Aerobic oxidation of isopropanol catalysed by peroxovanadium complexes: mechanistic insights

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Aerobic oxidation of Pr^iOH to acetone with parallel reduction of dioxygen to hydrogen peroxide is observed for acid $Pr^iOH–H_2O$ solutions of peroxovanadates. Spectroscopic evidence, obtained with a combined use of ^{51}V-NMR, UV–VIS and ESI-MS techniques, is presented for a monoperoxovanadium-catalysed inner-sphere oxidation of the alcohol coordinated to the metal center.

Introduction

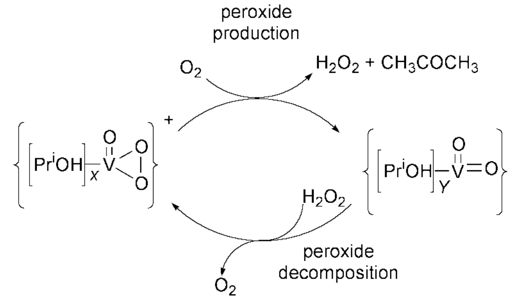
Reductive dioxygen activation mediated by transition metal ions is a fundamental step in oxidative reactions and biological processes.[1] In several instances, the involvement of peroxometal derivatives has been observed.[1] Studies aimed at characterising the structure of such intermediates are, therefore, key starting points for understanding synthetic and metabolic O_2 activation mechanisms. Furthermore, peroxometal complexes, and in particular peroxovanadium derivatives, are widely used in stoichiometric and catalytic oxidations of organic and inorganic substrates.[2]

Heretofore, we have reported[3,4] that V(V) and Mo(VI) peroxo complexes mediate, through a radical process, the oxidation of primary and secondary alcohols, along with the reduction of dioxygen to hydrogen peroxide. While in the Mo-catalysed reaction the H_2O_2 produced is quantitatively converted to products, carbonyl compounds and water, in the V-catalysed process the hydrogen peroxide accumulates. More recently, we have observed that with vanadium catalysis the reaction shows an oscillatory behavior,[4] *i.e.* the concentration of H_2O_2 as a function of time oscillates between phases of production and subsequent decomposition. Remarkably, the presence of acid ($HClO_4$, up to 2×10^{-4} mol L^{-1}) is essential for a suitable and reproducible rate of hydrogen peroxide production. In fact, in its absence an inconveniently low rate of increase of H_2O_2 concentration is observed.

Here we report spectroscopic evidence that points to the involvement of a vanadium monoperoxo complex as an effective catalyst for a one-electron oxidation of an alcohol molecule, occurring within the coordination sphere of the metal. The subsequent formation of hydrogen peroxide is due to a chain process initiated by the interception of dioxygen from a ketyl radical released in solution (Scheme 1).

Results and discussion

The model autoxidation reaction is carried out (see Experimental section for details) by dissolving the vanadium precursor, Bu_4NVO_3,[4,5] in wet Pr^iOH (H_2O up to 5 mol L^{-1}) in the presence of excesses of H_2O_2 and 2×10^{-4} mol L^{-1} $HClO_4$. The reaction mixture is kept at 40 °C, with stirring, under atmospheric oxygen pressure. The observed kinetic profile[4] is characterised by the presence of a periodic pattern, where the concentration of H_2O_2 oscillates as a result of a balance between subsequent production and decomposition processes (Scheme 1).



Scheme 1

The efficiency of the reaction can be measured as $([H_2O_2]_{t_{max}} - [H_2O_2]_0)/[cat]_0$, where t_{max} is the reaction time to detection of the first maximum in the H_2O_2 concentration kinetic profile[4] (see Table 1). Inspection of data in Table 1 shows that addition of water slows down the overall reaction rate (entries 1–4), but improves the efficiency of the process, as more than 4000 equivalents of H_2O_2 per vanadium catalyst are produced in the reaction containing 0.5 mol L^{-1} H_2O (entry 4, Table 1). On the other hand, by increasing the catalyst concentration (entries 5–8) the vanadium-catalysed decomposition of hydrogen peroxide becomes the dominant process.[6]

We have anticipated[4] that, under the adopted reaction conditions, speciation of the vanadium catalysts present in solution by the combined use of ^{51}V-NMR and ESI-MS techniques[7–9] is hampered in the presence of acid.† Yet, UV–VIS spectra provide a straightforward tool. The isosbestic behaviour in Fig. 1 shows that addition of acid transforms diperoxovanadium species, produced in the presence of an excess of hydrogen peroxide ($\lambda_{max} = 340$ nm),[10] to monoperoxo derivatives ($\lambda_{max} = 420$ nm).[10]

The catalytic effect of acid thus indicates monoperoxovanadium complexes as competent species for alcohol oxidation and O_2 activation. As in alcoholic solutions, in the absence of acid, vanadium monoperoxo species can be formed selectively by controlling the excess of hydrogen peroxide,[7] we have analysed solutions (Pr^iOH–0.5 M H_2O) containing

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† Accumulation of radical species in solution[3,4] causes the disappearance of ^{51}V-NMR signals. Besides, mono- and diperoxovanadium compounds do not survive the ESI conditions in acid media.[7–9]

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Table 1 H_2O_2 formation in the reaction of Bu_4NVO_3 and H_2O_2 in Pr^iOH (2×10^{-4} mol L^{-1} $HClO_4$), $T = 40$ °C, O_2 atmospheric pressure

Entry	$[cat]_0{}^a$/mol L^{-1}	$[H_2O_2]_0$/mol L^{-1}	$[H_2O]_0$/mol L^{-1}	$t_{max}{}^b$/h	$[H_2O_2]_{t_{max}}$/mol L^{-1}	Efficiency^c
1	0.00010	0.0050	0.5	80	0.130	1250
2	0.00010	0.0050	1.0	194	0.368	3630
3	0.00010	0.0050	2.5	240	0.408	4030
4	0.00010	0.0050	5.0^d	750	0.440	4350
5	0.00025	0.0125	0.5	40	0.085	290
6	0.00030	0.0150	0.5	50	0.081	220
7	0.00035	0.0175	0.5	30	0.030	36
8	0.00050	0.0250	0.5	50	0.020	^{e}

^{a} Catalyst = Bu_4NVO_3. ^{b} Time at which maximum formation of H_2O_2 is detected for the first time. ^{c} Efficiency = $([H_2O_2]_{t_{max}} - [H_2O_2]_0)/[cat]_0$. ^{d} $[H_2O_2]$ regularly increased in the observation period. ^{e} H_2O_2 decomposes.

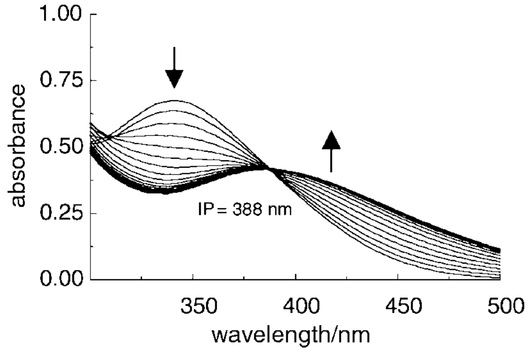
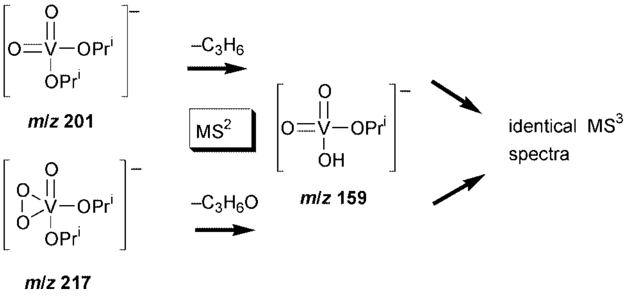


Fig. 1 UV–VIS spectra for solutions of Bu_4NVO_3 (1×10^{-3} mol L^{-1}) with H_2O_2 (5×10^{-2} mol L^{-1}) in Pr^iOH–H_2O (0.5 mol L^{-1}). $[HClO_4]$ increases from 0 to 2×10^{-3} mol L^{-1}.



Scheme 2

Bu_4NVO_3 (1×10^{-3} mol L^{-1}) and equimolar amounts of H_2O_2 by ESI-MS and ^{51}V-NMR techniques. In particular, ESI-MS has recently emerged as a powerful tool for the analysis and identification of many inorganic and organometallic derivatives, including species in rapid exchange.[7,9,11] The negative ion mode ESI-spectra of such systems show the occurrence of two major ionic species at *m*/*z* 201 and 217, respectively.‡ The peak at *m*/*z* = 201 is the predominant species observed in analogous conditions but in the absence of hydrogen peroxide. ^{51}V-NMR spectra obtained by dissolving Bu_4NVO_3 (1×10^{-3} mol L^{-1}) in Pr^iOH–0.5 M H_2O show a peak at δ −574, typical of vanadate alkyl esters in Pr^iOH.[12,13] Accordingly, the ion at *m*/*z* 201 can be attributed to the non peroxidic species $[O_2V(OPr^i)_2]^-$. In the presence of H_2O_2, further identification of the principal species in ESI-MS spectra was obtained by labelling experiments and collision-induced decomposition spectra (CID). In particular, replacement of water with $H_2{}^{17}O$ (*ca.* 50% isotope content) results in the formation of new peaks at *m*/*z* 202 (100% rel. int. *vs.* *m*/*z* 201) and 203 (50% rel. int. *vs.* *m*/*z* 201) next to 201, and at *m*/*z* 218 (50% rel. int. *vs.* *m*/*z* 217) next to 217, indicating a fast exchange, within the coordination sphere of the V(V) species, of two and one oxo oxygens, respectively.[14,15] In analogous conditions, ^{51}V-NMR spectra show again two major peaks, one at δ −574 already discussed, and one at δ −608, which can be attributed to a monoperoxovanadium derivative,[16,17] together with a smaller signal at δ −642, likely due to diperoxo alcohol-containing complexes.[12,18,19] The coupled use of ESI-MS and ^{51}V-NMR techniques hence allows the identification of the ion at *m*/*z* 217 as the monoperoxo complex $[OV(O_2)(OPr^i)_2]^-$.

CID experiments performed on the isolated ions at *m*/*z* 201 and 217 show the formation of a common ion at *m*/*z* 159. Moreover, such isobaric ions afford identical MS^3 spectra, thus indicating that a common fragment attributed to $[O_2V(OPr^i)(OH)]^-$ originates from both the vanadate precursor and the monoperoxo derivative (Scheme 2).

Interestingly, when the corresponding oxo-labelled species are mass selected, formation of the daughter ion at *m*/*z* 161 from 203 and *m*/*z* 160 from 218 is observed, confirming that the fragmentation does not takes place at the expense of the oxo ligands.

The pattern for the formation of the *m*/*z* 159 ion from the monoperoxo $[OV(O_2)(OPr^i)_2]^-$ derivative is particularly significant, since it consists of a 58 Da fragment expulsion, corresponding to the formal release of C_3H_6O. Previously,[3,4] we have proposed that the key step of the title oxidation is an inner-sphere hydrogen atom abstraction by the peroxometal complexes from the coordinated alcohol, thus forming a coordinated ketyl radical which, subsequently, evolves to acetone. Further support to our proposal has been obtained in the present study, where we have observed a marked decelerating effect in the presence of increasing amounts of water. Such behaviour is conceivably explained by the substitution, in the coordination sphere of the metal, of an alcohol molecule with one of water, a reaction that has been already observed with ESI-MS technique.[7] Furthermore, the outcome of the CID experiments, performed on the isolated $[OV(O_2)(OPr^i)_2]^-$ ion, represents the first compelling evidence of a monoperoxovanadium-catalysed inner-sphere oxidation of Pr^iOH to acetone (C_3H_6O).

The data reported above suggest the mechanism shown in Scheme 3 for the formation of acetone in the vanadium-catalysed oxidation of Pr^iOH.

Monoperoxovanadium compounds are known to act as one-electron acceptors.[20] Moreover, a correlation between the peroxidic oxygen–oxygen bond strength and their ability to act as one-electron acceptors has been observed.[20] On the basis of such a correlation it has been proposed that the most likely event caused by one-electron reduction is the homolytic rupture of the peroxidic bond.[20]

Formation of acetone, both in the gas phase and in solution, can be accordingly described as a sequence of one-electron transfer steps involving the peroxovanadium species leading to the radical anion intermediate reported in Scheme 3 path **a**. The data so far obtained, however, do not allow us to firmly exclude

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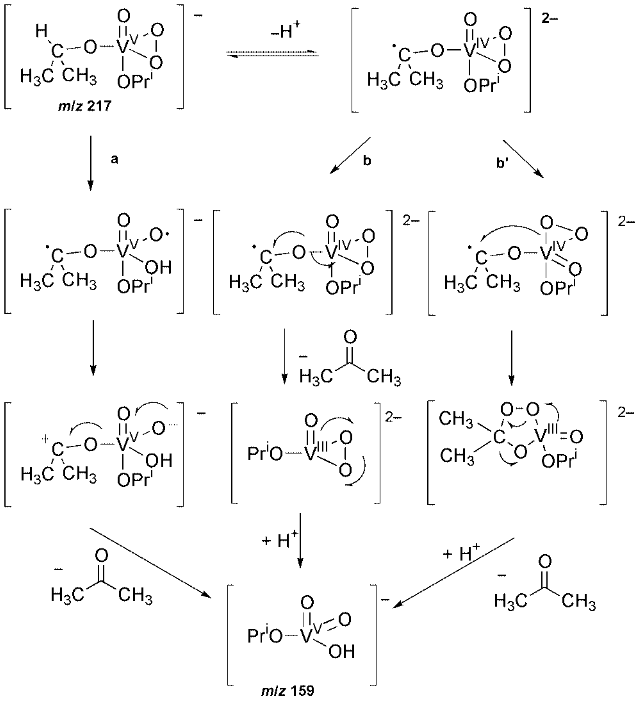
‡ Ions of rel. int. <10% are found at *m*/*z* 117 $[VO_3H_2O]^-$, 131 $[OV(O_2)_2]^-$ and 159 $[VO_3PrOH]^-$.



Scheme 3

the direct involvement of the metal centre in one-electron reduction processes. Such a circumstance is formally described by the intermediates of paths **b** and **b′** in Scheme 3.

Conclusions

The work presented in this paper provides conclusive evidence of the direct involvement of a monoperoxovanadium complex in the gas-phase oxidation of Pr^iOH to acetone occurring within the coordination sphere of the metal. In solution such a reaction gives rise to an autoxidation chain initiated by a one-electron oxidation of the coordinated substrate. A valuable outcome of the process is the *in situ* generation of H_2O_2[21] from O_2, which occurs under mild conditions and serves as primary oxidant for the activity of the vanadium catalyst.

Studies aimed at obtaining a better definition of the nature of the radical intermediates involved in the oxidation of alcohols with monoperoxovanadium derivatives are warranted.

Experimental

All reagents and solvents were of highest grade commercially available and were used purified or freshly distilled as reported in literature. Bu_4NVO_3 is synthesised accordingly to a previously reported[4,5] procedure. Hydrogen peroxide concentration is determined with standard iodometric titration.

The ESI-MS measurements (Thermoquest LCQ, San Jose CA) were performed by direct injection of Bu_4NVO_3 (1×10^{-3} mol L^{-1}) dissolved in Pr^iOH–0.5 M H_2O in the absence or in the presence of an equimolar amount of H_2O_2. For labeling experiments $H_2{}^{17}O$ with an isotope content of *ca.* 50% was used ($H_2{}^{18}O$ less than 4%). Solution flow rate 8 μL min^{-1}, capillary temperature 80 °C, spray voltage 2.2 kV, capillary voltage −5 to −10 V, tube lenses offset −55 V, nebulizing gas N_2 (40 units flow rate). The parameters related to octapoles and detector were achieved by the automatic set-up procedure. Collision-induced decompositions of selected ions were obtained by applying a supplementary r.f. voltage (tickle voltage) to the end cap electrodes of the ion trap (resonance activation).

NMR and UV–VIS spectra were obtained as already described[16] by using a Bruker AC 200 (4.69 Tesla) and Lambda 5 or Lambda 16 Perkin-Elmer instruments respectively.

The model autoxidation reaction has been carried out by dissolving the desired amount of Bu_4NVO_3 in wet Pr^iOH (H_2O 0.5–5 mol L^{-1}) in the presence of the corresponding excess of H_2O_2 (see Table 1 for concentrations), and 2×10^{-4} mol L^{-1} $HClO_4$. The reaction mixture is kept at 40 °C, with stirring, under atmospheric oxygen pressure. Variation of the peroxide content is analysed at chosen time intervals with standard iodometric titration. Reproducibility of the kinetic behaviour was checked with triplicate runs.

Acknowledgements

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References

1 Special thematic issue, *Metal-Dioxygen Complexes*, *Chem. Rev.*, 1994, **94**, 567.
2 T. Hirao, *Chem. Rev.*, 1997, **97**, 2707.
3 V. Conte, F. Di Furia and G. Modena, *J. Org. Chem.*, 1988, **53**, 1665.
4 M. Bonchio, O. Bortolini, M. Carraro, V. Conte and S. Primon, *J. Inorg. Biochem.*, 2000, **80**, 191.
5 V. W. Day, W. G. Klemperer and A. Yagasaki, *Chem. Lett.*, 1990, 1267.
6 M. Bonchio, V. Conte, F. Di Furia, G. Modena, S. Moro and J. O. Edwards, *Inorg. Chem.*, 1994, **33**, 1631.
7 O. Bortolini, V. Conte, F. Di Furia and S. Moro, *Eur. J. Inorg. Chem.*, 1998, 1193.
8 O. Bortolini, M. Carraro, V. Conte and S. Moro, *Eur. J. Inorg. Chem.*, 1999, 1489.
9 V. Conte, O. Bortolini, M. Carraro and S. Moro, *J. Inorg. Biochem.*, 2000, **80**, 41.
10 O. Bortolini, F. Di Furia, G. Modena and P. Scrimin, *J. Mol. Catal.*, 1980, **9**, 323.
11 R. Colton, A. D'Agostino and J. C. Traeger, *Mass Spectrom. Rev.*, 1995, **14**, 79.
12 D. Rehder, in *Vanadium in Biological Systems*, ed. N. D. Chasteen, Kluwer Academic Publishers, The Netherlands, 1990, ch. X, and references cited therein.
13 A. S. Tracey and M. J. Gresser, *Can. J. Chem.*, 1988, **66**, 2570.
14 M. Postel, C. Brevard, H. Arzoumanian and J. Riess, *J. Am. Chem. Soc.*, 1983, **105**, 4922.
15 A. Butler, M. J. Claugue and G. E. Meister, *Chem. Rev.*, 1994, **94**, 625.
16 V. Conte, F. Di Furia and S. Moro, *J. Mol. Catal.*, 1994, **94**, 323; V. Conte, F. Di Furia and S. Moro, *J. Mol. Catal., A: Chem.*, 1995, **104**, 159.
17 I. Andersson, S. Angus-Dunne, O. Howarth and L. Pettersson, *J. Inorg. Biochem.*, 2000, **80**, 51 and references cited therein.
18 V. Conte, F. Di Furia and S. Moro, *Inorg. Chim. Acta*, 1998, **272**, 62, and references cited therein.
19 J. S. Jaswal and A. S. Tracey, *Inorg. Chem.*, 1991, **30**, 3718.
20 M. Bonchio, V. Conte, F. Di Furia, G. Modena, S. Moro, T. Carofiglio, F. Magno and P. Pastore, *Inorg. Chem.*, 1993, **32**, 5797.
21 W. R. Thiel, *Angew. Chem., Int. Ed.*, 1999, **38**, 3157.