

Photochemical aerobic oxidation of alkanes promoted by iron complexes ¹

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Abstract. – Irradiation in air of an alkane MeCN/solution containing a catalytic amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ yields an alkyl hydroperoxide, which in the course of the reaction gradually decomposes to give an alcohol and a ketone. The proposed mechanism involves photolysis of the Fe–Cl bond and subsequent attack of the Cl^\bullet radical on the C–H bond. If MeCN is replaced by water and the reaction is carried out in an emulsion, cyclohexane in the presence of an iron salt is transformed into cyclohexanone and no cyclohexanol is detected by GLC.

Key words: alkanes, alkyl hydroperoxides, iron complexes, oxygenation, photocatalysis.

Introduction

The oxidation of saturated hydrocarbons by molecular oxygen to produce valuable products (peroxides, ketones, alcohols, etc.) is a very important field of contemporary chemistry from the point of view of both industrial and academic science ². In the last decades, in addition to well-known auto-oxidation processes, essentially new methods have been developed that allow oxygenation of alkanes under very mild conditions and with unusual selectivity ³ (the so-called Gif-chemistry is especially interesting and even a bit mysterious ⁴). Photochemical aerobic oxidation of saturated hydrocarbons (as well as some other compounds) ⁵, which is often promoted by certain soluble metal compounds ⁶, seems to be a very promising method for chemical transformation. Indeed, such oxidations usually proceed under an atmospheric pressure of dioxygen or even air at ambient temperature. In perspective, these oxidations could utilize solar irradiation.

Previously, we found that certain metal derivatives, soluble in organic solvents, can catalyze the photo-oxidation of alkanes and arylalkanes by air at room temperature. Acetonitrile, acetic acid, acetone and dichloromethane were used as solvents. Polyoxometalates (e.g., $\text{Na}_6\text{V}_{10}\text{O}_{28}$, $\text{Na}_5\text{H}_7\text{Mo}_6\text{V}_5\text{O}_{39}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$, Cr_4O_{13}) ⁷, UO_2Cl_2 ⁸, cyclopentadienyl iron complexes ⁹, and especially chloride derivatives of some transition metals (FeCl_3 ¹⁰, CuCl_2 ^{10c, e, 11}, HAuCl_4 ^{10b, 12}, CrCl_3 ^{10c, 13}, PtCl_6^{2-} ^{14a} and others ¹⁴) have turned out to be effective photocatalysts for aerobic alkane oxidation. Bromides

(FeBr_3 ^{10d}, CuBr_2 ^{11b}) also photocatalyze the aerobic oxidation of arylalkanes. Alkyl peroxides, alcohols and ketones (aldehydes) were formed as the main products in these reactions. Recently, we developed a “quinone – copper acetate – air” system that efficiently oxygenates alkanes into alkyl hydroperoxides under irradiation by visible light ¹⁵. Continuing our systematic investigations on the aerobic complex-photocatalyzed oxygenation of alkanes, we have studied in more detail the oxidation of some saturated hydrocarbons catalyzed by iron complexes. We report here on the photo-oxidation promoted by ferric chloride and perchlorate in acetonitrile solution as well as in an aqueous emulsion and some other solvents. Preliminary communications of some of this work have been published ¹⁰. The photoactivity of FeCl_3 is well-known and this compound has been used for various photochemical transformations of organic compounds (see, for example refs. 16). Certain other iron derivatives have been shown to induce photo-oxidation ¹⁷.

Experimental section

Alkanes and arylalkanes (“Fluka”, “Aldrich”, “Reakhim”) were purified by shaking with conc. sulfuric acid, subsequently washing with water, drying over CaCl_2 and distilling. Acetonitrile was distilled over P_2O_5 . Metal salts (from various sources) were used as received.

All photo-oxidations were carried out in air (a few exceptions are noted in the text and figure captures) in a cylindrical glass vessel

(internal diameter 2 cm, reaction solution volume 5 mL) with vigorous stirring and surrounded by a water cooling system (ca. 15 °C), and using the full spectrum of a 125 W luminescent street lamp ($\lambda > \text{ca. } 300 \text{ nm}$). It should be emphasized that the photoreaction rates depend more or less strongly on the distance between the reaction vessel and the light source, on the shape of the reaction vessel as well as on other factors (the presence or absence of a mirror behind the reaction vessel, the sort of glass of the reaction vessel, etc.). These data indicate that the reaction rate depends on the intensity of the absorbed light. Since in many cases we did not measure the intensity of the absorbed light and the position of the reaction vessel relative to the light source was fixed only within certain series of experiments, the quantitative results on oxidations may be correctly compared only within a set of experiments carried out simultaneously or with in one day (usually such data are given in the same figure in this paper; the data from different figures may be slightly different). The reaction rates do not depend on the stirring speed of the solution, which testifies that the studied reactions proceed in the kinetic regime i.e. the rate of dioxygen penetration into the solution is not the rate-determining step.

The oxidation reaction was monitored by withdrawing aliquots at specific intervals and analyzing them by GLC (each sample was analyzed twice, i.e. before and after addition of triphenylphosphine). For the analysis, a LKhM-80/6 chromatograph (column length 2 m, 5% Carbowax 1500 on Inerton AW-HMDS, argon carrier gas) was employed.

Results and discussion

Photo-oxidation in MeCN catalyzed by FeCl_3

We have found that irradiation ($\lambda > \text{ca. } 300 \text{ nm}$) in air of an alkane MeCN/solution in the presence of FeCl_3 produces various alkane oxygenation products; the main ones being cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide. We used the method of alkyl peroxide determination by GLC of samples *before* and *after* reduction with PPh_3 (we introduced this method in refs. 10f, 18 and it was successfully employed in subsequent investigations by us^{9b, 10g, h, 14b-d, 15, 19} and other scientists²⁰). One of the merits of this method is the possibility of estimating concentrations of alkyl peroxide formed from alkane even with excess oxidant (hydrogen peroxide, alkyl hydroperoxide or metal peroxide)¹⁹. Recently, we have obtained^{19f} direct evidence for the formation of alkyl hydroperoxides in the catalyzed oxidation of alkanes (*n*-heptane, cyclohexane, cyclooctane) by $\text{O}_2\text{-H}_2\text{O}_2$: alkyl hydroperoxide peaks were detected in the chromatograms of the reaction mixture untreated with PPh_3 . Retention times of these peaks are longer than those for corresponding alcohols. If the reaction solution is treated with PPh_3 the ROOH peaks disappear and the intensities of the corresponding alcohol peaks grow markedly.

The kinetics of the photo-oxidation of cyclohexane (taken in high concentration) is shown in Figure 1. The GLC analysis certifies the formation of cyclohexanol and cyclo-

hexanone. If the reaction solution was injected into the chromatograph without any preliminary treatment, the alcohol and ketone concentrations were approximately equal (Fig. 1, top; Fig. 2, left). However, as in our previous investigations^{9, 15, 18, 19}, the process was monitored by withdrawing aliquots at specific intervals and analyzing them by GLC, not only without any treatment but also after reduction with triphenylphosphine (Fig. 1, middle; Fig. 2, bottom). If excess solid triphenylphosphine is added to the solution of the alkane oxidation products 10-20 min before the GLC analysis, the resulting chromatogram differs drastically from that of a sample not subjected to the reduction with triphenylphosphine (two examples are shown in Figure 2). After reduction, the cyclohexanol peak rises markedly, while the intensity of the cyclohexanone peak decreases. The sum of alcohol and ketone concentrations in the reduced sample is approximately equal to the total concentration of products in the untreated solution. These results can be explained by the fact that the product mixture contains cyclohexyl hydroperoxide as the main component.

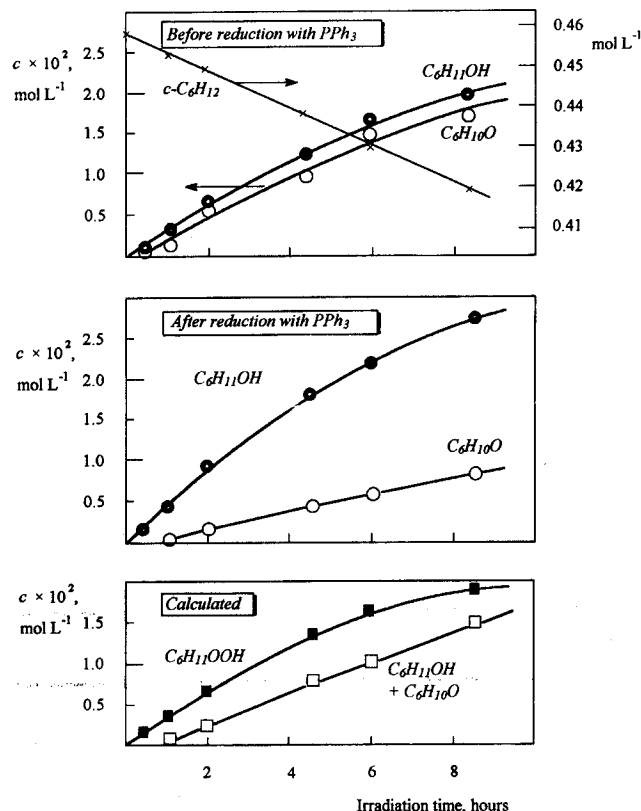


Figure 1. – Kinetics of the aerobic photo-oxidation of cyclohexane in MeCN in the presence of FeCl_3 ($5.0 \times 10^{-4} \text{ mol L}^{-1}$). *Top*: the accumulation of cyclohexanol (closed circles) and cyclohexanone (open circles) before the reduction with PPh_3 , as well as the consumption of starting cyclohexane (crosses). *Middle*: the same when the reaction solution is reduced with PPh_3 before GLC analysis. *Bottom*: concentration of cyclohexyl peroxide (closed squares) and the sum of cyclohexanol and cyclohexanone (open squares), estimated from the data shown at the top and in the middle of the figure, vs time.

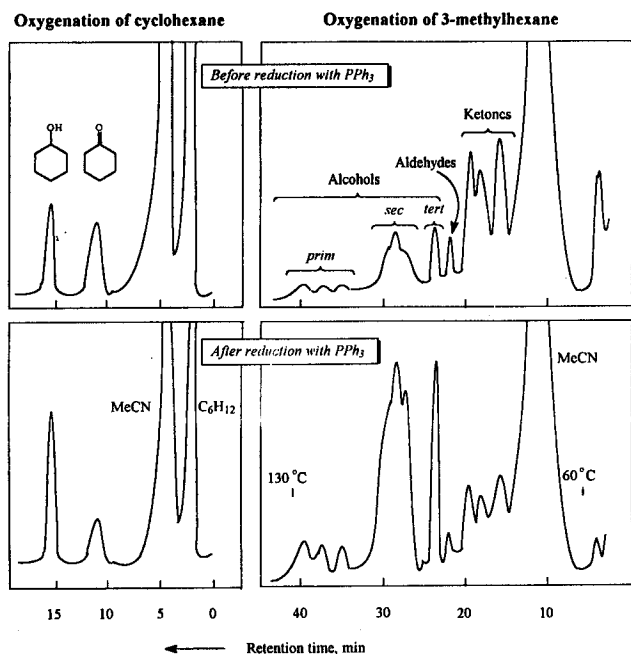
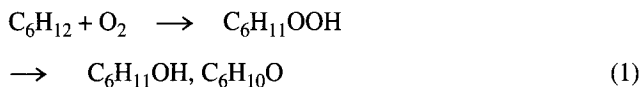


Figure 2. – Chromatograms of reaction mixtures for alkane photo-oxygenations catalyzed by FeCl_3 in MeCN (irradiation: 1 h in the case of cyclohexane and 6.5 h for 3-methylhexane).

Indeed, it is known²¹ that cyclohexyl hydroperoxide is totally decomposed in the chromatograph to produce cyclohexanol and cyclohexanone in a ca. 1:1 ratio. The peroxide is readily and quantitatively reduced by triphenylphosphine to yield cyclohexanol²¹.

Figure 1 (bottom) demonstrates that during the first hour of irradiation, only cyclohexyl peroxide is formed. These data testify that peroxide is the primary product in the cyclohexane oxidation whereas cyclohexanol and cyclohexanone are produced subsequent steps as the peroxide decomposes:



According to the results presented in Figure 1 (bottom), the rate of ROOH formation, W_0 , at least during the first four hours of reaction, is constant and equals $3.0 \times 10^{-3} \text{ mol L}^{-1} \text{ h}^{-1}$. Assuming that the ROOH decomposition proceeds as a pseudo-first-order reaction with the effective rate constant k_{dec} , the rate of formation of “stable” products (cyclohexanol and cyclohexanone) can be expressed as follows:

$$\frac{d[\text{C}_6\text{H}_{11}\text{OH}]}{dt} = \frac{d[\text{C}_6\text{H}_{10}\text{O}]}{dt} = k_{\text{dec}} [\text{ROOH}] \quad (2)$$

Since $[\text{ROOH}] = W_0 t$ we can write the following equation:

$$[\text{C}_6\text{H}_{11}\text{OH}] = [\text{C}_6\text{H}_{10}\text{O}] = \frac{k_{\text{dec}} W_0 t^2}{2} \quad (3)$$

The effective pseudo-first-order constant of the ROOH decomposition obtained from this equation equals 0.125 h^{-1} . Using this value of k_{dec} we can determine the value of the stationary ROOH concentration corresponding to its maximum concentration in the oxidation reaction ($2.4 \times 10^{-2} \text{ mol L}^{-1}$); the time required for this concentration to reach its half value is ca 5.5 h. It should be noted that the stationary ROOH concentration under the conditions used in the experiment shown in Figure 1 is not yet reached. This analysis can be complicated by the possible oxidation of “final” products (cyclohexanol and cyclohexanone).

In order to propose a mechanism for this process we determined the dependence of the oxygenation initial rate on the concentrations of various reactants; some additional experiments were also carried out. The initial rate of the reaction, W_0 , was determined as a function of the concentration, c , of all oxygenated products (measured by GLC) after relatively short irradiation periods (2 h or even 5 min; see figure captions).

There is a linear dependence of the initial oxygenation rate on the full light intensity. As shown in Figure 3, at low FeCl_3 content, the reaction rate is proportional to the catalyst concentration. However, when $[\text{FeCl}_3] > 3 \times 10^{-4} \text{ mol L}^{-1}$, the rate W_0 is almost independent of the catalyst concentration (moreover, W_0 slightly decreases when $[\text{FeCl}_3]$ increases). Data presented in Figure 3 are in accordance with an assumption that the reaction rate is proportional to the light intensity absorbed by ferric chloride. Indeed, for parallel monochromatic light, the absorbed light intensity is described by the following equation:

$$I_a = I_0(1 - 10^{-\epsilon lc}), \quad (4)$$

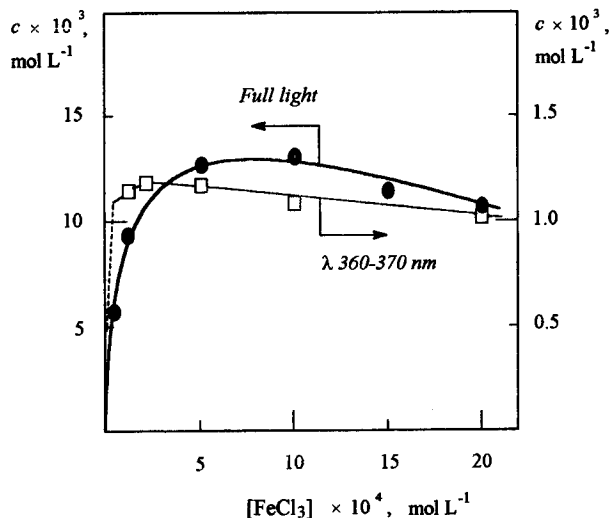


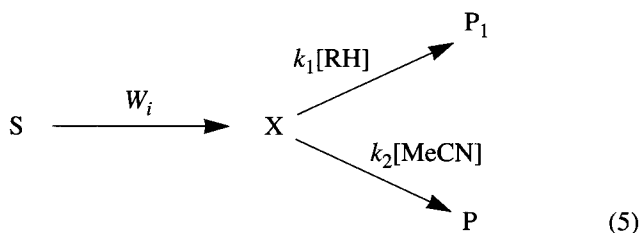
Figure 3. – Plot of the initial rate of the cyclohexane aerobic photo-oxidation in MeCN (determined as the concentration, c , of the sum of oxygenated products after 2 h irradiation) vs concentration of FeCl_3 . Full light (closed circles) and filtered light (λ 360–370 nm) (open squares) of a luminous street lamp was used for irradiation of the reaction solution.

where I_a and I_0 are the intensities of absorbed and irradiated light, ϵ is the extinction coefficient of the absorbing substance at a certain fixed wavelength, l is the optical length and c is the concentration of the absorbing substance. In accordance with equation (4), at low FeCl_3 concentrations the value of I_a is proportional to $[\text{FeCl}_3]$, and when ferric chloride is present in high concentrations we will have an approximate equality $I_a \approx I_0$, that is I_a does not depend on $[\text{FeCl}_3]$.

An approximate analysis shows that when filtered light is used, the plot of the reaction rate versus ferric chloride concentration exhibits a maximum at $[\text{FeCl}_3] \gg 2.0 \times 10^{-4} \text{ mol L}^{-1}$. At this concentration the optical density of the solution at $\lambda = 365 \text{ nm}$ in a plain parallel cuvette with $l = 2 \text{ cm}$ is more than 1.4, which corresponds to almost complete absorption of the light.

The shapes of the curves obtained in experiments using irradiation with full ($\lambda > \text{ca. } 300 \text{ nm}$) and filtered ($\lambda 360\text{--}370 \text{ nm}$) light are analogous. The main difference between the curves is due to the decrease of the total light intensity. The curves reach a plateau and when full light is used the plateau is attained at higher concentrations of FeCl_3 . This peculiarity testifies that the effect of the light increment with $\lambda > 370 \text{ nm}$ on the photo-oxidation is noticeable. This light is present in the full spectrum although it is absorbed less efficiently by FeCl_3 (see below, Fig. 6).

The dependence of W_0 on the initial cyclohexane concentration is presented in Figure 4 (top). This dependence can be linearized if the coordinates $1/[\text{cyclo-C}_6\text{H}_{12}]$ versus $1/W_0$ are used. In this case the straight line intercepts the ordinate at $1/c = 0.6 \times 10^3 \text{ L mol}^{-1}$. This result confirms the proposal that the active species, which induces the oxidation of cyclohexane into detectable products, also reacts with another component of the reaction system. This component is most likely the solvent, acetonitrile. From the following simple competitive scheme:



where X is the active transient species, W_i is its rate of formation, and S and P are the substrate and products, respectively, we can easily write the equation:

$$\left(-\frac{d[\text{RH}]}{dt} \right)^{-1} = \frac{1}{W_i} \left(1 + \frac{k_2[\text{MeCN}]}{k_1[\text{RH}]} \right) \quad (6)$$

which is in agreement with the experimental data presented in Figure 4. Taking into account these data and

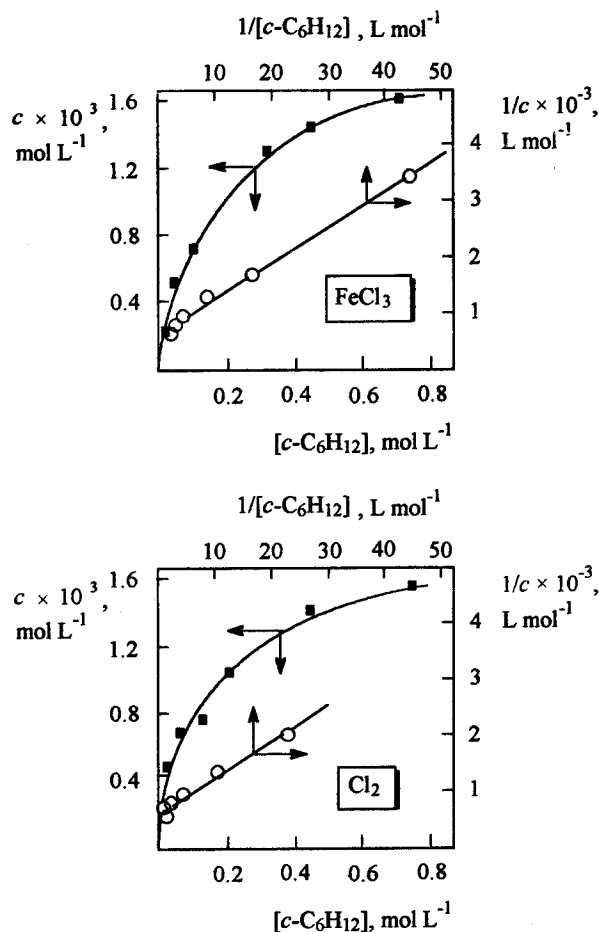


Figure 4. – Plots of the concentration, c , of the sum of oxygenated products formed after 25 min (in the case of FeCl_3) and 5 min (Cl_2) irradiation of cyclohexane solution in MeCN vs initial cyclohexane concentration (closed squares) as well as plots of $1/c$ vs $1/[\text{cyclohexane}]$ (open circles). The photo-oxidation is shown in the presence of FeCl_3 ($5.0 \times 10^{-4} \text{ mol L}^{-1}$) (top) and Cl_2 ($2.85 \times 10^{-3} \text{ mol L}^{-1}$) (bottom).

equation (6) one can calculate that $k_2[\text{MeCN}]/k_1 = 0.13 \text{ mol L}^{-1}$. Since $[\text{MeCN}] = 19 \text{ mol L}^{-1}$ the ratio $k_2/k_1 = 6.8 \times 10^{-3}$.

In order to evaluate the role of atmospheric oxygen in this reaction we carried out the photo-oxidation of cyclohexane in a closed vessel (Fig. 5). For comparison, in a special experiment molecular oxygen was bubbled through the reaction solution before closing the vessel and subsequently irradiating. However, no drastic difference has been noticed between the reactions under dioxygen or air. In both cases, during the first 2 h an almost linear accumulation of oxygenated products has been detected and the initial parts of both curves coincide. Consequently, the rate of cyclohexane oxygenation depends very little on the dioxygen concentration due to its small value. After ca. 2 h irradiation product accumulation stops due to the decrease of dioxygen dissolved in the reaction solution. Indeed, if addi-

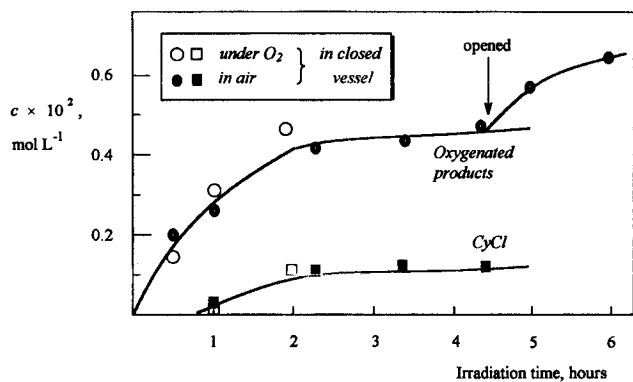


Figure 5.— Kinetics of the aerobic photo-oxidation of cyclohexane (0.46 mol L^{-1}) in MeCN in the presence of FeCl_3 ($5.0 \times 10^{-4} \text{ mol L}^{-1}$) in a closed vessel (no free volume over the solution) in air (closed symbols) and under molecular oxygen (open symbols). The accumulation of the sum of cyclohexanol, cyclohexanone and cyclohexyl peroxide (circles) and cyclohexyl chloride (squares) is shown. At the time, denoted by the arrow, the vessel was opened to air.

tional air is added to the system (by opening the vessel), oxygenation continues further, the oxidation rate being close to the initial one. In addition, the yield of oxygenated products at the moment when the reaction stops is close to that expected. It is known (see below, ref. 29a) that the solubility of dioxygen in acetonitrile is equal to $8.0 \times 10^{-3} \text{ mol L}^{-1}$ when its pressure is 1 atm at 300 K. At the partial pressure of dioxygen corresponding to its content in air, this concentration is $1.6 \times 10^{-3} \text{ mol L}^{-1}$. Since our experiments were carried out at ambient temperature (i.e., less than 300 K) one can expect some increase in solubility in comparison with this value. Consequently, if all dissolved molecular oxygen is used for the oxidation of cyclohexane to produce alcohol and ketone, the total concentration of the oxygenated products should be equal to twice the concentration of initially dissolved dioxygen, namely slightly higher than $3.2 \times 10^{-3} \text{ mol L}^{-1}$. The experimentally measured concentration of the oxygenated products (Fig. 6) is $4.2 \times 10^{-3} \text{ mol L}^{-1}$, which is close to the expected value.

The absorption spectrum of FeCl_3 dissolved in MeCN (Fig. 6) exhibits two bands, at 312 and 362 nm, and only negligible spectral changes occur in the 300–400 nm region during the 3 h exposure to light in the presence of cyclohexane. Thus the concentration of the iron chloride complex in the reaction solution is constant, which suggests that a form of the iron-containing catalyst, reduced by the action of light, is regenerated in the presence of dioxygen. The quantum yields (see ref. 10e) with respect to the oxygenated products are 0.03 (for irradiation of the cyclohexane solution under dioxygen with light $\lambda = 300 \text{ nm}$), 0.08 (365 nm) and 0.04 (436 nm).

The experiment with C_6D_{12} has shown that the oxidation reaction proceeds with a small kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.6$). Lowering the oxidation rate on going from

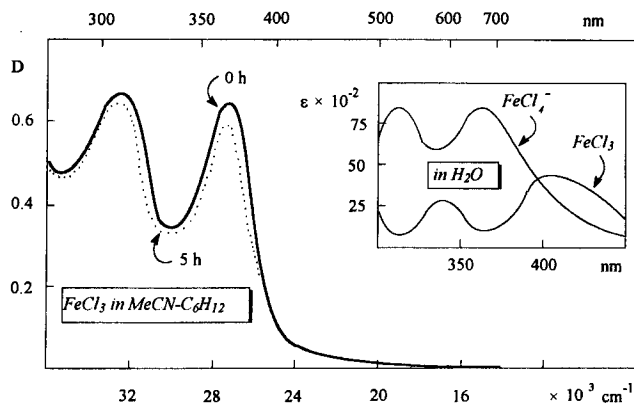


Figure 6.— Absorption spectra of the reaction solution containing FeCl_3 ($5.0 \times 10^{-4} \text{ mol L}^{-1}$) in MeCN in the presence of cyclohexane (0.46 mol L^{-1}) before and after 5 h irradiation in air. The samples of the reaction solution were diluted with MeCN (1:5) before recording the spectra (Specord UV-vis instrument). Spectra of FeCl_3 and FeCl_4^- in aqueous solution (taken from refs. 5h, 23) are shown in the upper right corner.

cyclohexane to its perdeuterated derivative can support the assumption that abstraction of a hydrogen atom from the alkane is the primary activation step. Indeed, in the case of ethyl alcohol the rate constant deuterium atom abstraction by hydroxyl radical is 1.4 times less than that for hydrogen^{22a}. Analogous values have been determined for reactions between hydrocarbons with chlorine atoms^{22b}. The photo-oxidation is only very slightly dependent on temperature. Comparison of the reaction rates in the interval 0–60 °C allows the effective activation energy to be estimated (13 kJ mol^{-1}).

Other alkanes and arylalkanes can easily be oxygenated by the system under discussion. Thus, a 5 h irradiation of *n*-hexane (0.46 mol L^{-1}) in MeCN in the presence of FeCl_3 ($5.0 \times 10^{-4} \text{ mol L}^{-1}$) gives the isomers of the corresponding alcohols and ketones (aldehydes), the total product concentration being $4.5 \times 10^{-2} \text{ mol L}^{-1}$ (the catalyst turnover number is 90). The selectivity of this oxidation (as well as the oxygenation of 3-methylhexane) is given in Table I. It may be concluded that the selectivities are comparable with those found for the oxygenations induced by hydroxyl radicals. (Hydroxyl radicals generated via pulse radiolysis give^{22c, d} the ratio $1^\circ:2^\circ:3^\circ = 1.0:1.2:2.4$ for the oxidation of 2-methylbutane). Under analogous conditions (3 h irradiation, GLC analysis without preceding reduction with PPh_3) toluene is transformed into a mixture of benzylic alcohol ($4.4 \times 10^{-3} \text{ mol L}^{-1}$) and benzaldehyde ($2.3 \times 10^{-2} \text{ mol L}^{-1}$) and ethylbenzene is oxidized into 1-phenylethanol and acetophenone. The competitive photo-oxygenation of cyclohexane (0.37 mol L^{-1}) and ethylbenzene (0.37 mol L^{-1}) during 4 h yields (without PPh_3 reduction) a mixture of cyclohexanol ($2.2 \times 10^{-2} \text{ mol L}^{-1}$), cyclohexanone ($1.6 \times 10^{-2} \text{ mol L}^{-1}$), 1-phenylethanol ($0.46 \times 10^{-2} \text{ mol L}^{-1}$) and acetophenone ($0.52 \times 10^{-2} \text{ mol L}^{-1}$). From this data the parameter Ψ , which we define

Table I. – Selectivities in the aerobic photo-oxygenations of linear and branched alkanes promoted by transition metal complexes and certain other reagents ^a.

Reagent	Solvent	Relative reactivity per C–H bond of the hydrocarbon, RH ^b					
		RH	C(1):C(2):C(3):C(4) ^c	RH ^d	1°:2°:3° ^e		
FeCl ₃ - <i>hν</i>	MeCN	<i>n</i> -Pentane	1:11:8	[10f]	3-MH	1:4:17	[10f]
		<i>n</i> -Hexane	1:5:5	[10f]		1:4:13	[tw]
		<i>n</i> -Heptane	1:4:4	[10b]			
	<i>i</i> -PrOH	<i>n</i> -Pentane	1:9:9:8	[10f]	3-MH	1:1:5:9	[10f]
		<i>n</i> -Hexane	1:2:5:2	[10f]			
		<i>n</i> -Heptane	1:1:5:3	[10f]			
CrCl ₃ - <i>hν</i>	MeCN	<i>n</i> -Hexane	1:2:2:3	[10f]	2-MB	1:14:9	[13]
		<i>n</i> -Hexane	1:3:3	[13]	3-MH	1:6:30	[18b]
		<i>n</i> -Hexane	1:10:7	[18b]			
H ₂ O ₂ - <i>hν</i>	MeCN	<i>n</i> -Pentane	1:7:7	[19d]	2-MP	1:9:40	[19d]
		<i>n</i> -Hexane	1:7:6	[19d]	3-MP	1:6:39	[19d]
H ₂ O ₂ -V ^V -PCA ^f	MeCN	<i>n</i> -Pentane	1:8:7	[18b]	3-MH	1:14:64	[18b]
		<i>n</i> -Hexane			3-MH	1:11:280	[tw]
Cl ₂ - <i>hν</i>	MeCN						

^a References are given in square parentheses; this work, tw. ^b Relative concentrations of isomeric alcohols formed in the reaction (in the cases where alkyl peroxide is formed, PPh₃ was added to reduce it into the corresponding alcohol) were determined and then normalized, taking into account the number of C–H bonds at each carbon atom of the hydrocarbon chain. ^c Relative reactivities of the C–H bonds at carbon atoms in positions 1, 2, 3 and 4 of the hydrocarbon chain. ^d 2-Methylbutane, 2-MB; 2-methylpentane, 2-MP; 3-methylpentane, 3-MP; 2-methylhexane, 2-MH; 3-methylhexane, 3-MH. ^e Relative reactivities of the C–H bonds at *primary*, *secondary* and *tertiary* carbon atoms of branched hydrocarbons. ^f Pyrazine-2-carboxylic acid, PCA.

as the ratio of the initial oxidation rates of the methylene groups in ethylbenzene and cyclohexane [normalized by taking into account the number of active hydrogens in each molecule according to eq. (7)] ²⁴, is found to be $\Psi = 1.55$. Values of Ψ determined by us for the oxidation of a mixture of cyclohexane and ethylbenzene by HO• radicals are the following: 2.9 for oxidation by H₂O₂ in MeCN–H₂O under irradiation, and 3.6 for oxygenation by Fenton's reagent (FeSO₄–H₂O₂ in MeCN–H₂O). The value of Ψ for attack by hydroxyl radicals generated via pulse radiolysis has been determined ^{22c, d} to be 10.

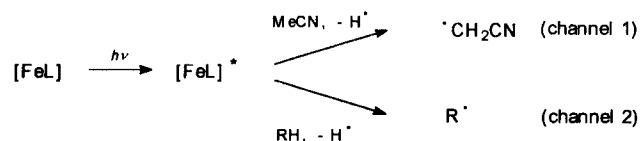
$$\Psi = \frac{k_{\text{PhCH}_2\text{CH}_3}}{k_{\text{C}_6\text{H}_{12}}} = \frac{6([\text{PhCHOHCH}_3] + [\text{PhCOCH}_3])}{[\text{C}_6\text{H}_{11}\text{OH}] + [\text{C}_6\text{H}_{10}\text{O}]} \quad (7)$$

The competitive oxidation of the methyl groups in the pairs *p*-CH₃C₆H₄CH₃–C₆H₅CH₃ and *p*-CH₃C₆H₄NO₂–C₆H₅CH₃ gave an estimation of the Hammett-Brown parameter $\rho^+(\sigma^+) = -1.1$.

On the basis of the results described above we can propose the following mechanism for alkane aerobic photo-oxidation catalyzed by FeCl₃ in MeCN. One may assume that upon dissolving FeCl₃·6H₂O in MeCN a number of species are formed, i.e. [FeCl_k(OH₂)_l(OH)_m(NCMe)_n]^{x+}, where *k*, *l*, *m* and *n* = 0–6. The first step of the process is the photoexcitation of the ferric complex. This process is well-known for iron(III) derivatives ²⁵ as well as for many other transition-metal-chloride complexes ²⁶. Then photoexcited iron-chloride species can react with the solvent, MeCN (channel 1) and the alkane, RH (channel 2) to produce the corresponding NCCH₂• and R• radicals (Scheme 1). Both radicals are capable of reacting further with molecular oxygen and other

components of the solution (i.e. R• can react with MeCN, whereas NCCH₂• attacks RH, the coupling of radicals also being possible). It seems that channel 2 is the predominant one (when the concentration of cyclohexane is high of course) and the concentration of products formed from MeCN is relatively small. In any case, we have not detected and investigated these products, in particular. However, we have kinetic evidence that MeCN also takes part in the photo-oxidation process (vide infra, see also Fig. 3).

The mode of interaction between hydrocarbon, RH, and photoexcited species depends on the nature of the latter. We suggest that the main route leading to the formation of R• radicals via hydrogen atom abstraction is the following. The photoexcitation of the ferric-chloride species induces electron transfer from the chloride anion to the iron(III) ion to generate a ferrous derivative (which is known to be relatively stable) and the extremely reactive chlorine radical, Cl•. The latter seems to be the crucial species in the whole process. Indeed, the chlorine radical is capable of attacking a hydrocarbon, RH, to produce an alkyl radical, R•. The other products are HCl (or H⁺ and Cl[–]). The arguments supporting the assumption about the key role of chlorine radical are given below.

**Scheme 1.** – Two possible channels for the interaction of the photoexcited iron-containing species with the components of the solution.

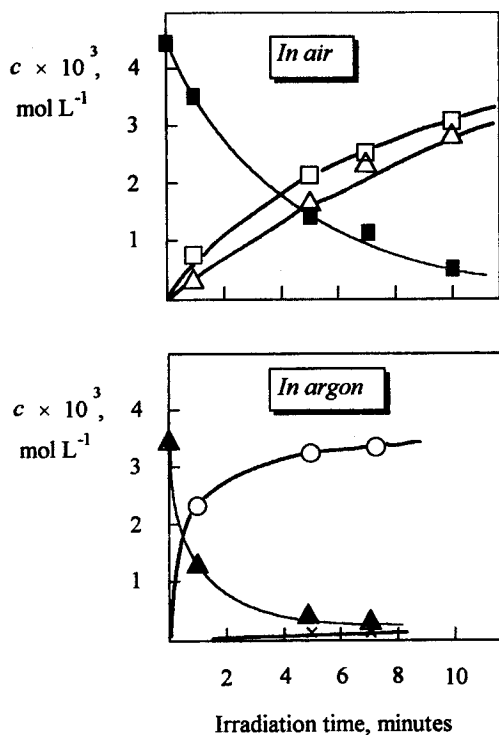
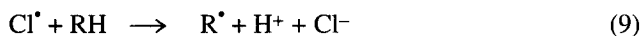


Figure 7. — Reaction of molecular chlorine with cyclohexane (0.46 mol L^{-1}) in MeCN in the presence of LiCl ($2.0 \times 10^{-2} \text{ mol L}^{-1}$) under irradiation in air (top) and in an argon atmosphere (bottom). The consumption of Cl_2 (closed squares and triangles), the accumulation of cyclohexanol (open squares), cyclohexanone (open triangles), cyclohexyl chloride (open circles), cyclohexyl chloride (open circles) and the sum of cyclohexanol and cyclohexanone (crosses) are shown. Samples were reduced by triphenylphosphine before GLC analysis.

We have found that irradiation in air of a solution of cyclohexane and molecular chlorine in MeCN (Fig. 7, top), like photo-oxygenation in the presence of FeCl_3 , yields oxygenated products with the dependencies of the initial reaction rates on $[\text{cyclo-C}_6\text{H}_{12}]_0$ being very similar (see Fig. 4). Assuming, as previously done that the dependence of the oxidation rate on $[\text{cyclo-C}_6\text{H}_{12}]_0$ reflects the competition between the hydrocarbon and acetonitrile in the interaction with the chlorine atom, we can obtain the ratio of the constants $k_{\text{RH}}/k_{\text{MeCN}} = 0.13$. The coincidence of this value with the parameter previously calculated for the transient species generated in the photolysis of FeCl_3 confirms that the cyclohexane oxygenation is induced by the chlorine atom. In accordance with the model described previously (eq. 6), the segment of the ordinate cut off by the straight line in the plot of $(-\text{d}[\text{RH}]/\text{dt})^{-1}$ versus $[\text{cyclo-C}_6\text{H}_{12}]_0^{-1}$ (Fig. 4) corresponds to the reciprocal rate of active species generation. Consequently, the data presented in Figure 4 allow one to conclude that under the conditions used the rate of Cl^\bullet generation from Cl_2 is 5 times higher than that in the photolysis of FeCl_3 .

The generation of alkylperoxy radicals photoinduced by molecular chlorine can be described by the following equations.

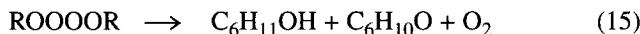
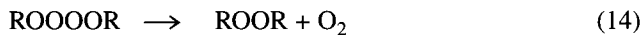


The primary active species (chlorine atom) is common to both systems under consideration.

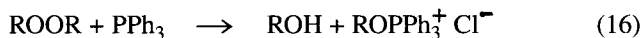
The first result corresponds to the regeneration of FeCl_3 , that is to the reoxidation by dioxygen or ROO^\bullet of FeCl_2 , which is produced in the primary photochemical step. In contrast, in the Cl_2 -stimulated reaction, species that might be reducing agents are not formed and regeneration of a photochemically active particle is impossible. This explanation helps in understanding the second distinction between the two systems. Indeed, in the FeCl_2 -containing system the alkyl hydroperoxide can be produced by the following route:



It is reasonable to assume that in the system with Cl_2 , dialkyl peroxide ROOR is a transient species that can be generated via the following mechanism (see, e.g., ref. 29b):



In this reaction solution, i.e. the solution that contains HCl, triphenylphosphine is apparently able to reduce dialkyl peroxide:



The fact that the concentrations of alcohol and ketone after addition of triphenylphosphine are equal testifies that ROOR and ROOH are present in the reaction solution only in small concentrations. This may be due to rapid decomposition of ROOR, which is less stable than ROOH, whereas the latter is not formed at all. An alternative route leading to the formation of an alkyl radical is electron transfer from the alkane to the photoexcited iron complex. Such a mechanism has been detected by laser pulse photolysis of the reaction between FeCl_4^- and ethanol^{25b, 28}. In our case, however, this route seems to be less probable due to the much higher ionization potentials of both MeCN and the alkane in comparison with that of aliphatic alcohols.

The third possible route to produce radical R^\bullet from the alkane RH does not involve chlorine ions and radicals at all as key intermediate species. In this mechanism, hydroxyl radical or the ferryl species $\text{Fe}^{\text{V}}=\text{O}$ may be assumed to be the crucial reactive intermediates capable of abstracting a

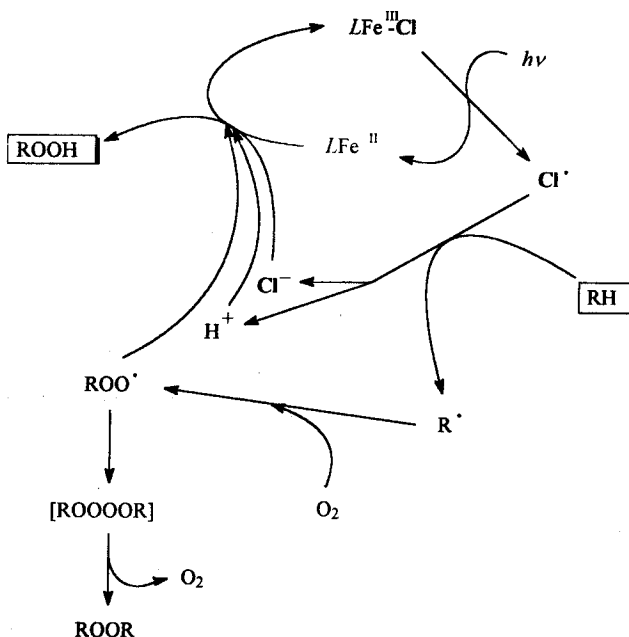
hydrogen atom from the alkane. Naturally, these possibilities become the only reasonable routes when going from the alkane photo-oxygenation promoted by FeCl_3 to that induced by the chlorine-free complexes (see below). Of course, in the case of FeCl_3 the latter two routes may be involved in the process to some extent, but we propose that their importance in the overall yield of oxygenated products is much less than that of the chlorine-mediated route. Indeed, the route involving hydroxyl radicals should photo-hydroxylate benzene into phenol. However, we have been unable to detect the formation of phenol when a benzene solution in MeCN was irradiated in the presence of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

It is well-known²⁹ that the alkyl radical adds molecular oxygen to give a new radical, ROO^\bullet . This is a fast step as rate constants for the reaction



at ambient temperature range from 10^6 up to 5×10^9 $\text{L mol}^{-1} \text{s}^{-1}$; for cyclohexyl radical this value is 3.4×10^9 $\text{L mol}^{-1} \text{s}^{-1}$ (see ref. 29a).

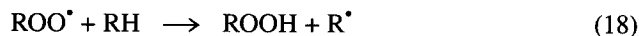
The peroxy radical, ROO^\bullet , formed in the reaction is most likely reduced by Fe(II) into the anion ROO^- , which can add a proton to produce alkyl hydroperoxide, the first relatively stable product of this oxidation. The oxidized iron species adds to chloride anion and is thus transformed into the initial catalytically active particle. The overall catalytic cycle is depicted in Scheme 2. The transformation in which the



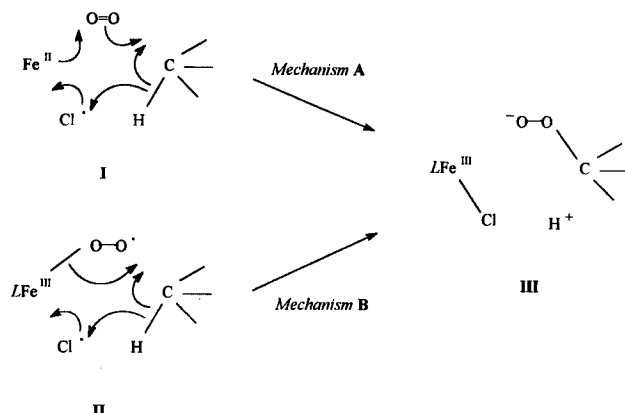
Scheme 2. – Proposed mechanism for FeCl_3 -catalyzed photo-oxygenation of alkane, RH , in MeCN. In addition to the chloride ligand, the iron ion bears any other ligand, L , present in the reaction system (Cl^- , HO^- ; H_2O , MeCN, OO^\bullet).

redistribution of electrons, within a complex formed between the excited iron species, a dioxygen molecule and the alkane, occurs simultaneously can be excluded (Scheme 3, Mechanism A). Indeed the reactivity of transient species in the presence of FeCl_3 and Cl_2 is the same. Moreover, the short lifetime of an excited state of the iron complex practically excludes the possibility of trimolecular interactions. However, the analogous mechanism involving an iron-peroxy complex instead of a free dioxygen molecule, as well as the reaction between Fe(II) with O_2 instead of reaction (11) (Scheme 3, Mechanism B), seems to be more probable. However, if this mechanism is really operative the similarity of the active transient species reactivities in the cases of FeCl_3 and Cl_2 is surprising.

It is important to note that the decomposition of alkyl hydroperoxide might initiate a radical chain auto-oxidation of a hydrocarbon. In order to investigate whether such a process really takes place we carried out the photo-oxidation of cyclohexane under the action of the system considered in this paper absence and in the presence of cyclohexyl hydroperoxide. It is clear that, should the alkyl peroxide decomposition give radicals that are reactive in the cyclohexane oxidation, the addition of ROOH would accelerate the accumulation of oxygenated products. Figure 8 demonstrates, however, that no increase in the reaction rate is noticed in the presence of cyclohexyl hydroperoxide. It also seems that in the case of cyclohexane (RH) at ambient temperature the effect of the radical chain route according to equations (17) and (18),



is negligible since the effective activation energy of the oxidation is low (ca. 13 kJ mol^{-1}) and since the addition of 2,6-di(*tert*-butyl)-4-methylphenol and methylmethacrylate, which are known as free-radical chain-reaction inhibitors³⁰, do not affect the rate of cyclohexane oxyge-



Scheme 3. – Tentatively assumed mechanisms for synchronous hydroperoxidation of the C–H bond in the alkane by the iron species and dioxygen molecule (Mechanism A) and by the excited iron peroxy complex (Mechanism B).

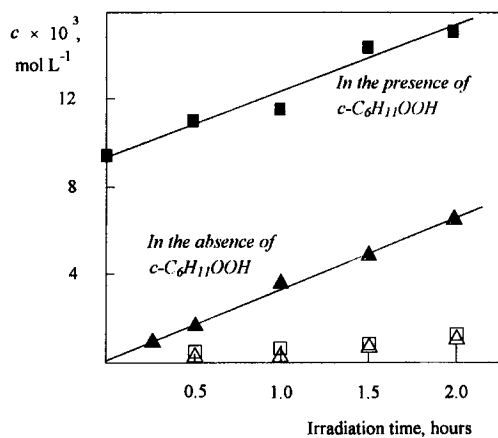


Figure 8. – Kinetics of the accumulation of cyclohexanol (closed symbols) and cyclohexanone (open symbols) in the photo-oxidation of cyclohexane (0.46 mol L^{-1}) catalyzed by FeCl_3 ($5.0 \times 10^{-4} \text{ mol L}^{-1}$) in the presence (initial concentration $9.5 \times 10^{-3} \text{ mol L}^{-1}$; squares) and in the absence (triangles) of cyclohexyl hydroperoxide. Samples of the reaction solution were reduced by triphenylphosphine before GLC analysis.

nation. In the case of ethylbenzene, and especially for cumene whose C–H bonds are weaker, the involvement of the free-radical channel (equations 1 and 2) in the overall oxidation process may be greater. Scheme 2 also shows a route in which ROO^\bullet radicals are transformed into ROOR dialkylperoxides. We propose that these compounds can be formed in the photocatalyzed oxygenation (see, e.g., ref. 22b), however in the present work, we have not attempted to identify them among the reaction products.

The alkyl peroxide formed in the alkane photo-oxygenation catalyzed by FeCl_3 is an unstable compound and decomposed (see, e.g., refs. 31) to produce mainly cyclohexanol and cyclohexanone, as well as other products, including C–C bond cleavage products (for example, adipic acid in the case of cyclohexane)³². The rate of pure cyclohexyl hydroperoxide decomposition is very low if the solution of the hydroperoxide in MeCN is irradiated in the absence of iron compound or in the presence of FeCl_3 in the dark. However, a rapid decrease of the peroxide concentration is noticed when the solution is irradiated in the presence of FeCl_3 . The plot of cyclohexanone concentration *versus* time exhibits a maximum at 1 h and even then, the maximum cyclohexanone concentration is only 1/4 of the initial concentration of starting cyclohexyl hydroperoxide. After 1 h the total concentration of starting cyclohexyl hydroperoxide and that of cyclohexanone plus cyclohexanol formed is ca. $0.4 \times 10^{-3} \text{ mol L}^{-1}$, whereas the initial concentration of cyclohexyl hydroperoxide was $0.75 \times 10^{-3} \text{ mol L}^{-1}$. After 3 h irradiation the concentration of cyclohexanone is ca. $0.1 \times 10^{-3} \text{ mol L}^{-1}$, the concentration of cyclohexanol (and cyclohexyl hydroperoxide) being negligible. These results testify that, in addition to the cyclohexanol and cyclohexanone detected by GLC, sufficient amounts of other products that have not been detected by GLC analysis are formed during the cyclohexyl hydroperoxide decomposition photocataly-

zed by FeCl_3 . One may assume that adipic acid and other products from oxidative cleavage of the C–C bond in the aliphatic ring are formed. No attempt to detect all these numerous products in the case of cyclohexane photo-oxygenation has been made in the present work.

Table II. – Photo-oxygenation of cyclohexane promoted by FeCl_3 ^a.

Run	Percentage of MeCN, v/v, %	Amount of oxygenated products, ^b mol		Ratio <i>allone</i>
		Cyclohexanone	Cyclohexanol	
1	0	1.8×10^{-6}	0	0
2	6	0.4×10^{-5}	0.1×10^{-3}	0.25
3	80	0.6×10^{-3}	3.4×10^{-3}	5.7

^a A mixture of 0.2 mL of cyclohexane, $1.25 \times 10^{-5} \text{ mol}$ of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and H_2O –MeCN (total 2 mL) was irradiated in air during 2.5 h. ^b After reduction with triphenylphosphine.

In the presence of excess cyclohexane the peroxide decomposes much more slowly to mainly produce cyclohexanone. Since the more or less rapid decomposition of ROOH is observed only under simultaneous action of light and FeCl_3 it is reasonable to assume that this process is induced by primary species that are formed during photolysis of FeCl_3 . If so, the higher rate of ROOH decomposition in the absence of cyclohexane is apparently due to the competition between ROOH and RH in their interaction with the chlorine atom.

Cumene is known to be easily oxidized to yield cumyl hydroperoxide, which decomposes to form acetophenone, a stable product easily detectable by GLC. We have found that irradiation of a solution of cumene in MeCN in the presence of FeCl_3 produces a mixture of oxygenated products. The composition of these products detected by GLC in samples untreated with PPh_3 is noticeably different from the composition of the reduced reaction mixture (Fig. 9). The main peculiarity of this oxygenation is the relatively slow decomposition of the cumene hydroperoxide formed to produce acetophenone. The oxygenation of cumene in aqueous emulsion photocatalyzed by $\text{Fe}(\text{ClO}_4)_3$ yields a much greater amount of acetophenone (see below).

FeCl₃ catalyzed photo-oxidation in other organic solvents

The photochemical alkane oxygenation catalyzed by FeCl_3 can be carried out not only in acetonitrile but also in other organic solvents such as acetone (Fig. 10), acetic acid, nitromethane, *tert*-butanol, dichloromethane (see refs. 10a–c) and even primary and secondary aliphatic alcohols^{10f}. As Figure 10 demonstrates, these oxidations give sufficient amounts of alkyl peroxides. Aliphatic alcohols apparently reduce peroxides *in situ*; due to this, hydroxylated alkanes

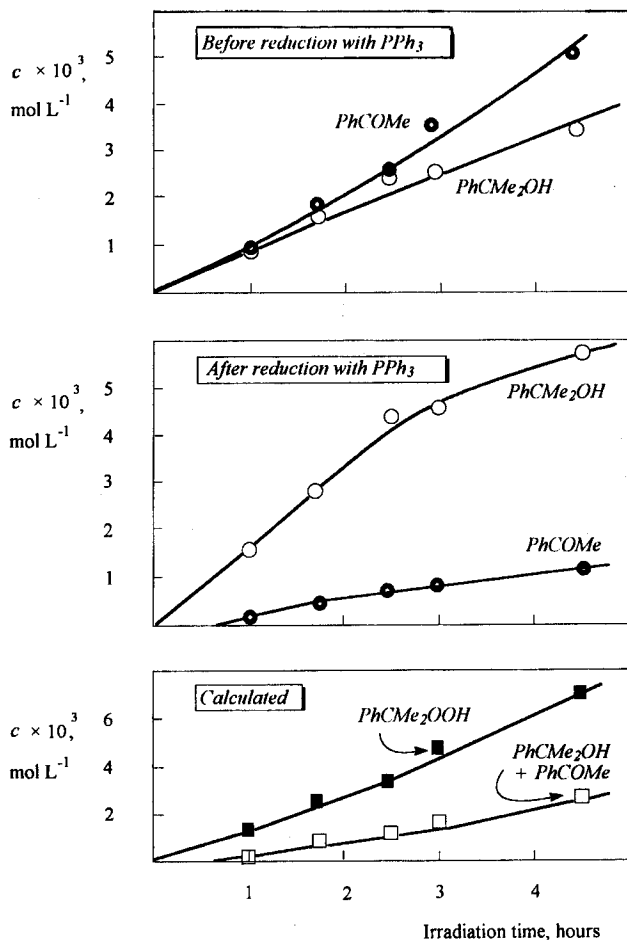


Figure 9.—Kinetics of the aerobic photo-oxidation of cumene (0.46 mol L^{-1}) in MeCN in the presence of FeCl_3 ($5.0 \times 10^{-4} \text{ mol L}^{-1}$). *Top:* the accumulation of cumyl alcohol (open circles) and acetophenone (closed circles) before reduction with PPh_3 . *Middle:* the same when the reaction solution is reduced with PPh_3 before GLC analysis. *Bottom:* concentration of cumene peroxide (closed squares) and the sum of cumyl alcohol and acetophenone (open squares), estimated from the data shown at the top and in the middle of the figure, vs time.

are predominant in the reaction solutions. Since $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is insoluble in dichloromethane the addition of an alkylammonium salt is necessary to introduce the catalytically-active species into solution. In this case, noticeable amounts of alkyl chlorides are also detected in the reaction mixture besides alcohol and ketone (aldehyde) ^{10b}.

Photo-oxidation in an aqueous emulsion catalyzed by $\text{Fe}(\text{ClO}_4)_3$ and FeCl_3 : ketonization of the C–H bond and “unusual” 1°:2°:3° selectivity

When investigating the photocatalytic behavior of FeCl_3 in alkane oxygenation it was important to check if other iron

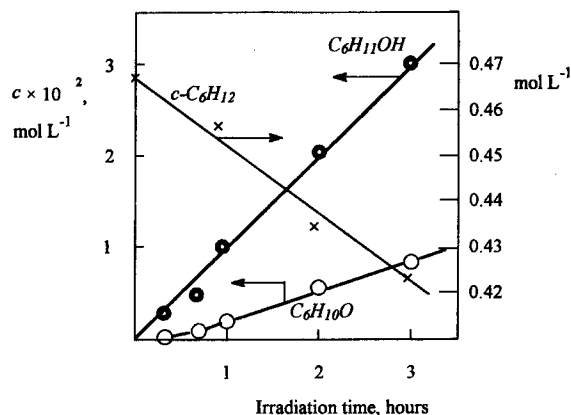


Figure 10.—Kinetic of the aerobic photo-oxygenation of cyclohexane (crosses) in acetone in the presence of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ($5.0 \times 10^{-4} \text{ mol L}^{-1}$). Concentrations of cyclohexanol (closed circles) and cyclohexanone (open circles) were determined by GLC in samples of the reaction solution after reduction with PPh_3 .

compounds were able to induce hydrocarbon oxidation under light irradiation. We have found that iron(II)-containing species, photochemically generated from various π -cyclopentadienyl and π -arene complexes in MeCN, do catalyze aerobic photo-oxidation of alkanes to give alkyl hydroperoxides, which partially decompose to produce the corresponding alcohols and ketones ⁹. It is clear that the mechanism of such a process is different from that proposed for the ferric chloride-catalyzed oxidation. Unfortunately, a simpler iron derivative, $\text{Fe}(\text{ClO}_4)_3$, is insoluble in acetonitrile or acetone. This fact prompted us to investigate the aerobic photo-oxygenation of cyclohexane catalyzed by $\text{Fe}(\text{ClO}_4)_3$ in aqueous acetone and an aqueous emulsion.

We have found that both FeCl_3 and $\text{Fe}(\text{ClO}_4)_3$ induce photochemical aerobic oxygenation of alkanes in solutions containing water. Figure 11 shows the kinetics for the accumulation of oxygenated products in the reaction catalyzed by $\text{Fe}(\text{ClO}_4)_3$ and carried out in aqueous acetone. Cyclohexane forms a homogeneous solution, although the iron derivative is present in the reaction mixture as a gel. Cyclohexanol and cyclohexanone have been detected by GLC in approximately equal concentrations in samples before the reduction with PPh_3 . It is thus obvious that cyclohexyl peroxide is the main primary oxidation product, which then gradually decomposes to yield cyclohexanol and cyclohexanone.

Another example is the oxygenation of cyclohexane in an aqueous emulsion. Although the oxidation in this case is not effective (turnover number based on the iron salt is < 1 after 3 h irradiation), the products detected by GLC turned out to be “unusual”. Indeed, cyclohexanone has been found to be the sole product of the reaction. Analogous selectivity has been found in the oxidation promoted by FeCl_3 . When a mixture of 0.2 mL ($1.85 \times 10^{-3} \text{ mol}$) of cyclohexane and 2.3 mL of aqueous solution containing

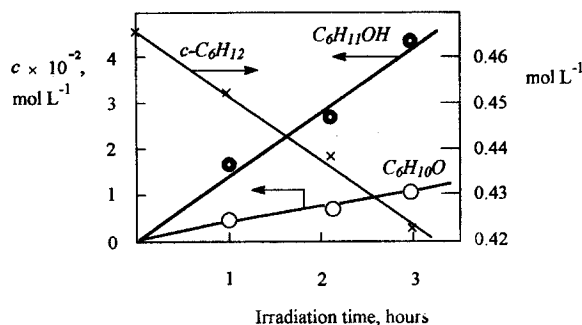


Figure 11. – Kinetics of the cyclohexane (0.125 mL) photo-oxidation in a acetone (2.125 mL)-water (0.25 mL) mixture in the presence of $\text{Fe}(\text{ClO}_4)_3$ (1.25×10^{-5} mol). Accumulation of cyclohexanol (closed circles) and cyclohexanone (open circles) and the conversion of cyclohexane (crosses) are shown. Samples of the reaction mixture were treated with PPh_3 before GLC analysis.

1.15×10^{-5} mol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was irradiated during 2.5 h, cyclohexanone (1.8×10^{-6} mol) was detected by GLC after extraction of the solution with chloroform. The amounts of cyclohexanol and cyclohexyl peroxide were not more than 10^{-8} mol.

If acetonitrile is present in the solvent a “usual” selectivity was noticed (i.e. cyclohexanol, cyclohexanone and cyclohexyl peroxide were detected in the reaction mixture), although the total yield of oxygenated products was much higher in this case (Table II). The latter feature is not surprising because in the presence of acetonitrile the solubility of cyclohexane is enhanced. As for the aqueous emulsion of cyclohexane, the aerobic photo-oxidation apparently occurs in a region close to the interface between the two phases. It should be noted that while iron(III) chloride and perchlorate exhibit comparable activities in the cyclohexane ketonization, iron(III) or iron(II) sulfate give only negligible amounts of oxygenation products ($< 2 \times 10^{-7}$ mol after 2 h irradiation).

Generally speaking, the oxygen atom that is inserted into the C–H bond of cyclohexane can come not only from atmospheric oxygen but also from water or the ClO_4^- anion. In order to check all these possibilities, we carried out the photo-oxidation of cyclohexane in the presence of $\text{Fe}(\text{ClO}_4)_3$ in a cyclohexane aqueous emulsion previously saturated with argon (argon was bubbled through the emulsion for 0.5 h before the oxidation and then during irradiation). It has been found, however, that irradiation in an argon atmosphere (1.85×10^{-3} mol of cyclohexane, 1.15×10^{-5} mol of iron perchlorate and 2.3 mL of water) for 2 h gives not more than 1.0×10^{-8} mol of cyclohexanone. Thus, it may be concluded that atmospheric dioxygen is the sole provider of the oxygen atom in the system under consideration.

Other alkanes are also oxygenated in aqueous emulsion to produce exclusively ketones (aldehydes). Thus, after irradiation in an aqueous solution of $\text{Fe}(\text{ClO}_4)_3$ under the

conditions described above, *n*-hexane gives a mixture of hexan-2-one and hexan-3-one (the ratio C-2:C-3 = 1:1.4) as the main products with a considerably smaller amount of hexanal. The oxidation of 3-methylhexane gave a complex mixture of products, with the relative amount of tertiary alcohol (after reduction with PPh_3) being small (the ratio 1°:2°:3° = 1:2.6:0.7). When the reaction solution was injected into the chromatograph without preliminary reduction with triphenylphosphine the peak corresponding to the tertiary alcohol was not observed at all. The photo-oxygenation of cumene in aqueous emulsion (Fig. 12) occurs with a long induction period and gives primarily cumene hydroperoxide, which then decomposes to yield predominantly acetophenone and a smaller amount of cumyl alcohol.

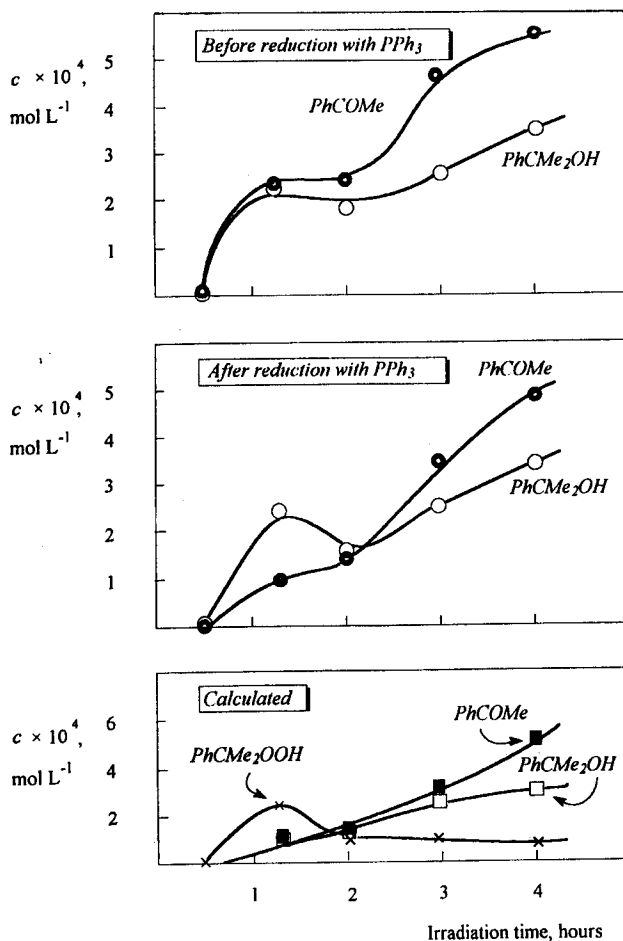
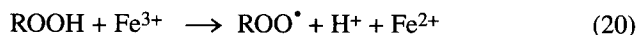
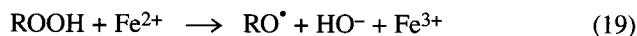


Figure 12. – Kinetics of the aerobic photo-oxidation of cumene (0.022 mol) in an aqueous emulsion (0.25 mL H_2O) in the presence of $\text{Fe}(\text{ClO}_4)_3$ (1.25×10^{-5} mol). *Top*: the accumulation of cumyl alcohol (open circles) and acetophenone (closed circles) before the reduction with PPh_3 . *Middle*: the same when the reaction solution is reduced with PPh_3 before GLC analysis. *Bottom*: concentration of cumene peroxide (crosses), cumyl alcohol (open squares) and acetophenone (closed squares), estimated from the data shown at the top and the middle of the figure, vs time. Concentrations are measured for the solution in cumene phase.

We propose that, like FeCl_3 , iron perchlorate induces the photo-oxygenation of alkane to give primarily alkyl hydroperoxide. In contrast to the FeCl_3 -photocatalyzed reaction in MeCN, in this case ROOH rapidly decomposes, affording ketone as the main or sole detectable product. Although the mechanism of the photo-oxidation promoted by FeCl_3 in MeCN seems to be more or less clear, we can only assume a few possible routes that lead to the formation of alkyl peroxide or ketone. We believe that the crucial step of the photo-oxidation in aqueous emulsion promoted by $\text{Fe}(\text{ClO}_4)_3$ is also the hydrogen atom abstraction from the alkane, RH, to produce the radical R^\bullet , which rapidly reacts with O_2 to finally give rise to ROOH. A species that abstracts the hydrogen atom might be the hydroxyl radical or a radical-like iron complex. Hydroxyl radicals are possibly not the only active species in the reaction under discussion (photohydroxylation of benzene in aqueous acidified solution promoted by the iron ion has been reported³³). These radicals apparently cannot be the key species in oxygenation.

We assume that alkyl hydroperoxide is a primary product of the reaction. It seems that this peroxide is selectively transformed into cyclohexanone under the conditions employed. To check this proposal, we investigated the decomposition of pure cyclohexyl hydroperoxide, ROOH, in aqueous solution. It turns out that in the dark at room temperature ROOH ($4.0 \times 10^{-2} \text{ mol L}^{-1}$) produces cyclohexanone very slowly even in the presence of $\text{Fe}(\text{ClO}_4)_3$ ($5.0 \times 10^{-2} \text{ mol L}^{-1}$) or HClO_4 ($5.0 \times 10^{-2} \text{ mol L}^{-1}$) (cyclohexanone concentration were $< 1.0 \times 10^{-4}$ and $7.0 \times 10^{-4} \text{ mol L}^{-1}$, respectively). The experiment with HClO_4 was carried out because the pH of an aqueous solution of $\text{Fe}(\text{ClO}_4)_3$ is 2.25 when its concentration is $8.0 \times 10^{-3} \text{ mol L}^{-1}$, due to the hydrolysis. However, perchloric acid does not affect the rate of ROOH decomposition, either in the dark or under irradiation. In contrast to the dark reaction, under irradiation $\text{Fe}(\text{ClO}_4)_3$ does induce the selective transformation of ROOH to cyclohexanone. Thus, after 7 h irradiation of an aqueous solution of cyclohexyl hydroperoxide (concentration $2.5 \times 10^{-2} \text{ mol L}^{-1}$) in the presence of $\text{Fe}(\text{ClO}_4)_3$ ($5.0 \times 10^{-2} \text{ mol L}^{-1}$), cyclohexanone ($2.1 \times 10^{-2} \text{ mol L}^{-1}$) was found in the reaction mixture and no cyclohexanol (concentration $< 10^{-4} \text{ mol L}^{-1}$) was detected by GLC. The cyclohexanone formed can apparently accelerate the transformation of peroxide^{31b}. It is also interesting that some compounds that are able to form hydrogen bonds with ROOH have been shown to catalyze the selective decomposition of hydroperoxides^{31c}. In our case, as mentioned above, when acetonitrile is added to an aqueous solution the selectivity of the process decreases. Earlier, we described the influence of the nature of the solvent on the selec-

tivity of alkane oxidation photocatalyzed by the system CrCl_3 / tetraalkylammonium chloride¹³. The mechanism of the alkyl hydroperoxide decomposition photocatalyzed by iron derivatives (both in MeCN and aqueous emulsion) is unclear. It may be a chain process analogous to those proposed for the Co-catalyzed thermal decomposition^{31e, f}:



The predominant formation of products arising from oxidative activation of the *secondary* C–H bond in branched hydrocarbons is evidently due to the extensive decomposition, in the course of the photoreaction, of the alkylhydroperoxide formed by attack at the *tertiary* position. Such a decomposition of *tert*-alkyl hydroperoxide yields products of the C–C bond splitting and consequently the relative amount of products oxygenated at the *tertiary* carbon is decreased. One may suspect that in some other cases, including reactions in the dark (e.g., Gif-systems⁴), “unusual” selectivity (i.e., predominant formation of ketones and the ratio $2^\circ > 3^\circ$) is also due to the selective decomposition of initially-formed alkyl hydroperoxide. Indeed, in preliminary experiments we have found that vigorous 2 h stirring in air of a mixture of cyclohexane (0.25 mL; $2.2 \times 10^{-3} \text{ mol}$), iron(III) perchlorate ($1.0 \times 10^{-5} \text{ mol}$), zinc dust (6.5 mg; $1.0 \times 10^{-4} \text{ mol}$) and water (2.5 mL) gave cyclohexanone ($1.5 \times 10^{-7} \text{ mol}$) and a noticeably smaller amount ($3.0 \times 10^{-8} \text{ mol}$) of cyclohexanol. Cyclohexyl peroxide is not formed since the reduction with triphenylphosphine does not affect the ketone:alcohol ratio, as detected by GLC of the reaction solution samples before and after reduction. It should be noted, however, that the good mass balance (see., e.g., ref 4d) may testify against the assumption that cleavage of the C–C bonds is the reason for the “unusual” ($2^\circ > 3^\circ$) selectivity in the Gif-type reactions.

Acknowledgments

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