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Catalytic Behavior of Niobium(V)–Tetraphenylporphyrin in the Oxidation of Cyclohexene with Hydrogen Peroxide Evaluated by ^{1}H NMR Spectroscopy†

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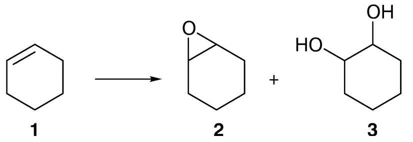
The catalytic efficiency of the niobium(V)–tetraphenylporphyrin complex in the oxidation reaction of cyclohexene with aqueous hydrogen peroxide was evaluated using ^{1}H NMR spectroscopy.

Oxidations promoted by synthetic porphyrin catalysts are of relevance to previous studies of the chemistry of cytochrome P-450 in living organisms.[1] Due to their importance, these biomimetic processes have received much attention in recent years.[2] In general the oxidant used is iodosylbenzene while the use of other oxidants such as alkyl hydroperoxides, molecular oxygen and hydrogen peroxide has also been investigated. The metal of the porphyrin ring can be iron, manganese, chromium or osmium. Previous studies have given the best results with iodosylbenzene or alkyl hydroperoxides and iron or manganese porphyrins.[2] Hydrogen peroxide gives good selectivities and conversions in the epoxidation of several alkenes in the presence of molybdenum or tungsten tetraryl- and octaethyl-porphyrins.[3] However, using molecular oxygen, visible light and tri-μ-oxo-niobium(V)–tetra-*p*-tolylporphyrin as catalyst the conversions are very low.[4] Using tri-μ-oxo-niobium(V)–tetraphenylporphyrin [$(NbTPP)_2O_3$] for the oxidation of cyclohexene by *tert*-butyl hydroperoxide led to total conversion in 12 h with 30% selectivity for the epoxide.[5] The present work presents the catalytic behaviour of the $(NbTPP)_2O_3$ complex in the oxidation reaction of cyclohexene **1** with aqueous hydrogen peroxide. ^{1}H NMR spectroscopy was used in place of the usual gas chromatography to examine this reaction.

All reactions were carried out in biphasic media formed from chloroform and aqueous H_2O_2 and taking an aliquot of the organic phase for the analysis at times and conditions as described in Table 1. The interesting point of these ^{1}H NMR analyses in $CHCl_3$ is that the possible products and also the substrate have at least one distinct signal between δ 3.0 and δ 7.2 due to the more deshielded protons: for example, cyclohexene (δ 5.76), cyclohexene oxide (δ 3.08), cyclohex-2-en-1-ol (δ 4.20), cyclohexene-1,2-diol (δ 3.78) and cyclohex-2-en-1-one (δ 7.16). The strong solvent signal at δ 7.90 does not interfere and therefore the lock was made by way of D_2O sealed in a capillary. Thus, deuterium solvent was not necessary. The conversion and selectivity were measured by signal integration based on the substrate. Calibration curves were not necessary although an internal standard can be used. The results show that due to the low oxidizing power of the hydrogen peroxide the reactions with equimolar quantities and with or without catalyst are unproductive (entries 2 and 1). Better conversions are obtained with an excess of the oxidant in the presence of the catalyst (compare entries 3 and 4). Small amounts of organic acids or bases and higher temperatures (entries 5 to 14) also led to better conversions. Acetic acid gave the best results although it has a major influence on the transformation of the epoxide **2** to the corresponding diol **3** (entries 9–12). We had also noted a slow and progressive decomposition of the catalyst in the presence of this acid (colour change from dark red to pale yellow and the characteristic bands disappear in the UV-VIS analysis).[5] In neither of the



Scheme 1

Table 1 Oxidation of cyclohexene by hydrogen peroxide in the presence of $(NbTPP)_2O_3$

Entry	Catalytic system[a]	T/°C	t/h	Epoxide **2**[d] (%)	Diol **3**[d] (%)	Turnover[b]
1	1eq H_2O_2[c]	40	24	<0.5	—	<1.0
2	1eq H_2O_2+0.1eq py	40	24	1.3	<0.5	2.6
3	10eq H_2O_2[c]	40	24	1.1	<0.5	2.3
4	10eq H_2O_2	40	24	4.5	<0.5	7.1
5	10eq H_2O_2+0.1eq py	40	24	9.3	1.0	14.7
6	10eq H_2O_2+0.1eq py	55	24	11.0	3.5	20.7
7	10eq H_2O_2+0.1eq py	55	48	23.4	6.7	43.0
8	10eq H_2O_2+0.1eq py	55	72	36.1	25.5	88.0
9	10eq H_2O_2+0.1eq AcOH	40	24	13.5	5.4	27.0
10	10eq H_2O_2+0.1eq AcOH	55	24	15.1	10.9	37.1
11	10eq H_2O_2+0.1eq AcOH	55	48	25.5	22.0	67.9
12	10eq H_2O_2+0.1eq AcOH	55	72	38.1	42.2	114.7
13	10eq H_2O_2+0.1eq EtOH	55	24	5.3	<0.5	8.3
14	10eq H_2O_2+0.1eq EtOH	55	48	12.2	2.9	21.6

[a] py = pyridine, AcOH = acetic acid, EtOH = ethyl alcohol. [b] Turnover = mmol products/mmol catalyst. [c] Without catalyst. [d] Scheme 1.

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experiments did we detect oxidation products formed by radical processes.

In conclusion the niobium(v) tetraphenylporphyrin showed catalytic activity in the oxidation of cyclohexene by aqueous hydrogen peroxide with a good selectivity but with long reaction times. Previous investigations using hydrogen peroxide as oxidant showed that the oxidation reaction is more efficient using porphyrin catalysts with metals from groups 5 to 8 (*e.g.* V, Mo, W, Fe, Mn).[2,3] However, the present case using niobium would appear to be an exception. The ^{1}H NMR analysis proved to be quick (<5 min) and easy to perform in comparison to traditional GC analysis (a cross check using an apolar capillary column give $t_r \sim 20$ min for the diol). The application of the NMR method to other catalytic processes must take into account: (1) the possibility of signal overlap, from the solvent, substrate and products and (2) nuclear relaxation, as it is necessary to leave a large enough delay time in order to prevent saturation and errors in the integration of the signals.[7]

Experimental

Chloroform, pyridine, acetic acid, ethanol, cyclohexene, and $NbCl_5$ were purchased from Aldrich and H_2O_2 (50% w/v in water) was purchased from Peróxidos do Brasil, in high purities and used without further purifications. $(NbTPP)_2O_3$ was prepared from $NbCl_5$ as described.[6] All reactions were carried out in a stirred biphasic system containing 10 ml of $CHCl_3$, 1 mmol of cyclohexene and 0.007 mmol of the catalyst with the other components added as described in Table 1. Aliquots of 0.5 ml of the organic phase were introduced in a 5 mm (o.d.) NMR tube containing a coaxial closed capillary tube with D_2O as the deuterium lock. The CG analyses were run on HP5890 equipment with an RTX-5 column. The ^{1}H NMR measurements were run using a Bruker Avance 300 spectrometer at using eight scans with a $\pi/3$ pulse, 2.5 s acquisition time with 4 s relaxation delay on 64k data points, and no sample spinning.

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