Short Communication

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CATALYTIC CONVERSION OF CYCLOHEXANE TO ADIPIC ACID USING OXYGEN UNDER MILD CONDITIONS

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The present paper is based on studies carried out for replacement of HNO_3 using oxo trinuclear complexes of Ru, Rh, Nb, Mo and Fe with dicarboxylic acids and the study of adipic acid preparation reaction mechanism.

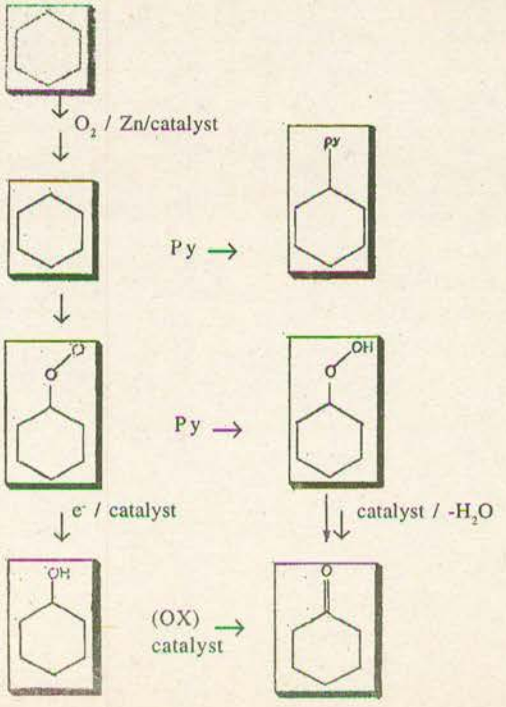
In Due Pont process, adipic acid is formed by oxidation of cyclohexane in two steps. Firstly, cyclohexane is oxidized to a mixture of cyclohexanol and cyclohexanone, then oxidized to adipic acid using nitric acid in the presence of Cu (II) and V(v) salts as catalysts. N_2O, NO_2, NO gases are produced as by products.

Adipic acid was first manufactured in 1902 from tetramethylene bromide. It was Deutsche Hydrierwerke to produce it from phenol in Germany. The process involved hydrogenation of benzene to cyclohexane followed by pressure oxidation of cyclohexane at low conversion to obtain acceptable yield of adipic acid (Linday 1954). The oxidation product like cyclohexanone-cyclohexanol (K A mixture), so produced was separated into the components and used to produce adipic acid. At present HNO_3 is being used as oxidant in the production of adipic acid (Linday 1954; Tanaka 1974). N_2O is produced as by-product with other gases such as NO_2 which causes ozone layer destruction. It is also believed that this gas can contribute to enhance green house effect by much as 10% (Linday 1954).

The oxotrinuclear complexes of Ru, Rh, Nb, Mo and Fe were prepared by standard methods and checked for purity by elemental analysis (CHN) and GLC-mass spectra. (Lal Khan *et al.* 1991; Glenmore *et al* 1994) The oxygenation reactions were carried out as reported elsewhere (Barton *et al* 1991; Glenmore *et al* 1994). The samples were analyzed by GC Hewlett Packerd using FID.Ultra violet and visible spectra were recorded on Perken Elmer Lambda-5 recording spectrophotometer.

The catalytic properties of three ruthenium species $[Ru_3O(CH_3COO)_6Py_3]^{+1}$, $[Ru_3O(CH_3COO)_6Py_2(CO)]$, and $[Ru_2O(CH_3COO)_2Py_6]^{+2}$ were compared with that of the iron trimer $[Fe_3O(CH_3COO)_6Py_3]^{+1}$. Cyclohexane was chosen as iron system carries on functioning probably until all the zinc is used up. An interesting finding in the studies is that with the use of the iron trimer as catalyst, major product is the ketone as found by Barton *et al* (1988) whereas the use of ruthenium trimer resulted in the alcohol as the major product. The results also show that catalyst $[Ru_3O(CH_3COO)_6Py_2(CO)]$, and $[Ru_2O(CH_3COO)_2Py_6]^{+2}$ gave predominantly the alcohol as the final product with trace amounts of the ketone. Apart from giving poorer yields, as it is evident from Table 1, the turnover numbers for these catalyst are very low in comparison to other complexes of ruthenium and further independent studies (Davis and Drago 1990) conducted in our laboratory have shown that with the iron trimer as catalyst, adipic acid and possibly other carboxylic acid are formed after 3-4 days as shown in Scheme 2. The adipic acid can be extracted in ~90% yield with ethylacetate and its identity confirmed by elemental analysis, NMR, melting point IR, and GCMS. This is probably the first time that cyclohexane has been catalytically oxidized to adipic acid using oxygen under mild conditions.

The ruthenium carboxylate species have somewhat higher solution stability than that of the iron species and this may be



Scheme 1

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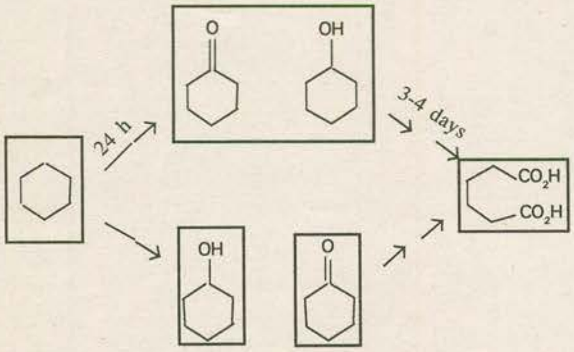
Table 1

Products of cyclohxane-cyclohexanol (KA mixture) by catalytical oxidation of cyclohexane

Complexes	Oxidation Products			
	Cyclohexane	Cyclohexanol	Adipic acid	Turnover number*
$[Fe_3O(CH_3COO)_6Py_3]^+$	7mmol	1mmol	4mmol	995
$[Ru_3O(CH_3COO)_6Py_3]$	1	2	0.5	885
$[Ru_2O(CH_3COO)_2Py_6]^{+2}$	1	1	0.5	725
$[Ru_3O(CH_3COO)_6Py_2(CO)]$	2	1	0.5	625
$[Mo_3O_2(CH_3COO)_6.(H_2O)_3]$	2	1	-	257
$[MoO_4(H_2O)_9]$	3	1	-	210
$[Nb_3O_4(H_2O)_9]$	-	-	-	-
$[W_3O_2(CH_3COO)_6.(H_2O)_3]$	-	-	-	-

$$^*\text{Turnover} = \frac{\text{Oxidized products in mmol}}{\text{Catalyst in mmol}}$$



(Adipic acid formation)

Scheme 2

in part responsible for the lower activity. It may be that the trinuclear species are precursors to the active catalyst involving reduction of one or more of the metal centres with retention of the U_3-oxo framework, formation of a dimeric or monomeric species, or even complete degradation of the trimer. Alternatively the redox properties of iron trimer though not as extensive as the ruthenium analogues, may contain the approximate potential which when coupled with the higher liability gives rise to the activity. It is conceivable that the greater yields of alcohol product in the Ru-Gif IV system could be due to the greater retention of reducing equivalents by the Ru_3 complex.

It is not as yet possible to assign a definitive mechanism for these oxidations. However, the oxidation may involve the formation of hydrocarbon radical, hydrogen atom abstraction, reaction of the radical with O_2 to form a hydroperoxide, and subsequent Haber- Weiss decomposition of the hydroperoxide. A similar mechanism was recently proposed to account for the air oxidation of alkanes by $[Ru_3O(pfb)_6(Et_2O_3]$ (pfb = $CF_3CF_2CF_2CO_2$-). Whether this mechanism (as given in Scheme 1) is relevent for both iron and ruthenium species remain to be clarified.

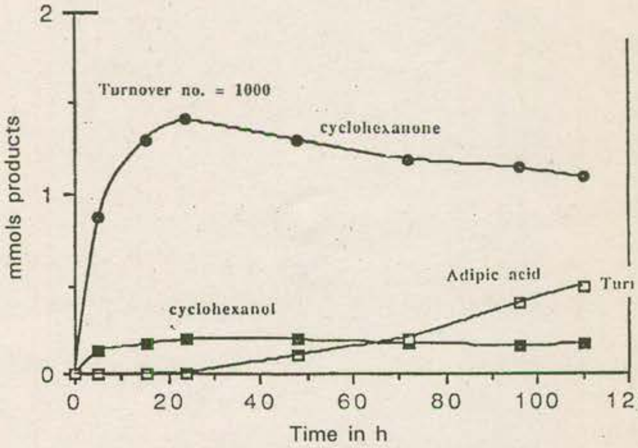


Fig 1 Formation of products with time during cyclohexane air oxidation catalysed by (1) (M=Fe) in pyridine acetic acid-Zn.

Conclusion

However, it may be concluded that: (i) Catalytic oxygenation of ketone and alcohol by substitution inert trinuclear iron complexes is in support of the evidence for a free radical mechanism involving generation and specific on word reaction of the hydroperoxide/hydroperoxy radicals. (ii) Adipic acid can be formed from cyclohexane via KA mixture using atmospheric oxygen in presence of catalyst instead of using HNO_3.

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