

## PHOTOCHEMICAL OXIDATION OF SATURATED AND ALKYLAROMATIC HYDROCARBONS BY ATMOSPHERIC OXYGEN IN CH<sub>3</sub>CN OR CH<sub>2</sub>Cl<sub>2</sub> SOLUTION, CATALYZED BY IRON(III) HALIDES\*†

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The liquid-phase oxidation of saturated and alkylaromatic hydrocarbons by oxygen with the formation of alcohols, ketones, aldehydes and carboxylic acids [4-7] is of great practical importance, permitting the elaboration of petrochemical synthesis to extremely valuable semi-products for organic synthesis. The oxygenation of hydrocarbons such as ethyl benzene and cyclohexane, proceeding by a radical chain mechanism, is normally initiated by transition metal compounds (for example, stearates) and carried out at a temperature above 70°C. It is of undoubted interest to research into fundamentally new selective reactions for the introduction of functional groups into alkanes and arylalkanes that can take place under mild conditions (i.e. at low temperature and pressure). Transition metal complexes can act as catalysts for such processes [7-12]. Promising in our view are light-initiated reactions of catalytic functionalization of alkanes, since, in theory, sunlight can be used as the energy source in these processes.

In recent years it has been established that, when irradiated with light at room temperature in an organic solvent or an aqueous solution, alkanes and arylalkanes are readily oxidized by oxygen or air in the presence of catalytic amounts of transition metal oxo complexes such as CrO<sub>3</sub> [3,13,14], Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Cr<sub>4</sub>O<sub>13</sub><sup>2-</sup> [3,15], VO<sub>3</sub><sup>-</sup> [3,16], PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> [3,13,16-18], W<sub>10</sub>O<sub>32</sub><sup>4-</sup> [19,20], UO<sub>2</sub><sup>2-</sup> [3,21] etc., and also the following compounds: Pt[NC<sub>6</sub>H<sub>5</sub>NC(S)SCH<sub>3</sub>]<sub>2</sub> [22], (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> [23]. A special place among similar metal complex photocatalysts is occupied by metal chlorides, the photoactivity of which is well-known [24]. Descriptions have recently been given of photooxidation reactions of alkanes and arylalkanes by atmospheric oxygen, catalyzed by FeCl<sub>3</sub> [1-3,25,26] (see [24]), CuCl<sub>2</sub> [1,3,27], AuCl<sub>4</sub><sup>-</sup> [1,3,28,29] and PtCl<sub>6</sub><sup>2-</sup> [1,3,29]. Note that FeCl<sub>3</sub> is an effective photocatalyst of different organic reactions (see, for example, [8,24,30-33]).

In the present work we have continued an investigation of the photooxygenation of alkanes and arylalkanes by air, catalyzed with FeCl<sub>3</sub> in acetonitrile, and some new data concerning this reaction are given. Furthermore, we have studied the photocatalytic action of such compounds as FeBr<sub>2</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub>.

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† Report XX from series "Photoinitiated reactions of organic compounds with metal complexes"; see [1] for report XIX. Preliminary results were published in [2,3].

## EXPERIMENTAL

Reactions were carried out in air in a cylindrical glass vessel with a casing cooled by running water ( $\sim 10^\circ\text{C}$ ) with intense stirring by means of a magnetic stirrer and irradiation using a medium-pressure (125 W) luminescent mercury lamp. The amount of products formed in the reaction was determined by means of GLC (2 m column, carrier gas argon,  $W = 60$  ml/min, sorbent Inerton AW-HMDS 0.25–0.315 mm, impregnated with 5% Carbowax 1500).

## RESULTS AND DISCUSSION

Irradiation of an  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution in acetonitrile (here and below, if not otherwise stipulated, the catalyst concentration was  $5 \times 10^{-4}$  mole/l) and cyclohexane (0.46 mole/l) with the full light of a luminescent mercury lamp (125 W) in air leads to the formation of cyclohexanol and cyclohexanone in roughly equal quantities. It must be noted that cyclohexyl hydroperoxide is formed in considerable quantity, and during elution this decomposes to form the corresponding ketone and alcohol. Accumulation in time occurs linearly, and, within 7 hr,  $3.25 \times 10^{-2}$  mole/l cyclohexanol and  $2.60 \times 10^{-2}$  mole/l cyclohexanone are formed. When the corresponding solution is irradiated in methylene chloride (in this case,  $5 \times 10^{-4}$  mole/l

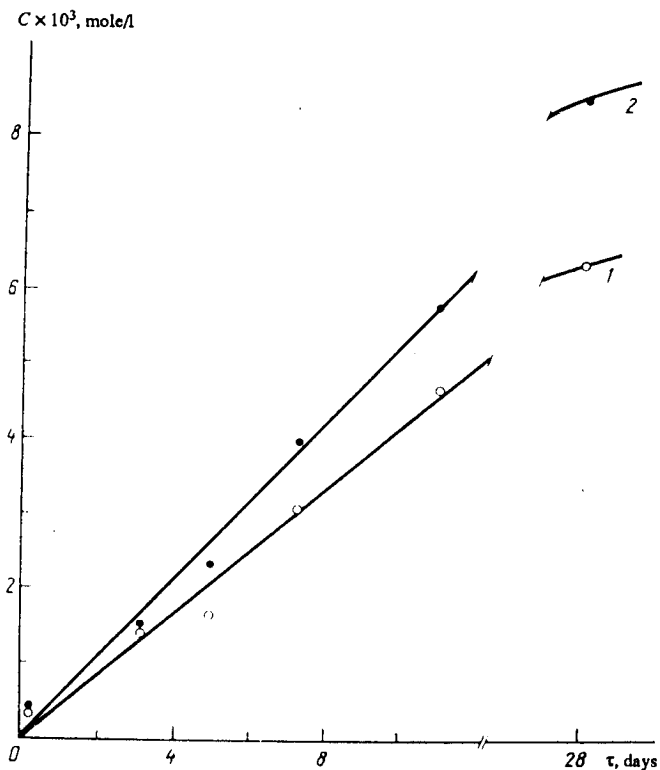


FIG. 1. Accumulation of cyclohexanol (1) and cyclohexanone (2) during irradiation of solution of cyclohexane (0.31 mole/l) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ( $0.17 \times 10^{-3}$  mole/l) in  $\text{CH}_3\text{CN}$  with sunlight in glass vessel ( $\sim 10^\circ\text{C}$ ).

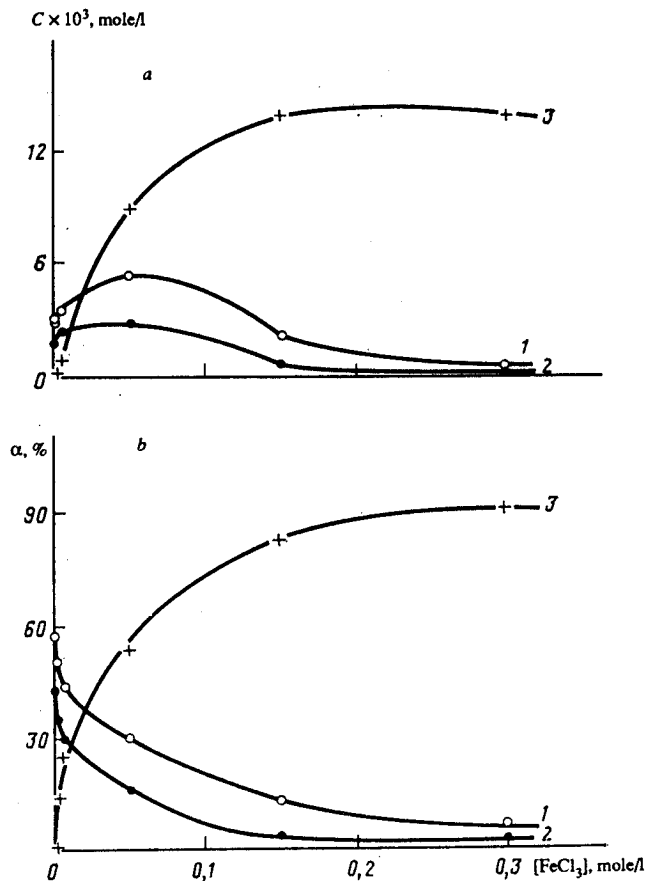


FIG. 2. Dependence of amount (absolute concentrations  $C$  and relative content  $\alpha$ , %) of products of oxidation of cyclohexane ( $0.46$  mole/l) – cyclohexanol (1), cyclohexanone (2) and cyclohexyl chloride (3) – on  $\text{FeCl}_3$  concentration during irradiation of solution in  $\text{CH}_3\text{CN}$  for 1.5 hr ( $\sim 10^\circ\text{C}$ ).

$\text{C}_6\text{H}_5\text{CH}_2(\text{C}_2\text{H}_5)_3\text{NCl}$  is added for dissolution of  $\text{FeCl}_3$ ), roughly the same amounts of oxygenation products are formed within the same time, and, furthermore, cyclohexyl chloride ( $0.45 \times 10^{-2}$  mole/l) is found in the reaction solution, the accumulation of which occurs after a certain induction period (roughly 3 hr). Note that slow oxygenation of cyclohexane is observed during irradiation of the reaction solution in a glass vessel by direct and scattered sunlight for a day (Fig. 1).

An investigation was made of the dependence of the oxygenation rate on the substrate concentration. It turned out that, with an increase in the cyclohexane concentration from 0 to  $0.2$  mole/l, the concentrations of the oxygenation products formed in the first 2 hr of irradiation increase linearly, but with  $[\text{C}_6\text{H}_{12}] > 0.3$  mole/l the reaction rate ceases to depend on the magnitude of this concentration [2]. With an increase in the  $\text{FeCl}_3$  concentration (the cyclohexane concentration is fixed) in the solution, the composition of the reaction products begins to change: the amount of oxygenation products falls, but then there is an appreciable increase in the concentration of cyclohexyl chloride formed (Fig. 2). Note that, when  $[\text{FeCl}_3] > 0.3$  mole/l, no oxygenation products are found, and the concentration of cyclohexyl chloride is

roughly halved by comparison with that for  $[\text{FeCl}_3] = 0.3$  mole/l. Thus, when the  $\text{FeCl}_3$  concentration is increased, the catalytic reaction of oxygenation is gradually superseded by the stoichiometric reaction of oxidative chlorination with the participation of ligands of the iron chloride complex.

The reaction rate depends very little on the temperature of the solution. Determination of the yields of oxygenation products during irradiation in the  $0\text{--}60^\circ\text{C}$  range made it possible to assess the apparent activation energy of the reaction (13 kJ/mole). By replacing cyclohexane with  $\text{C}_6\text{D}_{12}$  it was possible to reveal a slight kinetic isotopic effect ( $1.6 \pm 0.3$ ). The quantum yield of cyclohexanol (cyclohexanone) during irradiation in an atmosphere of pure oxygen with monochromatic light with a wavelength of 300, 365 and 435 nm amounts to  $0.017 \pm 0.003$  ( $0.013 \pm 0.001$ ),  $0.034 \pm 0.004$  ( $0.044 \pm 0.01$ ) and  $0.020 \pm 0.002$  ( $0.022 \pm 0.002$ ) respectively [1].

It is interesting that, with the addition of methyl methacrylate to the reaction solution, the cyclohexane oxidation rate not only does not fall, but even increases slightly. Thus, within 2 hr irradiation, the following oxygenation products are formed:

[Methyl methacrylate] $\times 10^3$ , mole/l	—	0.5	5	10	15
[Cyclohexanol] $\times 10^2$ , mole/l	90	108	118	102	64
[Cyclohexanone] $\times 10^4$ , mole/l	84	150	154	140	86

Other hydrocarbons are also oxygenated by irradiation of their solutions in acetonitrile in the presence of  $\text{FeCl}_3$ . The following products are formed from *n*-hexane (0.46 mole/l) within 5 hr irradiation (in brackets – concentration  $\times 10^3$ , mole/l): hexanol-1 (2.1), hexanol-2 (5.0), hexanol-3 (5.8), hexanal (4.9), hexanone-2 (14.4), hexanone-3 (12.6). Under similar conditions, benzyl alcohol ( $4.4 \times 10^{-3}$  mole/l) and benzaldehyde ( $2.3 \times 10^{-2}$  mole/l) are produced from toluene within 3 hr irradiation. 1-Phenylethanol and acetophenone are formed from ethyl benzene. During combined oxidation of ethyl benzene and cyclohexane (0.37 mole/l each), a mixture (in brackets – concentration  $\times 10^2$ , mole/l) of 1-phenylethanol (0.46), acetophenone (0.52), cyclohexanole (2.2) and cyclohexanone (1.6) was produced within 4 hr irradiation. From this it is possible to calculate the reactivity  $\Psi$  of a single C–H bond in  $\text{CH}_2$  groups:  $\Psi = k_{\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3}/k_{\text{C}_6\text{H}_{12}} = 1.55$ . Competing oxidation of pairs of alkylaromatic compounds *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3\text{--C}_6\text{H}_5\text{CH}_3$  and *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2\text{--C}_6\text{H}_5\text{CH}_3$  made it possible to assess the value of the Hammett–Brown parameter  $\rho^+ = -1.1$ . In an acetonitrile solution, styrene (0.46 mole/l) is photooxygenated in the presence of  $\text{FeCl}_3$ , yielding benzaldehyde ( $8 \times 10^{-3}$  mole/l within 2 hr irradiation).

During irradiation of a solution of cyclohexane in acetonitrile in the presence of  $\text{FeBr}_3$  salt, no oxidation of the hydrocarbon is observed even after 13 hr (Fig. 3). However, when hydroquinone is added to the solution, after an appreciable induction period the accumulation of oxygenation products begins, continuing for a few hours in all. In contrast to cyclohexane, ethyl benzene is oxidized readily under these conditions without an induction period (Fig. 4). Additions of radical chain oxidation inhibitors – ionol and methyl methacrylate – slow down the oxygenation process slightly (Fig. 4). It is significant that, even below room temperature, during photooxidation in the presence of  $\text{FeBr}_3$  benzaldehyde is formed, the amount of which increases with increasing temperature of the reaction solution (Fig. 5). Assessment of the apparent activation energy of ethyl benzene photooxidation in the  $18\text{--}60^\circ\text{C}$  temperature range gives a value of  $\sim 25$  kJ/mole.

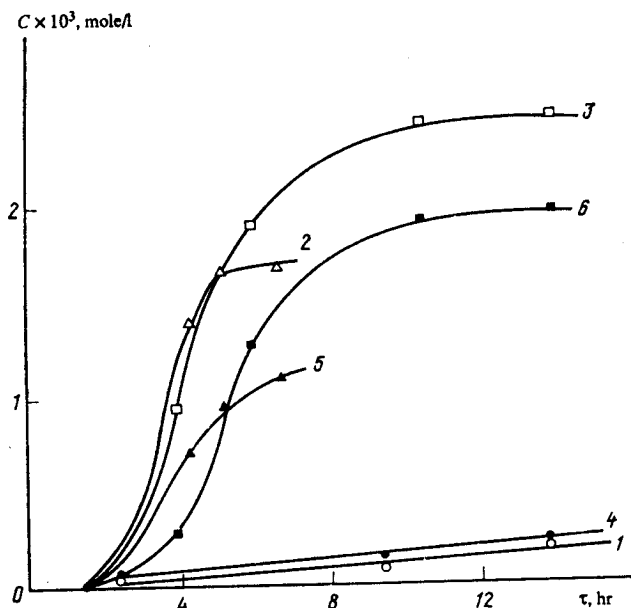


FIG. 3. Accumulation of cyclohexanol (1-3) and cyclohexanone (4-6) during irradiation of solution of cyclohexane (0.46 mole/l) in  $\text{CH}_3\text{CN}$  in presence of  $\text{FeBr}_3$  ( $5 \times 10^{-4}$  mole/l). Formation of oxygenation products with hydroquinone addition of  $10^{-3}$  (2, 5) and  $4 \times 10^{-3}$  mole/l (3, 6). Temperature  $\sim 10^\circ\text{C}$ .

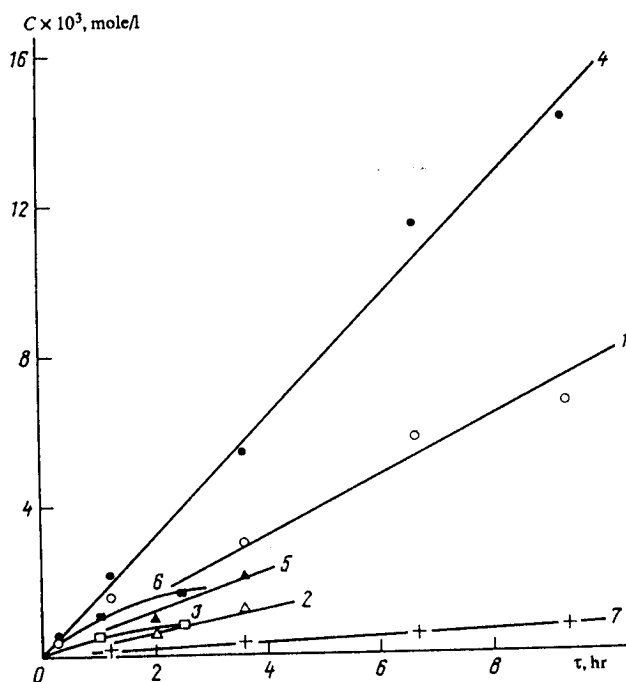


FIG. 4. Accumulation of 1-phenylethanol (1-3), acetophenone (4-6) and benzaldehyde (7) during irradiation of solution of ethyl benzene (0.41 mole/l) in  $\text{CH}_3\text{CN}$  in presence of  $\text{FeBr}_3$  ( $0.5 \times 10^{-3}$  mole/l). Formation of oxygenation products in presence of additions of  $2 \times 10^{-3}$  mole/l ionol (2, 5) and  $2 \times 10^{-3}$  mole/l methyl methacrylate (3, 6).

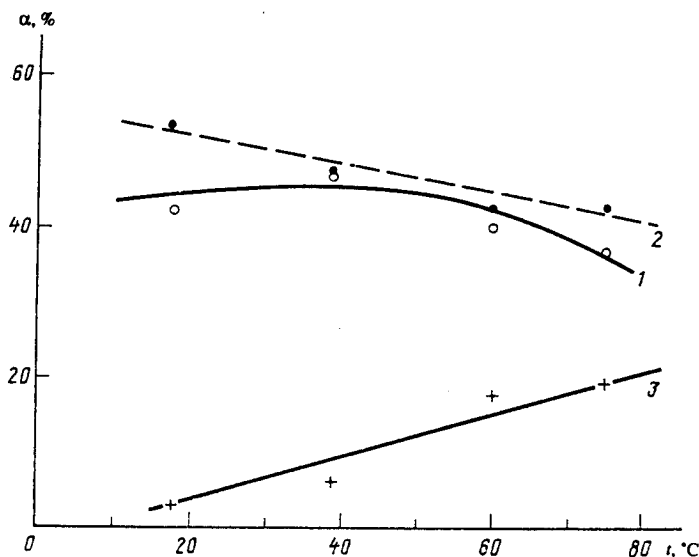


FIG. 5. Dependence of relative content of  $\alpha$ 1-phenylethanol (1), acetophenone (2) and benzaldehyde (3) in mixture of products of ethyl benzene oxygenation in presence of  $\text{FeBr}_3$  on temperature of irradiated solution in  $\text{CH}_3\text{CN}$ .

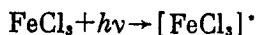
Irradiation of a solution of a mixture of ethyl benzene (0.46 mole/l) and cyclohexane (0.46 mole/l) in the presence of  $\text{FeBr}_3$  ( $5 \times 10^{-4}$  mole/l) leads to a situation where, besides ethyl benzene, cyclohexane is oxidized, but fairly slowly. Thus, 3 hr irradiation produces  $3 \times 10^{-3}$  mole/l of acetophenone,  $0.7 \times 10^{-3}$  mole/l of cyclohexanol, and  $0.4 \times 10^{-3}$  mole/l of cyclohexanone. Bearing in mind the initial formation rates of these products, it is possible to assess the reactivity of a single C-H bond in  $\text{CH}_2$  groups:  $\Psi = 108$ . As can be seen, this value is much greater than for the case of photooxidation in the presence of  $\text{FeCl}_3$ .

During irradiation of a mixture of toluene (0.46 mole/l) and *p*-xylene (0.23 mole/l) in the presence of  $\text{FeBr}_3$ , the corresponding alcohols and aldehydes are formed ( $\sim 10^\circ\text{C}$  (concentration  $\times 10^3$ , mole/l)):

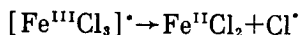
Irradiation time, hr	1	2	3	5
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	0.28	0.48	0.62	0.64
$\text{C}_6\text{H}_5\text{CHO}$	0.86	1.48	2.21	3.22
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	1.04	1.22	1.44	2.16
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CHO}$	2.30	3.86	5.24	7.74

On the basis of these data, it is possible (assuming the existence of correlation between the logarithms of the relative oxidation rates and constants  $\sigma^+$ ) to estimate the Hammett-Brown parameter ( $\rho^+ = -2.5$ ).

Taking account of the fact that the yield of products of oxygenation of hydrocarbons during irradiation in the presence of  $\text{FeCl}_3$  and also  $\text{FeBr}_3$  reaches several hundreds of moles per 1 mole photocatalyst, and that the spectrum of the solution of iron(III) chloride in a mixture of acetonitrile and cyclohexane hardly changes within the first few hours of irradiation [1], it is possible to assume the following mechanism of the process. At the first stage, under the action of light, excitation of the iron(III) complex occurs [24,34]



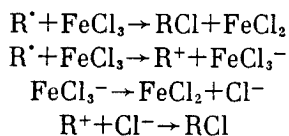
In an excited particle, electron transfer from ligand to complexing ion occurs, as a result of which a free chlorine atom can arise [35]



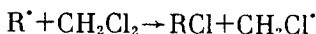
The degree of oxidation of iron per unit decreases in this case. The chlorine atom detaches the hydrogen atom from the alkane or arylalkane, and here an alkyl radical is formed [36]



Note that selectivity  $\Psi$  for the reaction of chlorine atoms with C-H bonds in ethyl benzene and cyclohexane amounts to 1.3 [37], which is similar to the  $\Psi$  value obtained in the present work (1.55). With a large concentration of compound  $\text{FeCl}_3$ , the concentration of molecular oxygen in the solution is considerable in relation to the  $\text{R}^*$  radicals formed. In this case, alkyl radicals react mainly with chloride complexes of iron(III), either detaching a chlorine atom from them or reducing them. By both routes, a chloride alkyl is formed (see [38,39])

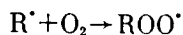


With a shortage of molecular oxygen and the reaction carried out in a chlorine-containing solvent,  $\text{R}^*$  radicals detach a chlorine atom from the solvent

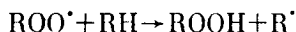


In all these cases, an alkyl chloride is one of the main products.

A different situation develops when an iron complex is present in low concentration. In this case the  $\text{R}^*$  radicals formed in low concentration rapidly react with the molecular oxygen in the solution, forming peroxide radicals



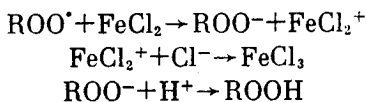
The reaction of radicals with a hydrocarbon molecule



which is the key stage in the radical chain oxidation occurring at increased temperature, seems to be unlikely in the case of photochemical oxygenation of cyclohexane, since photooxidation proceeds at low temperatures, and the activation energy of the process is very low (the activation energy of the reaction of a peroxide cyclohexyl radical with a cyclohexane molecule in gas phase amounts to 57.7 kJ/mole [40]; see also [41,42]). The contribution of the chain route is more probable for the oxidation of ethyl benzene. Since additions of inhibitors of radical

processes do not have a very great effect on the reaction rate, it is possible to assume that the reaction of chlorine atoms with hydrocarbon and then the addition of an oxygen molecule to alkyl radicals occur without the formation of such particles from a cell of the solvent.

Peroxide radicals can reoxidize reduced particles of the iron complex



Iron(II) can also be reoxidized by molecular oxygen. The iron(III) complex produced in this way can re-enter the catalytic cycle, while the hydroperoxide can break down (with the participation of light and/or iron complexes) with the formation of alcohol and ketone. It is also easy to imagine oxygenation of a new hydrocarbon molecule by hydroperoxide (and also by a peroxide radical or anion) during catalysis by an iron complex. This reaction should evidently occur with the intermediate formation of hydroxyl radicals.

The bromine atoms formed during photolysis of the Fe-Br bond in iron bromide at low temperature are insufficiently active and incapable of detaching hydrogen atoms from a cyclohexane molecule. However, ethyl benzene containing weaker C-H bonds in CH<sub>2</sub> groups readily enters into this reaction (note that selectivity Ψ for attack by bromine atoms amounts to 8143 [37]). Oxidation of cyclohexane in the presence of ethyl benzene becomes possible, for example, either on account of hydroxylation of cyclohexane by the peroxide formed from ethyl benzene or because ethyl benzene promotes the partial reduction of the iron(III) complex. Hydroquinone can fulfil the same function. The role of a complex of low-valency (bivalent) iron in oxygenation is less clear. It is possible that peroxide or oxo complexes of iron are formed from an iron(II) derivative and molecular oxygen, and these complexes oxygenate cyclohexane. To confirm or reject this reaction path, an additional investigation is required.

We also found that chlorides of some other metals in the presence of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>NCl in methylene chloride catalyze the oxygenation of cyclohexane by atmospheric oxygen during irradiation. Within 2 hr irradiation of a suspension of metal chloride in a quantity of 2.5 × 10<sup>-6</sup> mole in a 5 ml solution with an alkylammonium salt concentration of 5 × 10<sup>-4</sup> mole/l and a cyclohexane concentration of 0.46 mole/l, the following products were produced (concentration × 10<sup>3</sup>, mole/l):

Metal salt	MnCl <sub>2</sub> ·4H <sub>2</sub> O	CrCl <sub>3</sub> ·10H <sub>2</sub> O	CrCl <sub>3</sub>	RhCl <sub>3</sub> ·3H <sub>2</sub> O
Cyclohexanol	1.7	1.1	0.7	2.2
Cyclohexanone	0.6	0.5	0.2	1.4

Finally, during irradiation in the presence of 2.5 × 10<sup>-6</sup> mole K<sub>3</sub>[Fe(CN)<sub>6</sub>] in 5 ml of a solution of cyclohexane (0.46 mole/l) and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NCl (0.5 × 10<sup>-3</sup> mole/l) in methyl chloride, after an induction period, the following products are formed (concentration × 10<sup>3</sup>, mole/l):

Irradiation time, hr	1	2	3	4
Cyclohexanol	0.1	1.6	6.0	6.8
Cyclohexanone	0.1	1.2	4.4	4.6
Cyclohexyl chloride	0.0	0.3	1.5	3.5



Additional investigations are needed to establish the mechanism of this reaction.

### SUMMARY

Light irradiation in air of solutions of hydrocarbons in acetonitrile in the presence of catalytic amounts of  $\text{FeCl}_3$  leads to the formation of the corresponding alcohols and carbonyl compounds. The reaction proceeds in a similar manner in methylene chloride (with the addition of alkylammonium chloride for dissolution of iron salt), and here, besides oxygenation products, alkyl chlorides are produced. In the presence of photocatalyst  $\text{FeBr}_3$ , ethyl benzene gives 1-phenylethanol, acetophenone and benzaldehyde, while cyclohexane is not oxidized under these conditions. However, cyclohexane can be oxygenated if hydroquinone is added to the reaction solution. The mechanism proposed includes photohomolysis of the iron-halogen bond and detachment of the hydrogen atom by a halogen radical from  $\text{RH}$  with the formation of  $\text{R}^\cdot$ , which, adding  $\text{O}_2$ , yields  $\text{ROO}^\cdot$ . The latter (and/or  $\text{O}_2$ ) re-oxidizes the catalytic complex.

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