

Photocatalytic Oxidation of Alkanes with Dioxygen by Visible Light and Copper(II) and Iron(III) Chlorides: Preference Oxidation of Alkanes over Alcohols and Ketones

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Visible light irradiation of alkanes in acetonitrile with CuCl_2 and FeCl_3 catalysts under atmospheric dioxygen gave the corresponding alcohols and ketones effectively; in these reactions, the total selectivity of the products did not decrease so much with increase of alkane conversion. For example, cyclohexanol and cyclohexanone were formed with ca. 70% selectivity at 50% conversion, because overoxidation of the products took place more slowly than cyclohexane oxidation. The relative reactivity values of cycloalkanes increased as their ring-sizes decreased. In the oxidation of hexane, the reactivity ratio of $\text{C}^1\text{-}/\text{C}^2\text{-}/\text{C}^3\text{-H}$ was found to be 1.0/1.4/1.8 with CuCl_2 and 1.0/4.6/6.6 with FeCl_3 , respectively. Toluene and diphenylmethane were more reactive than cyclohexane with FeCl_3 , as expected, whereas the alkane was oxidized faster than the benzylic compounds in the separate reaction with CuCl_2 . Moreover, the alkane oxidation could be comparably performed by sunlight instead of an artificial lamp.

Oxidation of alkanes, particularly cyclohexane, with dioxygen is an important reaction in industry. However, the conversion should be kept at a very low level to get high product selectivity, as can be seen in the Du Pont process.¹ Much attention has been paid to photocatalytic reactions towards improvement of the oxidation, because they are potentially performable under environmentally benign conditions. Many photocatalysts have been used in the liquid-phase oxidation of cyclohexane. These include ammonium cerium(IV) nitrate,² titanium(IV) oxide,³ polyoxotungstate,⁴ iron(III) porphyrins,⁵ various transition metal chlorides,⁶ and alumina-supported vanadium(V) oxide.⁷ However, most of these studies were usually carried out under UV light irradiation,⁸ and focused on the initial stage of the reaction at very low conversion, which suggests that a photocatalytic approach also suffers from the dilemma of selectivity and conversion. Previously, we disclosed an efficient oxidation of cyclohexane and adamantane with dioxygen by visible light/ CuCl_2 and FeCl_3 systems, wherein fairly good selectivity for the corresponding alcohols and ketones was attained at over 50% conversion.⁹ We studied this system further using various alkanes and benzylic compounds and found a unique feature, particularly with CuCl_2 , in that alkanes are usually oxidized faster than alcohols, ketones, and benzylic substrates. Moreover, comparable results were obtained by the reaction under sunshine. We would like to report herein these results.

Results and Discussion

Irradiation of cyclohexane in acetonitrile by visible light (halogen lamp, >400 nm) with CuCl_2 catalysts (5 mol%) under atmospheric dioxygen at 13 °C gave cyclohexanol and cyclohexanone together with negligible amounts of cyclohexyl chloride, as shown in Fig. 1.¹⁰ Other products were not detect-

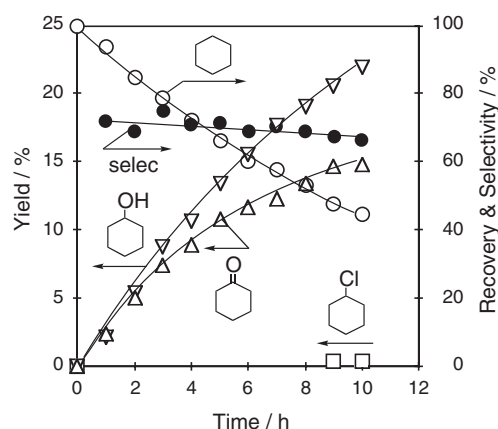
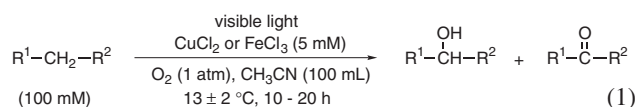


Fig. 1. Oxidation of cyclohexane by visible light/ CuCl_2 .

ed by GC in the liquid phase, though nonvolatile materials like dicarboxylic acids were not analyzed. Very little carbon dioxide was generated in the gas phase (ca. 3% yield based on the alkane), which was probably derived from the solvent, not from the alkane.⁹ Conversion of cyclohexane reached 55% after 10 h, but total selectivity of the alcohol and ketone was kept nearly unchanged at 70%. Various alkanes and benzylic substrates were oxidized under the standard conditions [Eq. 1], and these results are summarized in Table 1.



As can be seen in Fig. 1, the most striking feature of the present system is that the total selectivity of the alcohol and ketone does not diminish significantly as the conversion in-

Table 1. Initial Reaction Rate and Selectivity on the Oxidation of Various Substrates

Substrate	CuCl ₂				FeCl ₃			
	Consumption of substrate ^{a)}	Formation of alcohol ^{a)}	Formation of ketone ^{a)}	Selectivity ^{b)} /%	Consumption of substrate ^{a)}	Formation of alcohol ^{a)}	Formation of ketone ^{a)}	Selectivity ^{b)} /%
Cyclopentane	6.46	0.93	0.75	26	5.10	0.38	0.73	22
Cyclohexane	5.45	1.60	0.95	47	5.78	0.86	1.18	35
Cyclooctane	4.34	1.20	1.09	53	4.47	0.34	1.30	37
Cyclododecane ^{c)}	2.07	1.05	0.60	80	1.99	0.46	0.93	70
Hexane	4.71	0.23 (C ¹) 0.39 (C ²) 0.58 (C ³)	0.58 (C ¹) 0.38 (C ²) 0.38 (C ³)	54	6.94	0.02 (C ¹) 0.26 (C ²) 0.23 (C ³)	0.19 (C ¹) 0.38 (C ²) 0.70 (C ³)	26
Toluene	0.53	0.10	0.16	49	3.37	0.17	2.41 ^{d)}	77
Diphenylmethane	0.71	0.07	0.08	21	3.09	0.16	1.54	55
Tetralin	1.38	0.37 (α) 0.22 (β)	0.34 (α) 0.12 (β)	76	4.30	0.34 (α) 0 (β)	1.86 (α) 0 (β)	51
Cyclododecane ^{c,e)}	6.30	2.46	2.36	77	4.81	1.03	1.62	55

a) Unit: mM/h. b) Formation rate of (alcohols + ketones)/consumption rate. c) Cyclododecane (50 mM) and the catalysts (2.5 mM). d) Calculated from the results during the first 5 h. e) Carried out under sunshine at 20–40 °C.

	Cyclohexane	Cyclohexanol	Cyclohexanone
CuCl ₂	<u>1.0</u>	0.5	0.6
FeCl ₃	<u>1.0</u>	0.6	0.7

Scheme 1. Relative reaction rate on the oxidation of cyclohexane, cyclohexanol, and cyclohexanone.

creases, in contrast to the normal tendency observed for the alkane functionalization. These promising phenomena could be interpreted by the fact that overoxidation of the products took place more slowly than alkane oxidation (Scheme 1).^{11,12} Since the reaction rates were measured separately, the substrate alcohol and ketone may deactivate the catalysts to exhibit seemingly lower reactivities. However, when cyclohexanol, cyclohexanone, adipic acid, and hexanoic acid (2–3 equiv of the catalysts) were added to the reaction mixtures containing the Cu and Fe catalysts, no noticeable change in their UV–vis spectra was observed in the visible light region.¹³ Moreover, the consumption rate of cyclohexane and the formation rate of the products were not altered by these additives. Thus, these unusual results would be caused by the characteristics of the present system.¹⁴

Cyclopentane, cyclooctane, and cyclododecane were oxidized similarly to give the corresponding alcohols and ketones with preference for the former by CuCl₂ and for the latter by FeCl₃ as shown in Table 1, along with small amounts of chloroalkanes (<5% of the products). The relative reactivity of these cycloalkanes was determined by the competitive reactions using an equimolar mixture of all substrates (Scheme 2).¹¹ Interestingly, the normalized reactivity increases as the ring-size decreases with both catalysts, which is, though via a different mechanism, in agreement with the oxidative addition reaction with Ir catalyst.¹⁵ Of course, the reactivity order did not change in the separate reactions.

The normalized relative reactivity of tertiary to secondary C–H bonds found by the present system was 1.5 and 1.7 with the Cu and Fe catalysts, respectively; these were obtained in the reaction of adamantane.⁹ Compared to the ratios of 2.1–

					
CuCl ₂	1.3	<u>1.0</u>	0.6	0.3	(/ H)
FeCl ₃	2.2	<u>1.0</u>	0.6	0.4	(/ H)

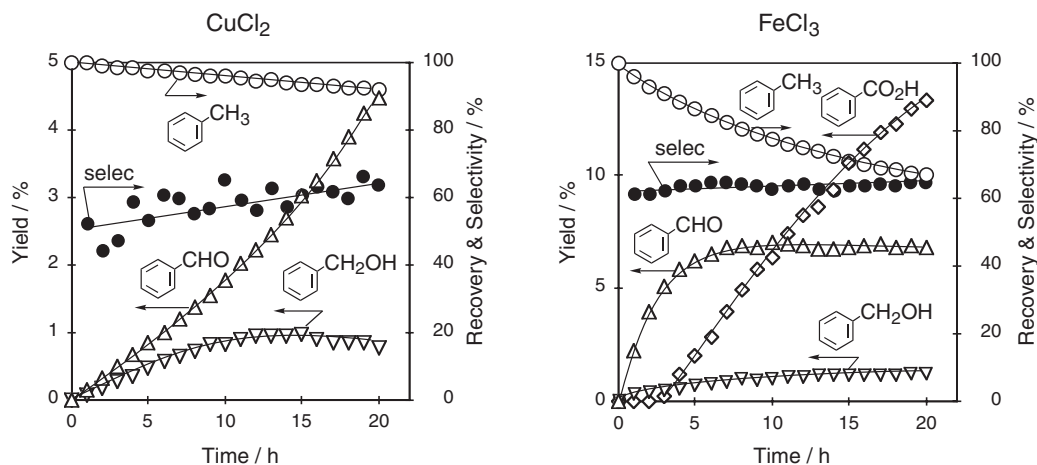
Scheme 2. Relative reactivity of cycloalkanes.

	C ¹	C ²	C ³	
CuCl ₂	<u>1.0</u>	1.4	1.8	(/ H)
FeCl ₃	<u>1.0</u>	4.6	6.6	(/ H)

Scheme 3. Relative reactivity of the C–H bonds of hexane.

7.1 reported for the typical radical reactions with hydroxyl, alkoxyl, alkylperoxyl, and chloro radicals, the present value seems to be small.¹⁶ The relative reactivity of secondary to primary C–H bond was investigated using hexane (Scheme 3).¹¹ With FeCl₃, C²- and C³-alcohols and ketones were totally produced 4.6 and 6.6 times faster than the C¹-products, respectively. On the other hand, these ratios were decreased to 1.4 and 1.8 with CuCl₂, which indicates that the terminal products are comparably formed as internal ones. The ratio of all secondary compounds to primary compounds with Cu is similar to that of hydroxylation of hexane with manganese(III) porphyrins.¹⁷

The present system was applied to the oxidation of the alkyl chains of aromatic compounds. Toluene was effectively oxidized with FeCl₃ to give benzaldehyde predominantly within 5 h, together with a small amount of benzyl alcohol, and then formation of the aldehyde was flattened and benzoic acid was produced as a major product (Fig. 2). The total selectivity of the three products was maintained at about 70%, but other products formed by the aromatic C–H bond oxidation and chlorinated compounds were not detected. On the other hand, the reaction with CuCl₂ was very slow; here conversion of the

Fig. 2. Oxidation of toluene by visible light/ CuCl_2 and FeCl_3 .

	Cyclohexane	Toluene	Diphenylmethane	
CuCl_2	1.0	0.4	0.8	(/H)
FeCl_3	1.0	2.3	3.2	(/H)

Scheme 4. Relative reactivity of sp^3 C–H bond of cyclohexane, toluene, and diphenylmethane.

substrate reached only 8% after 20 h under the standard conditions. Benzaldehyde and benzyl alcohol were formed together with a little benzyl chloride (8% of the two products), but benzoic acid was not formed. Similar results were obtained in the reaction of diphenylmethane, wherein benzophenone and benzhydrol were obtained in preference for the ketone without chlorinated compounds.

Reaction rates of toluene and diphenylmethane were compared with that of cyclohexane, separately measured under the identical conditions (Scheme 4).¹¹ With the Fe catalyst, toluene and diphenylmethane were oxidized 2.3 and 3.2 times faster than cyclohexane, respectively. Surprisingly, benzylic C–H bonds of the two aromatic compounds were less reactive than those of the alkane with CuCl_2 . Competitive reaction of cyclohexane and diphenylmethane gave, however, different results: the normalized ratio of diphenylmethane to cyclohexane was 1.4 and 3.5 with the Fe and Cu catalysts, respectively. That is, the order was the same with Fe, whereas the order reversed with Cu. The difference observed for the Cu-catalyzed reaction may be interpreted to result from the disturbing effect of the aromatic rings for alkane oxidation. However, this seems less likely, because the reaction rate of cyclohexane with CuCl_2 decreased slightly in the presence of benzene (5 equiv of CuCl_2). Instead, some intermediate like an alkyl radical, initially generated from cyclohexane, would be equilibrated with diphenylmethane. Moreover, oxidation of tetralin with FeCl_3 gave α -tetralol and α -tetralone with the preference for the latter, but the corresponding β -products were not detected. In the reaction with CuCl_2 , all four products were formed; here the ratio of total α - to β -products was 2.1.

The reaction mechanism of the present system was suggested previously by us⁹ and by another group.⁶ Irradiation of Fe(III) chloride would yield Fe(II) and $\text{Cl}^\bullet$, which abstracts

hydrogen from alkane to give an alkyl radical. The subsequent reaction of the radical with dioxygen, followed by reduction with Fe(II) and protonation yields alkyl hydroperoxide. Then, the alcohol and ketone are derived from the peroxide. Alternatively, the initial stage of the reaction would include an electron transfer process from alkane to photo-excited FeCl_3 to afford an alkyl radical cation and Fe(II) . However, these scenarios could not fully explain the regioselectivity and relative reactivity with CuCl_2 catalyst, which is a subject for further investigation.

Finally, the oxidation of cyclododecane with CuCl_2 was carried out under sunlight, and the results are compared with those obtained by a halogen lamp (Fig. 3). Sunlight showed better performance than the halogen lamp with respect to consumption rate of the alkane and formation rate of the products, wherein the alcohol and ketone were formed in nearly equal amounts. The selectivity was, however, decreased gradually as the reaction proceeded. Similar results were obtained with the Fe catalyst.

In summary, we have demonstrated that liquid-phase partial oxidation of alkanes with dioxygen can be effectively induced with CuCl_2 and FeCl_3 catalysts under visible light irradiation. A remarkable feature of the present system is that the corresponding alcohols and ketones were generally less reactive than the starting alkanes, and thus, product selectivities did not decrease so much despite high conversion. The relative reactivity of cycloalkanes increased with decrease of their ring-size. Particularly with the Cu catalyst, reactivity ratios of tertiary to secondary to primary C–H were smaller than those expected by normal radical reactions. Alkanes were oxidized faster than benzylic compounds in the separate reactions with CuCl_2 . In addition, the present system was simply conducted under sunshine, which is potentially useful for the exploitation of an environmentally benign process.

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, >400 nm) with double jackets of quartz (52 mm o.d.) for cooling water. The vessel was connected to a dioxygen balloon. The apparatus was placed in a thermostatic water bath with magnetic stir-

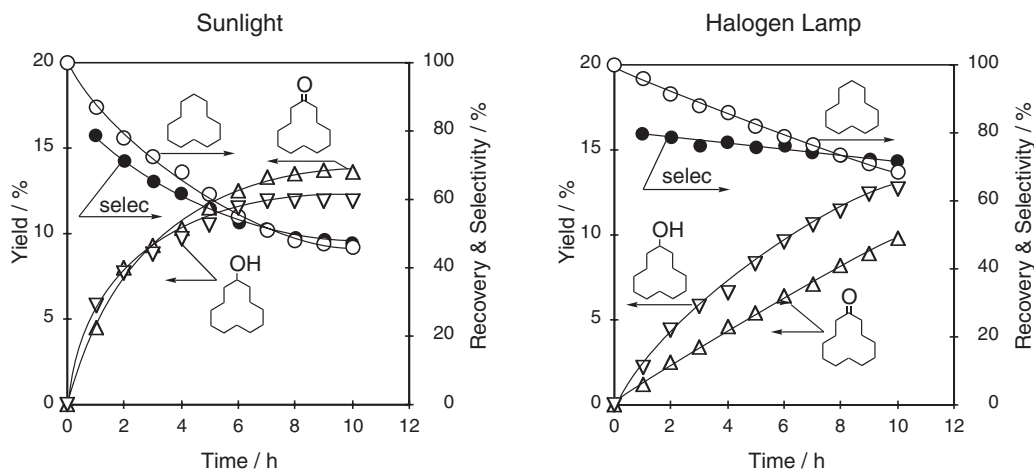


Fig. 3. Oxidation of cyclododecane with CuCl_2 by sunlight and halogen lamp.

ring. GC analyses were performed on a Shimadzu GC-17A equipped with an FID by using a $30 \text{ m} \times 0.25 \text{ mm}$ i.d. J & W capillary column (DB5.625) and a Shimadzu GC-14B with FID by using a $3 \text{ m} \times 3 \text{ mm}$ i.d. column of 15% of OV-17 on Chromosorb W. UV-vis spectra were recorded with a JASCO V-500 spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a Shimadzu GCMS-QP5050. The solvent, substrates, and authentic samples for the reaction products of high purity were commercially available and were used as received.

General Procedure for the Photocatalytic Oxidation. A solution of the substrate (10 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (85 mg, 0.5 mmol, 5 mol%) or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (135 mg, 0.5 mmol, 5 mol%) in acetonitrile (100 mL) was stirred for a while under dioxygen (1 atm), then irradiated by a halogen lamp with stirring at $13 \pm 2^\circ\text{C}$ as standard conditions. During the reaction, aliquots of the mixture (0.5 mL) were withdrawn with a micropipette at 1 h intervals over 10–20 h, and analyzed by GC with adequate internal standards such as mesitylene, *p*-xylene, benzene, and methyl benzoate. A more dilute solution of cyclododecane (842 mg, 5 mmol) in the solvent (100 mL) containing the catalyst (5 mol%) was used because of its low solubility. In the competitive reactions, a mixture of 5-, 6-, 8-, and 12-membered cycloalkanes (5 mmol each) with the catalyst (0.5 mmol), and that of diphenylmethane and cyclohexane (10 mmol each) with the catalyst (0.5 mmol) were irradiated. Oxidation of cyclohexanol and cyclohexanone was performed under the identical conditions to that of cyclohexane. The reaction of cyclododecane under sunshine was simply carried out by stirring of the standard solution in 300 mL Pyrex flask attached with dioxygen balloon outside in September, wherein the temperature of the mixture rose to 40°C . The initial reaction rates in Table 1 were obtained by the least squares method, and the relative reactivity and selectivity described in the text were determined based on these rates.¹¹

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- 10 The reaction was carried out using more dilute solution than the standard conditions indicated in Eq. 1, i.e., cyclohexane (20 mM) and CuCl_2 (1 mM) in CH_3CN (100 mL), which gave higher selectivity in general.
- 11 Relative reactivities in Schemes 1–4 were calculated as follows: Scheme 1, (consumption rate of cyclohexanol or cyclohexanone)/(that of C_6H_{12}), obtained by separate reaction; Scheme 2, (consumption rate of cycloalkane/number of C–H)/(that of $\text{C}_6\text{H}_{12}/12$), competitive reaction; Scheme 3, (total formation rate of C^n -alcohol and ketone/4)/(that of C^1 -alcohol and aldehyde/6); Scheme 4, (consumption rate of toluene or diphenylmethane/number of sp^3 C–H)/(that of $\text{C}_6\text{H}_{12}/12$), separate reaction.
- 12 Cyclohexanol and cyclohexanone were oxidized to unidentified nonvolatile materials directly, though a very small amount of the ketone was formed from the alcohol.

13 Absorption light at 462 nm for CuCl_2 and its shoulder over 400 nm for FeCl_3 are responsible for the present oxidation, see: Ref. 9.

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