

PHOTOOXIDATION OF ALKANES BY OXYGEN CATALYZED BY  $\text{CuCl}_2$   
IN ACETONITRILE

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*The irradiation of a solution of anhydrous  $\text{CuCl}_2$ , taken as a photocatalyst, and an alkane in acetonitrile in the air with visible light ( $\lambda > 320 \text{ nm}$ ) leads to the formation of alcohol and ketone products.*

Cyclohexane, hexane, and methane are oxidized to the corresponding alcohols and carbonyl compounds upon the irradiation in air of their solutions in acetonitrile in the presence of catalytic amounts of  $\text{HAuCl}_4$  or in  $\text{CH}_2\text{Cl}_2$  in the presence of  $(\text{C}_6\text{H}_5)_4\text{NAuCl}_4$  [1]. In the present work, preliminary results are given for a study of the photocatalytic properties of cupric chloride in the oxidation of alkanes.

Irradiation of a solution of  $5 \cdot 10^{-4}$  mole/liter anhydrous  $\text{CuCl}_2$  and 0.46 mole/liter cyclohexane in acetonitrile in the air with visible light for 6 h leads to  $1.70 \cdot 10^{-2}$  mole/liter cyclohexanol and  $1.65 \cdot 10^{-2}$  mole/liter cyclohexanone. The product accumulation was linear and the reaction rate did not decrease after 6 h irradiation. The reaction rate at 4-60°C was virtually independent of temperature (effective  $E_a < 15 \text{ kJ/mole}$ ). Experiments on the oxidation of cyclohexane- $d_{12}$  revealed a very slight kinetic isotope effect for this reaction  $k_H/k_D = 1.2 \pm 0.2$ . A low isotope effect (1.6) was also found when  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was used as the photocatalyst in analogous reactions.

Under analogous conditions, hexane was oxidized over 7.5 h to give  $0.15 \cdot 10^{-2}$  mole/liter 1-hexanol,  $0.28 \cdot 10^{-2}$  mole/liter 2-hexanol,  $0.26 \cdot 10^{-2}$  mole/liter 3-hexanol,  $0.39 \cdot 10^{-2}$  mole/liter hexanal,  $0.64 \cdot 10^{-2}$  mole/liter 2-hexanone, and  $0.66 \cdot 10^{-2}$  mole/liter 3-hexanone. The analogous reaction with ethylbenzene over 6 h gave  $0.34 \cdot 10^{-2}$  mole/liter 1-phenylethanol and  $1.1 \cdot 10^{-2}$  mole/liter acetophenone. The analogous reaction with styrene over 6 h gave almost exclusively  $1.05 \cdot 10^{-2}$  mole/liter benzaldehyde. The combined competitive oxidation of ethyl

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benzene and cyclohexane showed that the reactivity of the  $\text{CH}_2$  group in ethylbenzene relative to that of the analogous group in cyclohexane is 2.6. The corresponding reactivity is 1.7 in the reaction photocatalyzed by  $\text{FeCl}_3$ . The competitive oxidation method was used to show that the relative reactivity of the methyl group of substituted toluenes in the presence of  $\text{CuCl}_2$  decreases in the series:  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3$  (3.1) >  $\text{CH}_3\text{C}_6\text{H}_5$  (1.0) >  $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3$  (0.1). Hence, we find  $\rho^+ = -1.5$ . This value coincides with the values for  $\rho^+$  obtained for the photooxidation of the same substrates catalyzed by  $\text{FeCl}_3$  and  $\text{AuCl}_4^-$ .

An  $\text{R}^\cdot$  radical is presumably formed upon the reaction of photoexcited  $\text{CuCl}_2$  [2] with an alkane molecule [3]. This radical reacts rapidly with  $\text{O}_2$  to give  $\text{RO}_2^\cdot$  radicals, which decompose, possibly with the participation of metal complexes to alcohol and ketone products. The  $\text{Cu(I)}$  derivative formed may be reoxidized either by oxygen or  $\text{RO}_2^\cdot$  radicals.

#### EXPERIMENTAL

All the reactions were carried out in the air in a cylindrical glass vessel with a water jacket maintained at  $15^\circ\text{C}$  upon radiation with the full light of a 250-W DRL-250 (6) fluorescent lamp. The products were analyzed by gas-liquid chromatography on an LKhM-806 chromatograph on a 2-m column packed with 5% Carbowax 1500 on Inerton AW-HMDS with argon as the gas carrier and temperature programming at a rate of  $4^\circ\text{C}/\text{min}$  from  $50$  to  $180^\circ\text{C}$ .

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