React. Kinet. Catal. Lett., Vol. 41, No. 2, 239-243 (1990)

FERRIC CHLORIDE CATALYZED PHOTOOXIDATION OF ALKANES BY AIR IN ORGANIC SOLVENTS

G.B. Shul'pin and M.M. Kats

Institute of Chemical Physics, Moscow 117977, USSR

Received July 25, 1989
Accepted October 12, 1989

In the presence of catalytic amounts of $FeCl_3$, alkanes (cyclohexane, n-hexane), toluene and ethylbenzene are oxidized by air oxygen in CH_3CN, $(CH_3)_2CO$ or CH_2Cl_2 under visible light irradiation to yield ketones and alcohols.

В присутствии каталитических количеств $FeCl_3$ алканы (циклогексан, н-гексан), толуол и этилбензол окисляются кислородом воздуха в CH_3CN, $(CH_3)_2CO$ или CH_2Cl_2 при облучении видимым светом с образованием кетонов и спиртов.

Photochemical transformations of alkanes and alkylaromatic hydrocarbons into carbonyl compounds and alcohols are of great importance for syntheses. Transition metal complexes are known to catalyze oxidation of irradiated alkylaromatics and alkanes [1-10].

Here we present the results of studying the photooxidation of saturated and alkylaromatic hydrocarbons in organic solvents catalyzed by $FeCl_3$. Oxidations were carried out in air in a Pyrex cylindrical vessel with a water-cooled (~15°C) jacket under stirring. Total volume of the reaction solution was 5 cm^3. Light from a luminescent street lamp (125 W) was used for irradiation (daylight is also active in the reaction). Products were identified by gas-liquid chromatography.

small isotopic effect was observed: $k_{C_6H_{12}}/k_{C_6D_{12}} = 1.6 \pm 0.3$.

n-Hexane is also readily oxidized in the solution of CH_3CN (0.46 M) in the presence of $FeCl_3$ (5×10^{-4}) and yields the following products (in parentheses concentrations$\times 10^3$ M are given after 5 h irradiation): hexanol-1 (2.1), hexanol-2 (5.0), hexanol-3 (5.8), hexanone-1 (4.9), hexanone-2 (14.4) and hexanone-3 (12.6). The total yield of the products was 9.7% per n-hexane.

After 3 h irradiation the photooxidation of toluene (0.46 M solution in acetonitrile) in the presence of 5×10^{-4}M $FeCl_3$ produces benzaldehyde (2.3×10^{-2} M) and benzyl alcohol (4.4×10^{-3}M). Similarly, ethylbenzene is converted into a mixture of acetophenone and 1-phenylethanol. Competitive photooxidation of cyclohexane (0.37 M) and ethylbenzene (0.37 M) in acetonitrile after 4 h irradiation yields cyclohexanol (2.2×10^{-2} M), cyclohexanone (1.6×10^{-2} M), acetophenone (5.2×10^{-3} M) and 1-phenylethanol (4.6×10^{-3} M). These data can be used to calculate relative reactivity of one C-H bond in the CH_2 group:
$k_{C_6H_5CH_2CH_3}/k_{C_6H_{12}} = 1.55$.

The suggested reaction mechanism includes photoinduced electron transfer [1] from alkane to $[FeCl_3]^*$, proton detachment and a rapid reaction of formed alkyl radicals with dioxygen producing peroxo derivatives and ketones and alcohols as end products. Complexes of Fe(II) formed in the catalytic cycle can be reoxidized by dioxygen or peroxo radicals.

The authors are thankful to Prof. A.E. Shilov for his interest in this work and fruitful discussions.

REFERENCES

1. A.I. Kryukov, V.P. Sherstyuk, I.I. Dilung: Photoinduced Electron Transfer and its Applied Aspects. Naukova Dumka, Kiev 1982.
2. G.B. Shulpin: Organic Reactions Catalyzed by Metal Complexes. Nauka, Moscow 1988.

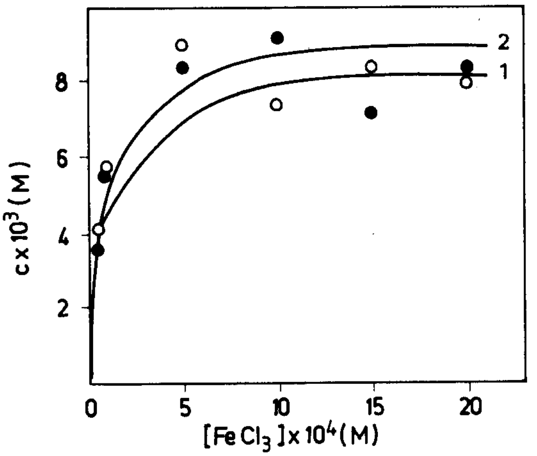

Fig. 2. Dependence of cyclohexanol (1) and cyclohexanone (2) concentrations formed in photooxidation of cyclohexane (0.46 M) in CH_3CN (after 2 h irradiation), on the concentration of $FeCl_3$

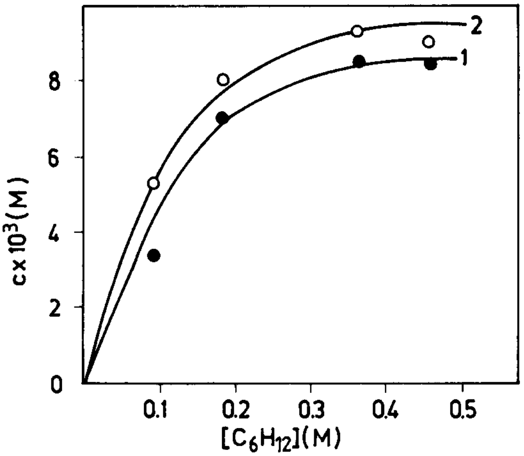

Fig. 3. Dependence of the concentration of cyclohexanol (1) and cyclohexanone (2) formed in photooxidation of cyclohexane in CH_3CN (after 2 h irradiation, $[FeCl_3] = 5\times10^{-4}$ M) on concentration of cyclohexane

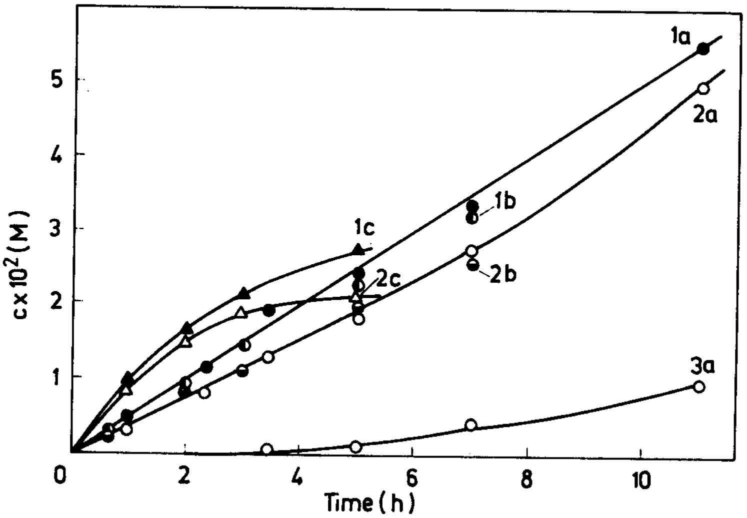

Fig. 1. Formation kinetics of cyclohexanol (1), cyclohexanone (2) and cyclohexyl chloride (3) in reaction of cyclohexane (0.46 M) with air in CH_2Cl_2 (in the presence of 5×10^{-4} M $C_6H_5CH_2N(C_2H_5)_3Cl$) (a), CH_3CN (b) and $(CH_3)_2CO$ (c) under irradiation. In all cases $FeCl_3\cdot6\ H_2O$ concentration was 5×10^{-4} M

Cyclohexane oxidation products cyclohexanol and cyclohexanone are formed in approximately equal amounts (Fig. 1). Oxidation rates of cyclohexane are weakly dependent on solvent (acetonitrile or methylene). In the case of methylene chloride, a tetraalkylammonium salt was added to dissolve an iron complex. In this solvent cyclohexyl chloride is also formed, and the kinetic curve of its accumulation has an induction period.

In the case of all three solvents, approximately 100 moles of oxidation products are obtained per 1 mol $FeCl_3$ after 5 h irradiation. Yield from cyclohexane is about 10%. In CH_2Cl_2 after 11 h irradiation the yield is above 20%.

Dependences of the oxidation rate on the initial concentration of $FeCl_3$ and cyclohexane are represented in Figs 2 and 3.

In experiments with C_6D_{12} in the acetonitrile solution a

3. A.E. Shilov, G.B. Shulpin: Usp. Khim., 56, 754 (1987).
4. M. Barbier: Helv. Chim. Acta, 67, 866 (1984).
5. E. Baciocchi, T. Del Giacco, C. Rol, G.V. Sebastiani: Tetrahedron Lett., 26, 3353 (1985).
6. A. Monaci: Gazz. Chim. Ital., 116, 339 (1986).
7. E. Baciocchi, T. Del Giacco, G.V. Sebastiani: Tetrahedron Lett., 28, 1941 (1987).
8. E.S. Rudakov, S.A. Mitchenko, N.A. Miroshnichenko: Kinet. Katal., 28, 187 (1987).
9. N.Z. Muradov, M.I. Rustamov: Kinet. Katal., 30, 248 (1989).
10. G.B. Shulpin, A.N. Druzhinina: Izv. Akad. Nauk SSSR, Ser. Khim., 1185 (1989).