

The oxidation of alkanols with air oxygen in the catalytic system copper(II) acetate—hydroquinone promoted by visible light

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2-Propanol or 1-propanol in acetonitrile, when exposed to air and irradiated with a tungsten lamp in the presence of catalytic amounts of copper(II) acetate and hydroquinone, are oxidized to give acetone or propanal, respectively.

Key words: photochemistry; propanols, oxidation with air oxygen; copper(II) complexes; metal complex catalysis.

Photoinduced transformations of organic substrates and, particularly, their oxidation in the presence of metal complex catalysts are of great interest as the basis for the synthesis of various organics.^{1–3} Among them, of special importance are the processes promoted by irradiation in the visible part of the electromagnetic spectrum. Earlier,⁴ the copper(II) acetate—hydroquinone system was shown to catalyze the effective and selective oxidation of alkanes to alkyl hydroperoxides by air oxygen promoted by irradiation with visible light. Complexes of other transition metals (*e.g.*, Fe, Ni, and Co) or copper salts with other anions, such as copper perchlorate, are much less active in this process or even devoid of any catalytic effect. The substitution of resorcinol or pyrocatechol for hydroquinone results in a total loss of photocatalytic activity.

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Here we report our first results obtained in the study of the use of the copper(II) acetate—hydroquinone system as a catalyst for the light-promoted air oxidation of aliphatic alcohols.

Experimental

All experiments were carried out in a cylindrical quartz vessel (1.5 cm in diameter), provided with a water jacket for cooling (to ~15 °C), magnetic stirring bar, and free access to the ambient air. Solutions containing the catalytic system and a substrate (total volume 5 mL) were illuminated with a standard tungsten lamp (100 W) and vigorously stirred. The reaction was monitored by gas chromatography using a DANI 86.10 instrument with a capillary column filled with Carbowax as the stationary phase; 0.1–0.2 mL aliquots were periodically taken out for analysis. The peak areas were measured by means of a Chrom Jet integrator (Spectra Physics). The acetonitrile and the other chemicals used in this work have been purchased from Fluka AG (Switzerland) and used without further purification.

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Results and Discussion

The irradiation of Pr^iOH or Pr^nOH , dissolved in MeCN, with the light of a standard tungsten lamp in the presence of catalytic amounts of copper(II) acetate and hydroquinone promotes the oxidation of these alcohols to acetone or propanal, respectively. The kinetic curves of the product accumulation are presented in Fig. 1. Evidently, both alcohols are oxidized at nearly the same rate, so that after 10 h of irradiation the yields of the products amount to ~70 mols per one mol of $\text{Cu}(\text{OAc})_2$. No oxidation occurs in the dark.

The initial rate of oxidation (determined from the concentration of acetone after 1 h of irradiation) is not dependent on the initial concentration of 2-propanol. Moreover, at high concentrations of Pr^iOH the rate of the reaction to some extent decreases as the alcohol concentration increases (data for $[\text{Cu}(\text{OAc})_2]_0$ $2 \cdot 10^{-4} \text{ mol L}^{-1}$ and $[\text{Hydroquinone}]_0$ $1 \cdot 10^{-4} \text{ mol L}^{-1}$):

$[\text{Pr}^i\text{OH}]_0/M$	0.5	1.0	1.5	2.0
$[\text{Me}_2\text{CO}] \cdot 10^3/M$	2.7	2.8	1.7	1.2

The dependence of the initial reaction rate of the same reaction on the concentration of hydroquinone is linear at hydroquinone concentrations of $0-4.4 \cdot 10^{-4} M$, but at higher concentrations of hydroquinone the rate tends to diminish (the data below relate to $[\text{Pr}^i\text{OH}]_0$ 1.0 mol L^{-1} and $[\text{Cu}(\text{OAc})_2]_0$ $2 \cdot 10^{-4} \text{ mol L}^{-1}$):

$[\text{Hydroquinone}]_0 \cdot 10^3/M$	0.0	0.2	0.4	1.0	2.0
$[\text{Me}_2\text{CO}] \cdot 10/M$	0.0	0.4	0.8	2.8	1.6

Such transition metal salts as copper(II) and nickel(II) perchlorates or cobalt(II) bromide in combination with hydroquinone show no photocatalytic activity in the air oxidation of alcohols, while iron(III) chloride is less effective than $\text{Cu}(\text{OAc})_2$.

The mechanism of the conversion of alkanols to ketones or aldehydes in the photocatalytic system under study is not yet clear. However, one can assume that the key stage in the process is the abstraction of a hydrogen atom from the hydroxylated carbon atom ($\text{H}-\text{C}-\text{OH}$) by a photoexcited species. This is followed by the interaction of the free radical formed with a molecule of dissolved oxygen.

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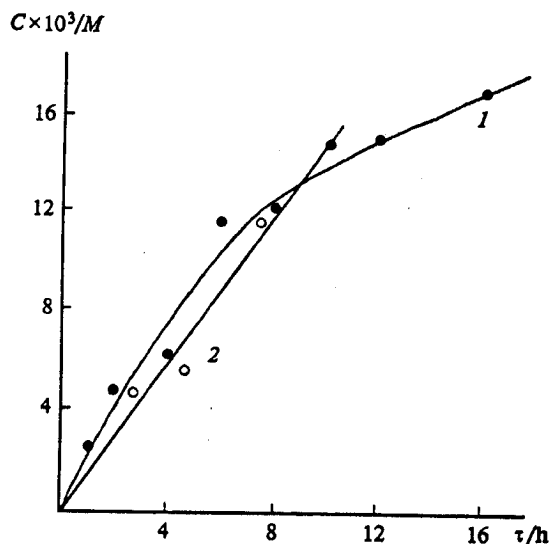


Fig. 1. Kinetic curves of the accumulation of acetone (1) and propanal (2) formed by the oxidation of 2-propanol or 1-propanol with air oxygen in the presence of the copper(II) acetate-hydroquinone system at 15°C promoted by visible light. $[\text{Cu}(\text{OAc})_2] = 2 \cdot 10^{-4} \text{ mol L}^{-1}$, $[\text{1,4-C}_6\text{H}_4(\text{OH})_2] = 1 \cdot 10^{-3} \text{ mol L}^{-1}$, $[\text{Pr}^i\text{OH}] = 0.5 \text{ mol L}^{-1}$.

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