

PHOTOCHEMICAL OXIDATION OF HYDROCARBONS BY ATMOSPHERIC OXYGEN
IN ACETONITRILE CATALYZED BY CYCLOPENTADIENYLIRON COMPLEXESA. N. Druzhinina, L. S. Shul'pina,
and G. B. Shul'pin

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$[(\pi\text{-ArH})\text{Fe}(\pi\text{-C}_5\text{H}_5)]^+\text{BF}_4^-$, where ArH is benzene or toluene, catalyzes the photochemical oxidation of hydrocarbons by oxygen in acetonitrile. Cyclohexane and ethylbenzene are oxidized to the alcohol and ketone derivatives, which are formed in different amounts (after gas-liquid chromatography); benzaldehyde is obtained from styrene. The proposed mechanism involves the formation of a peroxide radical from the organo-metallic complex, which is capable of hydrogen atom abstraction from the alkane.

The search for new pathways for the selective oxidation of hydrocarbons catalyzed by metal complexes holds great interest [1,2]. Upon irradiation by visible light hydrocarbons in acetonitrile, methylene chloride, acetone, and acetic acid are readily oxidized by atmospheric oxygen in the presence of catalytic amounts of ferric chloride [3,4], cupric chloride [5], and Au(III) chloride [6,7], et al. In all cases, the reaction begins with the reaction of a chlorine radical formed upon homologous dissociation of the M-Cl bond with the hydrocarbon (RH) to give a radical (R') and reduced form of the metal complex. This reaction may occur within a solvent cage. Radical R' rapidly reacts with an O₂ molecule to give ROO', which is capable of reoxidizing the complex to restore the catalytic activity of the complex species. However, the absorption spectra, form of the kinetic curves and long induction period for the oxidation reaction upon catalysis by metal bromides removed by addition of a reducing agent indicate that this reaction proceeds, at least upon catalysis by CuCl₂ and AuCl₃, partially or entirely by another mechanism involving the formation of a metal peroxide derivative from the reduced form of the catalyst and an O₂ molecule, which oxidizes RH. Such a mechanism does not presuppose the participation of the chloride ligand. Thus, in order to provide evidence for this mechanism, it was important to find an example of a photocatalytic effect of a metal complex not containing halide ligands in the oxidation of hydrocarbon.

In the present work, we found that the photochemical oxidation of hydrocarbons of atmospheric oxygen in acetonitrile is catalyzed by cyclopentadienyliron complexes. We used tetrafluoroborate salts of benzene- and toluenecyclopentadienyliron, $[(\pi\text{-ArH})\text{Fe}(\pi\text{-C}_5\text{H}_5)]^+\text{BF}_4^-$, as such complexes [8]. Cyclohexane, ethylbenzene, and styrene served as substrates. Cyclohexane and ethylbenzene are oxidized with a significant induction period to give the corresponding alcohol and ketone in approximately equal amounts (Fig. 1). Styrene is oxidized much more rapidly than cyclohexane and ethylbenzene and is converted mainly to benzaldehyde upon gas-liquid chromatography. The accumulation of benzaldehyde proceeds linearly. We should note that the oxidation of cyclohexane in the presence of the π -toluene complex proceeds at virtually the same rate and same induction period as in the presence of the π -benzene derivative. This finding indicates that the π -arene ligand is replaced by acetonitrile molecules upon the action of light even in the first minutes of the reaction [9]. A sharp increase at $\lambda = 300\text{-}450$ nm is observed in the absorption spectra of the reaction solution over the first 10 min. A gradual decrease in absorption in this region is then observed, although this absorption begins to increase slowly 1 h after the

*The alkyl hydroperoxide formed in this reaction (see below) decomposes upon gas-liquid chromatographic analysis with the apparent formation of the corresponding alcohol and ketone in equal amounts.

N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow.
A. N. Nesmeyanov Institute of Organometallic Compounds, Academy of Sciences of the USSR,
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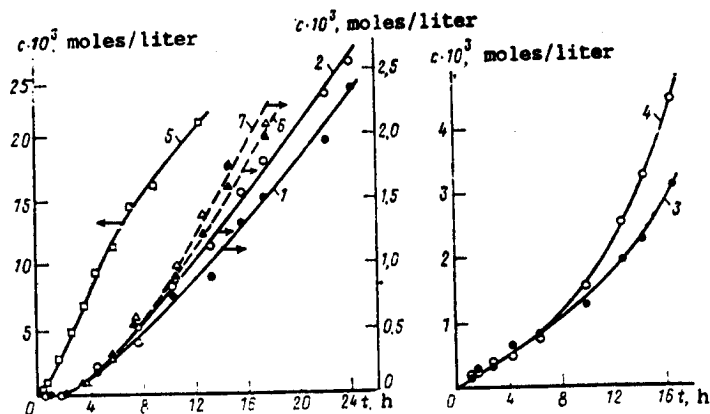
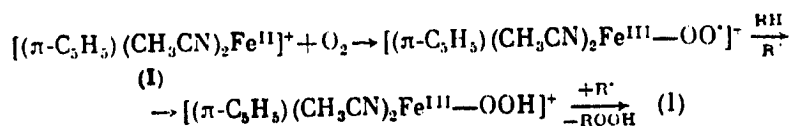


Fig. 1. Kinetic curves for the accumulation of the products of the oxidation of (0.46 mole/liter) hydrocarbons by atmospheric oxygen in acetonitrile upon irradiation in the presence of $5 \cdot 10^{-4}$ mole/liter $[\text{C}_6\text{H}_6\text{FeC}_5\text{H}_5] \cdot \text{BF}_4$ (1-5) or $[(\text{C}_6\text{H}_5\text{CH}_3)\text{FeC}_5\text{H}_5] \cdot \text{BF}_4$ (6,7): 1,6) cyclohexanol, 2,7) cyclohexanone (oxidation of cyclohexane), 3) 1-phenylethanol, 4) acetophenone (oxidation of ethylbenzene), and 5) benzaldehyde (oxidation of styrene).

reaction onset. Thus, a series of consecutive transformations of the starting complex occurs during the induction period.

In considering the reaction mechanism, we may assume that the formation of an incompletely coordinated species such as (I) occurs during the induction period by the action of light. This species upon the addition of O_2 forms a metal-containing peroxide radical, which then oxidized RH through initial hydrogen atom abstraction.



Radical R^\cdot in this scheme is capable of abstracting a peroxide radical (HOO^\cdot) from the metal complex similarly to the mechanism proposed for the abstraction of an HO^\cdot species from a cytochrome P-450 form by an R^\cdot radical [10]. The peroxide formed, ROOH , then either partially or completely decomposes to give approximately equal amounts of alcohol and ketone.

We note that irradiation of a solution of cyclohexane for 16 h under these conditions when the analogous ruthenium complex, $[(\pi\text{-C}_6\text{H}_6)\text{Ru}(\pi\text{-C}_5\text{H}_5)]^+\text{PF}_6^-$ [11], is used as the photocatalyst does not yield more than 10^{-4} mole/liter cyclohexanol + cyclohexanone. On the other hand, $3.0 \cdot 10^{-4}$ mole/liter cyclohexanol and $2.5 \cdot 10^{-4}$ mole/liter cyclohexanone are formed upon the irradiation of this solution in the absence of complex; the accumulation proceeds linearly. In this case, the oxidation is catalyzed by subanalytical amounts of transition metal compounds [12,13]. The lack of activity of the ruthenium complex may be a consequence either of the difficulty in exchanging the arene ligand by acetonitrile (the induction period in this case is more than 16 h) or the circumstance that this metal derivative is incapable of adding O_2 or abstracting a hydrogen atom from the alkane.

EXPERIMENTAL

The oxidation was carried out in the air in cylindrical glass vessels equipped with a jacket for cooling to -10°C with rapid stirring using a magnetic stirrer. The full light of an DRSh-1000 (1000 W) high-pressure mercury lamp was used for the irradiation. The amount of products formed was determined by gas-liquid chromatography on an LKhM-80-6 chromatograph on a $2 \text{ m} \times 4\text{-mm}$ column packed with 5% Carbowax 1500 on Inerton AW-HMDS (0.2-0.315 mm) with argon as the gas carrier.

LITERATURE CITED

1. G. B. Shul'pin, *Organic Reactions Catalyzed by Metal Complexes* [in Russian], Nauka Moscow (1988).
2. A. E. Shilov and G. B. Shul'pin, *Usp. Khim.*, 59, No. 9, 1468 (1990).
3. G. B. Shul'pin, M.M. Kats, and P. Lederer, *Zh. Obshch. Khim.*, 59, No. 12, 2742 (1989).
4. G. B. Shul'pin and M. M. Kats, *React. Kinet. Catal. Lett.*, 41, No. 2, 239 (1990).
5. G. V. Nizova, M. M. Kats, and G. B. Shul'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 3, 698 (1990).
6. G. V. Nizova and G. B. Shul'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 10, 2393 (1989).
7. G. B. Shul'pin and G. V. Nizova, *Zh. Obshch. Khim.*, 60, No. 9, 2121 (1990).
8. A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk SSSR*, 149, No. 3, 615 (1963).
9. A. M. McNair, J. L. Schrenk, and K. R. Mann, *Inorg. Chem.*, 23, No. 17, 2633 (1984).
10. A. E. Shilov and G. B. Shul'pin, *Usp. Khim.*, 56, No. 5, 754 (1987).
11. A. N. Nesmeyanov, N. A. Vol'kenau, I. N. Bolesova, and L. S. Shul'pina, *J. Organomet. Chem.*, 182, No. 2, C36 (1979).
12. J. Vepřek-Šiška, S. Luňák, I. Mach, and D. M. Wagnerová, *Oxid. Commun.*, 3, Nos. 1-2, 3 (1985/86).
13. D. M. Wagnerová, I. Mach, S. Luňák, and J. Vepřek-Šiška, *Collect. Czech. Chem. Commun.*, 54, No. 12, 3124 (1989).