# Aerobic oxidation of cumene photocatalyzed by iron salts

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Photooxidation of cumene by air in an aqueous emulsion in the presence of $Fe(ClO_4)_3$ results in the formation of considerable amounts of acetophenone, the product of the C—C bond cleavage.

**Key words:** photocatalysis, metal complex catalysis, oxidation with molecular oxygen, hydrocarbons, cumene, peroxides, activation of C—H and C—C bonds.

Photocatalytic oxidation of saturated and alkylaromatic hydrocarbons catalyzed by metal complexes under light irradiation can be a convenient method for the transformation of these hydrocarbons into valuable products (ketones, alcohols, peroxides, etc.).[1,2] In a continuation of the studies in this area,[3—8] we established that irradiation of an aqueous emulsion of cyclohexane in the presence of iron perchlorate in air resulted, according to the GLC data, in the formation of cyclohexanone, while only insignificant amounts of cyclohexanol and cyclohexyl hydroperoxide were present in the mixture of the reaction products.[9] It can be assumed that this "unusual" selectivity ("ketonization" of the $CH_2$ groups of this hydrocarbon) is caused by the fact that cyclohexyl hydroperoxide decomposes under the action of iron ions and light in the presence of considerable amounts of water to form only ketone and a complex mixture of products of oxidation followed by the cleavage of the C—H bond in alkane. It has been previously reported that up to 100 peaks of a mixture of reaction products are observed on the chromatogram upon the autooxidation of cyclohexane in the presence of metal complexes.[10] The identification of the products is sufficiently difficult.

In order to obtain additional information, which would allow one to explain the highly selective ketonization in the photochemical aerobic oxygenation of hydrocarbons promoted by an iron ion, it was important to study the oxidation of branched hydrocarbons (containing tertiary C—H bonds) under these conditions. Cumene seems to be an especially convenient model for investigation in which acetophenone is easily identified. In this work, the first results of this study are presented.

For the purpose of the subsequent comparison of the results, the photooxygenation of cumene was studied by the method developed previously (in acetonitrile in the presence of ferric chloride). Irradiation of a solution of cumene in acetonitrile in air in the presence of $FeCl_3 \cdot 6H_2O$ ($5.0 \cdot 10^{-4}$ mol $L^{-1}$) resulted in the forma-

tion of dimethylphenylcarbinol, acetophenone, and cumyl hydroperoxide (Table 1, method A). The two first products were determined by GLC. Relatively unstable cumyl hydroperoxide decomposes completely upon chromatography to form the two first compounds. Unfortunately, we did not manage to determine the concentration of cumyl hydroperoxide. However, the comparison[11—13] of the concentrations of stable products ($PhCMe_2OH$ and PhCOMe) before the reduction of a sample of the reaction mixture with triphenylphosphine (when $PhCMe_2OOH$ decomposing in a chromatograph to form both stable products is also present in the mixture) and after the reduction (when all hydroperoxide transforms quantitatively into alcohol) showed that cumyl hydroperoxide was formed in a noticeable concentration in the photooxidation, and at the irradiation time >1 h it decomposed in parallel with the accumulation to form $PhCMe_2OH$ and acetophenone (see Table 1, method A). It is likely that an iron ion and light strongly accelerate this decomposition. It is noteworthy that, as has been supposed,[3—7] the $FeCl_3$-catalyzed oxygenation of hydrocarbons in acetonitrile involves chlorine radicals at the key stage of the reaction.

Irradiation of an emulsion of cumene and an aqueous solution of $Fe(ClO_4)_3$ gives a considerable amount of PhCOMe and undecomposed $PhCMe_2OOH$ along with $PhCMe_2OH$ (see Table 1, method B). The oxidation occurs with a noticeable induction period and begins only in 0.5 h after irradiation. The maximum concentration of cumyl hydroperoxide is achieved in ~1.5 h; then its concentration begins to decrease, while the concentrations of cumyl alcohol and acetophenone increase monotonically. Unlike the reaction in acetonitrile, the oxidation in an aqueous emulsion gives an amount of acetophenone somewhat greater than the concentration of alcohol.

It is of interest that the photooxidation of cumene (0.16 mL, 0.46 $M$, homogeneous solution) in an aqueous solution of acetone (0.25 mL of $H_2O$ and 2.25 mL

**Table 1.** Photooxidation of cumene upon light irradiation

| Time /min | Concentrations of products according to the GLC data /mmol L$^{-1}$ | | | | Estimation of concentrations of products in the reaction solution$^b$/mmol L$^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| | before reduction$^a$ | | after reduction$^a$ | | | | |
| | PhCOMe | PhCMe$_2$OH | PhCOMe | PhCMe$_2$OH | PhCMe$_2$OOH | PhCMe$_2$OH | PhCOMe |
| | | | | Method *A* | | | |
| 60 | 0.94 | 0.85 | 0.12 | 1.69 | 1.55 | 0.12 | 0.12 |
| 105 | 1.89 | 1.60 | 0.49 | 2.88 | 2.61 | 0.49 | 0.49 |
| 150 | 2.60 | 2.34 | 0.71 | 4.26 | 3.52 | 0.71 | 0.71 |
| 180 | 3.66 | 2.55 | 0.94 | 4.69 | 4.33 | 0.94 | 0.94 |
| 270 | 4.98 | 3.41 | 1.20 | 5.80 | 6.88 | 1.20 | 1.20 |
| | | | | Method *B* | | | |
| 30 | 0.006 | 0.006 | 0 | 0.01 | 0.01 | 0 | 0 |
| 75 | 0.23 | 0.21 | 0.10 | 0.23 | 0.24 | 0.10 | 0.10 |
| 120 | 0.24 | 0.18 | 0.15 | 0.15 | 0.12 | 0.15 | 0.15 |
| 180 | 0.45 | 0.25 | 0.35 | 0.25 | 0.10 | 0.25 | 0.35 |
| 240 | 0.54 | 0.34 | 0.48 | 0.33 | 0.06 | 0.34 | 0.48 |

*Note.* *A*, photooxidation of a solution of cumene (0.46 *M*) in MeCN in the presence of FeCl$_3 \cdot 6H_2O$ (0.5 mmol L$^{-1}$) and *B*, photooxidation of its emulsion (2.25 mL, 22 mmol) with an aqueous solution (0.25 mL) of Fe(ClO$_4$)$_3$ (0.0125 mmol).
$^a$ Reduction was carried out for 15—20 min by an excess of solid triphenylphosphine added to a sample of the reaction solution; concentrations of the product (mmol L$^{-1}$) in a homogeneous solution of MeCN for experiment *A* and in a cumene solution for experiment *B* are presented. $^b$ By the GLC data; see Experimental.

of acetone) in the presence of Fe(ClO$_4$)$_3$ (0.0125 mmol, ferric salt in the form of gel) mainly results in the formation of cumyl hydroperoxide (concentrations of products, mmol L$^{-1}$):

| Time /min | Before reduction | | After reduction | |
|---|---|---|---|---|
| | PhCOMe | PhCMe$_2$OH | PhCOMe | PhCMe$_2$OH |
| 120 | 7.2 | 6.3 | 0.5 | 13.5 |
| 220 | 11.2 | 9.4 | 0.9 | 25.2 |

The photooxidation of cumene in an aqueous solution of the emulsion in the presence of Fe(ClO$_4$)$_3$ gives very small amounts of the products of hydroxylation at the phenyl ring. These products were not analyzed. Phenol (0.0075 mmol) was obtained by the hydroxylation (irradiation for 2 h) of benzene (25 mmol) in water (0.25 mL) in the presence of Fe(ClO$_4$)$_3$ (0.0125 mmol). It is known that a similar reaction gives phenol in a higher yield at the higher concentration of HO$^-$ ions.[14]

Preliminary results showed that irradiation of an emulsion (0.1 mL) of 3-methylhexane with an aqeuous solution of Fe(ClO$_4$)$_3$ (1.125 $\cdot$ 10$^{-5}$ mol in 2.5 mL of water) in air for 1.5 h results in the formation of a mixture of products, including oxo derivatives of 3-methylhexane, whose relative concentrations were determined after the reduction of a chloroform extract of the reaction solution with triphenylphosphine. The amount of tertiary alcohol is small. The ratio of the amounts of the obtained products of oxygenation (both alcohols and carbonyl compounds) to the C—H bonds of primary (1°), secondary (2°), and tertiary (3°) carbon atoms with consideration for the number of hydrogen atoms at these carbon atoms was 1 : 2.6 : 0.7. It is

noteworthy that the "normal series" of selectivity in oxygenation of branched alkanes is 1° < 2° ≪ 3°. When the reaction solution was chromatographed without preliminary reduction of the sample with triphenylphosphine, the peak corresponding to tertiary alcohol was not observed on the chromatogram.

Thus, the "unusual" selectivity (see, *e.g.*, Refs. 15—18) in hydrocarbon oxidation, *i.e.*, the predominant formation of ketones, the predomination of products of the oxidation of the secondary C—H bond (and, hence, a relatively low content of tertiary alcohols in the mixture of the products), can be caused in some cases by an increase in the contribution of the channel of decomposition of alkyl hydroperoxide accompanied by the cleavage of the adjacent C—C bond. The contribution of this channel increases as the solvent changes, and the cleavage of C—C bonds is fastest in water. Presently, we are carrying out the studies to elucidate whether this approach can be widely used for the explanation of selectivities in oxidation of alkanes by various systems.

## Experimental

and after the reduction with excess triphenylphosphine for 15—20 min) to determine alcohol, ketone, and alkyl hydroperoxide, as has been described previously.[11-13]

## References

1. G. B. Shul'pin, *Organicheskie reaktsii, kataliziruemye kompleksami metallov* [*Organic Reactions Catalyzed by Metal Complexes*], Nauka, Moscow, 1988, 280 pp.(in Russian).
2. A. E. Shilov and G. B. Shul'pin, *Aktivatsiya i kataliticheskie reaktsii uglevodorodov* [*Activation and Catalytic Reactions of Hydrocarbons*], Nauka, Moscow, 1995 (in Russian).
3. G. B. Shul'pin and M. M. Kats, *React. Kinet. Catal. Lett.*, 1990, **41**, 239.
4. G. B. Shul'pin and M. M. Kats, *Neftekhimiya*, 1991, **31**, 648 (in Russian).
5. P. Lederer, G. V. Nizova, M. M. Kats, and G. B. Shul'pin, *Coll. Czech. Chem. Commun.*, 1992, **57**, 107.
6. G. B. Shul'pin and A. N. Druzhinina, *Mendeleev Commun.*, 1992, 36.
7. G. B. Shul'pin and G. V. Nizova, *Neftekhimiya*, 1993, **33**, 118 (in Russian).
8. G. B. Shul'pin, A. N. Druzhinina, and L. S. Shul'pina, *Neftekhimiya*, 1993, **33**, 335 (in Russian).
9. G. B. Shul'pin and G. V. Nizova, *Mendeleev Commun.*, 1995, 143.
10. C. A. Tolman, J. D. Druliner, M. J. Nappa, and H. Herron, in *Activation and Functionalization of Alkanes*, Ed. C. L. Hill, Wiley-Interscience, New York, 1989, 303.
11. G. B. Shul'pin, D. Attanasio, and L. Suber, *J. Catal.*, 1993, **142**, 147.
12. G. B. Shul'pin and G. Süss-Fink, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1459.
13. G. B. Shul'pin, M. M. Bochkova, and G. V. Nizova, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1465.
14. K. Ohkubo, Y. Arikawa, and S. Sasaki, *J. Mol. Catal.*, 1984, **26**, 139.
15. D. H. R. Barton and D. Doller, *Acc. Chem. Res.*, 1992, **25**, 504.
16. A. Maldotti, C. Bartocci, R. Amadelli, E. Polo, P. Battioni, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1991, 1487.
17. A. Sobkowiak, H.-C. Tung, and D. T. Sawyer, *Progr. Inorg. Chem.*, 1992, **40**, 291.
18. C. Kang, A. Sobkowiak, and D. T. Sawyer, *Inorg. Chem.*, 1994, **33**, 79.