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Selective Photochemical Ketonization of Cyclohexane by Air in an Aqueous Emulsion in the Presence of Iron Ions

Georgiy B. Shul'pin* and Galina V. Nizova

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russian Federation.
Fax: +7 095 938 2156

Light irradiation of an emulsion of cyclohexane and an aqueous solution of iron(III) perchlorate (or chloride) in air produces exclusively cyclohexanone; no cyclohexanol or cyclohexyl hydroperoxide is detected.

Metal-promoted oxidations of saturated hydrocarbons by oxygen (and especially by air)[1] play a very important role since they are convenient routes in the transformation of oil and natural gas constituents into valuable chemical products. Such light-induced processes[2] seem to be useful not only for chemical synthesis and in industry but also in the solution of some environmental problems (*e.g.* the removal of oil contamination under solar irradiation[3]). The photooxidation of alkanes and alkylaromatics promoted by soluble metal salts and complexes[4] and TiO_2 semiconductor[5] has been intensively investigated in the past decade. Usually these reactions are not highly selective as far as products are concerned, giving rise to a complex mixture, the main products being alcohol, ketone (aldehyde) and alkyl hydroperoxides. (It should be noted that in previous work the peroxides formed were not apparently detected because they are easily decomposed in a chromatograph to produce ketone and alcohol in approximately equal amounts[6]). Only a few examples of selective ketone formation in photochemical[4d] and dark[7] oxygenation of alkanes have been described.

Earlier, we showed that irradiation of a solution of alkane in acetonitrile[8a,b] or even in alcohol[8c] in the presence of $FeCl_3$ or in acetonitrile in the presence of cyclopentadienyl complexes of iron(II)[8d] in air produces alkyl peroxides that are partially decomposed to form ketone (aldehyde) and alcohol. The amounts of the three products which could be estimated if concentrations of ketone and alcohol are measured by GLC before and after the reduction of peroxide to alcohol by triphenylphosphine (for details, see refs. 8*b* and 9) are comparable (*ca.* 1:1:1).

When we carried out the aerobic photooxidation of cyclohexane in the presence of $FeCl_3$ in an aqueous emulsion instead of a homogeneous solution in acetonitrile, we surprisingly detected cyclohexanone as the sole product. Thus, a mixture of 0.2 ml (1.85×10^{-3} mol) of cyclohexane and 2.3 ml of aqueous solution containing 1.15×10^{-5} mol of $FeCl_3{\cdot}6H_2O$ was irradiated[†] during 2.5 h. Cyclohexanone (1.8×10^{-6} mol) was detected after extraction of the solution with chloroform by GLC. The amounts of cyclohexanol and cyclohexyl peroxide were not more then 10^{-8} mol. Moreover, iron(III) perchlorate also turned out to be a rather effective promoter of cyclohexane ketonization although it does not contain chlorine ions which upon irradiation could be transformed into active chlorine radicals.[8a–c] Under analogous conditions [0.1 ml of cyclohexane, 2.0 ml of H_2O containing 1.25×10^{-5} mol of $Fe(ClO_4)_3$] cyclohexanone was the sole product detected:

Irradiation time/min	10	20	30	60	160
Cyclohexanone/10^{-6} mol	0.1	0.3	0.5	0.9	1.7

It is noteworthy that if acetonitrile was present in the solvent the '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 1). The latter feature is not surprising because in the presence of acetonitrile the solubility of cyclohexane is enhanced. As for an aqueous emulsion of cyclohexane, aerobic photooxidation apparently occurs in the region close to the border between the two phases. Unfortunately, our attempts to use phase-transfer catalysts have so far been unsuccessful due to the rapid decomposition of alkylammonium salts under the conditions employed. However, work directed towards improving the efficacy of the reaction is in progress. It should be noted that while iron(III) chloride and perchlorate exhibit comparable activities in cyclohexane ketonization, iron(III) or iron(II) sulfate or copper salts (chloride or sulfate) give only negligible amounts of oxygenation products ($< 2 \times 10^{-7}$ mol after 2 h irradiation).

Other alkanes are also oxygenated by the system under consideration, producing exclusively ketones (aldehydes). Thus, after irradiation with an aqueous solution of $Fe(ClO)_4$ under the conditions described above, *n*-hexane gives a mixture of hexan-2-one and hexan-3-one (ratio C-2:C-3 = 1:1.4) as the main products with a considerably smaller amount of hexanal.

Table 1 Photooxygenation of cyclohexane promoted by $FeCl_3$.[a]

Run	Percentage of MeCN, v/v (%)	Amounts of oxygenated products/mol[b]		
		Cyclohexanone	Cyclohexanol	Ratio -ol/-one
1	0	1.8×10^{-6}	0	0
2	6	0.4×10^{-5}	0.1×10^{-5}	0.25
3	80	0.6×10^{-3}	3.4×10^{-3}	5.7

[a] A mixture of 0.2 ml of cyclohexane, 1.25×10^{-5} mol of $FeCl_3{\cdot}6H_2O$ and H_2O–MeCN (total 2 ml) was irradiated in air during 2.5 h. [b] After reduction with triphenylphosphine.

Generally speaking, a source of oxygen which is inserted into the C–H bond of cyclohexane might not only be atmospheric oxygen but also water and ClO_4^- anion. In order to check all these possibilities, we carried out the photooxidation of cyclohexane in the presence of $Fe(ClO_4)_3$ in a cyclohexane aqueous emulsion previously saturated with argon (argon was bubbled through the emulsion during 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) during 2 h gives not more than 1.0×10^{-8} mol of cyclohexanone.

We believe that the crucial stage of the reaction described here is the hydrogen atom abstraction from alkane, RH, to produce radical $R^{\cdot}$, which rapidly reacts with O_2 giving rise finally to ROOH. A species which abstracts the hydrogen atom might be hydroxyl radical or a radical-like iron complex. Different possible stages leading to cyclohexyl hydroperoxide are the following:

$$\mathrm{Fe^{III}{-}OH} \xrightarrow{h\nu} \mathrm{Fe^{II}} + \mathrm{HO^{\cdot}} \tag{1}$$

$$\mathrm{HO^{\cdot}} + \mathrm{RH} \longrightarrow \mathrm{H_2O} + \mathrm{R^{\cdot}} \tag{2}$$

$$\mathrm{Fe^{II}} + \mathrm{O_2} \longrightarrow \mathrm{Fe^{III}{-}OO^{\cdot}} \tag{3}$$

$$\mathrm{Fe^{III}OO^{\cdot}} + \mathrm{RH} \xrightarrow{(h\nu?)} \mathrm{Fe^{III}{-}OOH} + \mathrm{R^{\cdot}} \longrightarrow \mathrm{Fe^{II}} + \mathrm{ROOH} \tag{4}$$

$$\mathrm{Fe^{III}} + \mathrm{HO^{\cdot}} \longrightarrow \mathrm{Fe^{IV}O} + \mathrm{H^+} \tag{5}$$

$$\mathrm{Fe^{IV}O} + \mathrm{RH} \longrightarrow \mathrm{Fe^{III}OH} + \mathrm{R^{\cdot}} \tag{6}$$

$$\mathrm{R^{\cdot}} + \mathrm{O_2} \longrightarrow \mathrm{ROO^{\cdot}} \tag{7}$$

$$\mathrm{ROO^{\cdot}} + \mathrm{Fe^{II}} + \mathrm{H^+} \longrightarrow \mathrm{ROOH} + \mathrm{Fe^{III}} \tag{8}$$

$$\begin{aligned} \mathrm{R'R''HC^{\cdot}} + \mathrm{O_2} + \mathrm{Fe^{II}} &\longrightarrow \mathrm{R'R''HC{-}OO{-}Fe^{III}} \longrightarrow \\ &\qquad \mathrm{R'R''C{=}O} + \mathrm{Fe^{III}{-}OH} \end{aligned} \tag{9}$$

Stages (1)–(6) demonstrate various possible routes to alkyl radical, $R^{\cdot}$. Stage (4) was initially proposed by us for alkane oxidation photocatalysed by cyclopentadienyl complexes of iron(II)[8d] and affords directly alkyl hydroperoxide. Stages (7)–(9) are concerned with possible ways from radical $R^{\cdot}$ to oxygenated products, step (9) being assumed[4d] for the mechanism of the reaction photocatalysed by iron porphyrinate and gives directly ketone. Stages (5) and (6) were proposed for the anaerobic cyclohexanol hydroxylation catalysed by iron(III) ion[10] and are identical with crucial steps in oxygenations catalysed by cytochrome P-450. If $R^{\cdot}$ reacts with $Fe^{III}OH$ the formation of ROH should be detected, which was not observed in our case.

As mentioned above, we assume that alkyl hydroperoxide is a primary product of the reaction. It seems that ROOH is selectively transformed into R′R″C=O under the conditions employed. To check this proposal, we investigated the decomposition of pure cyclohexyl hydroperoxide, ROOH, in aqueous solution. It turned out that in the dark at room temperature ROOH (4.0×10^{-2} mol dm^{-3}) produces cyclohexanone very slowly even in the presence of $Fe(ClO_4)_3$ (5.0×10^{-2} mol dm^{-3}) or $HClO_4$ (5.0×10^{-2} mol dm^{-3})

[†] *Experimental details.* The photooxidations were carried out in air in a Pyrex cylindrical vessel (internal diameter 2 cm) surrounded by a water-cooling jacket (*ca.* 20 °C) placed at a distance of 10 cm from the lamp. The full spectrum of a street luminescent lamp ('DRL', 125 W) was used for irradiation ($\lambda > ca.$ 300 nm). The emulsion was intensively agitated with magnetic stirrer. Cyclohexane and *n*-hexane ('Fluka') were purified by shaking with conc. H_2SO_4, washing with water, drying over $CaCl_2$ and subsequent distillation. Twice-distilled water was used. Acetonitrile was distilled over P_2O_5.

The process was controlled by extracting the reaction emulsion with chloroform, washing the chloroform solution with water, drying over Na_2SO_4 and analysing it by means of GLC (each sample was analysed twice, *i.e.* before and after the addition of triphenylphosphine). For the analysis, a LKhM-80/6 chromatograph (columns length 2 m, 5% Carbowax 1500 on Inerton AW-HMDS, carrier gas argon) was employed. The sensitivity of cyclohexanone and cyclohexanol detection was 10^{-5} mol dm^{-3}.

(concentrations of $R'R''C{=}O$ were $< 1.0 \times 10^{-4}$ and 7.0×10^{-4} mol dm^{-3}, respectively). The experiment with $HClO_4$ was carried out because due to hydrolysis the pH of an aqueous solution of $Fe(ClO_4)_3$ is 2.25 when its concentration is 8.0×10^{-3} mol dm^{-3}. However, neither in the dark nor under irradiation did $HClO_4$ affect the rate of ROOH decomposition. In contrast to the dark reaction, under irradiation $Fe(ClO_4)_3$ does induce the selective transformation of ROOH to cyclohexanone. Thus, after 7 h irradiation of aqueous solution of cyclohexyl hydroperoxide (concentration 2.5×10^{-2} mol dm^{-3}) in the presence of $Fe(ClO_4)_3$ (5.0×10^{-2} mol dm^{-3}) cyclohexanone (2.1×10^{-2} mol dm^{-3}) was found in the reaction mixture and no cyclohexanol (concentration $< 10^{-4}$ mol dm^{-3}) was detected by GLC. The cyclohexanone formed can apparently accelerate the transformation of peroxide.[11] It is also interesting that some compounds which are able to form hydrogen bonds with ROOH have been shown to catalyse the selective decomposition of hydroperoxides.[12] 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 a solvent on the selectivity of alkane oxidation photocatalysed by the system $CrCl_3$–tetraalkylammonium chloride.[13]

Hydroxyl radicals are not likely to be the only (if at all) active species in the reaction. This proposal is supported by an experiment on photooxidation of cyclohexane with hydrogen peroxide in an aqueous emulsion in a quartz vessel. Only 4.0×10^{-7} mol of oxygenated products was obtained after 2 h irradiation of a mixture of 0.2 ml of cyclohexane and 2.3 ml of aqueous H_2O_2 (concentration 0.19 mol dm^{-3}); the formation of the three products (*i.e.* cyclohexanol, cyclohexanone and cyclohexyl peroxide) was detected.

In conclusion, the reaction described here appears to proceed *via* formation of cyclohexyl hydroperoxide, which is highly selectively decomposed to produce cyclohexanone. One may suspect that in some other cases including reactions in the dark (*e.g.* Gif-systems[7c]) 'unusual' selectivity is due to selective decomposition of initially formed alkyl hydroperoxide (see, for example, ref. 14). Indeed, in preliminary experiments we have found that vigorous stirring in air for 2 h of a mixture of cyclohexane (0.25 ml; 2.2×10^{-3} mol), iron(III) perchlorate (1.0×10^{-5} mol), zinc dust (6.5 mg; 1.0×10^{-4} mol) and water (2.5 ml) gave cyclohexanone (1.5×10^{-7} mol) and a noticeably smaller amount (3.0×10^{-8} mol) of cyclohexanol. Cyclohexyl peroxide is not formed as detected by GLC of the reaction solution samples before and after reduction by triphenylphosphine: the reduction does not affect the ketone/alcohol ratio.

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