Selective Epoxidation of Terminal Alkenes with Diluted Hydrogen Peroxide Catalysed by Pt–OH Species

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An hydroxoplatinum(II) complex, recognized to behave as a base in protic media, catalyses the selective epoxidation of terminal alkenes with diluted H_2O_2.

The oxidation of terminal alkenes by transition metal peroxo species has received considerable attention[1] in recent years, mostly because of its potential use to the petrochemical industry. In this context the epoxidation of alkenes appears to be a prerogative of early transition metals in their higher oxidation states (acidic metal centres),[2] group 8 metal species leading almost invariably to ketonization.[3]

It has long been known that certain α,β-unsaturated ketones or aldehydes or other electronegatively substituted alkenes can be easily epoxidized with H_2O_2 under basic conditions (NaOH),[4] the key feature being the nucleophilic addition of the hydroperoxide anion to the carbon–carbon double bond promoted by the electron withdrawing substituent. From this point of view the base could in principle be a group 8 transition metal ion with the advantage of having a centre also capable of activating unsubstituted alkenes toward nucleophilic attack.

We have recently reported on the synthesis of some stable hydroperoxo and t-butylperoxo complexes of Pt^{II} of the type $P_2Pt(alkyl)(OOR)$ (P = tertiary phosphine, R = H, Bu^t)[5,6] and have accomplished the stoicheiometric ketonization of terminal alkenes with *trans*-t-butylperoxo species under

Table 1. Rate of epoxidation of alkenes with 35% H_2O_2 catalysed by (diphoe)Pt(CF_3)(OH).[a]

Alkene	Initial rate × 10^6 ($dm^3\ mol^{-1}\ s^{-1}$)	Solvent[b]
propene[c]	>10	THF
hex-1-ene	2.4	THF
oct-1-ene	1.8	THF
oct-1-ene	1.3	DME
oct-1-ene	4.9	EtOH
styrene	0.01	THF
cyclohexene	—	THF, EtOH
cis-hex-2-ene	—	THF, EtOH

[a] Reaction conditions: [Pt] 1.7×10^{-2} M; [alkene] 7.4×10^{-1} M; [H_2O_2] 4.2×10^{-1} M; *t* 20 °C; N_2 1 atm; selectivity >99%. [b] THF = Tetrahydrofuran, DME = dimethoxyethane. [c] Reaction conditions: same as footnote a except propene 1 atm instead of N_2.

anhydrous conditions.[7] Spectroscopic parameters for these complexes indicate a considerable covalent character for the Pt–O bond under anhydrous conditions. On the other hand Pt–OH complexes have been recognized to behave as strong bases in protic media,[8] and this behaviour has been confirmed by us for some of these species from conductivity data[7] thereby suggesting the important solvolytic role of water in promoting ionic dissociation [reaction (1)].

$$\text{Pt-OH} \overset{H_2O}{\rightleftharpoons} \text{Pt}^+ + \text{HO}^- \qquad (1)$$

We now wish to report the first successful epoxidation of terminal alkenes with diluted H_2O_2 under transition metal 'basic' conditions, which seems to represent a new approach to this class of reactions.

When an excess of 35% H_2O_2 was added to a solution of oct-1-ene in various solvents in the presence of (diphoe)Pt(CF_3)(OH) [diphoe = 1,2-bis(diphenylphosphino)ethylene] the catalytic epoxidation of the alkene took place. The reaction was carried out at 20 °C under an N_2 atmosphere; the selectivity was >99%, 1,2-epoxyoctane being the only detectable oxidation product. The reaction profile shown in Figure 1 was revealed from g.l.c. A linear initial rate, until about 35—40% conversion, can be envisaged. The epoxidation proceeded until complete consumption of H_2O_2 (100% conversion) indicating that no side reaction took place. Initial rates for different alkenes are reported in Table 1. Again epoxides were the only oxidation products. As shown only terminal alkenes can be epoxidized under the experimental conditions employed while internal alkenes are not.

This result represents the first success in the use of inexpensive, diluted solutions of H_2O_2 as the oxygen source for the epoxidation of simple linear alkenes; previous reports employed either more reactive substituted alkenes or highly concentrated (>70%) solutions of H_2O_2.[9] In these cases, using mostly early transition metals as catalysts, the use of water or alcohols as solvents strongly inhibited the process, at variance with our case (Figure 1). Moreover water is a necessary requirement to our system, since, as we have already observed, (diphoe)Pt(CF_3)(OOH) does not transfer oxygen to alkenes in a water-free system, even under more forcing conditions (90 °C).[5,6] However when 35% H_2O_2 was added to a solution of oct-1-ene in the presence of catalytic amounts of (diphoe)Pt(CF_3)(OOH) (experimental conditions as in Figure 1) a reaction identical to that reported in Figure 1 took place. These observations indicate that the Pt–OOH species, as such, is not the reactive intermediate of this oxidation reaction; moreover with Pd–OOH[10] or Ir–OOH[11] species where this class of reactions has been suggested to proceed *via* peroxymetallation, methyl ketones are invariably the oxidation products. Now since Pt–OH species undergo ionic dissociation in protic media, it is reasonable to assume a similar behaviour for Pt–OOH. This fact coupled with the unusual nature of the oxidation product strongly suggest the hypothesis of an external nucleophilic attack of the HOO⁻ anion to the co-ordinated alkene.

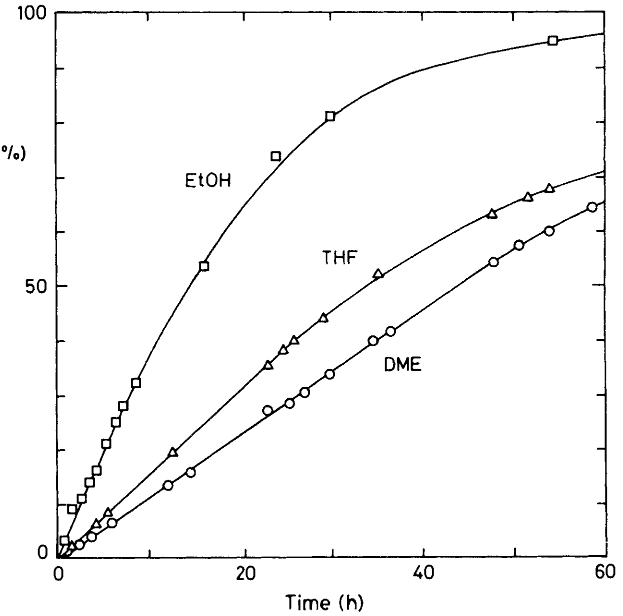

Figure 1. Epoxide formation from oct-1-ene and 35% H_2O_2 in various solvents catalysed by (diphoe)Pt(CF_3)(OH). Conversion (%) based on H_2O_2. Reaction conditions as in footnote a in Table 1.

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