Highly efficient one-step conversion of cyclohexane to adipic acid using single-site heterogeneous catalysts

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A solid source of 'active' oxygen (acetylperoxyborate, APB), when dissolved in aqueous solution in the presence of a single-site microporous catalyst containing redox centres (Fe^{III}AlPO-31, Mn^{III}AlPO-5, Fe^{III}AlPO-5), converts cyclohexane with high efficiency (*ca.* 88%) and exceptionally high selectivity (*ca.* 81%) to adipic acid at 383 K; this procedure is also effective in converting styrene to styrene oxide and α-pinene and (+)-limonene to their corresponding epoxides.

Oxidation reactions are central to numerous processes that convert bulk chemicals into useful, higher-value products.[1] But most of the current practices employed in industry suffer from several disadvantages, such as the use of aggressive oxidants, low selectivity, multiple-step reactions and the generation of excessive amounts of waste. There is a pressing need for new oxidants, especially if, by the parallel use of benign and inexpensive solid catalysts, highly selective oxidations may be effected under relatively mild conditions. It is acknowledged that the ideal oxidant is air or oxygen[2–4] and that the merits of hydrogen peroxide,[5] notwithstanding the practical problems associated with its transport, storage and use, are considerable. Many striking recent advances have been reported with this oxidant.[6]

Here we describe how a stable powder, acetylperoxyborate (APB), which has hitherto been used mainly for bleaching purposes,[7] may be used,[8] when dissolved in aqueous solution, to generate high yields of (i) adipic acid (an extremely important commodity chemical in the manufacture of urethanes and polyamides such as nylon 6,6), and (ii) a variety of epoxides, from their hydrocarbon precursors. Currently adipic acid is manufactured by a two-step process involving nitric acid oxidation of K-A oil, a mixture of cyclohexanol and cyclohexanone, the latter being produced from cyclohexane using a homogeneous cobalt-based catalyst.[9,10] Alternative synthetic routes have also been developed, such as the one-step oxidation of cyclohexane with either alkyl hydroperoxides or dioxygen.[11–13] The formation of styrene oxide from styrene has been used widely as a model reaction for demonstrating catalytic epoxidation. It is estimated that millions of lbs of styrene oxide are produced per annum in the USA alone for the production of styrene glycol and phenylethyl alcohol (perfumes), as a reactive diluent for epoxy resins and as a chemical intermediate for cosmetics, surface coatings, fibres and textiles. The solid redox catalysts that are eminently suitable for the generation of active oxygen from peroxy precursors are transition-metal-substituted microporous aluminophosphates[4b,14] (*e.g.* Fe^{III}AlPO-31, Mn^{III}AlPO-5 and Fe^{III}AlPO-5), which have been described[4b,14] (and used for other[15] benign oxidations) by us previously.

On the laboratory scale, we have shown previously[13] that, with a carefully designed framework-containing Fe^{III}AlPO-31 catalyst, aerial oxidation of cyclohexane may achieve some 65% selectivity towards adipic acid, but the conversion falls in the range of 3 to 8% at temperatures of 373 to 403 K. Many other heme and non-heme catalysts can facilitate the oxidation of cyclohexane in H_2O_2 or in alkylhydroperoxides, but the products are invariably a mixture of cyclohexanol and cyclohexanone.

We have carried out structural studies on APB both in the solid state and on dissolution in water. Powder XRD shows that APB is a crystalline material, but comprises a mixture of phases; the major constituent(s) of this mixture are of unknown structure.† Solid state NMR spectroscopy also substantiates the complexity of the solid material.‡ However, when APB is dissolved in water, the situation is substantially simpler, and it is clear that the different phases present in the solid state give rise to the same solution state species on dissolution in water. Thus, in aqueous solution, ^{13}C and ^{1}H NMR spectra reveal that acetic acid [CH_3CO_2H] and peroxyacetic acid [CH_3CO_3H] are the only carbon-containing species present (Fig. 1). The ^{11}B NMR spectrum shows a single peak characteristic of trigonal $B(O)_3$ species (probably representing the average over an equilibrium involving different species of this type, including boric acid [$B(OH)_3$]).

Integration of the ^{1}H NMR signal intensities (CH_3 groups) shows that, after dissolution in water, the ratio of peroxyacetic acid to acetic acid decreases relatively slowly as a function of time (Fig. 2), as the system moves towards establishing the following equilibrium:§ $CH_3CO_2H + H_2O_2 \rightleftharpoons CH_3CO_3H + H_2O$. Clearly, a decrease in the ratio [CH_3CO_3H]/[CH_3CO_2H] as the system approaches equilibrium leads to an increase in the concentration of hydrogen peroxide.

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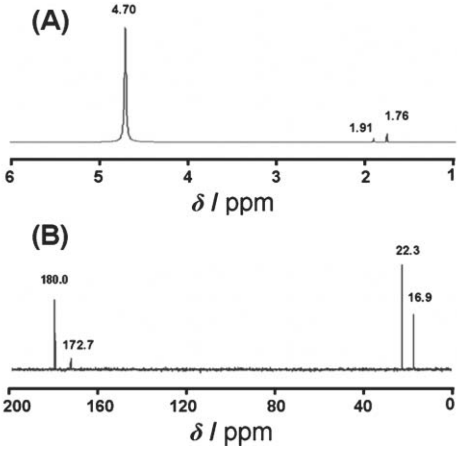

Fig. 1 (A) Solution state ^{1}H NMR spectrum of APB dissolved in D_2O [1.76 ppm: CH_3 of acetic acid (averaged over the equilibrium $CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$); 1.91 ppm: CH_3 of peroxyacetic acid (averaged over the equilibrium $CH_3CO_3H \rightleftharpoons CH_3CO_3^- + H^+$); 4.70 ppm: ^{1}H in D_2O (residual ^{1}H), $B(OH)_3$, H_2O_2, and the CO_2H groups of acetic acid and peroxyacetic acid, all of which undergo rapid exchange in the acidic solution]. (B) Solution state ^{13}C NMR spectrum of APB dissolved in D_2O [22.3 ppm: CH_3 of acetic acid; 180.0 ppm: C(O)O of acetic acid; 16.9 ppm: CH_3 of peroxyacetic acid; 172.7 ppm: C(O)OO of peroxyacetic acid; the ^{13}C signals are averaged over the equilibria shown above].

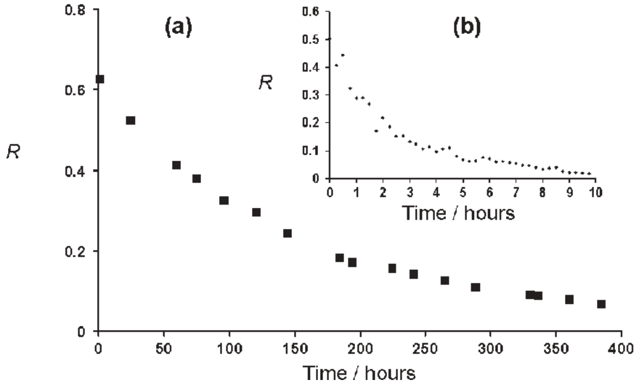

Fig. 2 Plot of the ratio $R = [CH_3CO_3H]/[CH_3CO_2H]$ (determined from solution state ^{1}H NMR) as a function of time after dissolution of APB in water at (a) 25 °C and (b) 65 °C.

Table 1 Oxidation of cyclohexane[a] using APB and Fe^{III}AlPO-31

				Product selectivity (mol%)			
Oxidant	pH	Time (h)	Conv. (mol%)	Cy-ol[c]	Cy-one[d]	Adipic acid	Other acids[b]
APB	5.2	3	49.0	11.2	71.5	17.1	—
		16	88.6	—	11.3	81.2	7.5
PAA	1.65	3	61.2	6.5	48.3	21.8	23.5
		16	97.0	—	—	33.1	56[e]
PAA + Neobor®	5.1	3	42.0	17.3	57.5	22.5	2.7
		16	82.6	3.3	17.7	72.5	6.5
PAA + NaOAc	5.1	3	48.0	13.5	49.7	17.5	19.2
		16	89.8	3.5	16.8	51.2	24.3[f]

[a] Cyclohexane ≡ 2.5 g; FeAlPO-31 ≡ 0.25 g; T ≡ 383 K; solid APB ≡ 3.49 g (shown by titration studies to liberate 0.701 g of peroxyacetic acid and 0.045 g of H_2O_2 immediately on dissolution); 20.5 g of double-distilled (d-d) water; PAA ≡ peroxyacetic acid (25% peroxyacetic acid solution in acetic acid) ≡ 4.2 g + 20.5 g of d-d water; PAA + Neobor® ≡ 4.2 g (25% peroxyacetic acid solution in acetic acid) + 1 g Neobor® + 1 g NaOH + 20.5 g of d-d water; PAA + NaOAc ≡ 4.2 g (25% peroxyacetic acid solution in acetic acid) + 0.934 g sodium acetate trihydrate + 1 g NaOH + 20.5 g of d-d water. [b] Other acids ≡ glutaric, succinic and valeric acids. [c] ≡ Cyclohexanol. [d] ≡ Cyclohexanone. [e] ≡ 10.5% CO_2. [f] ≡ 4.1% CO_2.

The key feature of the use of the novel solid oxidant APB is that the peroxyacetic acid, formed on dissolving APB, releases its active oxygen in the presence of the single-site[16] solid redox catalysts Fe^{III}AlPO-31, Mn^{III}AlPO-5 or Fe^{III}AlPO-5 and dissolved boron-containing species (see below). The active oxygen so liberated oxidizes cyclohexane and epoxidizes any alkene introduced to the sphere of reaction with high yields and high selectivities. Typical results for the oxidation of cyclohexane are presented in Table 1.

The Fe^{III}AlPO-31 microporous catalyst has a one-dimensional channel system with a pore aperture of 5.4 Å, which is significantly smaller than that of Fe^{III}AlPO-5 (7.3 Å). The more puckered inner walls therefore provide a constrained environment for the oxidation of cyclohexane and thus modify the selectivity of the reaction, as we have described earlier.[13] What we capitalize upon is "*product shape selectivity*" in a highly localized manner within the restricted environment, where the isolated catalytically active sites (M^{III} ions) are located. The use of the solid oxidant (APB) in conjunction with the Fe^{III}AlPO-31 catalyst improves the overall conversion by an order of magnitude (≅ 13 fold), but more interestingly the selectivity for adipic acid is also significantly enhanced (from 65% to 81%), compared to our earlier work[13] when air was used in combination with this catalyst.

For the purpose of comparison, the oxidation of cyclohexane was also carried out using neat peroxyacetic acid (PAA) rather than APB as the oxidant. Although high conversions are observed, the selectivity for adipic acid is reduced drastically. Fragmentation products such as succinic, glutaric and valeric acids, tar and CO_2 seem to predominate with PAA. In order to rule out the possibility that the decreased adipic acid selectivities observed with neat PAA are due to changes of pH, additional experiments were carried out by adjusting the pH to be the same as that in the experiments with APB. In one set of experiments, a combination of peroxyacetic acid, sodium acetate trihydrate and NaOH was used to bring the pH close to that for APB, while in another set, Neobor® borax pentahydrate ($Na_2B_4O_7{\cdot}5H_2O$; ex Borax Europe Ltd), an important component which is present in APB, was used. The addition of Neobor® significantly enhances the selectivity for adipic acid, whereas in the absence of Neobor®, fragmentation products and CO_2 are observed (in agreement with the result for neat PAA). In the experiments in which Neobor® is added to PAA, the conversions (activity) and selectivities for adipic acid are not as high as those observed with solid APB. Although Neobor® is a major component in the preparation of APB, we emphasize that other components (sodium perborate monohydrate and H_2O_2) are also involved in the preparation and may influence the activity and selectivity. However, this series of experiments shows that the boron (borate) component, contained in Neobor®, is critical for the high activities and selectivities observed when APB is used as the oxidant. Thus, while APB serves as a source of "active" oxygen for these catalytic oxidation processes, the role of key boron-containing species that arise from dissolution of APB is also implicated. Clearly, identification of these species and understanding their role is an important issue for future research.

Table 2 Liquid-phase epoxidation[a] of olefins and terpenes using APB

Substrate	Catalyst	Oxidant	pH	Time (h)	Conv. (mol%)	Product selectivity (mol%)			
						E[b]	Diol	B[c]	Others
Styrene	MnAlPO-5	APB	5.2	1	95.2	100	—	—	—
				4	98.8	86.5	13.5	—	—
Styrene	FeAlPO-5	APB	5.2	1	84.1	100	—	—	—
				4	99.1	87.3	12.5	—	—
Styrene	MnAlPO-5	PAA	1.65	1	97.6	15.5	35.2	39.7	9.5
Styrene	MnAlPO-5	PAA + Neobor®	5.1	1	73.0	87.3	12.5	—	—
				4	79.6	81.3	18.5	—	—
Styrene	MnAlPO-5	PAA + NaOAc	5.1	1	78.0	63.3	27.5	9.2	—
				4	92.7	43.5	29.7	11.3	14.2
α-Pinene	MnAlPO-5	APB	5.2	1	77.8	100	—	—	—
				4	88.6	68.7	—	—	31.2
(+)-Limonene	MnAlPO-5	APB	5.2	1	78.0	100	—	—	—
				4	93.7	61.3	—	—	38.5

[a] Styrene ≡ 2.8 g; α-pinene, (+)-limonene ≡ 3.7 g; MeAlPO-5 ≡ 0.25 g; T ≡ 338 K; solid APB ≡ 3.49 g (shown by titration studies to liberate 0.701 g of peroxyacetic acid and 0.045 g of H_2O_2 immediately on dissolution); 20.5 g of double-distilled (d-d) water; PAA ≡ (25% peroxyacetic acid solution in acetic acid) ≡ 4.2 g + 20.5 g of d-d water; PAA + Neobor ≡ 4.2 g (25% peroxyacetic acid solution in acetic acid) + 1 g Neobor® + 1 g NaOH + 20.5 g of d-d water; PAA + NaOAc ≡ 4.2 g (25% peroxyacetic acid solution in acetic acid) + 0.934 g sodium acetate trihydrate + 1 g NaOH + 20.5 g of d-d water. [b] E ≡ epoxide. [c] B ≡ benzaldehyde.

The liquid-phase epoxidations of styrene, α-pinene and (+)-limonene with Mn^{III}- and Fe^{III}AlPO-5 are summarized in Table 2. For styrene, both catalysts, at 65 °C and 1 h contact time, give very high conversions and close to 100% selectivity towards styrene oxide. Longer contact time, not surprisingly, yields some diol products and a corresponding diminution in selectivity towards the desirable styrene oxide. Blank experiments (in the absence of the solid catalysts) afford low conversions and virtually no styrene oxide is produced (only diols and polymeric products are observed), and a Mukaiyama style epoxidation[17] (entailing the use of sacrificial benzaldehyde for the *in situ* production of perbenzoic acid in the presence of the redox catalyst) is much less effective than the APB procedure.

Analogous experiments were performed with styrene to exclude the effect of pH and to investigate the importance of the boron (borate) component. As in the case of cyclohexane, the addition of Neobor® significantly improves the selectivity for the epoxide, whereas in the absence of Neobor®, cleavage, polymeric and other degradation products are observed (in good agreement with the result for neat PAA).

While previous uses of borates in the oxidation of organic compounds have been reported,[18] the use of the solid oxidant APB together with single-site framework-substituted metal aluminophosphate catalysts, reported for the first time in the present paper, represents a highly promising new opportunity for effecting a range of oxidation processes. Thus, the high activities and high selectivities observed using APB in the oxidation of cyclohexane to adipic acid and in the epoxidations of olefins and terpenes (Tables 1 and 2), coupled with the obvious advantages that this solid oxidant offers in handling, transport and storage, augur well for the future use of APB in a range of industrially significant reactions and processes.

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Notes and references

† The powder XRD pattern contains subsets of peaks that differ significantly in linewidth, suggesting that the material is a mixture of phases of differing crystallinity. The main intense peaks are comparatively broad. So far, successful indexing of the powder XRD pattern has not been achieved. Other narrower peaks of lower intensity are assigned as impurity phases, one of which is identified as $NaCH_3COO(CH_3CO_2H)_2$ (A. Perotti and V. Tazzoli, *J. Chem. Soc., Dalton Trans.*, 1981, 1768). The 2A phase of boric acid (W. H. Zachariasen, *Acta Crystallogr.*, 1954, **7**, 305) is probably also present as a minor impurity.

‡ The high resolution solid state ^{13}C NMR spectrum of APB indicates at least three different CH_3 environments and at least two different C=O environments, suggesting that there are several structurally distinguishable acetyl/acetate $[CH_3C(O)OZ/CH_3C(O)O^-]$ and/or peroxyacetyl/peroxyacetate $[CH_3C(O)OOZ/CH_3C(O)OO^-]$ groups in the material (where Z is probably a boron-containing moiety). Solid state ^{11}B NMR spectroscopy shows at least two different boron environments, and solid state ^{23}Na NMR spectroscopy confirms the presence of sodium in the material (the spectrum is broad due to quadrupolar interaction).

§ The reported equilibrium constant for this reaction at 25 °C (defined as $K = [CH_3CO_3H][H_2O]/[CH_3CO_2H][H_2O_2]$) is *ca.* 3.28 (see: K. Murai, G. Akazome and Y. Murakami, *Kogyo Kagaku Zasshi*, 1960, **63**, 1233). As $[H_2O] >> [H_2O_2]$ in aqueous solution, then at equilibrium, the ratio $[CH_3CO_3H]/[CH_3CO_2H]$ $(= K[H_2O_2]/[H_2O])$ must be << 1.

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