

BRIEF COMMUNICATIONS

PHOTOOXIDATION OF CYCLOHEXANE BY ATMOSPHERIC
OXYGEN IN 2-PROPANOL OR METHANOL CATALYZED BY
FeCl₃

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UDC 541.]

Cyclohexane is oxidized to cyclohexanol as well as cyclohexanone upon photoirradiation of its solution in 2-propanol or methanol in the presence of catalytic amounts of FeCl₃.

Keywords: photocatalysis, homogeneous catalysis, oxidation, alkanes, metal complexes, ferric chloride.

Aliphatic alcohols are usually oxidized by oxygen much more readily than alkanes [1]. Several examples have been reported when alkanes are oxidized in the presence of large alcohol concentrations [2, 3] (see the work of Hill et al. [4], who described the functionalization of alkanes in the presence of alcohols).

We have shown that alkanes are readily oxidized by atmospheric oxygen upon irradiation of their solutions in acetonitrile, acetone, methylene chloride, or acetic acid in the presence of catalytic amounts of FeCl₃ [5, 6]. The products of the oxidation of cyclohexane are cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone. The reaction apparently begins with the photolysis of a Fe-Cl bond [7] and formation of chlorine radicals in the solvent cage, which abstract hydrogen atoms from the alkane RH, to give R' radicals. These radicals react rapidly with O₂ molecules to give ROO' radicals, which are transformed into ROOH and also an alcohol and ketone (or aldehyde). The hydroperoxide decomposes upon gas-liquid chromatographic analysis to give alcohol and ketone in approximately equal amounts.

We attempted to expand the range of solvents for this reaction and carry out this photooxygenation in aliphatic alcohols.

We found that irradiation of a solution of 0.92 mole/liter cyclohexane in 2-propanol with $\lambda > 310$ nm in the presence of $5 \cdot 10^{-4}$ mole/liter FeCl₃·6H₂O (this catalyst concentration was used in all the subsequent work) in the air for 5 h gave $8.0 \cdot 10^{-3}$ mole/liter cyclohexanol and $1.2 \cdot 10^{-3}$ mole/liter cyclohexanone. Linear accumulation of the products was noted. In this case, 2-propanol was oxidized to give $2.7 \cdot 10^{-2}$ mole/liter acetone. In the cyclohexane concentration range from 0 to 4 moles/liter, the reaction is first-order relative to the substrate. The cyclohexane oxidation rate is virtually independent of the FeCl₃ concentration in the range from $2.5 \cdot 10^{-4}$ to $10 \cdot 10^{-4}$ mole/liter. Acetone was detected in the reaction mixture only when the cyclohexane concentration was less than 2 moles/liter. In contrast to the photooxidation of cyclohexane in other solvents [5, 6], in which a large amount of cyclohexyl hydroperoxide is formed, this hydroperoxide did not accumulate when the reaction was carried out in 2-propanol.

We obtained $2.4 \cdot 10^{-3}$ mole/liter acetophenone and $1.2 \cdot 10^{-3}$ mole/liter 1-phenylethanol from 0.46 mole/liter ethylbenzene in 2-propanol upon irradiation for 5 h. Only about $0.4 \cdot 10^{-3}$ mole/liter benzaldehyde is formed from toluene or styrene under these conditions after 4 h.

Methanol may also be used as the solvent. Thus, irradiation of 0.46 mole/liter cyclohexane in methanol over 5 h gave $7.4 \cdot 10^{-3}$ mole/liter cyclohexanol and $0.4 \cdot 10^{-3}$ mole/liter cyclohexanone. The combined oxidation of cyclohexane and ethylbenzene in 1:6 mole ratio over 1 h in methanol showed that the methylene C-H bond in ethylbenzene is 2.5 times more reactive than the same bond in cyclohexane.

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow. Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 2, pp. 436-437, February, 1992. Original article submitted April 4, 1991; revision submitted June 21, 1991.

It is interesting that about equal amounts of alcohol and ketone are obtained from cyclohexane in tert-butyl alcohol: $9.6 \cdot 10^{-3}$ mole/liter alcohol and $8.8 \cdot 10^{-3}$ mole/liter ketone after 5 h irradiation. Cyclohexyl hydroperoxide is not observed in the reaction mixture.

The authors express their gratitude to Khimfak for financial support for this work.

EXPERIMENTAL

The reactions were carried out in a cylindrical glass vessel maintained at a constant temperature of 15°C with irradiation by the full light of a DRL-125 fluorescent lamp in the air with stirring using a magnetic stirrer. The amounts of the products formed were analyzed by gas-liquid chromatography on an LKhM-80-6 chromatograph using 2-m columns packed with 5% Carbowax 1500 on Inerton AW-HMDS (0.25-0.315 mm). Argon served as the gas carrier. The peroxides were determined relative to the increase in the concentration of the corresponding alcohol after the addition of PPh_3 to the reaction solution [8].

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