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Oxidation of Alkanes with Dioxygen Induced by Visible Light and Cu(II) and Fe(III) Chlorides

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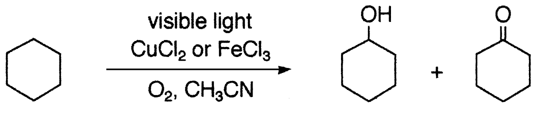
Cyclohexane and adamantane were oxidized in acetonitrile with dioxygen to the corresponding alcohols and ketones under irradiation of visible light in the presence of $CuCl_2$ or $FeCl_3$ catalyst. Fairly good selectivity of the products was attained with $CuCl_2$: ca. 50% for cyclohexane and 75% for adamantane at over 50% conversion. Alkyl hydroperoxides were detected during the reactions in 10% and 25% amounts of the products at maximum for the cyclohexane oxidation with $CuCl_2$ and $FeCl_3$, respectively. Moreover, the products were overoxidized by the present system at comparable or slower rates than the alkanes. Other features of the reaction, such as the rate of oxygen uptake and carbon dioxide liberation, isotope effect, and radical inhibitor effect, were also investigated.

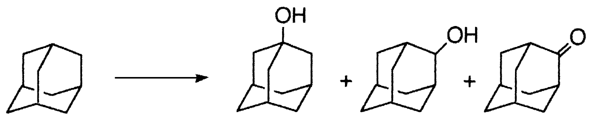
Selective oxidation of alkanes with molecular oxygen under mild conditions has attracted much attention in research laboratories and in industry, since these reactions usually suffer from lower selectivity at higher conversion as can be seen in cyclohexane oxidation by the Du Pont process.[1] Some promising catalytic systems for this transformation have been developed recently. These include autoxidation with *N*-hydroxyphthalimide,[2] co-oxidation with acetaldehyde by transition metal salts,[3] and reaction with modified polyoxometalates,[4] and zeolites.[5] Moreover, photoreactions by using various catalysts, such as ammonium cerium(IV) nitrate,[6] titanium(IV) oxide,[7] polyoxometalates,[8] iron porphyrins,[9] and transition metal chlorides,[10] have been found to be available for the oxidation of alkanes. Although these photocatalytic methods are potentially useful for the development of environmentally benign systems, the reactions were usually carried out under UV light irradiation[11] and the majority of the studies focused on the initial stage of the reaction at very low conversion; this means that behavior of the system at high conversion has rarely been investigated. Thus, we studied oxidation of cyclohexane and adamantane with dioxygen under visible light irradiation by using $CuCl_2$ and $FeCl_3$ catalysts;[12] we found that the reaction can proceed with similar selectivities to those attained by UV light at over 50% conversion. We report herein these results.

Results and Discussion

When a homogeneous solution of cyclohexane (**1**) (0.1 M) and $CuCl_2 \cdot 2H_2O$ (5 mol% of **1**) in acetonitrile was irradiated with a halogen lamp under oxygen (1 atm) at 13 °C for 18 h, cyclohexanol (**2**) and cyclohexanone (**3**) were formed in 14% and 13% yields, respectively, along with a small amount of cyclohexyl chloride (**4**) (1%), and the substrate **1** was recovered in 42% yield. Other volatile compounds were not detected by GC.[13] Visible light, the catalyst, and oxygen are essential for the reaction, i.e., no reaction took place in the absence of any one of these. An acetonitrile solvent can be substituted by propionitrile and CH_3CN–$CHCl_3$ (3/1) with a little decrease of the efficiency, but **1** was completely recovered unchanged in 1,2-dichloroethane and DMF as well as in neat reaction. Among the various copper salts tested, only $CuCl_2$ exhibited useful catalyst activity; such a result should be correlated to its solubility in CH_3CN and its ability to absorb visible light.[14]



1 **2** **3** (1)



5 **6** **7** **8** (2)

Encouraged by the above results, we examined the reactions of cyclohexane (**1**) and adamantane (**5**) with Cu(II) and Fe(III) chlorides under similar conditions (Eqs. 1 and 2); their time course is shown in Fig. 1. As cyclohexane (**1**) was monotonously consumed in the reaction with $CuCl_2$, the alcohol **2** and ketone **3** increased in preference of the former, wherein the total selectivity of **2** and **3** was maintained at almost 50% at over 50% conversion (Fig. 1, A). In contrast, the reaction with $FeCl_3$ gave the ketone **3** predominantly with decreased selectivity of ca. 25% (B). With respect to the oxidation of adamantane (**5**), high selectivity (ca. 75%) was attained by using the Cu catalyst. Here the yields of the products **6**–**8** increased in the order adamantanone (**8**) < 1-adamantanol (**6**) < 2-ada-

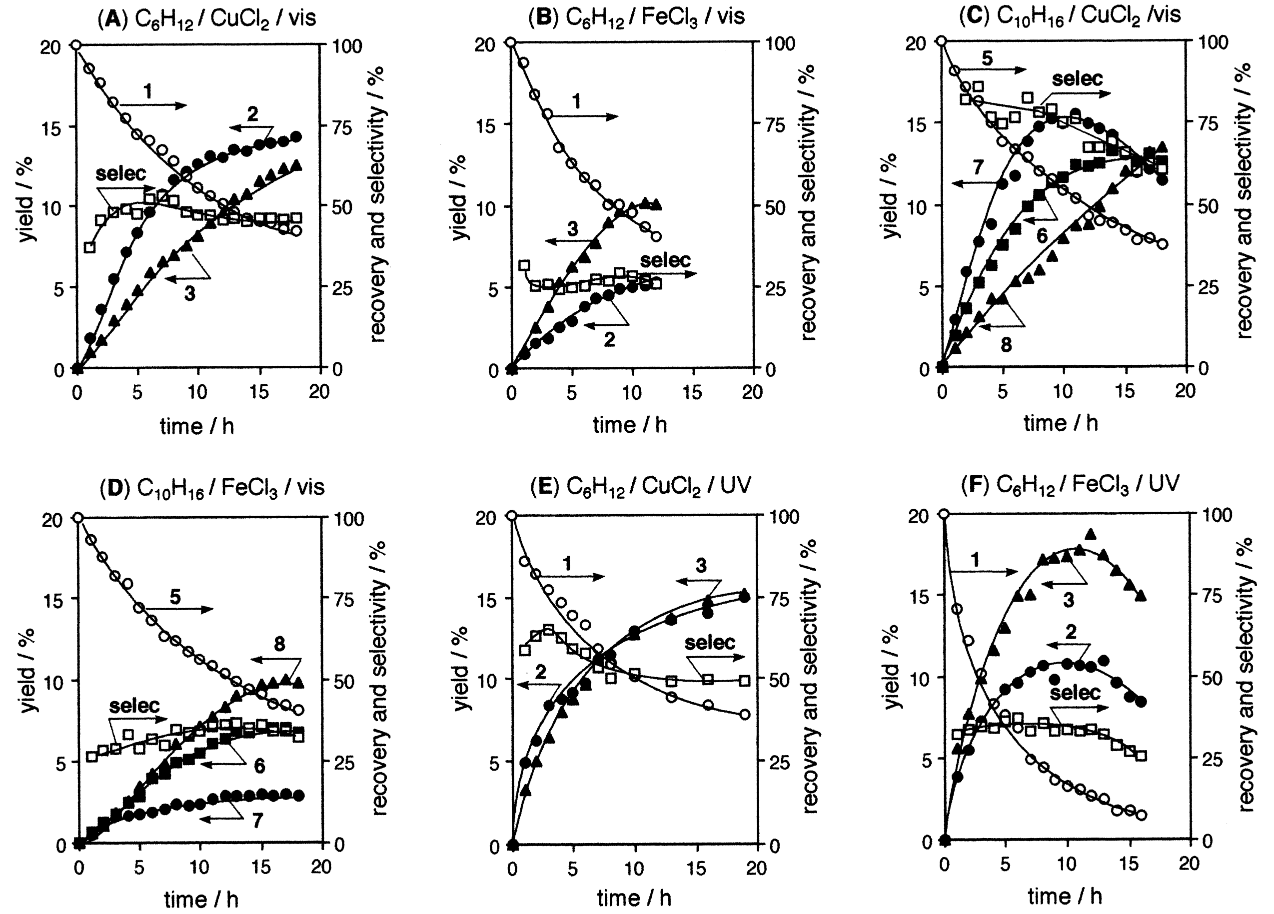


Fig. 1. Time course of the oxidation of cyclohexane (**1**) and adamantane (**5**) with $CuCl_2$ or $FeCl_3$. Conditions: C_6H_{12} (10 mmol), $C_{10}H_{16}$ (2.5 mmol), $CuCl_2$ and $FeCl_3$ (5 mol% of the substrates), CH_3CN (100 mL), O_2 (1 atm), 13 ± 2 °C, irradiated by halogen (A–D) or mercury lamp (E and F). The alkyl chlorides are omitted for clarity.

mantanol (**7**) (C). On the other hand, the order of the ketone **8** and 2-alcohol **7** was reversed with the Fe catalyst, as was the case for cyclohexane oxidation (D).

The oxidation of cyclohexane (**1**) under UV light irradiation was investigated for comparison with the vis light reaction (Fig. 1, E and F). With $CuCl_2$, the alcohol **2** and ketone **3** were formed in equal amounts, whereas preferential formation of **3** was not changed with $FeCl_3$. On the whole, reactions irradiated by UV were faster than those irradiated by vis, particularly in the reaction with $FeCl_3$, and the yields of the products **2**–**3** were higher. However, their total selectivities were nearly equal. Cu(II) and Fe(III) chlorides in acetonitrile exhibits λ_{max} at 310 and 455, and 310 and 360 nm, respectively, in UV-vis spectra. Emission of the halogen lamp used in this work distributes to a little below 400 nm (10% based on that of 700 nm). However, irradiation by the halogen lamp attached with an aqueous filter of $NaNO_2$ (> 400 nm) promoted the reaction with similar efficiency. Accordingly, absorbed light at 455 nm due to $CuCl_2$ and at a shoulder over 400 nm due to $FeCl_3$ should be responsible for the present oxidation.

Alkyl hydroperoxides, plausible precursors for the products, were not detected by normal GC analysis, because they should be readily decomposed to alcohols and ketones in the GC column. Thus, their amounts were estimated by double GC analysis: before and after addition of triphenylphosphine (see: Experimental).[10] The ratios of cyclohexyl hydroperoxide (**9**) to the total products **2** and **3** are shown in Fig. 2. The iron catalyst afforded more peroxide **9** than did copper. Comparing the two light sources, less **9** was detected by UV at an early stage of the reaction, but its ratio rapidly exceeded that detected by vis.

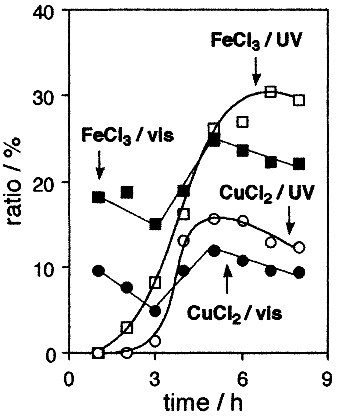


Fig. 2. Ratio of cyclohexyl peroxide (**9**) to the total amounts of cyclohexanol (**2**) and cyclohexanone (**3**).

Table 1. Initial Reaction Rate on the Oxidation of Cyclohexane (**1**), Cyclohexanol (**2**) and Cyclohexanone (**3**)[a),b)]

Catalyst	(1) $-\frac{d[\mathbf{1}]}{dt}$	(2) $\frac{d[\mathbf{2}]}{dt}$	(3) $\frac{d[\mathbf{3}]}{dt}$	(4) (2) + (3)	(5) (4)/(1)	(6) (2)/(3)	(7)[c)] $-\frac{d[\mathbf{2}]}{dt}$	(8)[c)] $-\frac{d[\mathbf{3}]}{dt}$
$CuCl_2$	0.62	0.19	0.10	0.29	0.48	1.9	0.33	0.39
$FeCl_3$	0.80	0.09	0.14	0.23	0.29	0.6	0.47	0.53

a) Unit: mmol/h. b) Conditions, see: Fig. 1. c) **2** and **3** were used as starting substrates under the identical conditions.

Table 2. Initial Reaction Rate on the Oxidation of Adamantane (**5**), 1- and 2-Adamantanol (**6**) and (**7**), and Adamantanone (**8**)[a),b)]

Catalyst	(1) $-\frac{d[\mathbf{5}]}{dt}$	(2) $\frac{d[\mathbf{6}]}{dt}$	(3) $\frac{d[\mathbf{7}]}{dt}$	(4) $\frac{d[\mathbf{8}]}{dt}$	(5) (2) + (3) + (4)	(6) (5)/(1)	(7) (3)/(4)	(8) [(3) + (4)]/(2)	(9)[c)] $-\frac{d[\mathbf{6}]}{dt}$	(10)[c)] $-\frac{d[\mathbf{7}]}{dt}$	(11)[c)] $-\frac{d[\mathbf{8}]}{dt}$
$CuCl_2$	0.18	0.048	0.069	0.029	0.146	0.81	2.4	2.0	0.16	0.17	0.14
$FeCl_3$	0.14	0.016	0.011	0.018	0.045	0.32	0.6	1.8	0.065	0.096	0.13

a) Unit: mmol/h. b) Conditions, see: Fig. 1. c) **6**, **7**, and **8** were used as starting substrates under the identical conditions.

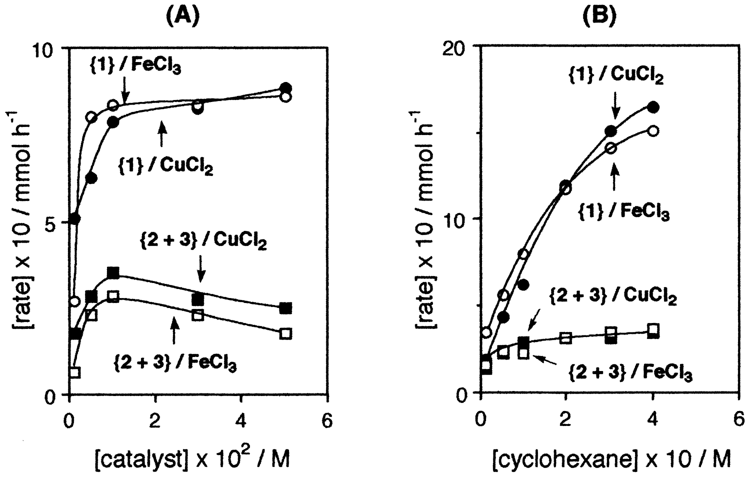


Fig. 3. Rate versus catalyst (A) and cyclohexane concentration (B). {**1**} and {**2** + **3**} denote ($-$d[**1**]/d*t*) and (d[**2**]/d*t* + d[**3**]/d*t*), respectively. $[C_6H_{12}] = 0.1$ M (A); [catalyst] $= 5 \times 10^{-3}$ M (B); other conditions, see: Fig. 1.

The initial consumption rate of cyclohexane (**1**) by vis light, the formation rates of the cyclohexanol (**2**) and cyclohexanone (**3**), and the overoxidation rates of **2** and **3** are summarized in Table 1. As can be seen in Table 1, the ratio of (4)/(1), total selectivity of **2** and **3**, was 0.48 and 0.29 with $CuCl_2$ and $FeCl_3$ catalysts, respectively (column 5); this result is in good agreement with the time course of the reaction depicted in Fig. 1, of course. The rate ratio of the alcohol **2** to ketone **3** was 1.9 and 0.6 with $CuCl_2$ and $FeCl_3$, respectively, which suggested that the catalysts would participate in the step to determine the ratio along with the absorption of the visible light (column 6). Surprisingly, comparing the consumption rate of **1** with that of **2** and **3** under the identical conditions, the alkane **1** was oxidized faster than the oxygenated products **2** and **3** (columns 1, 7, and 8). Moreover, it has been found that the ketone **3** was not mainly derived from the alcohol **2**, because a negligible amount of **3** was detected by the oxidation of **2**, i.e., formation rate of the former was only 8% of the consumption rate of the latter with $CuCl_2$ and 16% of that with $FeCl_3$.

Similarly, the initial reaction rate on the oxidation of adamantane (**5**) by vis light and the related ratios are shown in Table 2. The total selectivities of 81% and 32%, and the ratio of 2-adamantanol (**7**) to adamantanone (**8**) of 2.4 and 0.6 were observed for the reaction with $CuCl_2$ and $FeCl_3$, respectively (columns 6 and 7). Reactivity of the two alcohols **6** and **7** and ketone **8** is a little lower than or comparable to that of adamantane (**5**) (columns 1 and 9–11). Again, a negligible amount of the ketone **8** was detected by the oxidation of the 2-alcohol **7** under the present conditions. The ratio of [(3) + (4)]/(2), relative reactivity of the secondary to the tertiary C–H bond, was 2.0 and 1.8 (0.7 and 0.6 per H) with $CuCl_2$ and $FeCl_3$, respectively (column 8); such values are higher than the values of 0.5–1.2 reported for normal free radical autoxidation.[15]

The relation between the initial reaction rate and concentration of the catalysts and cyclohexane (**1**) is plotted in Fig. 3. The consumption rate of **1** and the total formation rate of the products **2** and **3** were increased with increasing the catalysts up to 1×10^{-2} M; then the former leveled off and the latter de-

Table 3. Dioxygen Uptake and Carbon Dioxide Liberation[a),b)]

Run	Substrate	Catalyst (amount/mmol)	(1) $-\frac{d[\text{substrate}]}{dt}$	(2) $-\frac{d[O_2]}{dt}$	(3)[c)] $-\frac{d[O_2]}{dt}$	(4) (1)/(2)	(5) $\frac{d[CO_2]}{dt}$	(6)[c)] $\frac{d[CO_2]}{dt}$
1	Cyclohexane	$CuCl_2$ (0.50)	0.62	0.23	0.060	2.7	0.021	0.020
2		$FeCl_3$ (0.50)	0.80	0.36	0.37	2.2	0.046	0.047
3	Adamantane	$CuCl_2$ (0.125)	0.18	0.19	0.062	0.9	0.024	0.020
4		$FeCl_3$ (0.125)	0.14	0.11	0.11	1.3	0.014	0.013
5		$FeCl_3$ (0.50)	0.28	0.38	0.37	0.7	—[d)]	0.047

a) Unit: mmol/h. b) Conditions, see: Fig. 1. c) Reaction in the absence of the substrates. d) Not determined.

creased slightly. Such tendencies are consistent with the results generally observed for the photocatalytic reaction (Fig. 3, A).[7,10] The consumption rate of **1** was proportional to its concentration: formally 0.5–0.6 order, whereas the formation rate of **2** and **3** was nearly constant (Fig. 3, B). Higher concentration of the substrate **1** may enhance some side reactions such as coupling reactions, which would result in a decrease of the product selectivity. In addition, substitution of dioxygen by air had little effect on the oxidation.

The initial rate of dioxygen uptake and carbon dioxide liberation were then measured (Table 3). Comparing the uptake of dioxygen with that of the substrates **1** and **5**, two to three times excess amounts of cyclohexane (**1**) were formally consumed per dioxygen (column 4, runs 1 and 2), whereas the ratio was nearly unity in the reaction of adamantane (**5**) (column 4, runs 3–5). In the absence of the alkanes **1** and **5**, a little oxygen uptake was also observed for acetonitrile containing $CuCl_2$: about 30% of the amount of the alkane oxidation, which was independent of the catalyst concentration (column 3, runs 1 and 3). In contrast, equal amounts of dioxygen were consumed in acetonitrile with $FeCl_3$ irrespective of the presence or absence of **1** and **5**, and the rate was proportional to the catalyst concentration (columns 2 and 3, runs 2, 4, and 5). Carbon dioxide was detected in small amounts during the reaction. This could be derived from the solvent rather than from the alkanes **1** and **5**, because the rate of liberation was not changed by the presence of **1** and **5** (columns 5 and 6). Similarly to the dioxygen uptake, the liberation rate of carbon dioxide was independent of the catalyst concentration in the case of $CuCl_2$ but, in contrast, depended on it with $FeCl_3$. These results imply that oxidation of the alkanes **1** and **5** and acetonitrile would occur independently with $CuCl_2$. On the other hand, the reaction with $FeCl_3$ is likely to proceed via activation of the solvent, for example, formation of $^{\bullet}CH_2CN$. Alternatively, the facile reaction of oxygen with photoactivated $FeCl_3$ would take place predominantly.

An obvious inhibitory effect of 2,4,6-tri-*t*-butylphenol was observed for the present reaction. For example, the consumption rate of cyclohexane (**1**) and the formation rate of the products **2** and **3** decreased to 62% and 35% of the original rates with $CuCl_2$ and 45% and 2% with $FeCl_3$, respectively, in the presence of equimolar amounts of the phenol. The reaction of adamantane (**5**) was retarded more drastically: 15% and 11% with $CuCl_2$ and 14% and no products with $FeCl_3$, respectively. Next, a competitive reaction of cyclohexane and cyclohexane-d_{12} was carried out by using their equimolar mixture accurately measured; the isotope effect was determined based on the individual reaction rates (Table 4). No isotope effect was observed with $CuCl_2$ catalyst. In the reaction with $FeCl_3$, a small but apparent effect of 1.7 was revealed in the formation of cyclohexanone (**3**), though such an effect could be negligible on the substrate consumption and on the total products formation.[16]

Table 4. Isotope Effect on the Oxidation of Cyclohexane (**1**)[a)]

Catalyst	Substrate consumption	Alcohol formation	Ketone formation	Total products formation
$CuCl_2$	1.1	1.0	1.1	1.0
$FeCl_3$	1.1	0.8	1.7	1.1

a) Conditions: C_6H_{12} (5.0 mmol), C_6D_{12} (5.0 mmol), and the catalyst (0.5 mmol); other conditions, see: Fig. 1.

As described above, it is apparent that the present reaction is most complicated and could not be adequately explained by a simple mechanism. However, a major process of producing the alcohols and ketones seems to be composed of the reactions shown in Eqs. 3–7. At first, irradiation of the catalyst could induce charge transfer to yield Cu(I) and chlorine radical (Eq. 3). Hydrogen abstraction from cyclohexane (**1**) by thus generated $Cl^{\bullet}$, followed by the reaction with dioxygen gave peroxy radical (Eqs. 4 and 5). Then, cyclohexyl hydroperoxide (**9**) was formed by the reduction of the radical with Cu(I) (Eq. 6). Finally, cyclohexanol (**2**) and cyclohexanone (**3**) were derived from the hydroperoxide **9**, probably catalyzed by copper (Eq. 7). Moreover, the process would be accompanied with other chain reactions through hydrogen abstraction from cyclohexane (**1**) by oxy radicals such as $C_6H_{11}O^{\bullet}$, generated from **9** with Cu(I), and $C_6H_{11}O_2^{\bullet}$. $FeCl_3$ could promote the reaction in a similar manner as $CuCl_2$ did, though predominant activation of the solvent or dioxygen prior to the formation of cyclohexyl radical would be involved. This scenario, fundamentally similar to the mechanism proposed by Shul′pin[10] except for the hydrogen abstraction by the oxy radicals, can explain the present results to a certain extent. However, a different mechanism may cooperate in the reaction of adamantane (**5**), because it showed higher reactivity ratio of 2°/3°-CH than that expected for a radical mechanism and a lower ratio of the substrate to dioxygen consumption than cyclohexane (**1**).

$$Cu^{II} - Cl \xrightarrow{h\nu} Cu^{I} + Cl^{\bullet} \tag{3}$$

$$C_6H_{12} + Cl^{\bullet} \longrightarrow C_6H_{11}^{\bullet} \tag{4}$$

$$\mathrm{C_6H_{11}^{\bullet}} + \mathrm{O_2} \xrightarrow{\qquad} \mathrm{C_6H_{11}O_2^{\bullet}} \tag{5}$$

$$\mathrm{C_6H_{11}O_2^{\bullet}} \xrightarrow{\mathrm{Cu^I/H^+}} \mathrm{C_6H_{11}OOH} \tag{6}$$

$$\mathrm{C_6H_{11}OOH} \xrightarrow{\qquad} \mathrm{C_6H_{11}OH} + \mathrm{C_6H_{10}O} \tag{7}$$

In summary, liquid phase oxidation of alkanes could be performed by visible light irradiation in the presence of $CuCl_2$ or $FeCl_3$ catalysts. Fairly good selectivity of the products does not decrease as the reaction proceeds, even at over 50% conversion, probably because overoxidation of the products is comparable to or slower than the alkane oxidation in this system. Alkyl hydroperoxides are the primary products of the reaction and the ratio of their decomposition to the alcohols and ketones depends on the catalysts used. Although further work is necessary to improve the efficiency of the reaction in terms of selectivity, turnover frequency, and quantum yield, the present results exhibit a possibility of an environmentally benign approach for alkane oxidation.

Experimental

General. All photoreactions were carried out in a three-necked cylindrical Pyrex glass vessel (74 mm ϕ, ca. 610 mL, net volume: 380 mL), containing an Eikohsha EHC-300 halogen arc (300 W) or a EHB-WU-100 high-pressure mercury arc (100 W) with double jackets of quartz (52 mm o.d.) for cooling water. On irradiation of mercury arc, the light source was surrounded by Pyrex filter tubes. The vessel was normally connected to a dioxygen balloon, and, in the case of measurement of its uptake, to a gas bullet. The apparatus was placed in a thermostatic water bath with magnetic stirring. GC analyses were performed on a Shimadzu GC-17A equipped with an FID by using a 30 m × 0.25 mm i.d. J & W capillary column (DB5.625) and a Shimadzu GC-14B with FID by using a 3 m × 3 mm i.d. column of 15% of OV-17 on Chromosorb W. UV-vis spectra were recorded with a Shimadzu UV-265 spectrophotometer.

Materials. Cyclohexane (**1**) was washed with H_2SO_4 and then with water, dried over $CaCl_2$, and distilled under N_2. Acetonitrile was dried over molecular sieves and distilled under N_2. Other materials of high purity were used as received.

General Procedure for the Photooxidation. A solution of cyclohexane (**1**) (1.08 mL, 10 mmol) and $CuCl_2\cdot 2H_2O$ (88.2 mg, 0.5 mmol, 5 mol%) or $FeCl_3\cdot 6H_2O$ (135.2 mg, 0.5 mmol, 5 mol%) in acetonitrile (100 mL) was stirred for a while under dioxygen, then irradiated by a halogen lamp. In the reaction of adamantane (**5**), a more diluted solution of the substrate (340.6 mg, 2.5 mmol) and the catalysts (0.125 mmol, 5 mol%) was used because of its solubility in the solvent. During the reaction, aliquots of the mixture (1.0 mL) were withdrawn with a micropipette at adequate intervals, and analyzed by GC with internal standards: *p*-xylene for **1** and naphthalene for **5**. Oxidation of cyclohexanol (**2**) and cyclohexanone (**3**) and of adamantanols **6** and **7** and adamantanone (**8**) were performed under identical conditions to that of the alkanes **1** and **5**, respectively. Carbon dioxide was measured by passing it through aqueous $Ba(OH)_2$ solution in a gentle stream of dioxygen. The isotope effect was calculated from the individual reaction rates of C_6H_{12} and C_6D_{12} obtained in the reaction by using their equimolar mixture (accurately 5.0 mmol each). Amounts of the alkyl hydroperoxides were determined by double GC analyses: before and after addition of excess Ph_3P; here the total amounts of the alcohols and ketones were nearly constant, and thus twice the difference of the ketones was estimated as the peroxide amounts, assuming that it decomposed to alcohols and ketones in a 1 : 1 ratio by GC.[10] For measurement of the initial reaction rate, analyses were done at 20-min intervals over 3 h for cyclohexane (**1**) and at 30-min intervals over 5 h for adamantane (**5**), and the data were obtained by the least squares method.

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16 Curiously, the isotope effect on the formation of cyclohexanol with $FeCl_3$ tends to lower a little, which may be attributed to the preferential decomposition of the deuterated cyclohexyl hydroperoxide survived (ca. 20%) to the corresponding alcohol on GC analyses, in contrast to the normal 1:1 ratio to the alcohol and ketone. Similarly, slow formation of the deuterated ketone from the peroxide, because of C–D bond fission, would cause an increase of the corresponding alcohol competitively.