Aerobic oxidation of alkanes and alkenes in the presence of aldehydes catalyzed by copper salts and copper–crown ether [1]

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Abstract

The oxidation of alkanes to the corresponding alcohols and ketones and the epoxidation of alkenes can be performed efficiently at room temperature with molecular oxygen (1 atm) in the presence of an aldehyde and a copper salt catalyst such as copper(II) hydroxide. Extremely high turnover numbers have been obtained for the oxidation of cyclohexane using a combination of copper(II) chloride and a crown ether as a catalyst.

Keywords: Oxidation of alkanes; Epoxidation of alkenes; Copper catalyst; Crown ether; Molecular oxygen; Aldehydes
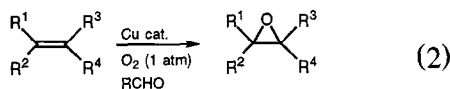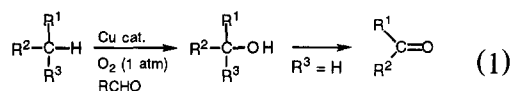
1. Introduction

Catalytic oxidations of hydrocarbons such as alkanes and alkenes have been explored by using various oxidizing agents, and oxidations with molecular oxygen under mild conditions are especially rewarding goals [1,2]. Copper as well as iron is predominantly contained in metalloenzymes that plays important roles in biological dioxygen metabolism [3]. Much effort has been devoted to mimicking heme-iron-containing enzymes such as cytochrome P-450; however, model studies for the copper-containing monooxygenases such as peptidylglyceine α-amidating monooxygenase, which catalyze the oxidation of aliphatic C–H bonds, are limited to

a few cases [4]. During the course of our systematic study on the simulation of enzymatic functions with metal complex catalysts [5], we found that aerobic oxidations of alkanes and alkenes with molecular oxygen can be performed highly efficiently with aldehydes and copper catalysts [6,7]. Copper(II) salt-catalyzed oxidation of alkanes with molecular oxygen (1 atm) in the presence of aldehydes under mild conditions gives the corresponding alcohols and ketones (Eq. (1)). Similar treatment of alkenes gives the corresponding epoxides (Eq. (2)). A combination of $CuCl_2$ and a crown ether has proven to be a highly efficient catalyst for the present aerobic oxidation of alkanes with acetaldehyde [7]. With this catalytic system extremely high turnover numbers were obtained for the aerobic oxidation of alkanes. As the catalytic intermediate, 2:1 complex of $CuCl_2$ and 18-crown-6 (**21**) are isolated and characterized. In this paper, full details of the copper-

catalyzed aerobic oxidations of alkanes and alkenes are described with respect to scope and mechanism.

$$R^2-\underset{\underset{R^3}{|}}{\overset{\overset{R^1}{|}}{C}}-H \xrightarrow[\substack{O_2\ (1\ atm)\\ RCHO}]{Cu\ cat.} R^2-\underset{\underset{R^3}{|}}{\overset{\overset{R^1}{|}}{C}}-OH \xrightarrow{R^3\ =\ H} \underset{R^2}{\overset{R^1}{>}}C=O \quad (1)$$

$$\underset{R^2}{\overset{R^1}{>}}C=C\underset{R^4}{\overset{R^3}{<}} \xrightarrow[\substack{O_2\ (1\ atm)\\ RCHO}]{Cu\ cat.} \underset{R^2}{\overset{R^1}{>}}\underset{}{\overset{O}{\triangle}}C\underset{R^4}{\overset{R^3}{<}} \quad (2)$$

2. Results and discussion

2.1. Aerobic oxidation of alkanes

The aerobic oxidation of alkanes is of importance from an enzymatic and synthetic point of view [1,2]. The direct functionalization of unactivated C–H bonds in saturated hydrocarbons usually requires drastic conditions such as high pressure and high temperature, and gives a mixture of products including polyoxygenated compounds [2]. Much effort has been devoted to

establish efficient catalytic systems for oxidation of alkanes using peroxides (iodosyl benzenes [8], hypochlorites and chlorites [9], hydrogen peroxide [10], KHSO$_5$ [11], alkylperoxides and peracids [12], amine *N*-oxide [13]); however, efficient aerobic oxidation is still remaining as a challenging topic (Pt–H$_2$ [14], sodium ascorbate [15], Zn [16], PhNHNHPh [17], photochemistry [18], aldehyde [19], hydroquinone [20], without reductant [21], NHPI [22]). Recently, we have found that a low valent ruthenium catalyst/peroxide system is efficient for the biomimetic oxidation of various substrates such as amines [23], amides [24], and hydrocarbons [25]. The catalytically active species of these reactions seems to be a low-valent oxo–ruthenium complex [5]. Further study revealed that the oxo–metal species seems to be generated by the reaction of low valent transition metal complexes with molecular oxygen in the presence of aldehydes [26,27]. As the consequence of our continuous study on the development of efficient aerobic oxidation reactions, we have found copper catalysts are effective for oxidation of alkanes with molecular oxygen in the presence of acetaldehyde.

The catalytic activity of various copper salts has been examined for the aerobic oxidation of

Table 1
Catalytic activity of various copper complexes for the oxidation of adamantane (1) with molecular oxygen in the presence of acetaldehyde [a]

Entry	Catalyst	Conv, [b] (%)	Yield, [b] (%)		
			1-adamantanol	2-adamantanol	2-adamantanone
			2	3	4
1	Cu(OCH$_3$)$_2$	32	24	1.3	1.1
2	Cu(OH)$_2$	29	25	1.5	0.9
3	Cu	27	22	1.1	0.4
4	Cu(acac)$_2$	26	21	0.9	trace
5	Cu(OAc)$_2$	26	21	1.0	0.4
6	Cu(OCHO)$_2$	19	16	0.8	0.4
7	Cu(OCOCF$_3$)$_2$	6.3	5.8	0	0
8	CuCl$_2$	4.0	4.0	0	0
9	CuSO$_4 \cdot$ 5H$_2$O	0.7	0.7	0	0
10	CuCl	20	16	0.9	0.3
11	Cu$_2$O	26	22	0.9	trace
12	CuO	10	9.9	0	0

[a] A mixture of 1 (2.00 mmol), catalyst (0.060 mmol), and acetaldehyde (6.00 mmol) in dry CH$_2$Cl$_2$ (12 mL) was stirred at room temperature under O$_2$ atmosphere (1 atm) for 17 h.
[b] Determined by GLC analysis based on the starting alkane.

Table 2
Effect of various aldehydes for the Cu(OH)$_2$-catalyzed oxidation of adamantane (1) with molecular oxygen [a]

Entry	Aldehyde	Conv,[b] %	Yield,[b] %		
			2	3	4
1	CH$_3$CHO	29	25	1.5	0.9
2	⋀⋀CHO	25	20	1.3	trace
3	⟩–CHO	22	18	1.3	0.5
4	⬡–CHO	17	14	1.2	trace
5	—⊢—CHO	13	11	1.0	0.3
6	⬡–CHO	29	21	1.9	trace
7	(CH$_3$CHO)$_3$	0	0	0	0

[a] A mixture of 1 (2.00 mmol), Cu(OH)$_2$ (0.060 mmol), and aldehyde (6.00 mmol) in dry CH$_2$Cl$_2$ (12 mL) was stirred at room temperature under O$_2$ atmosphere (1 atm) for 17 h.
[b] Determined by GLC analysis based on the starting alkane.

adamantane (1). The oxidation of 1 was carried out with molecular oxygen (1 atm) in the presence of a catalytic amount of copper salt and 3 equivalents of acetaldehyde in dry CH$_2$Cl$_2$ at room temperature. The conversion of 1 and the yields of 1-adamantanol (2), 2-adamantanol (3) and 2-adamantanone (4) were determined by GLC analyses. The representative results for the catalytic activity of various copper salts are shown in Table 1. Cu(OCH$_3$)$_2$ and Cu(OH)$_2$ have proven to be the most effective among examined (entries 1 and 2), and the effect of

copper salts is in the order of Cu(OMe)$_2$ ≈ Cu(OH)$_2$ > Cu(OAc)$_2$ ≫ Cu(OCOCF$_3$)$_2$ > CuCl$_2$, indicating that a copper salt bearing a more

Table 3
The Cu(OH)$_2$-catalyzed oxidation of various alkanes with molecular oxygen in the presence of acetaldehyde [a]

Entry	Substrate	Conv,[b] %	Product	Yield[b] (Selectivity),[c] %
1	⋀⋀⋀	3.2	heptanols	0.5 (16)[d]
			heptanones	2.7 (84)[e]
2	⋀⋀⋀⋀	4.6	decanols	0.7 (15)[f]
			decanones	3.8 (83)[g]
3	⬡	4.5	⬡–OH	1.7 (38)
			⬡=O	2.6 (58)
4	⬡	9.9	⬡–OH	0.9 (9)
			⬡=O	8.7 (88)
5	⬡–	8.6	methylcyclohexanols	5.8 (67)[h]
			methylcyclohexanones	2.5 (29)[i]
6	(adamantane)	29	adamantanol–OH	25 (86)
			adamantanol–OH	1.5 (5)
			adamantanone=O	0.9 (3)
7	⬡–CH$_3$	2.4	⬡–CH$_2$OH	0.3 (12)
			⬡–CHO	2.0 (85)
8	⬡–⋀	8.1	⬡–CH(OH)	2.3 (29)
			⬡–C(=O)	5.7 (70)
9	(indane)	27	(indanol) OH	6.1 (22)
			(indanone) =O	20 (75)

Notes to Table 3:
[a] A mixture of alkane (2.00 mmol), Cu(OH)$_2$ (0.060 mmol), and acetaldehyde (6.00 mmol) in dry CH$_2$Cl$_2$ (12 mL) was stirred at room temperature under O$_2$ atmosphere (1 atm) for 24 h.
[b] Determined by GLC analysis based on the starting alkane.
[c] Value in parenthesis corresponds to the yield based on the converted alkane.
[d] 2-ol:3-ol:4-ol = 40:34:26.
[e] 2-one:3-one:4-one = 40:43:17.
[f] 2-ol:3-ol:(4 + 5)-ols = 20:20:60.
[g] 2-one:3-one:(4 + 5)-one = 27:27:46.
[h] 1-ol:2-ol:3-ol:4-ol = 66:8:21:5.
[i] 2-one:3-one:4-one = 18:61:21.

basic or an electron donating ligand is suitable for the present oxidation. Cu powder also showed high catalytic activity because it is converted to a soluble copper salt during the reaction (entry 3). Addition of strong acids such as trifluoroacetic acid reduces the product yields, although acetic acid does not influence the oxidation.

The effect of various aldehydes was examined for the aerobic oxidation of **1** in the presence of $Cu(OH)_2$ catalyst (Table 2). The oxidation did not occur without an aldehyde. Acetaldehyde was found to be the most effective among examined (entry 1). Linear aldehydes such as butanal and aromatic aldehydes such as benzaldehyde also gave satisfactory results (entries 2 and 6), while the use of branched and cyclic aldehydes such as isobutyraldehyde, cyclohexanecarboxaldehyde and pivalaldehyde resulted in low conversions of adamantane (entries 3–5). Paraldehyde, trimer of acetaldehyde, is not effective for the present oxidation (entry 7). The use of acetaldehyde is practical because of its efficiency, low cost and easy separation of acetic acid formed from the reaction mixture. The effect of various solvents was examined for the $Cu(OH)_2$-catalyzed aerobic oxidation of **1** with acetaldehyde. CH_2Cl_2 has proven to be an excellent solvent. Other halogenated solvents such as 1,2-dichloroethane and CH_3CN gave good results, although polar solvents such as pyridine, methanol and DMF retarded the reaction.

The representative results of the $Cu(OH)_2$-catalyzed aerobic oxidations of alkanes in the presence of acetaldehyde are summarized in Table 3. Various alkanes including cycloalkanes and even poorly reactive linear alkanes such as *n*-heptane and *n*-decane are oxidized efficiently under oxygen atmosphere (1 atm) at room temperature to give the corresponding alcohols and ketones (entries 1–6). The distributions of the oxygenated products from adamantane and *n*-decane indicate that the selectivity of the present reaction is in the order of tertiary > secondary ≫ primary. Alkylated arenes are oxi-

dized at the benzylic position selectively (entries 7–9). The aldehydes under these conditions are converted into the corresponding carboxylic acids.

2.2. Aerobic epoxidation of alkenes

Since epoxides are useful synthetic intermediates, the aerobic oxidation of alkenes to epox-

Table 4
Catalytic activity of various copper salts for the oxidation of 1-decene with molecular oxygen in the presence of benzaldehyde [a]

Entry	Catalyst	Conv,[b] (%)	Yield of 1,2-epoxy-decane (**6**),[b] (%)
1	$Cu(OCH_3)_2$	53	30
2	$Cu(OH)_2$	51	32
3	Cu	42	26
4	$Cu(OAc)_2$	40	25
5	$CuCl_2$	16	10
6	CuCl	13	11
7	$Cu(OCHO)_2$	10	8.2
8	$Cu(OCOCF_3)_2$	7.7	6.1
9	Cu_2O	10	6.2
10	CuO	0	0

[a] A mixture of 1-decene (2.00 mmol), catalyst (0.020 mmol), and benzaldehyde (6.00 mmol) in dry CH_2Cl_2 (12 mL) was stirred at room temperature under O_2 atmosphere (1 atm) for 17 h.
[b] Determined by GLC analysis based on the starting alkene.

Table 5
Effect of various aldehydes for the $Cu(OH)_2$-catalyzed oxidation of 1-decene with molecular oxygen [a]

Entry	Aldehyde	Conv,[b] %	Yield of **6**,[b] %
1	⬡—CHO	51	32
2	⬡—CHO	32	27
3	⟩—CHO	38	22
4	⊣—CHO	27	10
5	∿∿—CHO	5.5	0.2
6	CH_3CHO	3.7	3.5

[a] A mixture of 1-decene (2.00 mmol), $Cu(OH)_2$ (0.020 mmol), and aldehyde (6.00 mmol) in dry CH_2Cl_2 (12 mL) was stirred at room temperature under O_2 atmosphere (1 atm) for 17 h.
[b] Determined by GLC analysis based on the starting alkene.

ides under mild conditions using metal catalysts has attracted much attention in recent years [28]. We tried to apply the present catalytic system to the oxidation of alkenes and found that aerobic epoxidation of alkenes can be performed efficiently [6]. Mukaiyama et al. reported that efficient aerobic epoxidation of alkenes proceeds using nickel(II) 1,3-diketone catalyst and an aldehyde [29]. Similar aerobic epoxidation of alkenes with aldehydes can be performed with other transition metal catalysts such as Ni [30], Fe [31], Mn [32], Co [33], and heteropolyoxometalate [34] or without a catalyst [35]. The present reaction provides a practical method for aerobic epoxidation of olefins with respect to high efficiency and mild conditions.

The catalytic activity of various copper salts has been examined for the oxidation of 1-decene (5) to 1,2-epoxydecane (6) with molecular oxygen (1 atm) in the presence of benzaldehyde at room temperature. The results are shown in Table 4. Electron donating ligands such as OCH_3 and OH enhance the catalytic activity, while electron withdrawing ligands such as CF_3COO reduce the product yields. As an aldehyde, benzaldehyde and cyclohexanecarboxaldehyde gave satisfactory results as shown in Table 5 (entries 1 and 2). Isobutyraldehyde and pivalaldehyde can be also used (entries 3 and 4). However, heptanal and acetaldehyde, which gave excellent results in the oxidation of alkanes, are not effective for the epoxidation of alkenes (entries 5 and 6). As solvents CH_2Cl_2, 1,2-dichloroethane and CH_3CN gave good results. The oxidation did not proceed in pyridine and DMF.

The representative results of the $Cu(OH)_2$-catalyzed aerobic oxidation of alkenes in the presence of cyclohexanecarboxaldehyde or benzaldehyde are summarized in Table 6. Various linear and cyclic alkenes can be converted into the corresponding epoxides. The oxidation of disubstituted alkenes gave epoxides in higher yields, although monosubstituted alkenes are less reactive (entry 1). The reactivity of alkenes is in the order of tri- > di- ≫ mono-substituted ones,

Table 6

The $Cu(OH)_2$-catalyzed oxidation of various alkenes with molecular oxygen in the presence of aldehyde [a]

Entry	Substrate	Product(s)	Conv.[b] %	Yield.[b] %
1			32	27 (32)[c]
2			100	79 (15)[c]
				0.4
				3.9
3			83	80[d]
4			96	82[e]
5			93	76[f]
6			81	64[g]
7			100	83

[a] A mixture of alkene (2.00 mmol), $Cu(OH)_2$ (0.020 mmol), and cyclohexanecarboxaldehyde (6.00 mmol) in dry CH_2Cl_2 (12 mL) was stirred at room temperature under O_2 atmosphere (1 atm) for 17 h.
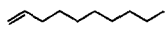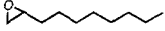[b] Determined by GLC analysis based on the starting alkene using an internal standard.
[c] Benzaldehyde was used instead of cyclohexanecarboxaldehyde.
[d] trans:cis = 100:0.
[e] trans:cis = 23:77.
[f] trans:cis = 100:0.
[g] trans:cis = 88:12.

indicating that the active copper species has an electrophilic character. Oxidation of cyclohexene gave 1,2-epoxycyclohexane selectively along with a small amount of 2-cyclohexene-1-ol and 2-cyclohexene-1-one (entry 2). The oxidations of trans-5-decene and trans-stilbene gave the corresponding trans-epoxides exclusively (entries 3 and 5); however, cis-5-decene and cis-stilbene gave a mixture of cis- and trans-epoxides (entries 4 and 6).

The stereochemistry of the epoxidation of cyclic allylic alcohols was examined (Eqs. (3) and (4)). The aerobic oxidation of 2-cyclohexen-1-ol (7) with cyclohexanecarboxaldehyde

proceeds with high *cis* selectivity to afford *cis*-2,3-epoxy-1-cyclohexanol (**8**) and *trans*-2,3-epoxy-1-cyclohexanol (**9**) in a ratio of 98.8 : 1.2. Similar *cis* selectivity has been observed in the oxidation of **7** with peracids such as mCPBA [36] and perbenzoic acid [37], although the selectivities are slightly low (**8**:**9** = 92:8). High *cis* selectivity of the epoxidation of **7** can be also achieved by several catalytic systems such as $Mo(CO)_6$–TBHP (98:2) [37], $VO(acac)_2$–TBHP (99.7:0.3) [38] and CF_3COCF_3–H_2O_2 (100:0) [39]. Reverse of the *cis/trans* selectivity was observed, when hydroxy group is replaced by bulky acetoxy group. Thus, the epoxidation of 2-cyclohexen-1-yl acetate (**11**) under the same conditions gives the *trans* epoxide predominantly (**12**:**13** = 31:69).

$$\text{(3)}$$

$$\text{(4)}$$
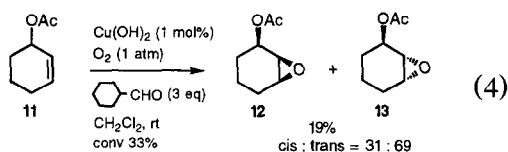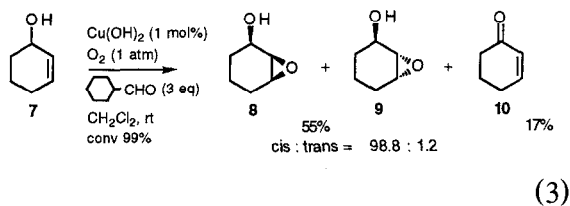
2.3. Aerobic oxidation of alkanes with copper–crown ether catalyst in the presence of acetaldehyde

These aerobic oxidations can be rationalized by assuming the sequence shown in Scheme 1. The copper-catalyzed radical chain reactions of an aldehyde with molecular oxygen affords the corresponding peracid [40]. The reaction of copper salts with peracids thus formed would give oxo–copper intermediate. Hydrogen abstraction of alkanes with oxo–copper salt followed by oxygen transfer to afford the corresponding al-

$$RCHO + O_2 \xrightarrow{Cu \text{ cat.}} RCO_3H$$

$$Cu^{II} + RCO_3H \longrightarrow {}^{\cdot}Cu^{III}\text{-O}{\cdot}^{\cdot} + RCO_2H$$

$${}^{\cdot}Cu^{III}\text{-O}{\cdot}^{\cdot} + RH \longrightarrow Cu + ROH$$
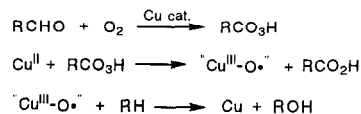
Scheme 1.

cohols. The alcohols are oxidized to the corresponding ketones under similar conditions. Relatively low yield of products and high conversions of aldehyde are due to the self decomposition of aldehyde with peracid, giving carboxylic acid as shown in Eq. (5) [41]. Based on assumption of the oxo–copper intermediate,

$$RCO_3H + RCHO \rightarrow 2RCO_2H, \tag{5}$$

the aerobic oxidation of aldehyde would be suppressed, if formation of high valent oxo–copper species, thus formed are getting much faster. For this purpose, we tried to stabilize high valent active copper species with a ligand bearing high electron donating ability. As described in the previous section, the catalytic activity of copper salts is in the order of $Cu(OH)_2 > Cu(OAc)_2 \gg Cu(OCOCF_3)_2 > CuCl_2$, indicating that a copper salt bearing more basic or electron donating ligand is suitable for the present oxidation. As Irving–Williams Series shows [42], divalent copper ions form the most stable complexes with the ligands among the second half of the first transition series. We thought crown ethers can be used as an electron donating ligand for the copper catalysts, although transition metals usually do not make a stable complex with crown ethers [43]. As a consequence of this study we found that the combination of a copper complex and a crown ether shows high catalytic activity for the present aerobic oxidation of alkanes with acetaldehyde (Eq. (6)).

$$R^1CH_2R^2 \xrightarrow[\text{CuCl}_2 \text{ (cat.)}]{RCHO, O_2} R^1CR^2 + R^1CHR^2$$

$$\tag{6}$$
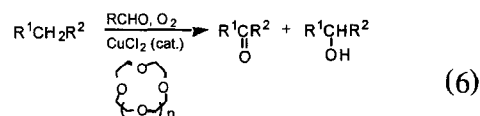
The catalytic activity of various combinations of metal catalysts and crown ethers (1:1) has

been examined for the oxidation of cyclohexane (14) with molecular oxygen (1 atm) in the presence of acetaldehyde (0.1 equivalent based on cyclohexane) in CH_2Cl_2 at room temperature. As shown in Table 7, the combined use of a copper salt and a crown ether increases the catalytic activity remarkably. A combination of $Cu(OH)_2$ and 18-crown-6 gives a higher turnover number (TN = 57) than the catalysts such as $Cu(OH)_2$ (TN = 12), Fe (TN = 22) [26] and $RuCl_3 \cdot nH_2O$ (TN = 20) [26] under the same conditions (entries 1–5).

The use of $CuCl_2$ with 18-crown-6 gave the best result (TN = 62) among those examined (entry 6). Particularly, high yield (78%) of oxygenated products based on acetaldehyde can be achieved, when the oxidation was carried out at 70°C (entry 7). The use of 1 equivalent of crown ether to $CuCl_2$ catalyst gave the best result, while 2 equivalents of crown ether do not influence the catalytic activity (TN = 63) and

0.5 equivalent of crown ether reduces the turnover number slightly (TN = 47) (entries 8 and 9). Other crown ethers such as dicyclohexyl-18-crown-6, dibenzo-18-crown-6, dibenzo-24-crown-8, 15-crown-5 and 12-crown-4 are also effective (entries 10–14), although the use of azacrown compounds results in no reaction (entry 15). Other ligands such as calixarenes, linear polyethers and carboxylic acids do not influence the turnover numbers (entries 16–18), while amines and their derivatives retard the oxidation reactions (entry 19). As an aldehyde, excellent results were obtained with aliphatic aldehydes such as acetaldehyde, isobutyraldehyde and pivalaldehyde. CH_2Cl_2 is proven to be the best solvent, although ethyl acetate, benzene and CH_3CN can also be used for the reaction.

The efficiency of the present catalysts is highlighted by extremely high turnover numbers in the aerobic oxidation of cyclohexane (14),

Table 7
Effect of crown ethers for the oxidation of cyclohexane (14) with molecular oxygen in the presence of acetaldehyde [a]

Entry	Catalyst	Yields, [b] (%) (based on CH_3CHO)			Turnover number [c]
		15	16	total	
1	Fe	5.8	2.6	8.4	22
2	$RuCl_3 \cdot nH_2O$	6.8	1.7	8.5	20
3	$Cu(OH)_2$	3.4	1.3	4.7	12
4	$CuCl_2$	3.0	1.1	4.1	10
5	$Cu(OH)_2$-18-crown-6 (1:1)	14	7.2	21	57
6	$CuCl_2$-18-crown-6 (1:1)	15	7.9	23	62
7	$CuCl_2$-18-crown-6 (1:1) [d]	66	12	78	177
8	$CuCl_2$-18-crown-6 (1:2)	16	8.0	24	63
9	$CuCl_2$-18-crown-6 (1:0.5)	13	5.4	18	47
10	$CuCl_2$-dicyclohexyl-18-crown-6 (1:1)	15	7.4	22	59
11	$CuCl_2$-dibenzo-18-crown-6 (1:1)	9.4	3.5	13	33
12	$CuCl_2$-dibenzo-24-crown-8 (1:1)	15	7.1	22	58
13	$CuCl_2$-15-crown-5 (1:1)	14	6.7	21	56
14	$CuCl_2$-12-crown-4 (1:1)	14	6.4	20	54
15	$CuCl_2$-cyclam (1:1)	0	0	0	0
16	$CuCl_2$-4-t-butylcalix [6] arene (1:1)	2.4	1.2	3.6	10
17	$CuCl_2$-1,2-dimethoxyethane (1:1)	3.4	1.0	4.4	11
18	$CuCl_2$–CH_3CO_2H (1:1)	2.6	1.8	7.0	17
19	$CuCl_2$-N-methylimidazole (1:1)	0	0	0	0

[a] A mixture of 14 (40.0 mmol), catalyst (0.010 mmol), and acetaldehyde (4.00 mmol) in dry CH_2Cl_2 (5 mL) was stirred at room temperature under O_2 atmosphere (1 atm) for 24 h.
[b] Determined by GLC analysis based on acetaldehyde. It was assumed that 2 mol of acetaldehyde were necessary for ketone formation.
[c] Results are given in mole of products formed per mole of catalyst.
[d] 70°C.

which is of importance in view of industrial aspects [44]. Actually, the oxidation of cyclohexane in the presence of $CuCl_2$ (2.50×10^{-4} mol%), 18-crown-6 (2.50×10^{-4} mol%) and acetaldehyde (10 mol%) at 70°C under O_2 atmosphere (1 atm) gave cyclohexanone (15) (61% yield based on acetaldehyde) and cyclohexanol (16) (10%) with turnover number of 1.62×10^4 (Eq. (7)). Although many catalytic systems for aerobic oxidation of alkanes have been reported, high catalytic efficiency has been achieved in a limited number of these systems such as $Fe(TPPF_{20}Br_8)-O_2$ [45] and Co–naphthenate–O_2–cyclohexanone [46], which require high reaction temperature and high pressure of O_2. The representative results of the $CuCl_2$-18-crown-6-catalyzed oxidation of alkanes with molecular oxygen (1 atm) and acetaldehyde in CH_2Cl_2 are shown in Table 8. Various alkanes and alkylated arenes can be converted into the

corresponding alcohols and ketones with high turnover numbers and high yields.
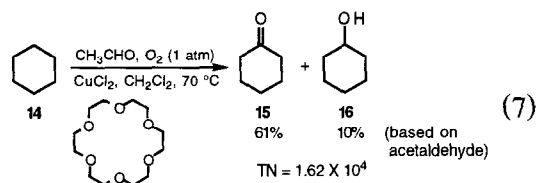
Aerobic epoxidation of olefins has been also examined using $CuCl_2$-18-crown-6-catalyst. The oxidation of cyclohexene (17) with cyclohexanecarboxaldehyde at room temperature affords 1,2-epoxycyclohexane (18, 68%) along with 2-cyclohexen-1-ol (19, 0.8%) and 2-cyclohexen-1-one (20, 10%), where the ratio of epoxidation to allylic oxidation $[18/(19+20)]$ is 6.3, while that with $Cu(OH)_2$ catalyst is 18 (Eq. (8)). The results suggest that oxo–copper species gener-

Table 8

$CuCl_2$-18-crown-6-catalyzed oxidation of alkanes with molecular oxygen in the presence of acetaldehyde [a]

Entry	Alkane	Temp. (°C)	Yields, [b] (%)		Turnover number [c]
			alcohol(s)	ketone(s)	
1	cyclohexane	70	10 [f]	61 [g]	1.62×10^4
2 [d]	cyclohexane	70	9.7 [f]	61 [g]	1.60×10^4
3	cyclooctane	70	9.1 [h]	74 [i]	1.86×10^4
4	n-hexane	70	2.3 [j]	44 [k]	9.77×10^3
5 [e]	ethylbenzene	rt	2.0 [l]	13 [m]	3.48×10^3
6 [e]	indane	rt	11 [n]	50 [o]	1.41×10^4
7 [e]	tetraline	rt	9.2 [p]	56 [q]	1.48×10^4

[a] A mixture of alkane (40.0 mmol), acetaldehyde (4.00 mmol), $CuCl_2$ (1.00×10^{-4} mmol), and 18-crown-6 (1.00×10^{-4} mmol) in CH_2Cl_2 (5 mL) was placed in an autoclave and reacted with stirring under O_2 atmosphere (1 atm) for 24 h.

[b] Determined by GLC analysis based on acetaldehyde. It was assumed that 2 mol of acetaldehyde were necessary for ketone formation.

[c] Results are given in mole of products formed per mole of catalyst.

[d] $(CuCl_2)_4(C_{12}H_{24}O_6)_2(H_2O)_2$ (21) (2.50×10^{-5} mmol) was used as a catalyst.

[e] Alkane (4.00 mmol) was used.

[f] Cyclohexanol.

[g] Cyclohexanone.

[h] Cyclooctanol.

[i] Cyclooctanone.

[j] 2-Hexanol and 3-hexanol (53:47).

[k] 2-Hexanone and 3-hexanone (49:51).

[l] 1-Phenylethanol.

[m] Acetophenone.

[n] 1-Indanol.

[o] 1-Indanone.

[p] α-Tetralol.

[q] α-Tetralone.

ated from copper–crown ether have ability to abstract hydrogen atoms from C–H bonds rather than oxygen transfer to olefins.

(8)
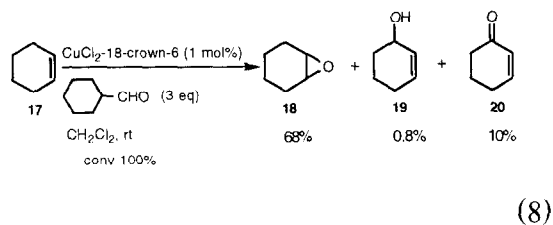
We succeeded in the isolation of a copper–crown ether complex, although stable transition metal complexes of crown ethers are rarely isolated (CuCl$_2$-12-crown-4 (1:1) complex [47], CuCl$_2$-benzo-15-crown-5 (1:1) complex [48]). When CuCl$_2$ was allowed to react with 18-crown-6 in CH$_2$Cl$_2$–ether at room temperature, a 1:1 complex of CuCl$_2$ and 18-crown-6, [(CuCl$_2$)$_4$(C$_{12}$H$_{24}$O$_6$)$_2$(H$_2$O)$_2$] (21) was obtained as a brown crystal. The structure of 21 was determined by X-ray crystal analysis as shown in Fig. 1. Crystallographic data, atomic coordinates, bond distances and angles are given in Tables 9–11, respectively. The complex 21 consists of tetrameric (CuCl$_2$)$_4$, two crown ethers and two H$_2$O molecules. The centrosymmetric molecule contains copper atoms in two distinct coordination geometries: the central pair of copper ions have 4 + 1 coordination, while the outer pair have a distorted-octahedral geom-

Table 9
Atomic coordinates of the non-hydrogen atoms

Atom	x	y	z	B_{eq}
Cu(1)	0.3382(2)	0.2771(2)	0.5853(1)	2.53(5)
Cu(2)	0.0447(2)	0.3807(1)	0.5174(1)	2.48(5)
Cl(1)	0.2328(4)	0.3963(3)	0.6481(3)	3.3(1)
Cl(2)	0.1981(4)	0.2851(3)	0.4556(3)	3.1(1)
Cl(3)	−0.0771(5)	0.2539(3)	0.5435(4)	4.3(1)
Cl(4)	−0.0856(4)	0.4940(3)	0.5801(3)	3.3(1)
O(1)	0.464(1)	0.2608(9)	0.7038(7)	3.2(3)
O(2)	0.262(1)	0.1385(10)	0.6695(9)	4.4(4)
O(3)	0.277(1)	0.0220(10)	0.5047(10)	4.8(4)
O(4)	0.354(1)	0.109(1)	0.3471(9)	4.9(4)
O(5)	0.519(1)	0.2714(9)	0.3870(7)	3.5(3)
O(6)	0.537(1)	0.3725(9)	0.5654(9)	3.6(3)
O(7)	0.440(1)	0.1757(7)	0.5328(7)	2.7(3)
C(1)	0.403(2)	0.223(2)	0.777(1)	5.5(6)
C(2)	0.337(2)	0.133(2)	0.755(1)	4.8(6)
C(3)	0.188(2)	0.052(2)	0.642(2)	6.1(7)
C(4)	0.179(3)	0.022(2)	0.560(2)	10(1)
C(5)	0.240(2)	−0.013(2)	0.416(2)	5.5(7)
C(6)	0.341(3)	0.005(2)	0.358(1)	5.6(7)
C(7)	0.449(2)	0.138(2)	0.293(1)	5.4(6)
C(8)	0.461(2)	0.247(2)	0.298(1)	4.5(5)
C(9)	0.523(2)	0.375(1)	0.401(1)	3.8(5)
C(10)	0.600(2)	0.397(1)	0.487(1)	2.6(4)
C(11)	0.619(2)	0.358(2)	0.645(2)	5.4(6)
C(12)	0.548(2)	0.337(2)	0.723(2)	5.7(6)

$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

etry. Each outer copper ion is hexacoordinate with three oxygen atoms of the crown ether, two bridged chlorine atoms and one oxygen atom of H$_2$O.

The catalytic activity of the isolated copper–crown complex 21 was examined for the oxidation of cyclohexane with acetaldehyde. The 21 catalyzed aerobic oxidation proceeds efficiently, the same as combined use of CuCl$_2$ and 18-crown-6. Thus, a similar high turnover number (1.60 × 10^4) was obtained (Table 8, entry 2), indicating ligation of crown ether is significant for the catalytic activity.

2.4. Reaction mechanism

In order to gain insight into the mechanism of the present oxidation of alkanes, the relative reaction rates of the Cu(OH)$_2$- and CuCl$_2$-18-
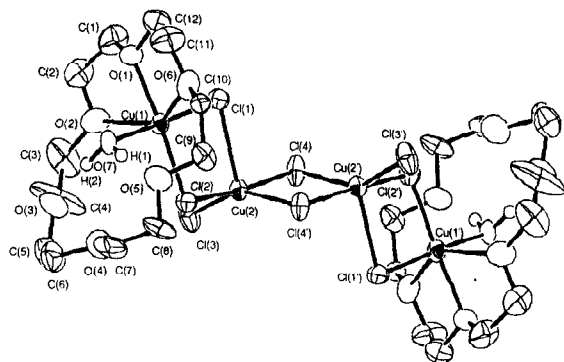

Fig. 1. The X-ray crystal structure [(CuCl$_2$)$_4$(18-crown-6)$_2$(H$_2$O)$_2$] (21). Hydrogen atoms on carbons are omitted for clarity. Atoms related by inversion center are primed.

crown-6-catalyzed oxidations of several substituted toluenes ($X–C_6H_4Me$, $X = p$-Me, H, p-Cl and m-Cl) with molecular oxygen in the presence of acetaldehyde in CH_2Cl_2 were deter-

Table 10
Selected bond distances (Å) and angles (deg) with their estimated standard deviations in parentheses

Bond	Length	Bond	Length
Cu(1)–Cl(1)	2.227(5)	Cu(1)–Cl(2)	2.289(5)
Cu(1)–O(1)	2.09(1)	Cu(1)–O(2)	2.45(1)
Cu(1)–O(6)	2.50(1)	Cu(1)–O(7)	1.96(1)
Cu(2)–Cl(1)	2.618(5)	Cu(2)–Cl(2)	2.329(5)
Cu(2)–Cl(3)	2.213(5)	Cu(2)–Cl(4)	2.322(5)
Cu(2)–Cl(4)	2.310(5)	O(1)–C(1)	1.40(2)
O(1)–C(12)	1.38(2)	O(2)–C(2)	1.42(2)
O(2)–C(3)	1.45(2)	O(3)–C(4)	1.38(3)
O(3)–C(5)	1.41(2)	O(4)–C(6)	1.44(2)
O(4)–C(7)	1.39(2)	O(5)–C(8)	1.43(2)
O(5)–C(9)	1.43(2)	O(6)–C(10)	1.42(2)
O(6)–C(11)	1.40(2)	C(1)–C(2)	1.44(3)
C(3)–C(4)	1.27(3)	C(5)–C(6)	1.45(3)
C(7)–C(8)	1.50(3)	C(9)–C(10)	1.47(2)
C(11)–C(12)	1.46(3)	O(7)–H(1)	0.77
O(7)–H(2)	1.01		

Bond	Angle	Bond	Angle
Cl(1)–Cu(1)–Cl(2)	90.6(2)	Cl(1)–Cu(1)–O(1)	91.5(3)
Cl(1)–Cu(1)–O(2)	99.1(3)	Cl(1)–Cu(1)–O(6)	96.7(3)
Cl(1)–Cu(1)–O(7)	176.8(4)	Cl(2)–Cu(1)–O(1)	176.5(4)
Cl(2)–Cu(1)–O(2)	104.2(3)	Cl(2)–Cu(1)–O(6)	110.2(3)
Cl(2)–Cu(1)–O(7)	91.7(3)	O(1)–Cu(1)–O(2)	72.8(5)
O(1)–Cu(1)–O(6)	72.3(4)	O(1)–Cu(1)–O(7)	86.2(5)
O(2)–Cu(1)–O(6)	141.8(4)	O(2)–Cu(1)–O(7)	82.4(4)
O(6)–Cu(1)–O(7)	80.5(4)	Cl(1)–Cu(2)–Cl(2)	80.7(2)
Cl(1)–Cu(2)–Cl(3)	109.8(2)	Cl(1)–Cu(2)–Cl(4)	94.6(2)
Cl(1)–Cu(2)–Cl(4)	102.9(2)	Cl(2)–Cu(2)–Cl(3)	93.3(2)
Cl(2)–Cu(2)–Cl(4)	171.6(2)	Cl(2)–Cu(2)–Cl(4)	89.9(2)
Cl(3)–Cu(2)–Cl(4)	94.9(2)	Cl(3)–Cu(2)–Cl(4)	147.2(2)
Cl(4)–Cu(2)–Cl(4)	84.4(2)	Cu(1)–Cl(1)–Cu(2)	90.0(2)
Cu(1)–Cl(2)–Cu(2)	96.2(2)	Cu(2)–Cl(4)–Cu(2)	95.6(2)
Cu(1)–O(1)–C(1)	112(1)	Cu(1)–O(1)–C(12)	115(1)
C(1)–O(1)–C(12)	116(1)	Cu(1)–O(2)–C(2)	108(1)
Cu(1)–O(2)–C(3)	133(1)	C(2)–O(2)–C(3)	115(1)
C(4)–O(3)–C(5)	113(1)	C(6)–O(4)–C(7)	115(1)
C(8)–O(5)–C(9)	111(1)	Cu(1)–O(6)–C(10)	132(1)
Cu(1)–O(6)–C(11)	105(1)	C(10)–O(6)–C(11)	114(1)
O(1)–C(1)–C(2)	112(1)	O(2)–C(2)–C(1)	111(1)
O(2)–C(3)–C(4)	120(1)	O(3)–C(4)–C(3)	125(2)
O(3)–C(5)–C(6)	109(1)	O(4)–C(6)–C(5)	108(1)
O(4)–C(7)–C(8)	108(1)	O(5)–C(8)–C(7)	107(1)
O(5)–C(9)–C(10)	109(1)	O(6)–C(10)–C(9)	113(1)
O(6)–C(11)–C(12)	111(1)	O(1)–C(12)–C(11)	110(1)
Cu(1)–O(7)–H(1)	102.8	Cu(1)–O(7)–H(2)	104.7
H(1)–O(7)–H(2)	117.1		

Table 11
Crystallographic data

	$(CuCl_2)_4(18\text{-crown-}6)_2(H_2O)_2$
Molecular formula	$Cu_4Cl_8C_{24}H_{52}O_{14}$
Formula weight	1102.47
Crystal dimensions (mm)	$0.30 \times 0.30 \times 0.10$
Crystal color	brown
Crystal system	monoclinic
Space group	$P2_1/n$ (# 14)
a (Å)	10.460(7)
b (Å)	13.727(5)
c (Å)	14.738(7)
β (°)	95.88(5)
Cell volume (Å^3)	2104(1)
Z	2
$F(000)$	1120
D_{calc} (g/cm^3)	1.739
Temperature (K)	293
Radiation (Å)	graphite monochromated Mo Kα ($\lambda = 0.71069$)
μ(Mo Kα) (cm^{-1})	25.56
Scan type	$\omega - 2\theta$
Scan rate	16.0°/min (in ω) – up to 3 scans
Scan width (°)	$1.84 + 0.30\tan\theta$
Scan range (°)	$25.2 < 2\theta < 29.6$
Total number of unique reflections	3149
Unique observed reflections with $I > 3\sigma(I)$	1661
No. of variables	221
Final R and R_w indices [a]	0.082, 0.083

[a] $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$, $R_w = [\Sigma\omega(|F_0| - |F_c|)^2/\Sigma\omega F_0^2]^{1/2}$.

mined by GLC analyses of the products (Fig. 2). The rate datum correlate well ($\gamma = 0.957$ and 0.999) with the Hammett linear free-energy relationship with use of σ^+ values. The ρ values for the reactions with $Cu(OH)_2$ and $CuCl_2$-18-crown-6 are -1.21 and -1.59, respectively. These are close to the values of -1.6 (cytochrome P-450) [49], -1.69 (Fe(TPP)Cl-PhIO) [50], and -1.36 (Mn(TPP)Cl-PhIO) [50], strongly suggesting that the character of active species in the present reaction is similar to that of oxo–metal (M = O) species.

The intramolecular deuterium isotope effects of the $Cu(OH)_2$- and $CuCl_2$-18-crown-6-catalyzed oxidation of 1,1-dideuterio-1,2-diphenylpropane (**22**) were determined by means of GC-MS analysis of the products (Eq. (9)). The k_H/k_D values obtained are 3.6 for $Cu(OH)_2$
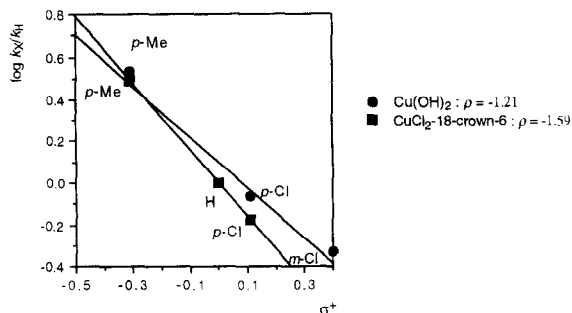
Fig. 2. Hammett correlation of Cu(OH)$_2$- and CuCl$_2$-18-crown-6-catalyzed aerobic oxidation of substituted toluenes in the presence of acetaldehyde; Cu(OH)$_2$: log k_X / k_H (X, σ^+), 0.535 (p-Me, −0.31), 0 (H, 0), −0.066 (p-Cl, 0.11), −0.333 (m-Cl, 0.40). CuCl$_2$: 18-crown-6: log k_X / k_H (X, σ^+), 0.493 (p-Me, −0.31), 0 (H, 0), −0.177 (p-Cl, 0.11).

and 4.1 for CuCl$_2$-18-crown-6, which are smaller than that observed with cytochrome P-450 (11) [51]. The intermolecular isotope effects of the oxygenations of cyclohexane were determined to be 1.8 (Cu(OH)$_2$) and 1.5 (CuCl$_2$-18-crown-6) by GLC analysis of the products obtained from the competitive reaction of cyclohexane (14) and cyclohexane-d_{12} (25) (Eq. (10)).

(9)

(10)
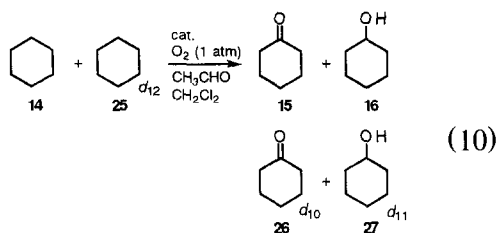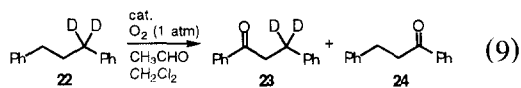
The present oxidation can be rationalized by assuming the following three sequential pathways (Scheme 2): (i) formation of peracids by a copper-mediated radical chain reaction of aldehydes with molecular oxygen, (ii) formation of oxo–copper species by the reaction of copper with peracids, and (iii) oxidations of alkanes and alkenes by oxo–copper species. Thus, the

reaction of aldehyde 28 in the presence of copper catalyst gives acyl radical 29, which reacts with molecular oxygen to afford the acylperoxy radical 30. The radical 30 abstracts hydrogen from 28 to give peracid 31 and radical 29. Kinetic studies on the metal-catalyzed aerobic oxidation of aldehydes affording peracids have revealed that the reactions proceed via radical chain mechanism as shown in Eq. (i) of Scheme 2 [40]. Intermediacy of peracetic acid has been confirmed by ^{1}H NMR (270 MHz) analysis of the mixture of Cu(OH)$_2$-catalyzed aerobic oxidation of adamantane with 3 equivalents of acetaldehyde in CD$_2$Cl$_2$ at room temperature. After 1.5 h the signal of methyl protons of peracetic acid was observed as a singlet at δ 2.13 along with those of acetic acid (δ 2.07s), acetaldehyde (δ 2.15, d, J 2.9 Hz), and paraldehyde (δ 1.32, d, J 5.1 Hz), all of which are confirmed by comparison with those of authentic samples.

The reaction of copper(II) salt 32 with peracid formed in situ would give acylperoxy copper(II) complex, followed by heterolytic O–O bond cleavage [52] to give oxo–copper species Cu(III)–O$^\cdot$ (33) or Cu(IV)=O (34). It has been postulated that oxo–copper intermediate can be formed by homolytic scission of the μ-peroxo bridge in tyrosinase [53] and of hydroperoxo copper group in dopamine β-hydroxylase [54]. The intermediacy of oxo–copper species are also postulated in the aerobic oxidations of alka-
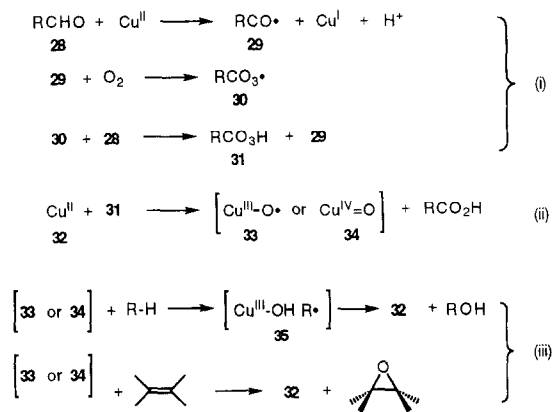
Scheme 2.

nes [55] and amines [56] and the hydroxylation of pyridine rings with PhIO [57]. Hydrogen abstraction of alkanes with **33** or **34** would give radical intermediate **35**. Small inter- and intra-molecular deuterium isotope effects in the present oxidation suggest that the mode of hydrogen abstraction has ionic character [58]. Hydroxy ligand transfer to the radical **35** would give alcohol and Cu(II) (**32**) to complete the catalytic cycle. Alcohols can be converted into ketones under the same conditions.

An alternative mechanism is the hydrogen abstraction by hydroxy radical caused by homolytic scission of peracid thus formed. To check these possibility, $3°/2°$ selectivity in the oxidation of adamantane has been examined. The $3°/2°$ selectivity is denoted by the ratio of 1-adamantanol per tertiary C–H bond (4) to 2-adamantanol and 2-adamantanone per secondary C–H bond (12). The $Cu(OH)_2$- and $CuCl_2$-18-crown-6-catalyzed oxidations afford the value of 30 and 21, respectively, while that obtained in the oxidation of adamantane with free OH radical is 10 [59]. The significant difference from the oxidation with hydroxy radical indicates that the present oxidation does not proceed via a free radical mechanism.

The higher catalytic activity of a combination of $CuCl_2$ and a crown ether seems to be due to the stabilization of the oxo–copper intermediates **33** or **34**, which promotes efficient consumption of peracid **31** by the reactions in Eq. (ii) of Scheme 2. The resulting low concentration of **31** leads to prevent self decomposition of aldehyde as depicted in Eq. (5), which would result in the high yields based on aldehydes and extremely high turnover numbers.

In the presence of an alkene, the oxo–copper intermediate **33** or **34** would react with an alkene to afford epoxide and copper salt to complete catalytic cycle. The non-stereospecific epoxidation of *cis*-olefins indicates that the present epoxidation is not due to the direct reaction with peracids formed in situ (Table 6, entries 4 and 6), since the epoxidation with peracid proceeds with high stereospecificity [60].

In conclusion, we have found efficient catalytic system for aerobic oxidations of alkanes and alkenes using copper catalyst and acetaldehyde. Extremely high catalytic activity can be achieved in the aerobic oxidation of alkanes using ligation of a crown ether. Our oxidation reaction provides a powerful strategy, since acetaldehyde can be readily prepared by the Wacker oxidation of ethylene. These principles would lead to the development of other efficient systems for aerobic oxidation of various organic compounds.

3. Experimental

3.1. General

All melting points were determined in capillary tubes and are uncorrected. IR spectra were measured by Shimadzu FTIR-4100 spectrometer. Analytical GLC evaluations of product mixtures were carried out on Shimadzu GC-12A gas chromatograph using a 30 m × 0.25 mm glass capillary column (TC-WAX, df = 0.25 μm) and Shimadzu GC-17A gas chromatograph using a 30 m × 0.25 mm glass capillary column (SPB-20, df = 0.25 μm) both of which were operated under the conditions of injection temperature (200°C), column temperature (initially 60°C, then increased 5°C/min, and finally 250°C), and helium gas pressure (1.0 kg/cm^2, sprit ratio = 100:1). GC-MS analyses were performed on a JEOL JMS-DX303 and a Shimadzu GCMS QP1000 mass spectrometer.

3.2. Materials

Benzene was distilled over benzophenone ketyl under argon atmosphere. CH_2Cl_2, 1,2-dichloroethane, pyridine, CH_3CN and DMF were distilled over calcium hydride under argon atmosphere. Methanol was distilled over magnesium turnings. Adamantane, *cis*-stilbene and *trans*-stilbene were commercially available and purified by recrystallization from CH_2Cl_2. 1,1-

Dideuterio-1,3-diphenylpropane (22) was prepared according to the reported procedure [51]. Other commercially available alkanes and alkenes were purified by distillation.

3.3. General procedure for Cu(OH)₂-catalyzed oxidation of alkanes and alkylated arenes with molecular oxygen in the presence of acetaldehyde

In a 50 mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar connected to a three-way stopcock were placed substrate (2.00 mmol), Cu(OH)$_2$ (5.9 mg, 0.060 mmol), acetaldehyde (264 mg, 6.00 mmol) and dry CH$_2$Cl$_2$ (12 mL). After the flask was flushed with oxygen, the mixture was vigorously stirred at room temperature under oxygen atmosphere (1 atm, balloon) for 17 h. The conversion of alkane or alkylated arene and the yields of the oxygenated products were determined by GLC analyses using an internal standard. The identities of the products were verified by coinjection with authentic samples and GC-MS analyses. The results are shown in Table 3. The effects of copper salts and aldehydes were examined by the oxidation of adamantane (1) under the similar conditions. These results are shown in Tables 1 and 2. The effect of solvents was also examined under the similar conditions using various dry solvent (12 mL). The results are as follows. CH$_2$Cl$_2$ (conversion 29%, yield of 1-adamantanol (2) 25%, yield of 2-adamantanol (3) 1.5%, yield of 2-adamantanone (4) 0.9%), ClCH$_2$CH$_2$Cl (13%, 13%, 0%, 0%), CH$_3$CN (9.3%, 9.2%, 0%, 0%), EtOAc (1.4%, 1.4%, 0%, 0%), benzene (1.3%, 1.3%, 0%, 0%), pyridine (0%, 0%, 0%, 0%), CH$_3$OH (0%, 0%, 0%, 0%), DMF (0%, 0%, 0%, 0%).

3.4. General procedure for Cu(OH)₂-catalyzed oxidation of alkenes with molecular oxygen in the presence of aldehyde

A mixture of alkene (2.00 mmol), Cu(OH)$_2$ (2.0 mg, 0.020 mmol), aldehyde (6.00 mmol) and dry CH$_2$Cl$_2$ (12 mL) was vigorously stirred

at room temperature under oxygen atmosphere (1 atm, balloon) for 17 h. The conversion of alkene and the yield of the oxygenated products were determined by GLC analyses using an internal standard. The identities of the products were verified by coinjection with authentic samples and GC-MS analyses. The results are shown in Table 6. The effect of copper salts and aldehydes were also examined under similar conditions. The results are shown in Tables 4 and 5.

trans-5,6-*epoxydecane*. Mass spectrum (CI), m/e (relative intensity) 158 (M$^+$+ 2, 10), 157 (M$^+$+ 1, 88), 156 (M$^+$, 3), 139 (86), 97 (34), 87 (71), 83 (100).

cis-5,6-*epoxydecane*. Mass spectrum (CI), m/e (relative intensity) 157 (M$^+$+ 1, 100), 85 (85), 83 (88), 80 (33).

trans-α,β-*epoxystillbene*. Mass spectrum (EI), m/e (relative intensity) 197 (M$^+$+ 1, 10), 196 (M$^+$,67), 195 (M$^+$-1, 53), 167 (M$^+$-CHO, 100), 90 (C$_6$H$_5$CH$^+$, 36), 89 (44).

cis-α,β-*epoxystilbene*. Mass spectrum (EI), m/e (relative intensity) 197 (M$^+$+ 1, 9), 196 (M$^+$, 63), 195 (M$^+$-1, 50), 167 (M$^+$-CHO, 100), 90 (C$_6$H$_5$CH$^+$, 48).

2,3-epoxypinane. Mass spectrum (EI), m/e (relative intensity) 152 (M$^+$, 3), 137 (M$^+$-CH$_3$, 51), 109 (74), 95 (31), 83 (55), 82 (43), 69 (30), 67 (100), 43 (C$_3$H$_7^+$, 41), 41 (41).

cis-2,3-*epoxy*-1-*cyclohexanol* (8). Mass spectrum (EI), m/e (relative intensity) 114 (M$^+$, 1), 96 (M$^+$-H$_2$O, 4), 95 (5), 71 (13), 70 (100), 69 (13), 68 (9), 67 (12), 58 (45), 57 (78), 55 (13), 41 (22).

trans-2,3-*epoxy*-1-*cyclohexanol* (9). Mass spectrum (EI), m/e (relative intensity) 96 (M$^+$-H$_2$O, 8), 95 (10), 71 (50), 70 (100), 69 (15), 68 (16), 67 (18), 58 (16), 57 (35), 42 (45).

3.5. General procedure for the aerobic oxidation of alkanes with copper–crown ether catalyst in the presence of acetaldehyde

A 300 mL stainless steel autoclave equipped with a Teflon-coated magnetic stirring bar was

charged with $CuCl_2$ (0.0134 mg, 1.00×10^{-4} mmol), 18-crown-6 (0.0264 mg, 1.00×10^{-4} mmol) and dry CH_2Cl_2 (5 mL). After stirring for 20 min, alkane (40.0 mmol) or alkylarene (4.00 mmol) and acetaldehyde (176 mg, 4.00 mmol) were added, and the autoclave was flushed with molecular oxygen (initial pressure, 1 atm). The mixture was stirred at 70°C for 24 h under oxygen atmosphere. The yields of oxygenated products were determined by GLC analyses using an internal standard. The identities of the products were verified by coinjection with authentic samples and GC-MS analyses. The results are shown in Table 8.

3.6. Effect of crown ethers for the aerobic oxidation of cyclohexane (14) with metal catalysts in the presence of acetaldehyde

A mixture of **14** (3.37 g, 40.0 mmol), metal catalyst (0.010 mmol), crown ether (0.010 mmol) and acetaldehyde (176 mg, 4.00 mmol) in dry CH_2Cl_2 (5 mL) was stirred at room temperature under oxygen atmosphere (1 atm, balloon) for 24 h. The yields of cyclohexanone (**15**) and cyclohexanol (**16**) were determined by GLC analyses using internal standard (acetophenone). The results are shown in Table 7.

3.7. Preparation of [(CuCl₂)₄(18-crown-6)₂(H₂O)₂] (21)

A mixture of $CuCl_2$ (67 mg, 0.50 mmol) and 18-crown-6 (145 mg, 0.55 mmol) in dry CH_2Cl_2 (30 mL) was stirred at room temperature for 1 h. After the resulting insoluble material was filtered off, ether (30 mL) was added to the filtrate. The solution was allowed to stand at room temperature overnight to afford complex **21** as brown microcrystals. mp 138°C (decomp.). IR (KBr): 3449, 2911, 1617, 1472, 1350, 1283, 1250, 1105, 963, 835 cm^{-1}. The structure of **21** was unequivocally established by X-ray structure analysis as shown in Fig. 1. Crystallographic date, atomic coordinates and selected bond distances and angles are listed in Tables 9–11.

3.8. X-ray crystallographical studies

X-ray analysis was performed on Rigaku AFC7R diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinements using the setting angles of 25 carefully centered reflections in the range $25.16 < 2\theta < 29.61°$ corresponding to a primitive monoclinic cell with dimensions. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. The structure was solved by direct method (SHELXS-86 [61]) and expanded using Fourier techniques [62]. Neutral atom scattering factors were taken from Cromer and Waber [63]. Anomalous dispersion effect were included in F_{calc} [64]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [65]. An empirical absorption correction based on azimuthal scans of several reflections were applied which resulted in transmission factors ranging from 0.72 to 1.00. The data were corrected for Lorentz and polarization effects. The values for the mass attenuation coefficients are those of Creagh and Hubbell [66]. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were included in fixed positions. The ORTEP drawings [67] are shown in 50% probability thermal ellipsoid.

3.9. Competitive reactivities of substituted toluenes (X–C₆H₄Me, X = p-Me, H, p-Cl and m-Cl) for the copper-catalyzed oxidation with molecular oxygen in the presence of acetaldehyde

An equimolar mixture of toluene (92 mg, 1.00 mmol) and substituted toluene (1.00 mmol), copper catalyst (0.0010 mmol), acetaldehyde (4.0 mg, 0.10 mmol) in dry CH_2Cl_2 (12 mL) was vigorously stirred at room temperature under oxygen atmosphere (1 atm, balloon) for 24

h. The relative ratio of oxygenated products were determined by GLC analyses using internal standard (acetophenone or cyclohexanone). The identities of the products were verified by coinjection with authentic samples and GC-MS analyses. The ρ values of Hammett linear free-energy relationship with σ^+ value are -1.21 ($\gamma = 0.957$) for $Cu(OH)_2$ and -1.59 ($\gamma = 0.999$) for $CuCl_2$-18-crown-6, respectively, as shown in Fig. 2.

3.10. Intramolecular isotope effect for the copper-catalyzed oxidation of 1,1-dideuterio-1,3-diphenylpropane (22) with molecular oxygen in the presence of acetaldehyde

A mixture of 1,1-dideuterio-1,3-diphenylpropane (**22**, 20 mg, 0.10 mmol), catalyst ($Cu(OH)_2$ (0.98 mg, 0.010 mmol) or $CuCl_2$ (1.3 mg, 0.010 mmol)-18-crown-6 (2.6 mg, 0.010 mmol)), acetaldehyde (18 mg, 0.40 mmol) and dry CH_2Cl_2 (5 mL) was vigorously stirred at room temperature under oxygen atmosphere (1 atm) for 24 h. The relative ratio of 3,3-dideuterio-1,3-diphenyl-1-propanone (**23**, M$^+$, 212) to 1,3-diphenyl-1-propanone (**24**, M$^+$, 210) (k_H/k_D) were determined to be 3.6 and 4.1 by GC-MS analyses of the reaction mixture.

3.11. Intermolecular isotope effect for the copper-catalyzed oxidation of cyclohexane with molecular oxygen in the presence of acetaldehyde

The competitive reaction of an equimolar mixture of cyclohexane (42 mg, 0.50 mmol) and cyclohexane-d_{12} (48 mg, 0.50 mmol) was carried out in the presence of catalyst ($Cu(OH)_2$ (2.9 mg, 0.030 mmol) or $CuCl_2$ (4.0 mg, 0.030 mmol)-18-crown-6 (7.9 mg, 0.030 mmol)), acetaldehyde (44 mg, 1.0 mmol) and dry CH_2Cl_2 (3 mL) at room temperature under oxygen atmosphere (1 atm, balloon) for 24 h. The relative ratio of (cyclohexanol + cyclohexanone) to (cyclohexanol-d_{11} + cyclohexanone-d_{10}) (k_H/k_D) were determined to be 1.8 and 1.5 by

GLC analyses. The products were identified by GC-MS analyses.

Cyclohexanol-d_{11}. Mass spectrum (EI), m/e (relative intensity) 111 (M$^+$, 5), 92 (29), 91 (22), 79 (15), 77 (21), 74 (38), 63 (17), 62 (6), 61 (100).

Cyclohexanone-d_{10}. Mass spectrum (EI), m/e (relative intensity) 109 (M$^+$ + 1, 5), 108 (M$^+$, 100), 90 (12), 88 (10), 80 (7), 78 (9), 76 (24), 74 (35), 62 (11), 60 (17), 58 (60).

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