

Iron(III) Chloride Catalysed Photooxygenation of Alcohol Solutions of Alkanes by Atmospheric Oxygen

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Alkanes (cyclohexane, pentane, hexane, heptane, 3-methylhexane) have been oxidised to the corresponding alcohols, together with minor amounts of ketones (aldehydes) by irradiation of solutions of the alkanes in aliphatic alcohols in air in the presence of catalytic amounts of FeCl₃: unusual selectivity in the reaction is revealed.

Liquid phase oxidation of saturated hydrocarbons by dioxygen catalysed by transition metal complexes under mild conditions, which requires activation of an inert C—H bond, is an area of continuing interest (reviews¹ and recent original papers²). Functionalisation of alkanes and arylalkanes under visible irradiation in the presence of high-valent metal complexes as catalysts is one of the most intriguing problems.³

Previously, we have found that alkanes can be oxygenated when irradiated in air in the presence of catalytic amounts of transition metal chlorides (FeCl₃, CuCl₂, PtCl₆²⁻, AuCl₄⁻, CrCl₃, etc.).⁴ Relatively inert solvents (MeCO₂H, MeCN, CH₂Cl₂, Me₂CO) were used in these oxidations.

We report here the oxygenation of alkanes by atmospheric oxygen, using aliphatic alcohols as solvents. Alcohols are easily oxidisable substrates and only a few examples of alkane oxygenation in the presence of alcohols are known⁵ (catalytic photo-functionalisation of cyclooctane in the presence of butan-2-ol has also been reported⁶).

Irradiation of a solution of cyclohexane in an alcohol in the presence of a catalytic amount of FeCl₃·6H₂O in air affords cyclohexanol and a smaller amount of cyclohexanone. The reaction was carried out in a glass vessel (volume of reaction solution 5 ml) surrounded by a water-cooling jacket (15 °C) with stirring, and using the full spectrum of a 1000 W high-pressure mercury lamp ($\lambda > 310$ nm). The data are summarised in Table 1. It should be noted that both alcohol and ketone are accumulated linearly with time, a significant prevalence of cyclohexanol being observed. The reaction is first order in alkane concentration.

The alcohol used as the solvent is also oxidised to afford a ketone or aldehyde (detected in Runs 3–6). The amount of the carbonyl compound formed from the solvent decreases with increasing initial concentration of cyclohexane. The turnover number in the FeCl₃-photocatalysed oxygenation of cyclohexane is ca. 60 h⁻¹. It is noteworthy that, in contrast to the reaction in acetonitrile, the oxygenation of cyclohexane in alcohols affords no cyclohexyl hydroperoxide. Similarly, when carried out in *tert*-butyl alcohol, which contains no active C—H bonds, the reaction produces no hydroperoxide, but in this case a large amount of cyclohexanone is formed (Run 7).

Linear alkanes can also be easily oxygenated in alcohols as solvents under the conditions described above. Heptane (2.76 mol dm⁻³), for example, gives rise after 1 h irradiation to 10.8 mmol dm⁻³ of a mixture of isomeric alcohols

Table 1 Photooxygenation of cyclohexane catalysed by FeCl₃^a

Run	Solvent	Products		
		Cyclohexane /mol dm ⁻³	Cyclohexanol /mmol dm ⁻³	Cyclohexanone /mmol dm ⁻³
1	MeOH	0.46	10.7	0.3
2	MeCH ₂ OH	0.46	3.0	1.1
3 ^b	Me ₂ CHOH	0.46	11.3	1.7
4 ^b	Me ₃ CHOH	2.76	30.6	5.9
5 ^c	MeCH(OH)CH ₂ Me	0.46	5.2	0.9
6 ^c	MeCH(OH)CH ₂ Me	2.76	30.3	9.5
7	Me ₃ COH	0.46	10.1	10.0
8 ^d	MeCN	0.46	22.3	20.4

^a Concentration of FeCl₃ 0.2 mmol dm⁻³, 3 h irradiation. ^b Acetone was also formed: 26.0 (Run 3) and 6.3 mmol dm⁻³ (Run 4). ^c Methyl ethyl ketone was also formed: 66.4 (Run 5) and 23.1 mmol dm⁻³ (Run 6). ^d Cyclohexyl hydroperoxide was also formed: 32.0 mmol dm⁻³.

(2.8 mmol dm⁻³ of heptan-1-ol) and 10.0 mmol dm⁻³ of carbonyl derivatives. The relative reactivities of the C—H bonds at the first, second, third and fourth carbon atoms of the hydrocarbon chains of pentane, hexane and heptane are given in Table 2. It can be seen that when propan-2-ol is used as a solvent the relative reactivity of the C—H bond at carbon atom C-1 is higher than that when acetonitrile is used as a solvent. However, the most striking feature of the reaction in alcohol solution is the enhanced reactivity of the C—H bonds at C-3 in comparison with those at C-2 in hexane. Similarly, the C—H bonds at C-4 in heptane are more reactive than those at C-2 and C-3. In the photo-oxygenation of 3-methylhexane, the distribution of isomeric alcohols formed by attack on primary, secondary and tertiary C—H bonds changes on passing from acetonitrile (1°:2°:3° = 1.0:3.8:16.9) to propan-2-ol (1°:2°:3° = 1.0:1.4:9.1) as solvents.

One may propose the following mechanism for the reaction under discussion. Photohomolysis of the Fe—Cl bonds⁷ affords extremely reactive chlorine radicals⁸ which abstract hydrogen atoms from alkane RH or alcohol R'R''CHOH to yield radicals R' or R'R''COH respectively, the reactivities of alkane and alcohol in this process being approximately equal. Indeed, the reactivity of the CH₂ groups in ethylbenzene relative to that in

Table 2 Selectivities in photooxygenations of linear alkanes catalysed by FeCl₃^a

Alkane	Solvent	Relative reactivity per C—H bond ^b			
		C-1	C-2	C-3	C-4
Pentane	MeCN	1.0	10.9	8.2	—
	Me ₂ CHOH	1.0	2.5	2.3	—
Hexane	MeCN	1.0	4.7	5.0	—
	Me ₂ CHOH	1.0	1.5	3.1	—
Heptane	MeCN	1.0	8.6	9.1	7.8
	Me ₂ CHOH	1.0	1.7	1.6	3.2

^a Concentrations: FeCl₃ 0.5 mmol dm⁻³; alkane 0.76 mol dm⁻³ in MeCN and 2.76 mol dm⁻³ in Me₂CHOH; 1 h irradiation. ^b Relative concentrations of isomeric alcohols formed in the reaction (after addition of PPh₃ to reduce hydroperoxides in the case of MeCN) were determined and then normalised, taking into account the number of C—H bonds at each carbon atom of the hydrocarbon chain.

cyclohexane in the FeCl₃-photocatalysed oxygenation in methanol turned out to be 2.5. Similar values were obtained for hydroxylation by hydrogen peroxide under UV irradiation (2.9) and by Fenton's reagent (3.6), which appear to involve attack by hydroxyl radicals. Alkyl and hydroxyalkyl radicals thus formed in the photocatalysed oxygenation react rapidly with dioxygen to produce peroxy radicals which are then transformed into the final products. Dioxygen and/or peroxy radicals can reoxidise the Fe^{II} formed by photolysis of FeCl₃.

Radical chain oxygenation of the alkane is improbable because the photooxygenation proceeds at low temperature and the effective activation energy of the FeCl₃-photocatalysed reactions is usually less than 5 kcal mol⁻¹† (see ref. 9). The addition of 2,6-di-*tert*-butyl-4-methylphenol (concentrations up to 5.4 mol dm⁻³) to the reaction solution (conditions as in Run 1 in Table 1) did not reduce the rate of cyclohexanol (and cyclohexanone) accumulation. However, hydrogen atom abstraction from R'R''CHOH by ROO' appears to be possible. Moreover, alcohol R'R''CHOH is apparently capable of reducing ROO' to give ROH, which explains the predominant formation of alcohols at the expense of ketones when alcohols are used as solvents.

† 1 cal = 4.184 J.

In conclusion, the high reactivity of FeCl₃ as a photocatalyst provides a method for oxidising both alkanes and alcohols at approximately equal rates and provides a new method for the oxygenation of alkanes at low temperature when alcohols are used as solvents. The unusual selectivity observed in the photooxidation of linear alkanes in alcohol solutions requires explanation, however.

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