Alkane Oxidation by Polynuclear Non-haem Iron Complexes—an Imidazole Effect†

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Binuclear and trinuclear non-haem iron complexes efficiently transfer oxidizing equivalents from *tert*-butyl hydroperoxide to cyclohexane; imidazole in excess greatly increases the yield of the reaction and the ketone : alcohol ratio.

Binuclear oxo-bridged non-haem iron complexes (containing the Fe–O–Fe unit) have recently received much attention.[1] They provide structural models for diiron sites in several proteins involved in oxygen storage (hemerythrin) and oxygen activation (ribonucleotide reductase and methane monooxygenase).[2] However, very few polynuclear iron complexes have been shown to act as catalysts for alkane oxidation by dioxygen or single oxygen atom donors. Previous work has included studies using $[Fe_3O(OAc)_7]$–HOAc–pyridine–O_2,[3] $[Fe_2O(OAc)_2(bipy)_2Cl_2]$–tbhp[4] and $[\{Fe(HBpz_3)(hfcac)\}_2O]$–Zn–$O_2$.[5] On the other hand, a (μ-oxo)diiron(III) intermediate has been proposed as the active species during the selective oxidation of saturated hydrocarbons to ketones by Gif-type systems.[6]

Here we report that simple binuclear and trinuclear oxo-bridged complexes are good catalysts for oxidation of cyclohexane to cyclohexanol and cyclohexanone by tbhp and that addition of imidazole improves the efficiency and the selectivity of the reaction.

In a typical reaction cyclohexane (0.2 ml = 1.8 mmol) was allowed to react with tbhp (300 μmol) in acetonitrile (2 ml) in the presence of iron catalyst (15 μmol; tbhp : catalyst 20 : 1) at 25 °C under 1 atm of oxygen-free argon. The reaction was completed after *ca.* 3 h and the amounts of both cyclohexanol and cyclohexanone were estimated quantitatively by GLC in the presence of an internal standard. In this study, the binuclear iron complexes $[Fe_2OCl_6](NEt_4)_2$ **1** and $[Fe_2O(phen)_4(H_2O)_2](ClO_4)_4$ **2**, and the trinuclear iron complex $[\{Fe(ala)_2(H_2O)\}_3O](ClO_4)_7$ **3** were tested as catalysts. They were selected since (*i*) they are easily prepared,[7] (*ii*) they are soluble in acetonitrile, and (*iii*) they contain accessible coordination sites.

In the absence of imidazole, **1** or $FeCl_3$ were not active. On the other hand, the trinuclear complex **3** showed some activity, albeit low when compared to a standard well known catalytic system containing an iron porphyrin complex, [Fe(tpp)Cl], as a catalyst.[8] The best catalyst was complex **2**, with a turnover number of 8 after 3 h reaction. The ketone to alcohol ratio was close to 1 : 1, twice that found with the porphyrin system.

Addition of imidazole in excess markedly improved the efficiency of the iron complexes during oxidation of cyclohexane by tbhp. Complex **1** became very active with a total yield, based on tbhp, of 45% and a turnover number of 10 after 3 h reaction. Cyclohexanone was the major product with a ketone

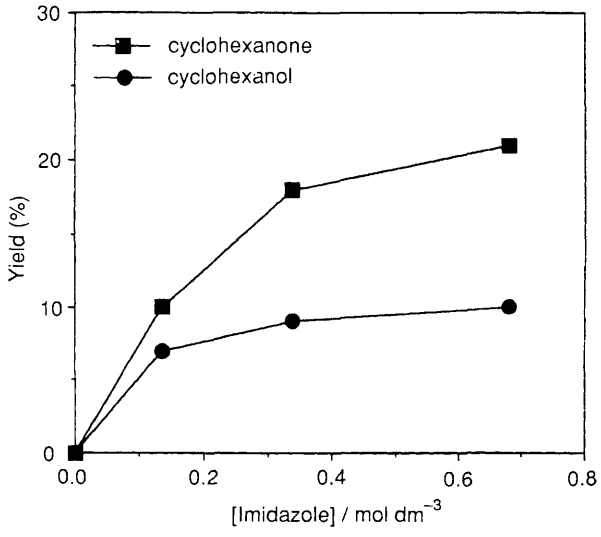

Fig. 1 Effect of imidazole on cyclohexanone (■) and cyclohexanol (●) yields. Conditions were the same as indicated in Table 1. Complex **1** was used as a catalyst and products were analysed after 3 h reaction.

† bipy = bipyridine, $HBpz_3$ = hydrotris-1-pyrazolylborate, hfacac = hexafluoroacetylacetonato, phen = phenanthroline, tpp = tetraphenylporphyrin, tbhp = *tert*-butyl hydroperoxide, ala = alanine, edta = ethylenediaminetetraacetate.

Table 1 Oxidation of cyclohexane by tbhp

Conditions[a]	Yield (%)[b] Cyc–OH	Cyc–O	Total[c]
1	0	0	0
1 + Imidazole	9	18	45
1 + Pyridine, edta or phenanthroline	0	0	0
$FeCl_3$	0	0	0
$FeCl_3$ + Imidazole	8	21	50
2	13	12	37
2 + Imidazole	12	18	48
3	5	3	11
[Fe(tpp)Cl]	25	12	49

[a] Complete system: catalyst (15 μmol), imidazole or pyridine edta, phenanthroline (750 μmol), where indicated and tbhp (300 μmol) in acetonitrile (2 ml) and cyclohexane (0.2 ml), under argon. [b] Yields based on starting tbhp; cyc–OH = cyclohexanol, cyc–O = cyclohexanone. [c] Total yield is calculated assuming that 1 and 2 molecules of tbhp respectively are used for alcohol and ketone formation.

to alcohol ratio of close to 2 : 1. Fig. 1 shows the dependence of cyclohexanone and cyclohexanol yields on the concentrations of imidazole. Both the yields and the ketone to alcohol ratio were increased on increasing the excess of imidazole. The requirement for imidazole was specific since pyridine, edta or phenanthroline did not lead to activation of complex **1** as did imidazole. It is noteworthy that similar results were obtained with iron(III) chloride as a catalyst. In that case, imidazole was also essential (Table 1). Addition of imidazole to the tbhp–complex **2** system had a smaller effect but also resulted in an increased ketone to alcohol ratio. The ketone to alcohol ratios observed in this work are much larger than those previously obtained with comparable systems.[4,5,9] However, they are still lower than those of the Gif-type oxidations.

Addition of acid (trifluoroacetic acid) did not affect the reaction. The yield of cyclohexanol was unchanged while that of cyclohexanone was significantly increased (1.3–1.4 fold) when the reaction was carried out under aerobic conditions. Complexes **1**, **2** and **3** were not capable of catalysing the oxidation of cyclohexane by hydrogen peroxide or iodosylbenzene. Both oxidants were dismutated in the presence of the iron complexes.

On the basis of these results, polynuclear non-haem iron complexes such as **2** appear to be promising catalysts for alkane oxidation by alkyl hydroperoxides even though it is impossible to come to a conclusion concerning the identity of the actual catalyst. Our data indicate that a nitrogen-rich environment provided by imidazole or phenanthroline is required for an active iron. Recently a mononuclear non-haem iron complex, with tripodal nitrogen ligands, was found to catalyse oxidation of cyclohexane by tbhp.[9] Such coordination patterns are reminiscent of those frequently provided by histidines in metalloenzymes. The origin of the remarkable effect of imidazole has yet to be identified. A comparable effect had been observed previously with metalloporphyrin dependent systems but never with non-haem iron.[10]

Received, 16th April 1991; Com. 1/01781K

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