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Electrocatalytic C-C Double Bond Cleavage Reaction of Styrene with Molecular Oxygen Mediated by $CuCl_2$

Toshihiro KOYAMA, Akira KITANI, Sotaro ITO, and Kazuo SASAKI
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724

The electrocatalytic oxidation of styrene with molecular oxygen in the presence of $CuCl_2$ in an acetonitrile solution promotes C-C double bond cleavage reaction to form benzaldehyde. Continuous supply of Cl^- is required to keep the catalytic activity.

Transition metal catalyzed oxidation of olefins with molecular oxygen is one of the attractive subjects in synthetic and mechanistic points of view.[1] Many methods have been reported for epoxidation with molecular oxygen using transition metals as catalyst.[2-4] Transition metal catalyzed C-C double bond cleavage reactions, however, are quite limited.[5-7] In this paper, we would like to describe an oxidative C-C double bond cleavage reaction of styrene with molecular oxygen catalyzed by $CuCl_2$ to form benzaldehyde.

An acetonitrile solution (50 ml) containing 1 mmol copper salt and 5 mmol styrene was refluxed for 1 hour under O_2 atmosphere. Products were identified with GC-MASS and NMR and quantitatively analyzed with a HPLC. Cu^+ was determined colorimetrically by the bathocuproine disulfonate method.[8]

As shown in Table 1, $CuCl_2$ gave benzaldehyde and phenacyl chloride as oxidized products, where the selectivity of benzaldehyde was 17% (Entry 1). It is interesting that the selectivity of benzaldehyde increased to 54% when 0.25 mmol of $CuCl_2$ was used (Entry 2). The reaction was greatly suppressed under N_2 atmosphere (Entry 3). $CuBr_2$ also gave benzaldehyde and phenacyl bromide (Entry 4), while others gave no products. Other solvents, such as ethanol, THF, DMF, acetone, and a mixture of acetonitrile (80% by volume) and water, were not efficient for the present oxidation.

Table 1. Oxidation of styrene in the presence of several copper salts

Entry	Salt	Yield / μmol		
		PhCHO	$PhCOCH_2X$[a]	Total
1	$CuCl_2$	13	64	77
2	$CuCl_2$[b]	28	24	52
3	$CuCl_2$[c]	-	2.2	2.2
4	$CuBr_2$[d]	10	29	39
5	$Cu(ClO_4)_2$	-	-	-
6	CuCl[d]	-	-	-

a) X=Cl or Br. b) 0.25 mmol. c) N_2 atmosphere. d) Partly left insoluble.
Reaction conditions: Solution 50 ml, Salt 1 mmol, Styrene 5 mmol, Refluxed temp, Time 1 h, Atmosphere O_2.

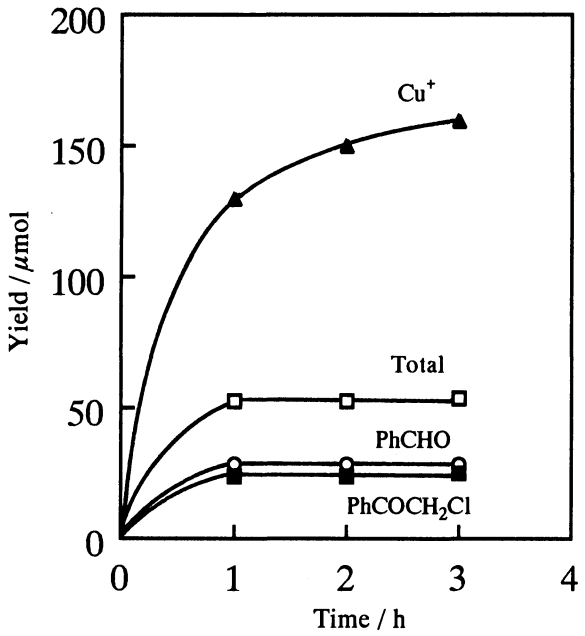


Fig.1. The time course of the reaction in CH_3CN solution. Reaction conditions: Solution 50 ml, $CuCl_2$ 0.25 mmol, Styrene 5 mmol, Refluxed temp, Atmosphere O_2.

Figure 1 shows the time course of the reaction using 0.25 mmol $CuCl_2$. Yields reached to steady values within 1 hour and further increases of yields were not observed in a prolonged reaction. It is found that Cu^+ accumulated in the reaction mixture, as represented at the most upper curve in Fig.1

If there is an appropriate method of regeneration of Cu^{2+} from Cu^+, the yield may exceed the amount of $CuCl_2$ initially added. In order to oxidize Cu^+ accumulated in the reaction mixture, electrochemical oxidation was performed. The reaction was conducted in an H type cell divided with cation exchange membrane equipped with a reflux condenser. A reaction mixture (50 ml) containing 0.25 mmol $CuCl_2$, 5 mmol styrene, and 5 mmol (0.1 mol•dm^{-3}) $NaClO_4$ as supporting electrolyte was refluxed for 1 hour, then anodic oxidation was carried out at 1.0 V vs. Ag. During the electrolysis, reaction temperature was kept at the refluxed temperature. As shown in Fig.2 (■), where the total yield was plotted against electricity, the total yield increased with increasing the electricity and reached to 0.57 mmol, which was larger than the amount of $CuCl_2$ initially added. The selectivity of benzaldehyde rose to 70% during the course of electrolysis. This result indicates that Cu^+ is efficiently oxidized and regenerated Cu^{2+} promotes the further oxidation. The yield, however, reached to steady value when electricity was beyond 30 C. This may be caused by composition change of active species arisen from consumption of Cl^- to form phenacyl chloride. If Cl^- concentration is maintained at proper level, such inactivation may not occur. As shown in Fig.2 (○ and ●), the yield increased with increasing the amount of Et_4NCl added and finally reached to 1.4 mmol (turnover number of Cu^{2+} was 5.6). It is notable that the selectivity of benzaldehyde was constant (ca.70%) regardless of the amount of Et_4NCl. The substrate will be completely oxidized if a sufficient amount of Et_4NCl is added.

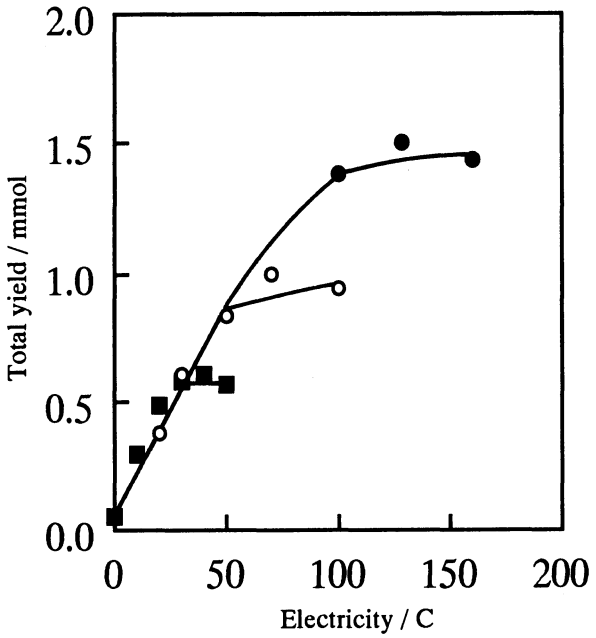


Fig.2. Effect of Cl^- on total yield of electrocatalytic oxidation of styrene in CH_3CN solution. Reaction conditions: (■) 0.25 mmol $CuCl_2$, (○) 0.25 mmol $CuCl_2$ + 0.25 mmol Et_4NCl, (●) 0.25 mmol $CuCl_2$ + 0.75 mmol Et_4NCl, Styrene 5 mmol, Working electrode Pt.

As stated above, styrene is oxidized to benzaldehyde. The key species of the present catalytic system is assumed to be an oxo-complex consisted of Cu^{2+} and Cl^-, which forms only in an acetonitrile solution. In order to confirm the role of Cl^-, the reaction was carried out with $Cu(ClO_4)_2$ in the presence of Et_4NCl (reaction conditions were the same as those in Table 1). As shown in Table 2, the reaction took place even in the presence of small amount of Et_4NCl (Entry 1), indicating clearly that the active species consists of Cu^{2+} and Cl^-. The yields were relatively high as expected from the amount of Et_4NCl added. When more Et_4NCl was added (Entry 2,3), the yields increased, but the selectivity of benzaldehyde decreased with increasing the amount of Et_4NCl.

Table 2. Oxidation of styrene with $Cu(ClO_4)_2$ in the presence of Et_4NCl[a)]

Entry	Et_4NCl / mmol	Yield / μmol		
		PhCHO	$PhCOCH_2Cl$	Total
1	0.1	51	22	73
2	0.5	71	73	144
3	1	86	112	198

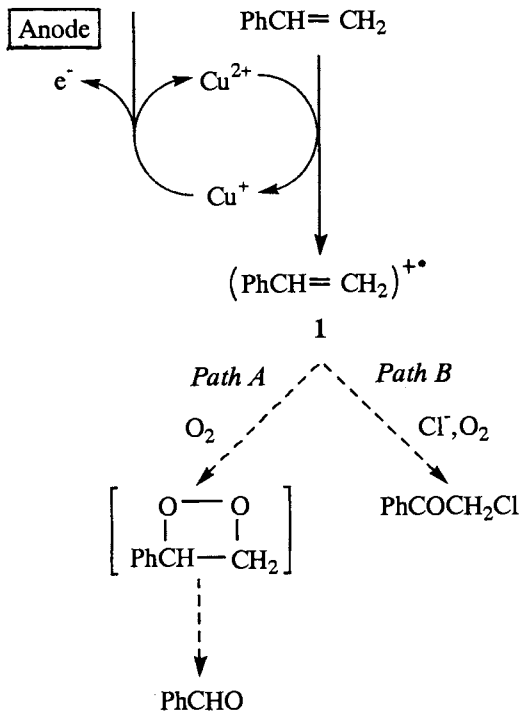
a) Reaction conditions: Solution 50 ml, $Cu(ClO_4)_2$ 1 mmol, Styrene 5 mmol, Refluxed temp, Time 1 h, Atmosphere O_2.

Likewise, the oxidation of *trans*-stilbene using 1 mmol $CuCl_2$ gave benzaldehyde (138 μmol) and 2-chloro-2-phenylacetophenone (100 μmol) under the conditions described in Table 1. Since only benzaldehyde was obtained as C-C double bond cleavage product, the counterpart of benzaldehyde in the oxidation of styrene would be formaldehyde.

From these observations, we propose a possible reaction mechanism as shown in Scheme 1. Firstly, styrene is oxidized by Cu^{2+} to form a styrene radical cation (**1**). The radical cation then reacts with oxygen to give dioxetane, which decomposes to benzaldehyde (*Path A*). On the other hand, phenacyl chloride is obtained when the radical cation reacts with Cl^- followed by oxygen attack (*Path B*). The copper species may be an oxo-complex as mentioned above.

This catalytic system is particularly interesting since reducing agents are not required for activation of molecular oxygen.

We have also found that $FeCl_3$ promoted the same kind of cleavage reaction and further studies concerning this oxidation system are extensively in progress.



Scheme 1.

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