons over CBT (Figure 2a). In contrast, no signal corresponding to Cl-PBN$^\bullet$ was observed when BT was irradiated. This result implies that the chlorine radicals formed over the irradiated CBT system are responsible for its higher photocatalytic activity in hydrocarbon oxygenation. Moreover, when the CBT catalyst was irradiated with higher-energy UV light ($\lambda > 320$ nm), the intensity of the signals for the chlorine radical increased greatly (Figure 2b), and the conversion of hydrocarbons into oxygenated products was higher (see Table S3).

To further corroborate the important role of chlorine radicals in the reaction, we added CCl_4, which is believed to generate chlorine radicals through homolytic cleavage upon UV irradiation (see Figure S2), to a reaction system containing a substrate (toluene or cyclohexane), a solvent, and O_2, but without a photocatalyst. Both oxygenated and chlorinated products as well as HCl were obtained under UV irradiation (see Tables S4 and S5). However, in the absence of CCl_4 or under irradiation with visible light, no products were detected, which suggests that chlorine radicals produced by the UV irradiation of CCl_4 are essential for C−H activation in this system. Selectivity for the formation of the corresponding aldehyde or ketone was poor in this homogeneous system, since both oxygenated and chlorinated products were obtained. It was also found that the introduction of CCl_4 into reaction systems containing the BT photocatalyst led a significant enhancement of the conversion of both toluene (1.9-fold) and cyclohexane (32-fold) in Btf under UV irradiation in comparison with the use of BT alone (see Table S4). However, in systems containing CCl_4, the formation of chlorinated products was unavoidable. The extremely low conversion of toluene observed under irradiation with visible light in the absence of chlorine radicals (see Figure S3) also demonstrated their dominant role in the transformation of alkanes in the BT/CCl_4 system. The direct participation of the semiconductor photocatalyst in the hydrocarbon oxygenation over CBT irradiated with visible light was also confirmed by an experiment in which chlorine radicals were quenched. The addition of PBN to the reaction system led to a significant decrease in the formation of the aldehyde or ketone, but did not totally inhibit the reaction (Figure 2c). Therefore, it is clear that the oxygenation of hydrocarbons over CBT is induced by both chlorine radicals and direct semiconductor photocatalysis.

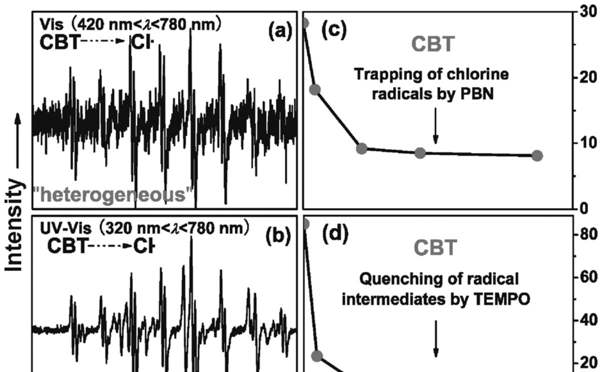
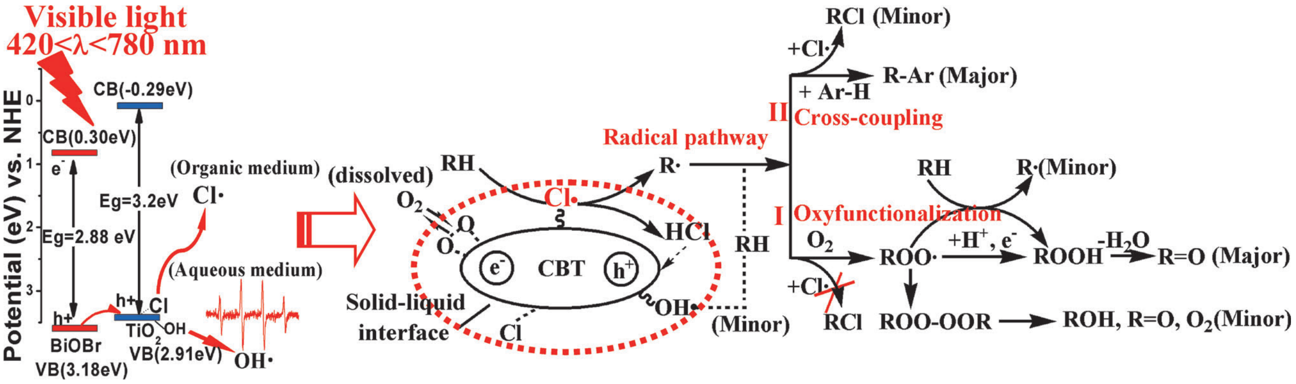


Figure 2. a,b) Evidence for the formation of chlorine radicals on the CBT photocatalyst under irradiation with visible light (a) and UV light (b). c,d) Influence of the trapping agents PBN (c) and TEMPO (d) on the formation of oxygenated products in the photocatalytic reaction (the concentration of the trapping agent is given on the *x* axis).

The proposed existence of a dominant pathway involving radicals in the oxygenation of hydrocarbons over the current CBT system was corroborated by the addition of tetramethylpiperidine *N*-oxide (TEMPO), a typical radical scavenger, to the reaction system. The transformation of a substrate into the corresponding oxygenated products decreased as the amount of TEMPO was increased, and when TEMPO was added at a concentration of 64 mmol L^{-1}, the conversion of the substrate was almost completely inhibited (Figure 2d; see also Table S6). A comparison of the transformations of toluene, cyclohexane, ethylbenzene, and *p*-xylene revealed that the conversion activity over CBT is inversely proportional to the C−H bond strength, which suggests that the cleavage of the C−H bond in the hydrocarbon is an important step in the oxygenation reactions. An experiment carried out to determine the kinetic isotopic effect (KIE) showed a significant k_H/k_D value of 4.6 for the oxidation of toluene in our CBT system (see Table S7). We could therefore conclude that C−H bond cleavage is probably the rate-determining step. Furthermore, although a range of substituted toluene derivatives underwent oxygenation to form the corresponding aldehydes, the reaction rate was higher for a toluene derivative with an electron-donating *para* substituent (CH_3) than for substrates with electron-withdrawing *para* substituents (Cl, Br, and CF_3; see Table S8). Thus, more strongly electron withdrawing substituents on the benzene ring drastically deactivate the aromatic system for hydrogen abstraction.

On the basis of the above experimental evidence, the following mechanism is proposed for the selective oxidation of hydrocarbons over the CBT catalyst (Scheme 1): BiOBr with a narrow band gap (E_g) can be excited to produce electron and hole pairs under irradiation with visible light.[10] When BiOBr is coupled to TiO_2 and chlorinated, the photogenerated holes can transfer to TiO_2 as a result of the more negative valence band of BiOBr. On TiO_2 these holes are trapped by chlorine or hydroxy groups chemisorbed on the



Scheme 1. Proposed mechanism for the chlorine-radical-mediated photocatalytic activation of hydrocarbons and their further functionalization. CB = conduction band, NHE = normal hydrogen electrode, VB = valence band.

catalyst surface to produce chlorine radicals or hydroxyl radicals. Both types of radicals can abstract hydrogen from alkanes to give alkyl radicals, but in organic media the production of hydroxyl radicals is very limited. Since chlorine radicals are more reactive than hydroxyl radicals in hydrogen-abstraction reactions,[11] the presence of chlorine radicals during the aerobic oxidation of alkanes will lead to the production of more alkyl radicals. These alkyl radicals can either react with O_2 to form $ROO^\bullet$ or react with chlorine radicals to give alkyl halides. In the CBT system, these chlorine radicals remain surface-bound in a similar way to that described for hydroxyl radicals by Xu et al.[12] Surrounded by a large excess of the alkane, most of the chlorine radicals are consumed to form alkyl radicals and stable HCl at the solid–liquid interface. Owing to the presence of an ample O_2 supply, including the adsorbed O_2 on the catalyst surface and a continuous supply of O_2 from the solution at the interface (see Figure S4), the possibility of the reaction between chlorine radicals and alkyl radicals to form alkyl halides is highly suppressed, and oxygenated products are obtained exclusively, although DFT calculations imply that the alkyl halides should be the main products (see Figure S5 and Table S12). In contrast, in the reactions involving CCl_4 under UV irradiation, collisions between chlorine radicals and alkyl radicals to form alkyl halides can not be avoided, since the chlorine radicals generated homogeneously in solution can migrate freely. As a result, lower selectivity for the formation of the oxygenated products is observed.

The $ROO^\bullet$ radicals formed can either combine to form ROOOOR or be reduced by the photogenerated electrons on the photocatalyst and undergo reaction with H^+ to yield ROOH.[4c] The former pathway leads to the formation of alcohols and ketones in almost equal amounts through the decomposition of ROOOOR and is commonly observed in selective oxygenation reactions. However, the formation of aldehydes or ketones as the dominant products with the CBT catalyst indicates that in our system the $ROO^\bullet$ radical favors the reductive pathway to form ROOH. DFT calculations revealed that the process to form ROOH is very exothermic, whereas the formation of ROOOOR is slightly endothermic. Furthermore, the elevated concentration of protons derived from preadsorbed HCl and generated through the reaction of chlorine radicals with the hydrocarbon should help to direct the reaction to yield ROOH. The dehydration of ROOH to yield the aldehyde or ketone can occur readily, since this process is highly exothermic. A clearly enhanced yield of the alcohol product was observed when the preferred reductive pathway to form ROOH via $ROO^\bullet$ was blocked by the addition of a typical electron acceptor (quinine) as a result of the consumption of the photogenerated electrons by quinine. The surface chlorination of other semiconductors, such as WO_3 and WO_3/TiO_2, also led to significant improvements in these photocatalysts for the selective oxygenation of both toluene and cyclohexane (see Table S11).

Since the chlorine radicals generated over irradiated CBT can promote the formation of alkyl radicals, we expected that the CBT photocatalytic system could also be applied to C–C coupling reactions involving alkyl radicals: another important application of C–H activation. In the absence of O_2, toluene was transformed over CBT irradiated with visible light into a range of coupling products dominated by 1-benzyl-4-methylbenzene, 1-benzyl-2-methylbenzene, and 1,2-diphenylethane, whereas the coupling reaction between toluene and benzene led to diphenylmethane as the major product (see Figure S8). In contrast, only a trace amount of the desired coupling product was obtained if CBT was replaced with BT. Thus, the surface chlorination of BT plays a pivotal role in the reaction. These preliminary studies on this propagation reaction pathway involving aryl radicals show that our reaction mode provides an alternative approach to C–C bond construction directly from hydrocarbons without prefunctionalization of the starting materials.[13] The optimization of this synthetic route and further detailed mechanistic studies are under way.

In summary, we have developed a highly effective photocatalytic reaction mode involving chlorine radicals generated on a semiconductor system upon irradiation with visible light for the transformation of alkanes into oxygenated products, even under solvent-free conditions. This system can also be applied to other synthetic reactions involving alkyl radicals. The current study represents a conceptual breakthrough in direct C–H functionalization by photocatalysis.

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Keywords: C—H activation · chlorine radicals · photocatalysis · solvent-free conditions · visible light

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