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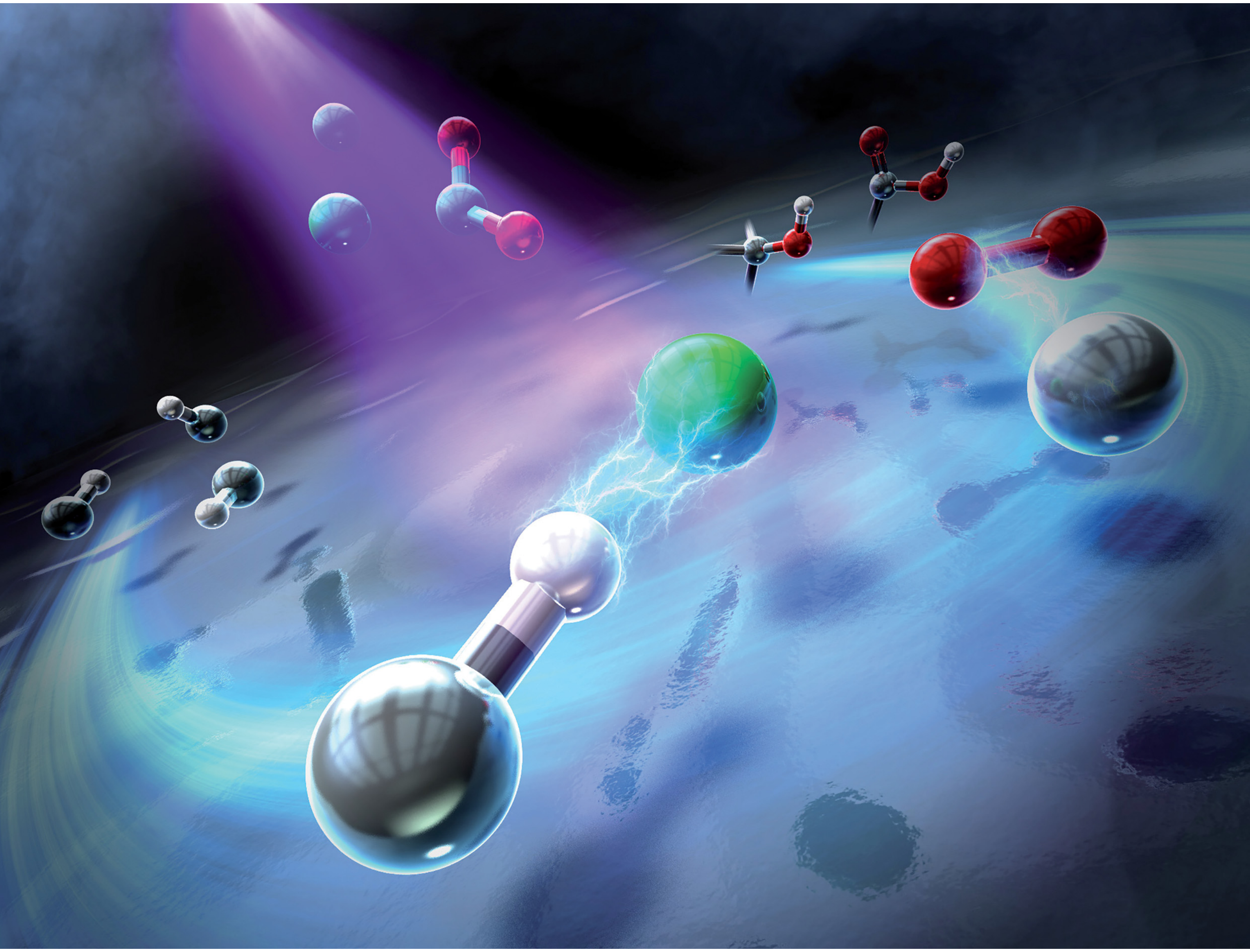

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FEATURE ARTICLE
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Chlorine-radical-mediated C–H oxygenation reaction under light irradiation

Yuki Itabashi, [a] Haruyasu Asahara *[bc] and Kei Ohkubo *[ac]

The oxygenation of C(sp^3)–H bonds is a key chemical reaction in the production of fine chemicals and pharmaceuticals. Hydrogen atom transfer has recently gained significant attention for its ability to functionalise C–H bonds. The C–H bond can be activated by transferring the H radical to a hydrogen acceptor such as the chlorine radical (Cl$^•$). Thus, the Cl$^•$ generated by light irradiation can be used to initiate C–H oxygenation reactions, in which molecular oxygen is used as the oxidant. In this review article, we have summarised the recent advances in the field of Cl$^•$-mediated C–H oxygenation reactions. Reactions with catalysts such as metal chlorides, organophotoredox catalysts (acridinium ions), and chlorine dioxide radicals under light irradiation have been discussed. We conclude the review by providing suggestions for future research studies in the field. We expect that this review article will provide valuable information for the development of Cl$^•$-mediated C–H oxygenation reactions, contribute to the understanding of the reactivity of Cl$^•$, and inspire other useful synthetic chemical applications for C–H oxygenation reactions.

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1. Introduction

The oxygenation of C(sp^3)–H bonds is a key chemical reaction in the production of fine chemicals and pharmaceuticals.[1–4] As shown in Table 1, these reactions typically require harsh conditions such as a high temperature and/or high pressure and strong oxidants owing to their high bond dissociation energies (BDEs, $>$90 kcal mol^{-1}).[5] The use of molecular oxygen (O_2) as an oxidant is favourable as it is eco-friendly and

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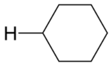
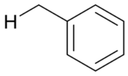
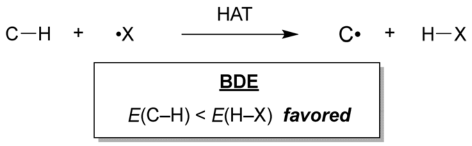
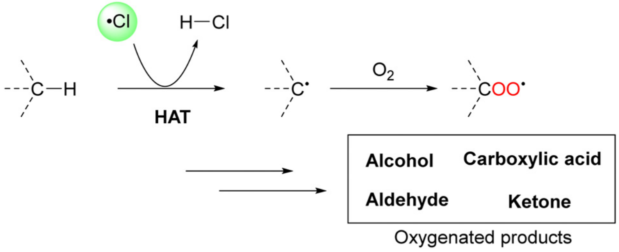
Table 1 Bond dissociation energies (kcal mol^{-1}) of C–H bonds in alkanes and those of H–X bonds[5]

C–H bond				H–X bond	
$H–CH_3$	105		100	H–Cl	103
$H–CH_2CH_3$	101			H–Br	88
$H–CH(CH_3)_2$	98		90	H–I	71
$H–C(CH_3)_3$	96				
$H–CCl_3$	96				



Scheme 1 Hydrogen atom transfer (HAT).

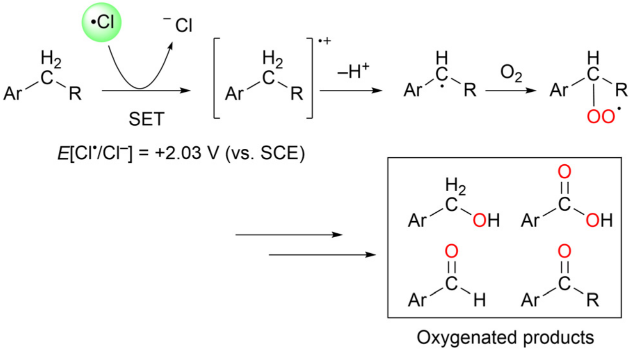


Scheme 2 C–H oxygenation *via* HAT by the action of Cl$^•$.

sustainable;[6] however, O_2 cannot activate C–H bonds under mild conditions.

Hydrogen atom transfer (HAT) is one of the most effective tools to cleave the C–H bond and activate it.[7] HAT has recently garnered significant attention owing to its ability to functionalise complex molecules *via* C–H bond activation. As a fundamental radical reaction, HAT involves the transfer of a hydrogen atom from a hydrogen donor (C–H) to a hydrogen acceptor ($X^•$), which is also known as the radical reagent. The progress of HAT reactions can be estimated by comparing the BDEs of the bonds that would be cleaved (C–H) and those that would be formed (H–X), as shown in Scheme 1. Therefore, a radical reagent that forms more stable bonds than those that would be cleaved can enable direct functionalisation through HAT. Several radical species ($X^•$), including O-, N-, S-, B-, and halogen-centred radicals, are known to be suitable HAT reagents.[8–11] Halogen radicals have attracted much attention owing to their easy accessibility and high reactivity.

In particular, a chlorine radical ($Cl^•$) is a powerful hydrogen acceptor and valuable HAT agent. HAT from hydrocarbons to $Cl^•$ affords HCl with a H–Cl bond stable to homolytic cleavage. The C–H BDEs of the hydrocarbons listed in Table 1 are generally lower than the bond formation energy of H–Cl (103 kcal mol^{-1}). Thus, $Cl^•$ can easily cleave the C–H bonds of alkanes. However, $Br^•$ and $I^•$ have little or no ability to induce HAT from alkanes owing to the low bond formation energies of H–Br and H–I (88 and 71 kcal mol^{-1}, respectively).[12] The formation of two $Cl^•$ radicals from Cl_2 upon UV irradiation or heating is a well-established synthetic organic radical reaction for the chlorination of hydrocarbons.[13,14] However, Cl_2 gas is not suitable for the synthesis of fine chemicals because of its poor site selectivity and potential hazards. In this context, different methods for the generation of $Cl^•$ have been developed for the photocatalytic oxidation of Cl^- and photo-cleavage of the M–Cl bond in the past decade, which has increased the synthetic utility of $Cl^•$. Carbon radicals produced by the action of $Cl^•$ readily react with molecular oxygen under O_2 atmosphere to produce oxygenated products (Scheme 2). $Cl^•$ is a strong oxidant that enables the transfer of one electron from an electron-rich substrate. Substrates containing benzyl groups can undergo single-electron transfer (SET) to form a radical cation, which subsequently deprotonates to form a stable benzyl radical (Scheme 3). The likelihood of SET can be estimated by comparing the redox potentials of the substrate and chlorine radical ($E[Cl^•/Cl^-]$ = +2.03 V *vs.* SCE (saturated calomel electrode)).[15] The addition of oxygen to these benzyl radicals yields oxygenated products, as shown in Scheme 2. Therefore, the oxygenation of benzyl radicals may involve the SET mechanism.



Scheme 3 C–H oxygenation *via* SET with Cl$^•$.

Kei Ohkubo

Dr Kei Ohkubo, Chemistry Doctor (PhD-engineering), now is a Professor of Chemistry of Institute for Advanced Co-Creation Studies and Open and Transdisciplinary Research Initiatives, Osaka University, Japan. He earned his PhD degree from Graduate School of Engineering, Osaka University in 2001. He was working as a JSPS fellow and a JST research fellow at Osaka University (2001–2005), a designated associate professor in Osaka University (2005–2014) and a specially appointed professor at Osaka University (2014–2017). He has been a full professor at Osaka University since 2017. His research fields are photochemistry, organic photocatalysis and oxygenation chemistry.

Molecular oxygen (O_2) is an ideal reagent for economical and environmentally benign oxygenation reactions because of its abundant availability and nontoxicity.[16–20] O_2 does not react with hydrocarbons because the reaction of triplet oxygen ($^3O_2$ $^3\Sigma_g^-$) with a singlet organic substrate is a spin-forbidden process. Nevertheless, O_2 can be converted to reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$) by energy transfer or superoxide anion ($O_2^{\bullet -}$) by electron-transfer reduction, to facilitate a spin-allowed process for the oxygenation of hydrocarbons. However, the direct activation of O_2 to produce ROS without a transition metal catalyst is challenging[21–24] because it requires a photosensitiser under light irradiation. In addition, ROS do not react with hydrocarbons such as alkanes and aromatic substrates.

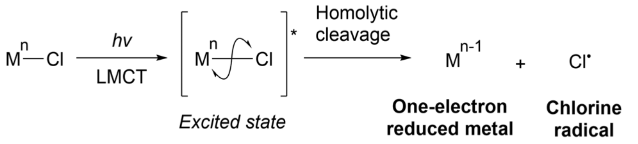
In this review article, we summarise the recent progress in the field of $Cl^\bullet$-mediated C–H oxygenation reactions under light irradiation. However, reactions initiated by the addition of $Cl^\bullet$ to alkenes are not discussed. As previous review articles have provided an overview of C–C bond-formation reactions,[25] this article focuses only on C–H oxygenation reactions. We discuss C–H oxygenation reactions initiated by metal chlorides (iron, copper, and cerium), organophotoredox catalysts (acridinium ion), and chlorine dioxide radicals. Finally, we suggest future directions for research in the field.

2. Chlorine-radical-mediated C–H oxygenation reactions

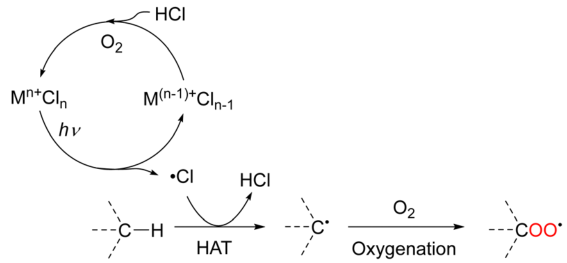
2.1 Metal chlorides

Transition metal chlorides can be excited by UV- or visible-light irradiation, resulting in ligand-to-metal charge transfer (LMCT) electronic transitions. These transitions involve the transfer of an electron from an occupied orbital of a chlorine ligand to a vacant orbital of the metal,[24–27] which must be on a lower energy level; high-valent metals such as Fe(III), Cu(II), and Ce(IV) are suitable for these transitions. The transfer of an electron from a M–Cl bonding molecular orbital to a vacant metal orbital and from a Cl lone pair to a M–Cl antibonding molecular orbital ultimately lead to homolytic cleavage and subsequent formation of a one-electron-reduced metal (M^{n-1}) and $Cl^\bullet$ (Scheme 4). Kochi first applied this process to organic synthesis in 1962. $CuCl_2$ undergoes photolysis to produce $Cl^\bullet$, which oxidises isopropanol and chlorinates the benzyl and allyl positions.[28]

HAT from aliphatic C–H bonds to $Cl^\bullet$ produces HCl and carbon radical species. Under O_2 atmosphere, carbon radicals react with molecular oxygen to afford oxygenated products because the reaction is thermodynamically favourable. Finally, the catalyst is regenerated *via* the oxidation of molecular oxygen by HCl (Scheme 5). In recent years, several metal-catalysed reactions other than oxygenation that are initiated by HAT from C–H bonds to chlorine radicals have been reported.[29–43]

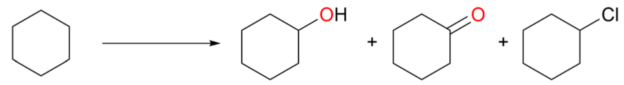


Scheme 4 $Cl^\bullet$ generation *via* photoinduced ligand-to-metal charge transfer (LMCT).



Scheme 5 Mechanism of transition–metal–chloride-catalysed oxygenation *via* HAT.

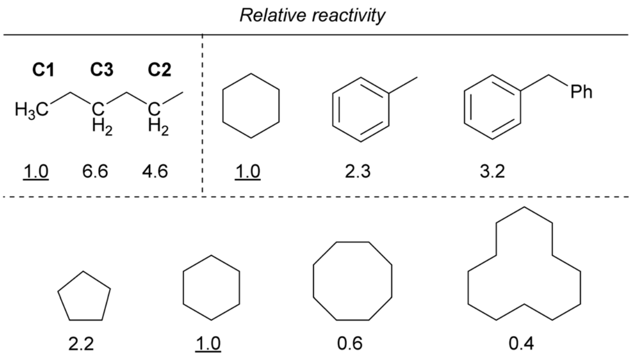
2.1.1 Iron(III) chloride. Imoto *et al.* first reported the photocatalysis of $FeCl_3$ in the oxidation of ethylene glycol derivatives[44–46] and benzylic chlorination of toluene; the effect of water on this reaction was subsequently reported.[47] Shul'pin *et al.* reported that cyclohexane was oxidised by 1 mol% $FeCl_3$ (and an ammonium salt to dissolve it) upon light irradiation in air and CH_2Cl_2 to yield the corresponding alcohol and ketone in the same ratio (Scheme 6, entry 1).[48] A small amount of the chlorinated product was also obtained. Notably, the use of isopropanol as the reaction solvent improved the product selectivity of alcohols and ketones in the direct oxidation of alkanes (Scheme 6, entry 2).[49] When hexane was used as the substrate in acetonitrile (MeCN), a mixture of alcohols and ketones with oxygen atoms at the 1-, 2-, and 3-positions was obtained. Toluene and ethylbenzene were oxidised in the same manner to afford the corresponding alcohols and ketones. Takaki *et al.* reported the relative reactivities of different C–H bonds in the oxygenation reaction in the presence of $FeCl_3$. C2 and C3 were 4.6 and 6.6 times more reactive than C1 in hexane, respectively (Table 2).[50] A five-membered ring was more reactive than larger cycloalkanes. Moreover, the relative reactivities of toluene and diphenylmethane in the oxygenation reaction were 2.3 and 3.2 times higher than that of cyclohexane, respectively. These results agree with the general reactivity of radical species.

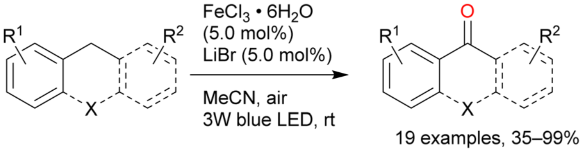


Entry	catalyst	conditions	conv.	Product ratio (-OH : =O : -Cl)
1	$FeCl_3 \cdot 6H_2O$ (1 mol%), $BnN(C_2H_5)_3Cl$ (1 mol%)	DCM, air, 15 °C, 11 h, 125 W street lamp	20%	5 : 5 : 1
2	$FeCl_3 \cdot 6H_2O$ (50 mol%)	*i*-PrOH, 15 °C, 3 h, 1000 W Hg lamp,	3%	11 : 2 : 0

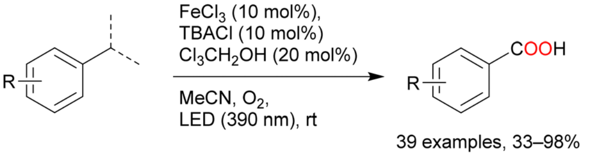
Scheme 6 Oxygenation of cyclohexane with iron chloride.

Table 2 Relative reactivities of substrates in iron-catalysed C–H oxygenation reactions





Scheme 8 Iron-catalysed oxygenation of benzyl C–H to a ketone.



Scheme 9 Iron-catalysed oxygenation of benzyl C–H to carboxylic acid.

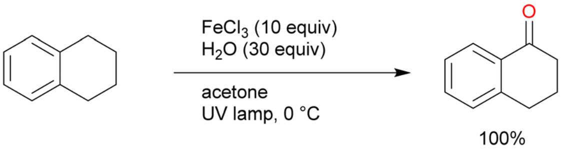
The kinetic isotope effect estimated using C_6H_{12} and C_6D_{12} was 1.6 ± 0.3, which indicates the occurrence of C–H bond cleavage.

A reaction mechanism for the oxidation reaction was reported in a subsequent study: $Cl^•$ and $FeCl_2$ are formed from $FeCl_3$ under light irradiation, and hydrogen is abstracted from the alkane by $Cl^•$.[51] The C–H bond at the benzyl position can be more easily cleaved than those at the other alkane positions, thus contributing to efficient oxygenation at this position. A primary C–H bond at the benzyl position is typically oxidised to the corresponding alcohol or aldehyde and even carboxylic acid, whereas secondary and tertiary C–H bonds are oxidised to the corresponding alcohols or ketones. Further oxidation to carboxylic acid in the latter case occurs *via* C–C bond cleavage only under certain conditions. Barbier *et al.* reported an early example of benzylic C–H oxygenation, where a secondary C–H bond afforded a ketone. Tetralin afforded 1-tetralone in high yield in the presence of 10 equivalents of $FeCl_3$ and 30 equivalents of water under UV irradiation (Scheme 7).[52] Indan and diphenylmethane also tolerated the oxidation reaction well, but the oxidation of toluene and ethylbenzenes afforded <10% product yields. Therefore, the scope of this reaction was narrow. Jiang *et al.* developed the secondary benzylic C–H oxygenation to ketones. The oxidation of substrates such as ethylbenzene, fluorene, and xanthene at the benzyl position in the presence of $FeCl_3 \cdot 6H_2O$ and LiBr under blue-light irradiation afforded moderate to high yields of the desired products (Scheme 8).[53] The addition of an equal amount of LiBr to the that of the iron catalyst improved the reaction to afford the desired oxygenated products in higher yields than when only $FeCl_3$ was used. However, the authors explained that the reaction mechanism did not involve HAT by the $Cl^•$ generated by the photoexcitation of $FeCl_3$; instead, the reaction occurred *via* SET from the substrate to the photoexcited iron. This was confirmed by the same oxygenation reactions proceeding well in the presence of $Fe(NO_3)_2$ and $FeSO_4$.[54] However, since $Cl^•$ can be generated in oxidation reactions using $FeCl_3$ as the photocatalyst, it cannot be ruled out that both HAT and SET mechanisms are involved in this reaction simultaneously.

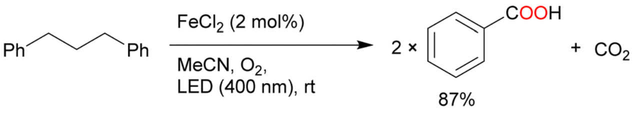
Oxygenation reactions of primary, secondary, and tertiary C–H bonds directly afford carboxylic acids in the presence of catalytic amounts of $FeCl_3$, tetrabutylammonium chloride, and 2,2,2-trichloroethanol (Scheme 9). Many toluene derivatives possessing electron-withdrawing or electron-donating groups and heterocyclic aromatics such as thiophene and pyridine have been oxidised at the benzyl position; even substrates with secondary and tertiary benzyl C–H bonds afforded carboxylic acids *via* C–C bond cleavage.[55]

The oxidation of 1,3-diphenylpropane by $FeCl_2$ under O_2 atmosphere afforded benzoic acid in a high yield (87%) with CO_2 as a by-product *via* C–C bond cleavage (Scheme 10).[56] In addition, polystyrene and its derivatives [styrene-allyl alcohol copolymer, poly(styrene-*co*-acrylonitrile), ABS (acrylonitrile-butadiene-styrene), and styrene-maleic anhydride copolymer] afforded benzoic acid in moderate yields *via* oxidative degradation of the substrate with 100% conversion. Stache *et al.* further developed methods to degrade the high-molecular-weight polystyrene (MW > 90 000) to a molecular weight of less than 1000 and obtained up to 23 mol% benzoyl products using 10 wt% $FeCl_3$ as the catalyst and acetone as the solvent under white-light irradiation. Commercially available polystyrenes were efficiently degraded by this method and have been used in a photoflow process.[57]

2.1.2 Copper(II) chloride. After Kochi *et al.* reported $CuCl_2$ photolysis, Takaki *et al.* reported differences in the reactivities

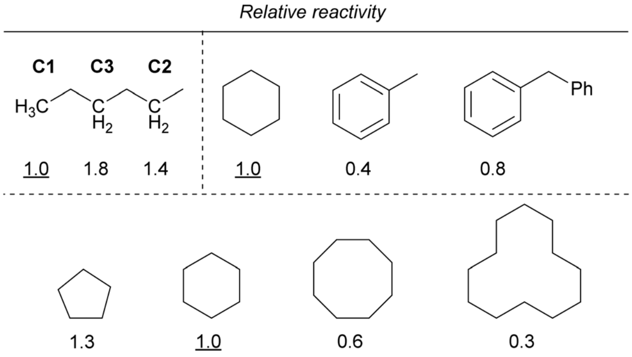


Scheme 7 Benzylic C–H oxygenation in the presence of the $FeCl_3$ catalyst.



Scheme 10 Oxygenation of 1,3-diphenylpropane by $FeCl_2$ for polymer degradation.

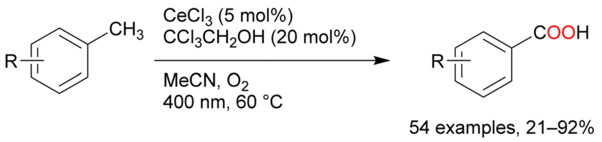
Table 3 Relative reactivities of substrates in iron-catalysed C–H oxygenation reactions



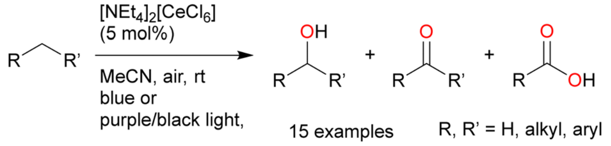
of different C–H bonds towards oxygenation in the presence of a $CuCl_2$ catalyst (Table 3).[50] Unlike that observed for iron, the difference between the reactivities of primary and secondary C–H bonds in the oxidation of hexane was not large; the reactivities of C2 and C3 were 1.4 and 1.8 times higher than that of C1, respectively.

Furthermore, the reactivity of the C–H bond at the benzyl position was lower than that of the C–H bond at the alkane position. In addition, the reactivity decreased as the ring size of the cycloalkanes increased, similar to that observed for iron. If the reaction proceeds *via* C–H bond cleavage by the $Cl^•$ generated by the light irradiation of copper, the relative reactivities should not be different from those in the case of iron. Therefore, other mechanisms are also probably involved in addition to the $Cl^•$-mediated mechanism.

2.1.3 Cerium(III) chloride. The $CeCl_3$-catalysed direct conversion of the C–H bond at the benzyl position to a carboxylic acid was achieved under O_2 atmosphere and irradiation at 400 nm (Scheme 11).[58] This reaction was tolerated well by many substituted benzenes with electron-donating or electron-withdrawing groups and heterocycles. Xylene, mesitylene, and durene produced the desired products in good yields even with multiple steps. Secondary and tertiary substrates such as ethylbenzene and cumene afforded benzoic acids *via* C–C bond cleavage. Conversely, ethylbenzene and diphenylmethane derivatives afforded the corresponding ketones without further oxidation to carboxylic acid in water under blue-LED irradiation with catalytic amounts of $CeCl_3$ and PEG4000 in air.[59] The use of a cerium catalyst with PEG4000 under air atmosphere led to controlled reactivity. Cerium(IV) chloride complexes such as $[NEt_4]_2[CeCl_6]$ successfully catalysed the oxygenation of benzylic C–H bonds in arenes (such as toluene derivatives), liquid alkane substrates, and gaseous alkanes (such as methane and ethane) to the corresponding oxygenated products (Scheme 12).[60]



Scheme 11 Cerium-catalysed benzyl C–H oxygenation.



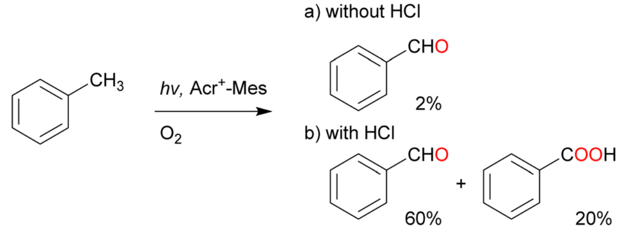
Scheme 12 Cerium-catalysed aliphatic C–H oxygenation.

2.2 Organophotoredox catalysts

Over the past half century, organic dyes have been used for strong-electron-transfer oxidation or reduction, where the dyes are irradiated with UV or visible light to generate an excited state. Organophotoredox catalysts have received considerable attention as a 'green tool' for conducting various organic transformations such as oxidation, C–C coupling, and C–hetero atom bond formation.[61,62] The metal-free functionalisation of alkanes is challenging because the activation of chemically stable alkanes requires a powerful $C(sp^3)$–H abstraction reagent. $Cl^•$ can cleave C–H bonds to yield alkyl radicals under mild conditions (*vide supra*). $Cl^•$ can be photochemically and electrochemically generated from $Cl^−$ as an inexpensive and safe HAT-active source *via* one-electron oxidation.[63,64] The one-electron oxidation potential of $Cl^−$ is +1.15 V *vs.* SCE in MeCN.[65–67] An appropriate photocatalyst will have a more positive one-electron reduction potential than that of $Cl^−$ in the photoexcited state to facilitate the negative free energy change of electron transfer ($\Delta G_{et} < 0$). Consequently, the alkyl radical generated by the electron transfer oxidation of $Cl^−$ reacts with molecular oxygen to produce alkyl peroxyl radicals.

2.2.1 Acridinium photocatalyst. Acridinium salts are good organophotoredox catalysts with a strong oxidising ability in the photoexcited state. For example, the one-electron reduction potential of 10-methylacridinium perchlorate at the singlet excited state is 2.72 V *vs.* SCE in MeCN. This value is enough to oxidise tetrabutylammonium chloride ($TBA^+Cl^−$) (E_{ox} = +1.15 V *vs.* SCE) by photoinduced electron transfer. Metal-free photocatalytic oxygenation reactions of alkyl aromatic compounds such as toluene, *p*-xylene, and 4,4′-dimethylbiphenyl with molecular oxygen in the presence of an organic photocatalyst, 9-mesityl-10-methylacridinium perchlorate (Acr^+–Mes),[68,69] *via* photoinduced electron-transfer have been previously reported.[70–76] These substrates have a lower one-electron oxidation potential than the photocatalyst Acr^+–Mes (E_{red} = 2.06 V *vs.* SCE). The radical cation ($RH^{•+}$) formed by the photoinduced electron transfer oxidation of the substrate (RH) deprotonates to form an alkyl radical ($R^•$). $R^•$ is oxygenated by O_2 to form an alkyl peroxyl radical ($ROO^•$), leading to the formation of oxygenated products such as aldehydes and benzyl alcohols.

Visible-light irradiation of the absorption band of Acr^+–Mes in an O_2-saturated MeCN solution containing toluene using a xenon lamp afforded benzaldehyde in 2% yield (Scheme 13).[77] The one-electron oxidation potential of toluene (2.20 V *vs.* SCE) is more positive than that of Acr^+–Mes. Hence, the electron



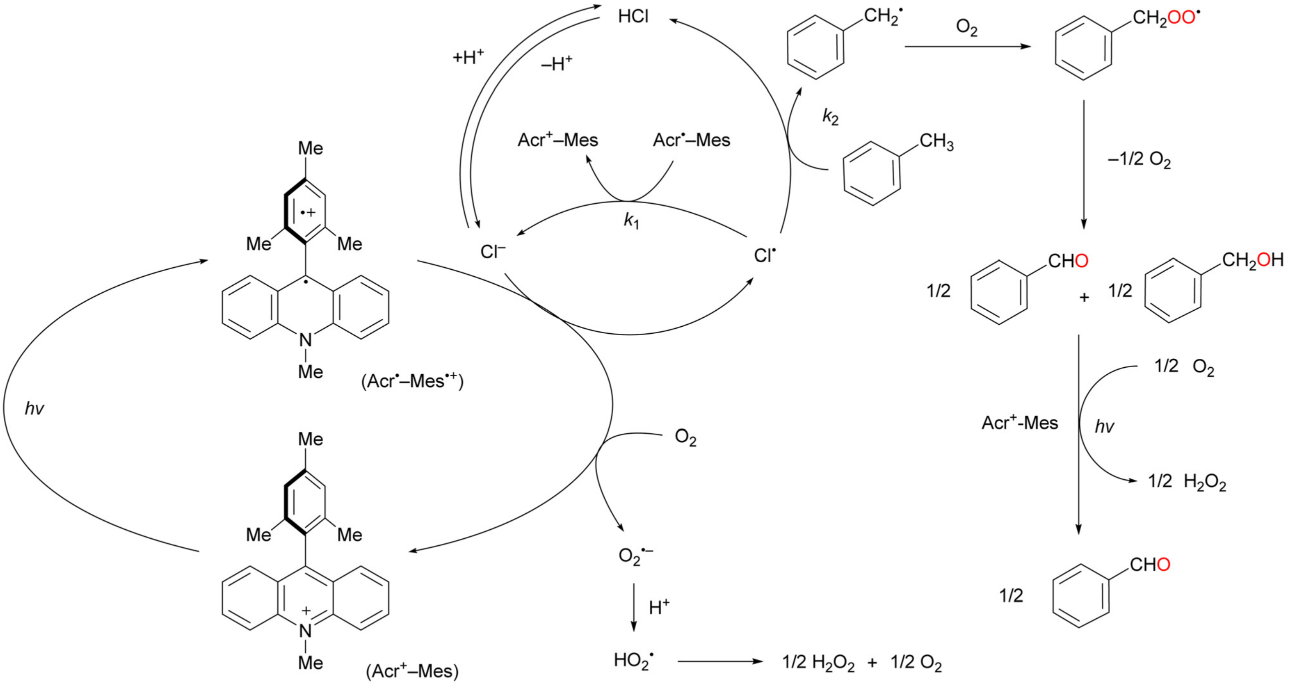
Scheme 13 Acr$^+$–Mes catalysed photo-oxygenation of toluene with or without HCl.

transfer oxidation of toluene did not occur in this case. However, in the presence of HCl under the same irradiation conditions, toluene underwent oxidation to concomitantly produce benzaldehyde (60%), benzoic acid (20%), and H_2O_2 (60%) after 7 h of light irradiation (Scheme 13). The photocatalytic mechanism of the oxygenation of toluene catalysed by Acr$^+$–Mes and HCl is shown in Scheme 14. The photoexcitation of Acr$^+$–Mes affords the long-lived electron-transfer state Acr$^•$–Mes$^{•+}$ *via* intramolecular electron transfer from the strongly reducing mesitylene moiety to the strongly oxidising acridinium moiety (E_{red} = 2.06 V and E_{ox} = −0.57 V *vs.* SCE, respectively). The Acr$^•$ and Mes$^{•+}$ moieties reduce and oxidise O_2 and Cl$^-$ to produce $O_2^{•-}$ and Cl$^•$, respectively. The hydrogen of the methyl group of toluene is abstracted by Cl$^•$ to afford the benzyl radical, which is followed by rapid O_2 addition to afford the peroxyl radical. This peroxyl radical produces benzaldehyde and benzyl alcohol *via* disproportionation. Benzyl alcohol is readily oxygenated by Acr$^•$–Mes$^{•+}$ to yield benzaldehyde, while $O_2^{•-}$ disproportionates in the presence of protons to yield H_2O_2 and O_2. Further oxygenation of benzaldehyde by Acr$^+$–Mes and HCl yields benzoic acid *via* the abstraction of hydrogen from the formyl group of benzaldehyde by Cl$^•$.

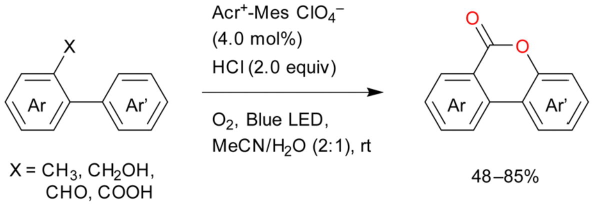
The visible-light-mediated oxidative lactonisation of 2-methyl-1,1′-biaryls produces benzocoumarins (Scheme 15).[78] Multiple C–H functionalisation processes occur in this reaction in the presence of oxygen. Other 1,1′-biaryl derivatives such as 2-aldehydes, alcohols, and carboxylic acids also produce good results in this reaction.

Unlike the one-electron oxidation potentials of aromatic substrates, those of C1–C6 alkanes are too positive (E_{ox} >3.0 V *vs.* SCE) because of the large ionisation potential. As Cl$^•$ can cleave strong C–H bonds, it has been used to activate the C–H bond of alkanes such as cyclohexane to afford C–C or C–Cl bonds in a photochemical reaction.[79,80] The combination of the acridinium photoredox catalyst and HCl produces an HAT-active Cl$^•$ for the C–H oxygenation of cyclohexane.[81] The photooxygenation of cyclohexane by O_2 occurs efficiently in an O_2-saturated MeCN solution containing Acr$^+$–Mes and HCl under visible-light irradiation to yield cyclohexanone, cyclohexanol, and H_2O_2.

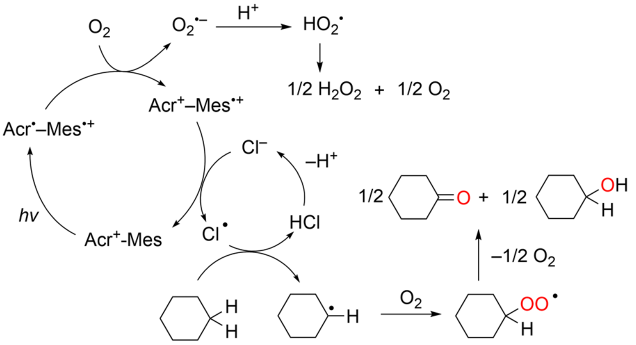
The photocatalytic mechanism of Acr$^+$–Mes-catalysed cyclohexane oxygenation is shown in Scheme 16. The reaction is initiated by intramolecular photoinduced electron transfer from the mesitylene moiety to the singlet excited state of the acridinium ion moiety of Acr$^+$–Mes to form an electron transfer state (Acr$^•$–Mes$^{•+}$).[68,69] The Mes$^{•+}$ moiety oxidises Cl$^-$ to Cl$^•$, whereas the Acr$^•$ moiety reduces O_2 to $O_2^{•-}$. The produced Cl$^•$ reacts with cyclohexane to form a cyclohexyl radical *via* C–H bond dissociation.[82] The cyclohexyl radical undergoes O_2 addition to afford the peroxyl radical, which disproportionates to the final oxygenated products, cyclohexanol and cyclohexanone.



Scheme 14 Reaction mechanism of the photooxygenation of toluene catalysed by Acr$^+$–Mes and HCl.



Scheme 15 Reaction mechanism for the photooxygenation of toluene catalysed by Acr^+–Mes and HCl.



Scheme 16 Photocatalytic mechanism of Acr^+–Mes-catalysed cyclohexane oxygenation.

Although the cleavage of the C–H bonds of cyclohexane is difficult because of the high BDE (97 kcal mol^{-1}), the $Cl^•$ generated by the light irradiation of Cl_2 in the gas phase can readily cleave them. In addition, $O_2^{•-}$ disproportionates in the presence of protons to yield H_2O_2 and O_2.

2.3 Chlorine-dioxide-mediated C–H oxygenation reactions

2.3.1 Oxygenation of CH_4. Activation of the C–H bond in CH_4 with a BDE of 105 kcal mol^{-1} requires a powerful HAT reagent. Even though $Cl^•$ can cleave the C–H bond of CH_4, the methyl radical ($CH_3^•$) generated by HAT is a highly reactive radical that induces radical chain reactions to produce chlorinated products such as CH_3Cl and CH_2Cl_2. In addition, oxygenation products are not observed even under aerobic conditions because of the efficient radical chain reaction triggered by $Cl^•$. The lifetime of $CH_3^•$ as an intermediate is also too short to access molecular oxygen for oxygenation.

The chlorine dioxide radical ($ClO_2^•$), which is composed of chlorine and oxygen, is prepared by the oxidation of sodium chlorite ($NaClO_2$) with HCl (Eq. 1). It is a photochemically reactive yellow gas that absorbs UV-visible light (λ_{max} = 358 nm), as shown in Fig. 1.[83]

The photoexcitation of $ClO_2^•$ affords one molecule each of $Cl^•$ and singlet oxygen ($^1O_2$).[84] Singlet oxygen has a higher reactivity than ground state triplet oxygen. $Cl^•$ then reacts with CH_4 to form $CH_3^•$ and HCl *via* C–H bond dissociation. The addition of singlet oxygen to $CH_3^•$ occurs rapidly, affording the methyl peroxyl radical ($CH_3OO^•$). Thus, $ClO_2^•$ is an effective initiator of CH_4 oxygenation without chlorination.

The photochemical oxygenation of CH_4 occurs in a two-phase system comprising perfluorohexane (PFH) and water under ambient conditions (298 K, 1 atm). PFH is an effective solvent for the oxygenation of CH_4 as only the substrates and intermediates such as CH_4, O_2, and $ClO_2^•$ dissolve in PFH but not the products methanol and formic acid, thus facilitating product isolation. The yields of methanol and formic acid were 14% and 85%, respectively. The CH_4 conversion was 99% and the selectivity for CH_3OH and HCOOH formation was >99% based on the initial concentration of CH_4. The formation of further oxygenated products, such as CO and CO_2, was not observed under the reported reaction conditions.[84] The reaction mechanism for the oxygenation of CH_4 with $ClO_2^•$ is shown in Scheme 17. $ClO_2^•$ photochemically converts $Cl^•$ and singlet O_2 *via* bond rearrangement from Cl–O–Cl to Cl–O–O.[85] The bimolecular reaction of $CH_3OO^•$, generated by the addition of singlet oxygen to $CH_3^•$, affords the methoxy radical ($CH_3O^•$). $CH_3O^•$ reacts with CH_4 to yield CH_3OH and regenerate $CH_3^•$. The rearrangement from $CH_3O^•$ to $CH_2(OH)^•$ also competes with the reaction with CH_4. The second radical chain reaction (B) with O_2 and CH_4 *via* $CH_2(OH)OO^•$ produces methyl hydroperoxide (CH_3OOH) and regenerates $CH_2(OH)^•$. Finally, CH_3OOH decomposes to HCOOH. The chain reactions are terminated by the disproportionation of $CH_3OO^•$ to yield CH_3OH and HCHO. However, HCHO is not observed as a product because it is immediately oxidised to HCOOH by autoxidation or Pinnick oxidation.[86]

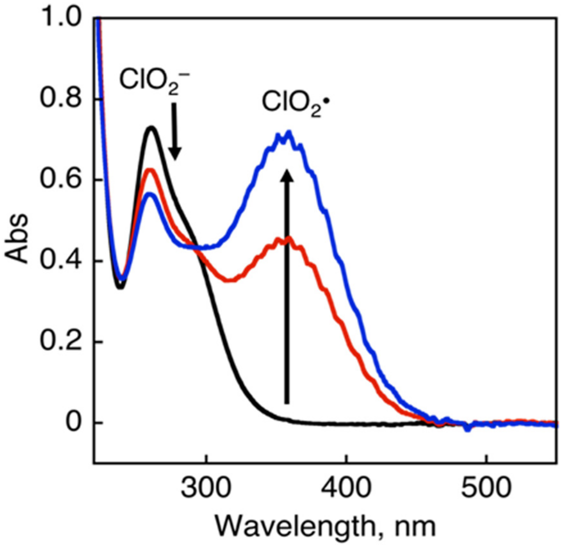
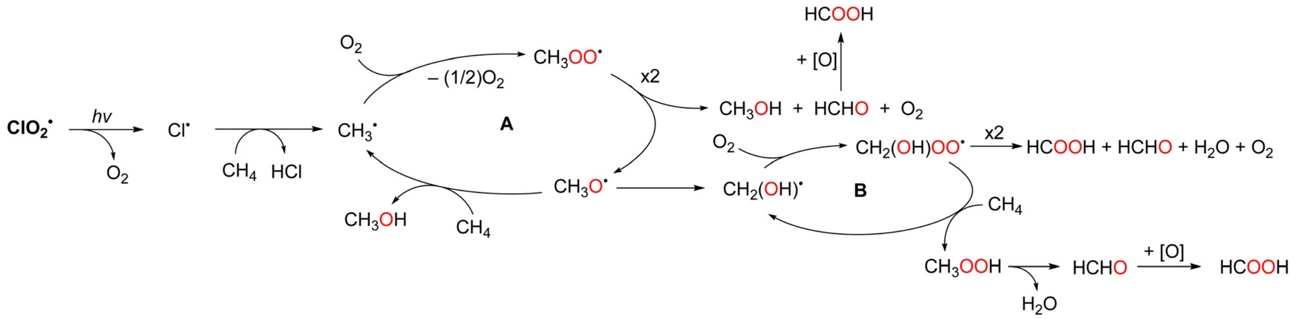
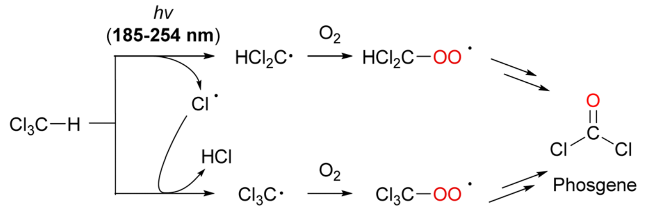


Fig. 1 UV-Vis absorption spectral change of $ClO_2^•$ generation in the reaction of $NaClO_2$ with HCl.

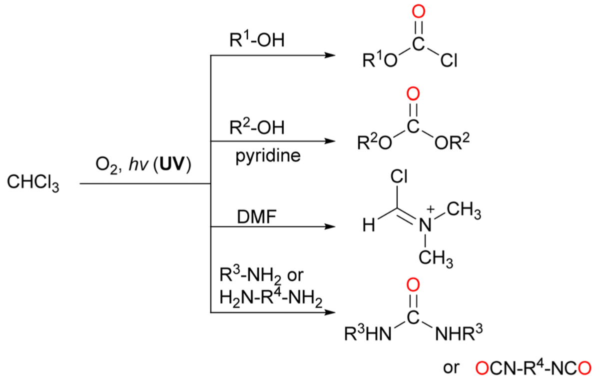
2.3.2 Oxygenation of $CHCl_3$. $CHCl_3$ is a common organic solvent used in many chemical processes owing to its stability and ability to dissolve a wide variety of organic compounds. However, it easily decomposes under UV irradiation or heat in the presence of oxygen, yielding phosgene ($COCl_2$, Scheme 18).[87,88] The C–H BDE of $CHCl_3$ is 95.7 kcal mol^{-1},[89] which is lower than that of CH_4 (104 kcal mol^{-1}). Therefore, C–H hydrogen abstraction by $Cl^•$ and subsequent oxygenation proceed under appropriate reaction conditions. Tsuda *et al.* previously reported the synthesis of carbonates,[90–92] chloroformates,[93] Vilsmeier



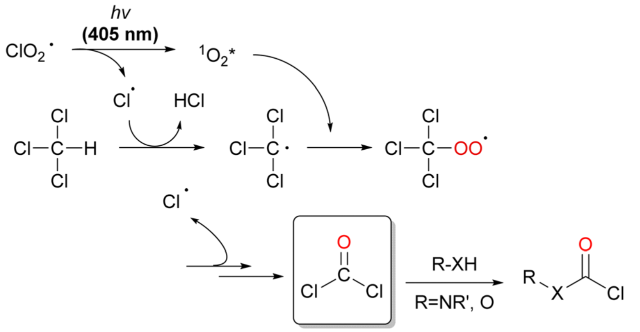
Scheme 17 Radical chain reactions during the $ClO_2^{\bullet}$ oxygenation of CH_4 to CH_3OH and HCOOH.



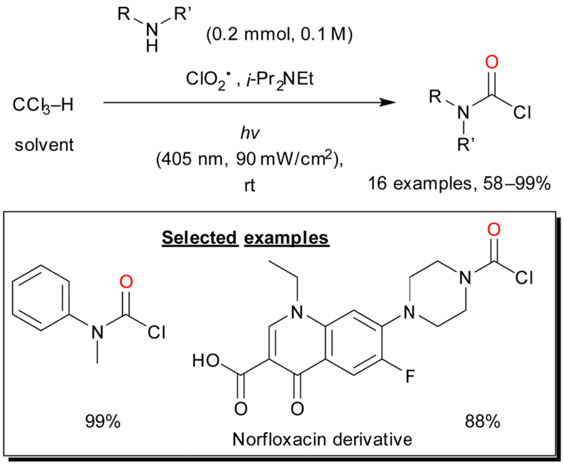
Scheme 18 Generation of phosgene ($COCl_2$) by the oxidative degradation of $CHCl_3$ under UV-light irradiation.



Scheme 19 Synthetic organic reactions using $COCl_2$ generated by the oxidative decomposition of $CHCl_3$.



Scheme 20 $COCl_2$ generation *via* the formation of $ClO_2^{\bullet}$ under visible-light irradiation and its synthetic applications.

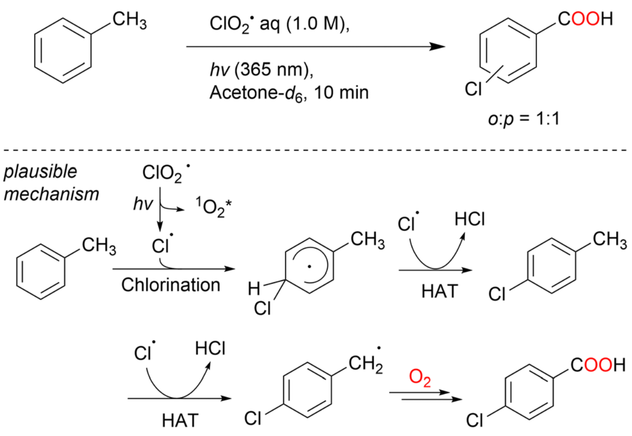


Scheme 21 *In situ* preparation of $COCl_2$ through $CHCl_3$ oxygenation using visible-light-activated $ClO_2^{\bullet}$ and further reaction with amines to afford carbamoyl chlorides.

reagents,[94] urea and isocyanate (Scheme 19) by the *in situ* generation of $COCl_2$ *via* the oxygenation of $CHCl_3$ initiated by $Cl^{\bullet}$ under UV-light irradiation.[95] More recently, they have also reported $CHCl_3$ oxygenation under visible-light irradiation using trace amounts of Cl_2 as an initiator.[96,97] In addition, our research group has developed a $CHCl_3$ oxygenation reaction *via* the photoactivation of $ClO_2^{\bullet}$ (Scheme 20).[98] Carbamoyl chlorides were synthesised from a wide substrate range by the phosgenation of amines under visible-light irradiation ($\lambda > 400$ nm) as $ClO_2^{\bullet}$ exhibits a strong absorption band in the visible-light region (Fig. 1). Various aromatic and aliphatic amines were successfully phosgenated in high yields using this method (Scheme 21). This method was applicable even to substrates containing an olefinic or benzyl moiety, as well as substrates with complex structures such as pharmaceutical derivatives. For a long time, the use of $COCl_2$ in the synthesis of fine chemicals has been avoided owing to the difficulty in handling a gas molecule and its high toxicity. Therefore, triphosgene[99–102] has generally been used as a phosgene equivalent in small-scale synthesis despite its hazards, which have been noted in recent years.[103] However, this photooxygenation method, which can gradually generate $COCl_2$ from $CHCl_3$ *in situ* and directly achieve the phosgenation of nucleophiles, is a promising alternative to the conventional method.

2.3.3 Chlorocarboxylation of toluene. Although the one-step oxidation of C(sp^3)–H and functionalisation of the C(sp^2)–H of an alkyl-substituted aromatic compound would be synthetically useful, to the best of our knowledge, no examples have been reported thus far. Recently, our research group reported the photoinduced chlorocarboxylation of toluene initiated by $ClO_2^{\bullet}$ at room temperature without the use of a metal catalyst (Scheme 22).[104] Based on the results of various control experiments, we proposed a reaction mechanism initiated by the reaction of $Cl^{\bullet}$ with the aromatic ring of toluene to form an aryl radical. Subsequently, another $Cl^{\bullet}$ abstracts hydrogen from the aryl radical to form chlorotoluene. Hydrogen is then abstracted from the C(sp^3)–H bond of chlorotoluene by another $Cl^{\bullet}$, resulting in the formation of a benzyl radical, which is converted to chlorobenzoic acid upon subsequent oxygenation. The excess amount of $Cl^{\bullet}$ generated *in situ* would be involved in chlorination and two HAT processes.

2.3.4 Oxygenation of polymer surfaces. The surface function of polymer materials has been actively studied in many fields such as medical supplies, packing materials, and the automotive industry, as the polymer surfaces come into contact with different materials.[105–108] Therefore, the surface modification of polymers is essential to impart various functions such as hydrophilicity, biomolecular affinity, metal affinity, antifouling properties, and adhesiveness to the moulded polymer. An advantage of surface modification is that the chemical and physical surface properties of polymers can be selectively modified without affecting their bulk properties. Traditional physicochemical processes such as plasma and corona discharge treatments are widely used surface modification techniques owing to their simple operation and high treatment efficiency, but these methods have a trade-off with material surface degradation. Therefore, the development of milder techniques is necessary. In this context, our research group has applied the abovementioned chlorine dioxide photooxidation to polymer materials for surface modification. $ClO_2^{\bullet}$ is an efficient reagent for the oxygenation of the surfaces of polypropylene (PP) and polyethylene (PE) (Fig. 2).[109]



Scheme 22 Chlorocarboxylation of toluene using $ClO_2^{\bullet}$ under LED (365 nm) irradiation.

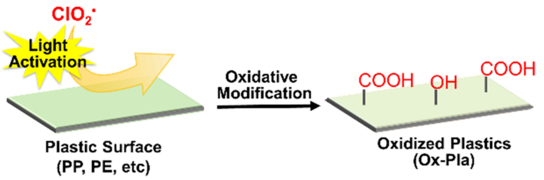


Fig. 2 Polymer surface oxygenation by photoactivated $ClO_2^{\bullet}$.

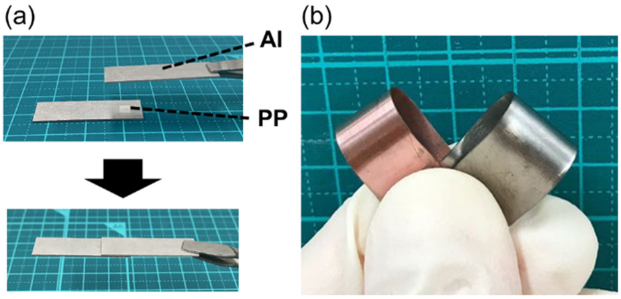
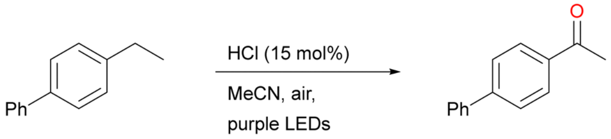


Fig. 3 Photographs of (a) the oxidized polypropylene (PP) films before and after the thermocompression bonding of Al/PP/Al without any adhesive and (b) Cu and Ni electroless plated PP films.

This is the first convenient chemical method for the surface C–H oxygenation of olefinic plastics such as PP and PE without the use of heavy metal oxides. Oxygen functional groups such as carboxyl groups were introduced onto the polymer surface *via* this surface oxidative modification, and cationic dyes were immobilised. In addition, the polar oxygen functional groups introduced on the polymer surface can facilitate metal adhesion; for instance, the oxidised PP film exhibits good adhesion of an aluminium plate without any adhesives (Fig. 3(a)).[110] In addition, this modification method has been used to successfully develop electroless metal plating without exfoliation (Fig. 3(b)). The functional groups on the oxygenated polymer surface allow for further modification with various organic compounds, which could have significant implications in synthetic polymer chemistry. For instance, our research group successfully immobilised cyclodextrins on PP nonwoven fabrics *via* the ester coupling reaction of carboxyl groups that are introduced by photooxidation.[111] This highly functional PP nonwoven fabric can sustainably load and release drugs. This surface modification has also been applied to polycarbonate (an engineering plastic),[112] ABS resin,[113] and polyhydroxyalkanoic acid (a biomass plastic).[114]

2.4 Others

Recently, C–H oxygenation reactions using the abundant and inexpensive HCl as the $Cl^{\bullet}$ source without metal or organocatalysts have also been developed. Wang *et al.* reported the benzyl oxidation of alkylarenes using HCl as the catalyst and molecular oxygen as the oxidant (Scheme 23).[115] They attributed this reaction to the generation of singlet oxygen from the photoexcitation of the substrate and the consequent formation of $Cl^{\bullet}$ from Cl^{-}. However, direct excitation of the substrates is unlikely under visible-light irradiation (395–400 nm) as the



Scheme 23 HCl-catalysed aerobic oxidation of alkylarenes.

substrates do not absorb visible light. In addition, energy transfer from the excited substrate to oxygen has not been sufficiently investigated using techniques such as cyclic voltammetry. Further follow-up studies are expected.

3. Conclusion and outlook

The direct oxygenation of C(sp^3)–H bonds is an important chemical conversion process in industrial and fine chemical synthesis. It can be a step-, time-, and energy-saving method in the construction of complex organic compounds compared with the classical synthetic approach. Oxygenation using molecular oxygen is an optimal method for economic and environmental reasons because O_2 is abundant and non-toxic. However, O_2 cannot react directly with hydrocarbons and should be converted to singlet oxygen to facilitate C–H bond cleavage. In this article, we reviewed C–H oxygenation reactions initiated by the $Cl^\bullet$ generated by light irradiation and molecular oxygen. $Cl^\bullet$ is an attractive HAT reagent and electron acceptor (SET source) as it has strong oxidative properties, and the Cl atoms form strong bonds with hydrogen atoms. In addition, the generation of $Cl^\bullet$ by light irradiation is effective in terms of the energy required and ease of controlling the reaction. These features meet the increasing demand for sustainable and environment-friendly chemical processes and $Cl^\bullet$-mediated oxygenation reactions are expected to be further developed in the future.

Further development is expected to complement the current electrochemical techniques.

Future studies can focus on the following topics:

(1) Selective oxygenation reactions of alkyls can be developed by controlling steric hindrance using reactive ligands, which exhibit selectivity even when the C–H bonds have similar bond strengths (radical stability).[116] On the other hand, the following points should be noted in $Cl^\bullet$-mediated oxygenation using metal chlorides as the Cl source: reactions where metal chlorides are used as the $Cl^\bullet$ source can proceed *via* SET from the substrate to the metal. This should be confirmed by conducting the reaction in the presence of metal species other than chlorides (*e.g.*, sulfates and nitrates) and $Cl^\bullet$ trapping experiments. Both HAT and SET are possible mechanisms for the benzylic C–H oxygenation. Even though elucidating the reaction mechanism is challenging owing to competing reactions, the presence or absence of SET can be validated by determining the redox potentials, and the presence of radical cations can be detected by electron spin resonance (ESR). In addition, density-functional-theory-based mechanistic studies have been demonstrated to be useful in most of the original papers in this review.

(2) The use of acridinium and other organic photocatalysts can potentially improve the reaction efficiency and selectivity. However, these photocatalysts need to have the appropriate oxidation ability and chemical stability.

(3) Reactions of chlorine dioxide, such as methane oxidation and plastic surface modification, should be developed as industrial processes. Scale-up and safety assessment are topics to be studied in the future.

We hope that this review will encourage interest in C–H oxygenation reactions with Cl radicals and contribute to the understanding of the reactivity of Cl radicals, thereby facilitating their use in further useful and wide-range synthetic chemical applications.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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