Direct synthesis of adipic acid by mono-persulfate oxidation of cyclohexane, cyclohexanone or cyclohexanol catalyzed by water-soluble transition-metal complexes

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A catalytic system consisting of water-soluble metal sulfophthalocyanines (MPcS) or various ruthenium complexes and mono-persulfate as the oxidant was effective in the oxidation of cyclohexanone, cyclohexanol and cyclohexane to adipic acid with different yields and selectivity. Oxidations were conducted at room temperature and under atmospheric pressure in aqueous media (or, in the case of cyclohexane, in a water–neat substrate double phase). The oxidation of cyclohexanol involved step-by-step formation of cyclohexanone, ε-caprolactone and 6-hydroxyhexanoic acid, all of which have been identified in the reaction mixtures; in selected cases moderate over-oxidation of adipic acid to glutaric and succinic acid was also observed. Various MPcS catalysts were examined (M = Fe, Co, Ni, Cu and Ru), and the ruthenium derivative exhibited the best performances in terms of rate and selectivity. Mono-persulfate was found to be a more convenient oxidizing reagent than hydrogen peroxide; related patterns were observed when H_2O_2 was used, however extended dismutation of the oxidant limited the overall yields. Cyclohexane underwent slow oxidation when reacted with persulfate (water–substrate double phase) in the presence of the water-soluble metal catalysts; adipic acid was selectively produced (95%) in the presence of RuPcS catalyst with yields as high as 21% (48 h). The catalytic performance of simpler ruthenium derivatives, such as $[RuCl_2(DMSO)_4]$ (RuDMS) and $K_5[Ru(H_2O)P_{11}O_{39}]$ (RuPW), was also examined for comparison purposes. A kinetic scheme for cyclohexane oxidation is proposed.

Adipic acid is an important building block for a variety of commercially useful products. Currently, adipic acid is manufactured mainly by a two-step process involving stoichiometric nitric acid oxidation of a cyclohexanol–cyclohexanone mixture, which is aerobically generated from cyclohexane using a homogeneous cobalt-based catalyst. Research has particularly focused on tuning alternative synthetic routes to obtain cleaner technology and compliance with increasingly stringent environmental laws.[1] In this context the major issue concerning adipic acid synthesis is the replacement of the toxic reactant nitric acid, which generates nitrous oxide, which in turn is associated with important environmental problems.[2] The scientific challenge is to devise a one-step synthesis operating at room temperature in an environmentally friendly solvent system, such as water, and using green co-oxidants, such as oxygen (air) or hydrogen peroxide. The substrate of choice is cyclohexane, but much attention has been paid to the development of one-step catalytic oxidation of cyclohexanol and/or cyclohexanone with alternate oxidants, such as alkylhydroperoxides and hydrogen peroxide. Recently, metal catalysts were proposed for the oxidation of cyclohexane using molecular oxygen, in the presence of homogeneous ruthenium and iron catalysts,[3] or of heterogeneous counterparts, such as cobalt molecular sieves[4] and aluminophosphate molecular sieves containing iron(III) ions.[5] A recent improvement of the SbF_3-catalyzed oxidation of cyclohexanone to ε-caprolactone using hydrogen peroxide as an oxidant by supporting the catalyst on mesoporous silica has been reported.[6]

Over the last few years we have been interested in using ruthenium complexes as catalysts for the oxidation with mono-persulfate of a number of organic substrates.[7,8] More recently, we achieved a substantial improvement by using the water-soluble ruthenium(II) derivative RuPcS (where PcS is tetrasodium 2,3-tetrasulfophthalocyaninate) to effectively promote the oxidation of chlorophenols,[9] chloro-olefins[10] and alcohols[11] in aqueous media and in the presence of either mono-persulfate or hydrogen peroxide. Related metal sulfophthalocyanines (M = Fe, Mn) have been successfully used by Meunier *et al.* for the oxidation of chlorophenols,[12] chloroanilines[13] and catechols[14] with persulfate or hydrogen peroxide in aqueous acetonitrile, whereas various metal phthalocyanines, encapsulated in zeolites[15] or other inorganic supports,[16] have also been successfully tested for the direct oxidation of cyclohexane. We present here a series of metal sulfophthalocyanines and other simple ruthenium complexes, among them a Keggin-type heteropolyoxotungstate, that catalyze the one-pot oxidation of cyclohexanone, cyclohexanol or cyclohexane to adipic acid using mono-persulfate or hydrogen peroxide as the oxidizing sources, under very mild conditions and in an entirely aqueous phase. Polyoxometallates were recently reported to catalyze the oxidation of cyclohexane by molecular oxygen[17] and hydrogen peroxide.[18]

Experimental

RuPcS and CoPcS were prepared by template synthesis starting from $RuCl_3 \cdot 3H_2O$ or $CoSO_4 \cdot 7H_2O$, sodium 4-sulfophthalate and urea, following early general procedures for the synthesis of metal sulfophthalocyanines;[19] *cis*-$[RuCl_2\{(CH_3)_2SO\}_4]$ (RuDMS)[20] and $K_5[Ru(H_2O)PW_{11}O_{39}]$ (RuPW)[21] were prepared using published

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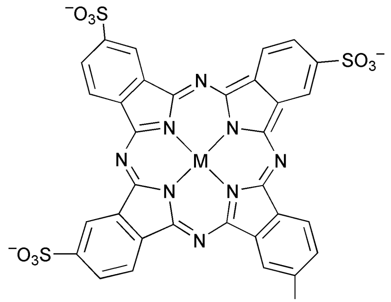


MPcS

procedures. Organic substrates, chromatographic and spectroscopic standards and FePcS, NiPcS and CuPcS complexes were obtained from Aldrich.

A procedure for the catalytic oxidations is as follows. (a) A water solution (10 ml) containing cyclohexanone or cyclohexanol (50 mM) and the metal catalysts (0.1–1 mM) was stirred magnetically in a vial together with commercial Oxone®, corresponding to a 0.5 N concentration of active oxygen as $KHSO_5$, or an equivalent amount of hydrogen peroxide, as determined by iodometric titration. (b) Neat cyclohexane (0.5 ml) was added to 2.5 ml of a water solution containing the metal catalysts (1–5 mM) and $KHSO_5$ (0.5 N) and the double-phase mixture stirred magnetically in a vial. The reactions were carried out at 20 °C and were not affected by the presence of air.

Organic analyses were performed on an HP 6890 GLC instrument equipped with a FID, using a 30 m HP-5 capillary column (0.32 mm i.d.; 0.25 film thick) with the injection port kept at 250 °C (carrier gas: He) on aliquots withdrawn with a microsyringe from the aqueous reaction mixtures either as such or diluted 1 : 10 with acetone. Commercial products were used for all gas chromatographic standardizations. The reaction mixtures were treated by standard procedures with a 10 : 1 excess of 2-methyl-1-butanol to analyze the dicarboxylic acids formed as their isobutyl esters. The identity of each product was confirmed by comparison of the fragmentation patterns in the mass spectra obtained with a MD 800 Fisons mass spectrometer operating in the electron ionization mode at 70 eV. The reactions were also followed by ^1H NMR on a Bruker Avance 300 MHz instrument, by adding a small amount of D_2O to the reaction mixtures; water suppression was carried out by a presaturation sequence using a composite pulse (zgcppr Bruker sequence). A co-axial capillary tube containing a 30 mM water (D_2O) solution of 3-(trimethylsilyl)-propionic-2,2,3,3-d_4 acid sodium salt (TSP) was used as reference. The identity of each product and their quantitation were confirmed by comparison of the position and intensity of suitable signals after adding measured amounts of the pure compounds to the reaction mixtures. Average reproducibility of quantitative measurements was within 5%.

Results and discussion

Oxidation of cyclohexanone and cyclohexanol

Persulfate oxidations of cyclohexanone took place at room temperature in a completely aqueous phase containing an excess of the peroxidic oxidant (Oxone®), typically 0.5 N (pH *ca.* 2), and the substrate (50 mM). The MPcS catalysts (M = Fe, Co, Ni, Cu and Ru) were added at the 0.2–2 mol% level with respect to the substrate (Table 1). It should be recalled that mono-persulfate alone is able to easily perform the uncatalyzed Baeyer–Villiger oxidation of cyclohexanone to the corresponding lactone; in the reaction conditions quantitative transformation of cyclohexanone to ε-caprolactone (and/or its hydrolysis product, 6-hydroxyhexanoic acid) was achieved within minutes. Some of the MPcS complexes investigated were able to further oxidize the alcoholic function of 6-hydroxyhexanoic acid to adipic acid, with various rates and selectivity. With FePcS (1 mM) conversion into adipic acid was indeed observed, although slow (34% yield after 24 h). The result was nevertheless interesting, since "naked" iron ions, for example iron(III) sulfate, are inactive for the oxidation of the lactone. CoPcS was more active, leading to adipic acid in a 62% yield, but glutaric and succinic acid were also formed, arising from significant over-oxidation of adipic acid. Adipic and succinic acid oxidation by the metal sulfophthalocyanine–persulfate catalytic systems (Table 2) suggested that the rate of the oxidative decarboxylation of the dicarboxylic acids followed the trend: glutaric acid > adipic acid > succinic acid. In the presence of RuPcS (1 mM), cyclohexanone was quantitatively transformed into adipic acid within a few hours and with a selectivity close to 90%; glu-

Table 1 Oxidation of cyclohexanone by metal catalysts and $KHSO_5$[a]

Catalyst	[cat]/mM	Time/h	Yield w.r.t. the oxidant[b]/equiv.%	Product selectivity[c]/mol%				
				A	B	C	D	E
None[d]	—[e]	3[f]	10	—	100	—	—	—
FePcS	0.1	3	10	8	92	—	—	—
		24	10	—	100	—	—	—
	1	3	10	—	100	—	—	—
		24	34	—	66	34	tr	—
CoPcS	0.1	3	10	2	98	—	—	—
		24	30	—	75	25	—	—
	1	3	33	2	65	33	—	—
		24	68	—	21	62	6	11
RuPcS	0.1	3	10	7	93	—	—	—
		24	45	—	43	55	—	2
	1	3	64	—	6	89	tr	5
		24	72	—		90	tr	10
RuPW	1[g]	3	92	—		54	14	32

[a] Conditions: catalyst cyclohexanone 50 mM, and $KHSO_5$ 0.5 N, in water (non-buffered solutions, pH *ca.* 2); 20 °C. Yields determined by ^1H NMR and GC. [b] Consumed (calc.) over available oxidant (equiv./equiv.). Equivalents of oxidant necessary for the formation of each mol of product from cyclohexanone were calculated to be: ε-caprolactone and 6-hydroxyhexanoic acid (2); adipic acid (6); glutaric acid (12); succinic acid (18). In all reported cases, substrate conversions are quantitative. [c] Product abbreviation: A, ε-caprolactone; B, 6-hydroxyhexanoic acid; C, adipic acid; D, glutaric acid; E, succinic acid. [d] Same results with NiPcS, CuPcS and $Fe_2(SO_4)_3$ (1 mM). [e] Substrate 31 mM. [f] Reaction no longer running. [g] Substrate 31 mM; $KHSO_5$ 0.36 N.

Table 2 Oxidation of adipic acid by MPcS catalysts and $KHSO_5$[a]

Catalyst	Time/h	Substrate conv. (%)	Products/mol%[b] D	E
FePcS[c]	6	64		
	24	64	12	88
CoPcS	6	42		
	24	57	2	78
RuPcS	6	23		
	24	42	19	81

[a] Conditions: catalyst 1 mM, substrate 50 mM, and $KHSO_5$ 0.6 N, in water (non-buffered solutions, pH *ca.* 2); 20 °C. Yields by ^1H NMR. [b] Product abbreviation: D, glutaric acid; E, succinic acid. [c] Oxidation of succinic acid gave 9% conversion after 24 h.

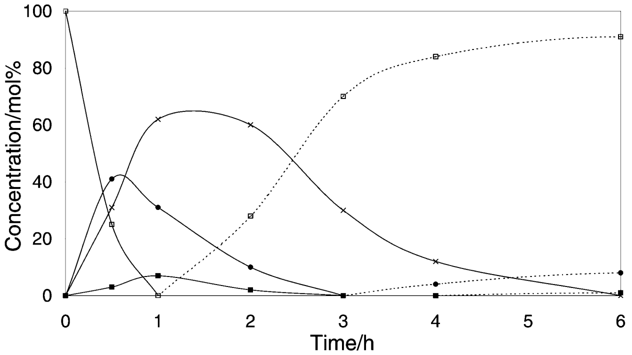


Fig. 1 Time course for cyclohexanol oxidation. Reaction conditions: RuPcS catalyst (1 mM), cyclohexanol (45 mM), $KHSO_5$ (0.5 N in water) 20 °C. Cyclohexanol (—□—); cyclohexanone (—■—); ε-caprolactone (—●—); 6-hydroxyhexanoic acid (—×—); adipic acid (- - □ - -); glutaric acid (- - ■ - -); succinic acid (- - ● - -).

taric and succinic acid were the only other products detected in the final reaction mixture. By lowering the catalyst concentration to 0.1 mM, the reaction definitely slowed down and the reaction mixtures at 24 h showed formation of adipic acid (55%), with only a trace of succinic acid, but significant amounts of unreacted ε-caprolactone or 6-hydroxyhexanoic acid. A simple water-soluble derivative of ruthenium, RuPW, tested for comparison purposes, also effected the oxidation of cyclohexanone, but the reaction was rather unselective, involving massive over-oxidation (*ca.* 50%) of the formed adipic acid.

The good results obtained for the cyclohexanone oxidation prompted us to test the persulfate oxidation of cyclohexanol in the presence of FePcS, CoPcS and RuPcS. NiPcS and CuPcS, which were unable to promote the oxidation of ε-caprolactone or 6-hydroxyhexanoic acid and were also found to be poor catalysts for the oxidation of cyclohexanol (Table 3). In the presence of 1 mM FePcS, cyclohexanol was rapidly and quantitatively converted into 6-hydroxyhexanoic acid, which remained however the overwhelmingly major product even after 24 h; CoPcS behaved better, leading to a 37% yield of adipic acid (24 h). The reaction in the presence of 1 mM RuPcS was very fast and complete disappearance of the substrate occurred within minutes, with quantitative formation (*ca.* 90%) of adipic acid after a few hours. The time course for the oxidation of cyclohexanol (Fig. 1), which was followed by ^1H NMR (Fig. 2), clearly showed the formation and disappearance of all the expected reaction intermediates (cyclohexanone, ε-caprolactone, 6-hydroxyhexanoic acid) in the early stages of the reaction and slow formation of the over-oxidation products of adipic acid (glutaric and succinic acids) at longer times. With 0.1 mM RuPcS, only a 45% conversion was achieved after 24 h. Kinetic isotope effects for the oxidation of cyclohexanol-d_{12} *vs.* cyclohexanol were measured, but with both RuPcS and FePcS at 0.1 mM concentration, almost undetectable differences were found ($r_H/r_D = 1.1$ for RuPcS and 1.2 for FePcS). The observed absence of detectable KIEs strongly indicates a concerted oxygen transfer from the oxidizing metal species to the alcoholic substrate, likely coordinated to the metal.[22]

Hydrogen peroxide oxidations of cyclohexanol and cyclohexanone were conducted at room temperature in an aqueous phase containing the substrates (50 mM) and an excess of hydrogen peroxide (*ca.* 10 equiv. mol^{-1}), both in acidic (pH *ca.* 2) and in neutral media, with the MPcS catalysts (M = Fe, Ru) added in at 2 mol% with respect to the substrates. Typical conversions, oxidation rates and product distributions are reported in Table 4. Contrary to the experiments with persulfate, where yields to the oxidant were generally close to the stoichiometric requirement, extensive dismutation of H_2O_2 was observed, even in the acidic media, thus considerably limiting the yields of the reactions; cyclohexanol was oxidized only into cyclohexanone and in very low yields. FePcS caused the least amount of decomposition of H_2O_2 (1 and 0.1 mM solutions of FePcS induced dismutation of 0.25 M solutions of H_2O_2 with half-times of 12 and 6 h, respectively). However, the overall conversions of cyclohexanone by FePcS and

Table 3 Oxidation of cyclohexanol by MPcS catalysts and $KHSO_5$[a]

Catalyst	[cat]/mM	Time/h	Substrate conv. (%)	Yield w.r.t. the oxidant[b]/equiv.%	Product selectivity[c]/mol% A	B	C	D	E
FePcS	1	1	100	35	6	42	52	—	—
		24		36	—	—	100	tr	—
CoPcS	1	1	34	10	35	64	1	—	—
		24	100	49	—	—	63	37	tr[d]
NiPcS	1	24	20	5	65	35	tr	—	—
CuPcS	1	24	5	2	—	100	—	—	—
RuPcS	1	0.5	75	22	3	59	38	—	—
		24	100	87	—	—	—	86	14[d]
	0.1	1	12	4	30	70	—	—	—
		24	45	27	—	—	35	65	—

[a] Conditions: catalyst, cyclohexanol, 45 mM, and $KHSO_5$, 0.5 N, in water (non-buffered solutions, pH *ca.* 2); 20 °C. Yields determined by ^1H NMR and GC. In the absence of catalysts, 1% conversion of the substrate to cyclohexanone within 24 h. [b] Consumed (calc.) over available oxidant (equiv./equiv.). Equivalents of oxidant necessary for the formation of each mol of product from cyclohexanol were calculated to be: cyclohexanone (2), ε-caprolactone and 6-hydroxyhexanoic acid (4); adipic acid (8); succinic acid (20). [c] Product abbreviation: A, cyclohexanone; B, ε-caprolactone; C, 6-hydroxyhexanoic acid; D, adipic acid; E, succinic acid. [d] Also traces of glutaric acid.

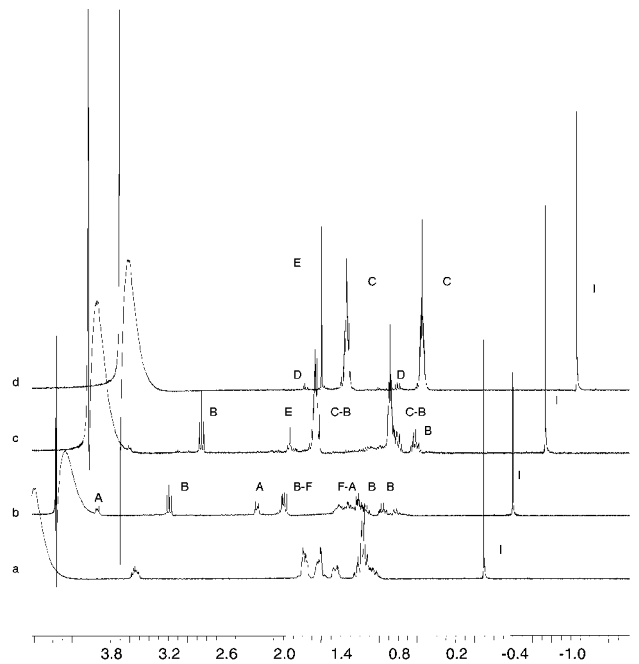


Fig. 2 ^{1}H NMR spectra during cyclohexanol oxidation (for reaction conditions, see Fig. 1): a: $t = 0$ min; b: $t = 60$ min; c: $t = 180$ min; d: $t = 24$ h; A = ε-caprolactone, B = 6-hydroxyhexanoic acid, C = adipic acid, D = glutaric acid, E = succinic acid, F = cyclohexanone, I = TSP (reference in a co-axial capillary tube).

Table 4 Oxidation of cyclohexanone and cyclohexanol by MPcS catalysts and H_2O_2[a]

Catalyst	Substrate conv. (%)	Product selectivity[b,c]/mol%		
		A	B	C
Cyclohexanone				
FePcS	21[d]	99	1	
	68[e]	99	1	
	100[f]		15	
RuPcS	30	10		
	60[e]	50	1	
	47[f]	5		
Cyclohexanol				
FePcS	16[d]			100
RuPcS	5			100

[a] Conditions: catalyst 1 mM, substrate (cyclohexanone 42 mM or cyclohexanol 45 mM) and H_2O_2 0.5 N, in water (non-buffered solutions, pH *ca.* 7, unless otherwise stated); 20 °C, unless otherwise stated. Yields at 24 h, determined by ^{1}H NMR and GC. No detectable substrate conversion within 24 h in the absence of catalyst or in the presence of NiPcS, CuPcs, RuPW, RuDMS or $Fe_2(SO_4)_3$ (1 mM) or RuPcS or FePcS catalysts (0.1 mM). [b] CO_2, CO and other VOCs are also present in the gas phase. [c] Product abbreviation: A, 6-hydroxyhexanoic acid; B, adipic acid; C, cyclohexanone. [d] Oxidant still present. [e] Acidified (pH *ca.* 2) by adding H_2SO_4. [f] At 60 °C.

RuPcS (1 mM) were comparable, likely due to an intrinsically higher catalytic activity of RuPcS. In all cases yields in adipic acid were definitely small. Higher temperature (60 °C) sped up the reactions, leading to higher conversions of the substrate, but with low yields of adipic acid.

Oxidation of cyclohexane

The promising results obtained with persulfate prompted us to test the possibility of a direct, one-step oxidation of cyclohexane to adipic acid. The oxidations were conducted in a double phase system, with the catalysts and persulfate dissolved in the aqueous phase and the organic phase consisting of the neat substrate, in large excess to the oxidant. Addition of conventional phase-transfer agents, such as trimethylcetylammonium hydrogen sulfate, was useless, because of fast oxidation of the organic chain. Nevertheless, oxidation of cyclohexane also took place in the absence of phase-transfer agents, although slowly (days) and in the presence of high concentrations (1–5 mM) of the catalysts (Table 5). FePcS and CoPcS were poor catalysts, with small overall conversion of cyclohexane. Moreover, FePcS led to the formation of 6-hydroxyhexanoic acid only, whereas CoPcS promoted an effective over-oxidation of the formed adipic acid. With

Table 5 Oxidation of cyclohexane by metal catalysts and $KHSO_5$[a]

Catalyst	[cat]/mM	Time/h	Yield w.r.t. the oxidant[b]/equiv.%	Products[c]/mM (in the aqueous phase)			
				A	B	C	D
FePcS	5	24	18	15	—	—	—
		48	20	17	—	—	—
CoPcS	5	24	6	—	1.9	tr	0.5
		48	7	—	2.5	tr	0.5
RuPcS	5	24	8	tr	4.0	—	—
		48	17	—	8.5	—	tr
		72	22	—	10	tr	0.4
	1	24	8	2.4	2.8	—	tr
		48	9	1.3	3.4	tr	0.2
RuPW	5	24	28	—	11	—	1.4
		48	53	—	18	—	3.8
		72[d]	100	—	25	6	7.0
	1	24	8	4.5	1.5	—	—
		48	9	3.4	2.4	—	—
		72	12	2.5	3.6	—	0.3
RuDMS	5	24	41	—	12.5	tr	3.7
		48[e]	53	—	13	3.0	4.0

[a] Conditions: 2.5 mL of water (non-buffered, pH *ca.* 2) containing the catalyst and persulfate 0.5 N, stirred with 0.5 mL of cyclohexane. Yields determined by ^{1}H NMR. [b] Consumed (calcd) over available oxidant. Equivalents of oxidant necessary for the formation of each mol of product from cyclohexane were calculated to be: 6-hydroxyhexanoic acid (6); adipic acid (10); glutaric acid (16); succinic acid (22). [c] Product abbreviation: A, 6-hydroxyhexanoic acid; B, adipic acid; C, glutaric acid; D, succinic acid. [d] On addition of a further 5 mequiv. of fresh oxidant to the reaction mixture and reaction for a further 72 h, the following products are detected: adipic acid, 25; glutaric acid, 6; succinic acid, 45 mM. [e] Reaction no longer running after 48 h.

RuPcS progressive and selective accumulation of adipic acid was observed in the aqueous phase, accounting for a *ca.* 20% yield after 72 h (calculated with respect to the oxidant), with the reaction still running; only smaller amounts (5%) of glutaric and succinic acid were detected in the reaction mixtures. Two other ruthenium derivatives, RuDMS and RuPW, both soluble in water, were tested for comparison purposes; adipic acid was produced in both cases, although with lower selectivity. Moreover, in the presence of RuDMS the reaction stopped at *ca.* 50% of the available oxidant, likely because of poisoning of the catalyst (*vide supra*); on the contrary, RuPW was active for several days, up to quantitative consumption of the available oxidant.

Fate of the catalyst

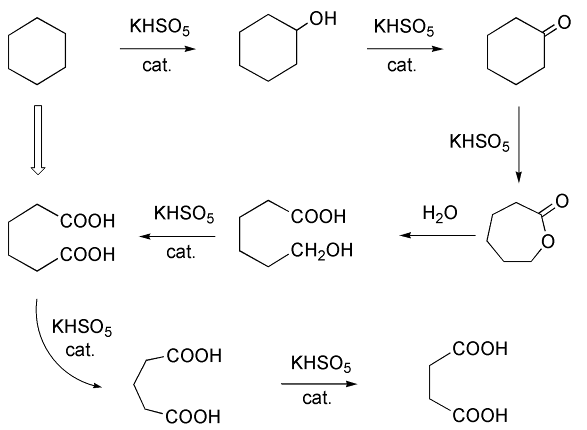
In all reported cases, the metal complexes used underwent rapid degradation in the oxidizing reaction media, giving rise to new species, likely the catalytically active ones; the fact that different catalytic behaviors were exhibited (for example, by the various ruthenium derivatives) strongly indicates that degradation did not lead to the same, totally uncomplexed aqueous metal species. Only RuDMS behaved as a true precursor of a 'naked' metal species, likely RuO_4; in the presence of persulfate the diagnostic ^1H NMR signals of the RuDMS complex[23] were completely replaced within 30 min by a sharp singlet at 3.05 ppm, assigned to dimethylsulfone, a poor metal-coordinating ligand.

The fate of the RuPW catalyst was less clear-cut; ^{31}P NMR spectra (measured under the same reaction conditions, *i.e.* at pH *ca.* 2 for H_2SO_4) showed complete disappearance of the diagnostic signal of the compound, at -11.4 ppm, within 1 h upon addition of persulfate. A new signal appeared as a singlet at -12.8 ppm, whereas no other species, apart from moderate amounts of H_3PO_4 (singlet at $+1.1$ ppm), were detected after 48 h reaction. The nature of the new species is elusive, although the above data should rule out massive fractionation of the heteropolyoxometallate moiety, at least to the level described in the literature for simpler Keggin derivatives; polyoxometallates are indeed generally considered to be very sensitive to peroxolytic degradation,[24,25] but significant and recent exceptions have been reported.[26–28] The catalytically active solutions containing the 'RuPW' compound could be reused in the experiments of cyclohexane oxidation, but at longer reaction times succinic, and not adipic acid, was the dominant product.

RuPcS (and the other MPcS derivatives used) also behaved as a pre-catalyst; we have already reported[10] that peroxidic oxidants rapidly and irreversibly turn the deeply colored compounds into yellow species, with complete disappearance of the diagnostic absorptions due to the π-conjugated aromatic system of the phthalocyanine ring (Q band). This change is accompanied by the formation of ammonia, roughly in a 1 : 1 molar ratio with the complex. This unexpected feature suggests that selective cleavage at one of the nitrogen atoms of the phthalocyanine ring occurs, strongly reminiscent of the celebrated oxidative degradation of heme to verdoheme and biliverdin[29] and also observed in relevant iron porphyrin model compounds.[30] Detailed investigations are under way, aiming to define the nature of the species resulting upon degradation of the phthalocyanine ring.

Conclusion

The oxidation pathway for the present catalytic cyclohexane oxidation consists of the conventional multistep process (Scheme 1), involving two catalytic oxidations (first to cyclohexanol and then to cyclohexanone), followed by two uncatalyzed steps (Baeyer–Villiger oxidation of cyclohexanone to ε-caprolactone and acid hydrolysis of the latter to 6-hydroxyhexanoic acid) and finally the catalytic oxidation of 6-hydroxyhexanoic acid to adipic acid. In the case of RuPcS, fast and quantitative conversions of cyclohexanone or cyclohexanol were observed at catalyst loadings down to 0.2%, with selectivities in adipic acid of up to 90%. RuPcS is also active and equally selective for the direct oxidation of cyclohexane to adipic acid, whereas RuPW and RuDMS shows poorer selectivity. Oxidation of 6-hydroxyhexanoic acid appears to be the crucial step, which was effectively promoted only by CoPcS and the ruthenium derivatives. However, since oxidation of cyclohexanol to cyclohexanone by CoPcS was scarcely effective and major problems arose with RuPW and RuDMS, because of effective decarboxylation of the formed adipic acid, RuPcS turns out to be the pre-catalyst of choice for the overall process, leading to adipic acid when starting from both cyclohexanol and cyclohexane with acceptable selectivity (Fig. 3).



Scheme 1 Proposed reaction pathway for the oxidation of cyclohexane.

As the authors of a very recent review claim in the title itself, "cyclohexane oxidation continues to be a challenge",[31] a survey of the recent literature on liquid phase oxidations of cyclohexane to adipic acid did indeed show conflicting results. With molecular oxygen moderate conversions, low selectivity in adipic acid and, often, severe reaction conditions were generally reported;[5,6,32] when milder conditions were used, only cyclohexanol or cyclohexanone were detected as oxidation products.[33,34] Persulfate oxidation of cyclohexane or cyclohexanol, promoted by manganese porphyrins, only led, and after long reaction times (up to 160 h), to ε-caprolactone;[35] on the contrary, oxidations effected by hydrogen peroxide (in the presence of heteropolytungstates[18]) or by TBHP (over cerium-containing silicates[36]) produced cyclohexanol and cyclohexanone (or cyclohexyl hydroperoxide). The good selectivity in adipic acid reported for the present RuPcS pre-catalyst and

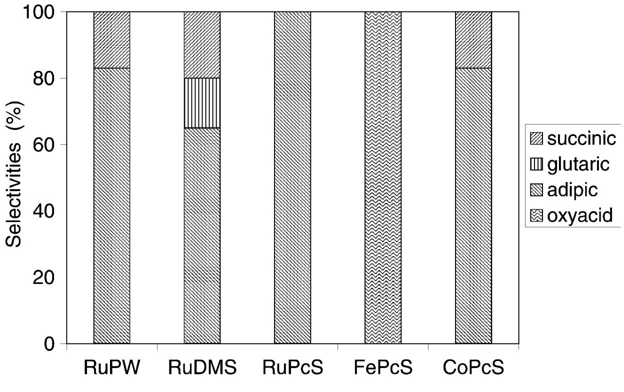


Fig. 3 Bar chart comparing the product selectivity (mol%) upon persulfate oxidation of cyclohexane with various metal catalysts (48 h reaction).

the mild conditions used may allow one to envisage its use as an alternative possibility for the direct synthesis of adipic acid.

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References

1 M. Freemantle, *Chem. Eng. News*, 2000, **78**, 7.
2 K. D. Draths and J. W. Forst, in *Green Chemistry*, ed. P. T. Anastas and T. C. Williamson, Oxford University Press, Oxford, UK, 1998, p. 58.
3 C. Xu, J. Oyloe and D. E. Richardson, *Abstracts of the 218th Meeting of the American Chemical Society*, ACS, Washington, DC, 1999, p. 569-INOR.
4 I. Belkhir, A. Germain, F. Fajula and E. Fache, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 1761.
5 M. Dugal, G. Sankar, R. Raja and J. M. Thomas, *Angew. Chem., Int. Ed.*, 2000, **39**, 310 and references therein.
6 A. Lambert, D. J. Macquarrie, G. Carr and J. H. Clark, *New J. Chem.*, 2000, **24**, 485.
7 M. Bressan, L. Forti and A. Morvillo, *New J. Chem.*, 1995, **19**, 951.
8 M. Bressan, L. Forti and A. Morvillo, *J. Chem. Soc., Chem. Commun.*, 1994, 253.
9 M. Bressan, N. d'Alessandro, L. Liberatore and A. Morvillo, *Coord. Chem. Rev.*, 1999, **185–186**, 385.
10 M. Bressan, N. Celli, N. d'Alessandro, L. Liberatore, A. Morvillo and L. Tonucci, *J. Organomet. Chem.*, 2000, **593–594**, 416.
11 N. d'Alessandro, L. Liberatore, L. Tonucci, A. Morvillo and M. Bressan, *J. Mol. Catal. A: Chem.*, 2001, in press.
12 A. Hadash, A. Sorokin, A. Rabion and B. Meunier, *New J. Chem.*, 1998, **22**, 45.
13 A. Hadash and B. Meunier, *Eur. J. Inorg. Chem.*, 1999, 2319.
14 A. Sorokin, L. Fraisse, A. Rabion and B. Meunier, *J. Mol. Catal. A: Chem.*, 1997, **117**, 103.
15 R. Raja and P. Ratnasamy, *Catal. Lett.*, 1997, **48**, 1.
16 E. Armengol, A. Corma, V. Fornes, H. Garcia and J. Primo, *Appl. Catal. A*, 1999, **181**, 305.
17 C. Nozaki, M. Misono and N. Mizuno, *Chem. Lett.*, 1998, 1263.
18 M. M. Q. Simoes, C. M. M. Conceicao, J. A. F. Gamelas, P. M. D. N. Domingues, A. M. V. Cavaleiro, J. A. S. Cavaleiro, A. J. V. Ferrer-Correia and R. A. W. Johnstone, *J. Mol. Catal. A: Chem.*, 1999, **144**, 461.
19 J. H. Weber and D. H. Busch, *Inorg. Chem.*, 1965, **4**, 469.
20 I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 204.
21 M. Bressan, L. Forti, F. Ghelfi and A. Morvillo, *J. Mol. Catal.*, 1993, **79**, 85.
22 R. Mello, L. Cassidei, M. Fiorentino, C. Fusco, W. Hummer, V. Jager and R. Curci, *J. Am. Chem. Soc.*, 1991, **113**, 2205.
23 E. Alessio, G. Mestroni, G. Nardin, W. M. Attia, M. Calligaris, G. Sava and S. Zorzet, *Inorg. Chem.*, 1988, **27**, 4099.
24 C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **143**, 407.
25 L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Doromieux-Morin, G. Gottard, H. Ledon, Y. Jeannin and J.-M. Bregeault, *Inorg. Chem.*, 1994, **33**, 871.
26 R. Neumann and A. M. Khenkin, *J. Mol. Catal. A: Chem.*, 1996, **114**, 169.
27 W. P. Griffith, N. Morley-Smith, H. I. S. Nogueira, A. G. F. Shoair, M. Suriaatmaja, A. J. P. White and D. J. William, *J. Organometal. Chem.*, 2000, **607**, 146.
28 J. Server-Carrio, J. Bas-Serra, M. E. Gonzalez-Nunez, A. Garcia-Gastaldi, G. B. Jameson, L. C. W. Baker and R. Acerete, *J. Am. Chem. Soc.*, 1999, **121**, 977.
29 L. Avila, H.-W. Huang, J. C. Rodriguez, P. Moenne-Loccoz and M. Rivera, *J. Am. Chem. Soc.*, 2000, **122**, 7618 and references therein.
30 T. N. St. Claire and A. L. Balch, *Inorg. Chem.*, 1999, **38**, 684 and references therein.
31 U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. de Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinace and E. L. Fires, *Appl. Catal. A*, 2001, **211**, 1.
32 M. Besson, A. Blackburn, P. Gallezot, O. Kozynchenko, A. Pigamo and S. Tennison, *Top. Catal.*, 2000, **13**, 253.
33 K. Teramura, T. Tanaka, T. Yamamoto and T. Funabiki, *J. Mol. Catal. A: Chem.*, 2001, **165**, 299.
34 N. Perkas, Y. Q. Wang, Y. Koltypin, A. Gedanken and S. Chandrasekaran, *Chem. Commun.*, 2001, 998.
35 L. Cammarota, S. Campestrini, M. Carrieri and F. Di Furia, *J. Mol. Catal. A: Chem.*, 1999, **137**, 155.
36 E. L. Pires, U. Arnold and U. Schuchardt, *J. Mol. Catal. A: Chem.*, 2001, **169**, 157 and references therein.