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Peroxidative oxidation of benzene and mesitylene by vanadium catalysts

Patrícia M. Reis, José Armando L. Silva, João J.R. Fraústo da Silva, Armando J.L. Pombeiro*

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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Dedicated to Professor J.J. Ziólkowski, on the occasion of his 70th birthday, as a recognition of his achievements.

Abstract

Benzene and mesitylene (1,3,5-trimethylbenzene) are oxidized to phenol and to the corresponding aldehyde (3,5-dimethylbenzaldehyde), respectively, in CH_3CN at room temperature, by aqueous hydrogen peroxide, in acidic medium, in reactions catalyzed by vanadium(IV or V) compounds with *N*,*O*-ligands (such as *Amavadine* models and related ones), namely of the types triethanolamine and (hydroxyimino)dicarboxylic acid (basic forms) or comparable ligands. The effects of the ligands, of the relative amounts of reagents and of the temperature are also reported.

Keywords: Vanadium catalysts; Hydroxylation; Oxidation; Hydrogen peroxide; Benzene; Mesitylene; Aromatics; Amavadine

1. Introduction

The conversion of hydrocarbons into oxygenated derivatives such as alcohols, aldehydes, ketones and carboxylic acids has been extensively studied over the last decades, because such products are of a high industrial significance [1–4]. However, industrial oxidation processes usually exhibit limitations, namely in terms of selectivity, yield or energy demand. For instance, phenol is currently produced from cumene (Hock process) and by toluene oxidation [5,6]. In the former process, acetone is produced in equimolar amount and in the latter the yield is low. Therefore, there is a need for the search of new processes to produce phenol without by-products, with a high selectivity and in conditions as mild as possible.

Hydroxylation of benzene is a conceptually attractive alternative and a number of authors have used vanadium and other metal complex catalysts [7–25], which in the presence of hydrogen peroxide, form peroxo complexes that can oxidize hydrocarbons and are postulated as active intermediates in the catalytic processes. Hydrogen peroxide, besides molecular oxygen, is the most attractive oxidation reagent because it is of comparatively low cost and gives only water as by-product. In the last few years, most of the articles dealing with the hydroxylation of benzene to form phenol are based on heterogeneous catalysts, which require high temperatures [26–28].

We now report that a series of vanadium(IV or V) complexes with *N*,*O*-donor ligands act as catalysts (or catalyst precursors) for such a conversion at room temperature, using hydrogen peroxide as the hydroxylating agent in acidic medium. They are also effective for the peroxidative oxidation, at room temperature, of mesitylene (1,3,5-trimethylbenzene), a substrate with two different types of groups (aliphatic alkyl and aromatic benzene) both susceptible to oxidation, which curiously appears to occur selectively only at one of the methyl groups to afford 3,5-dimethylbenzaldehyde.

The vanadium catalysts are of the types of those we have previously found to be active for the peroxidative hydroxylation, oxygenation and halogenation of alkanes, such as cyclohexane [29], and for the carboxylation of methane to acetic acid [30]. They are *Amavadine* models and related complexes, and the current study extends their catalytic ac-

* Corresponding author. Tel.: +351 21 841 92 37; fax: +351 21 846 44 55.
E-mail address: pombeiro@ist.utl.pt (A.J.L. Pombeiro).

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tivity to the abovementioned oxidation reactions of benzene and mesitylene, thus providing further testimony for a possible peroxidase behaviour of that natural bare vanadium complex whose biological role still remains elusive.

2. Experimental

2.1. Materials

The following compounds were used as received from the supplier: V_2O_5 (Aldrich), $VOSO_4{\cdot}5H_2O$ (Merck), V_2O_4 (Merck), benzene (Merck), mesitylene (Aldrich), CH_3CN (Riedel-deHaën), H_2O_2 (30%) (Fluka), HNO_3 (65%) (Riedel-deHaën) and diethyl ether (Riedel-deHaën). $[VO\{N(CH_2CH_2O)_3\}]$ [31,32], $Ca[V(hida)_2]$ (hida = basic form of 2,2′-(hydroxyimino)diacetic acid) [33], Ca[V(hidpa)] (hidpa = basic form of 2,2′-(hydroxyimino)dipropionic acid, racemic mixture) [33], $[VO(ada)(H_2O)]$ (ada = basic form of *N*-(2-acetamido) iminodiacetic acid) [34] and $[VO(Hheida)(H_2O)]$ (Hheida = dibasic form of *N*-(2-hydroxyethyl)iminodiacetic acid) [34] were prepared according to literature.

2.2. Instrumentation

Gas chromatographic (GC) measurements were carried out on a Fisons model 8160 equipped with a FID detector and a capillary column (DB-WAX; column length: 30 m; internal diameter: 0.32 mm). The temperature of injection was 240 °C. The column temperature profile was typically as follows: the initial temperature was maintained at 100 °C for 1 min, then raised 10 °C/min to 180 °C and held at this temperature for 1 min. In tests for benzoic acid, the temperature was raised up to 200 °C instead of 180 °C. Helium was used as the carrier gas. GC–MS measurements were carried out in a mass spectrometer Trio 2000 Fisons Instruments with a coupled gas chromatograph Carlo Erba Instruments: Auto/HRGC/MS. ^{13}C NMR-$\{^1H\}$ spectra were recorded at 22 °C on a Varian UNITY 300 spectrometer, using TMS as internal standard.

2.3. Typical oxidation procedures and products analysis

The oxidation reactions of benzene and mesitylene were carried out in Schlenk tubes and in a dinitrogen atmosphere. In a typical experiment, 0.010 mmol of catalyst were dis-

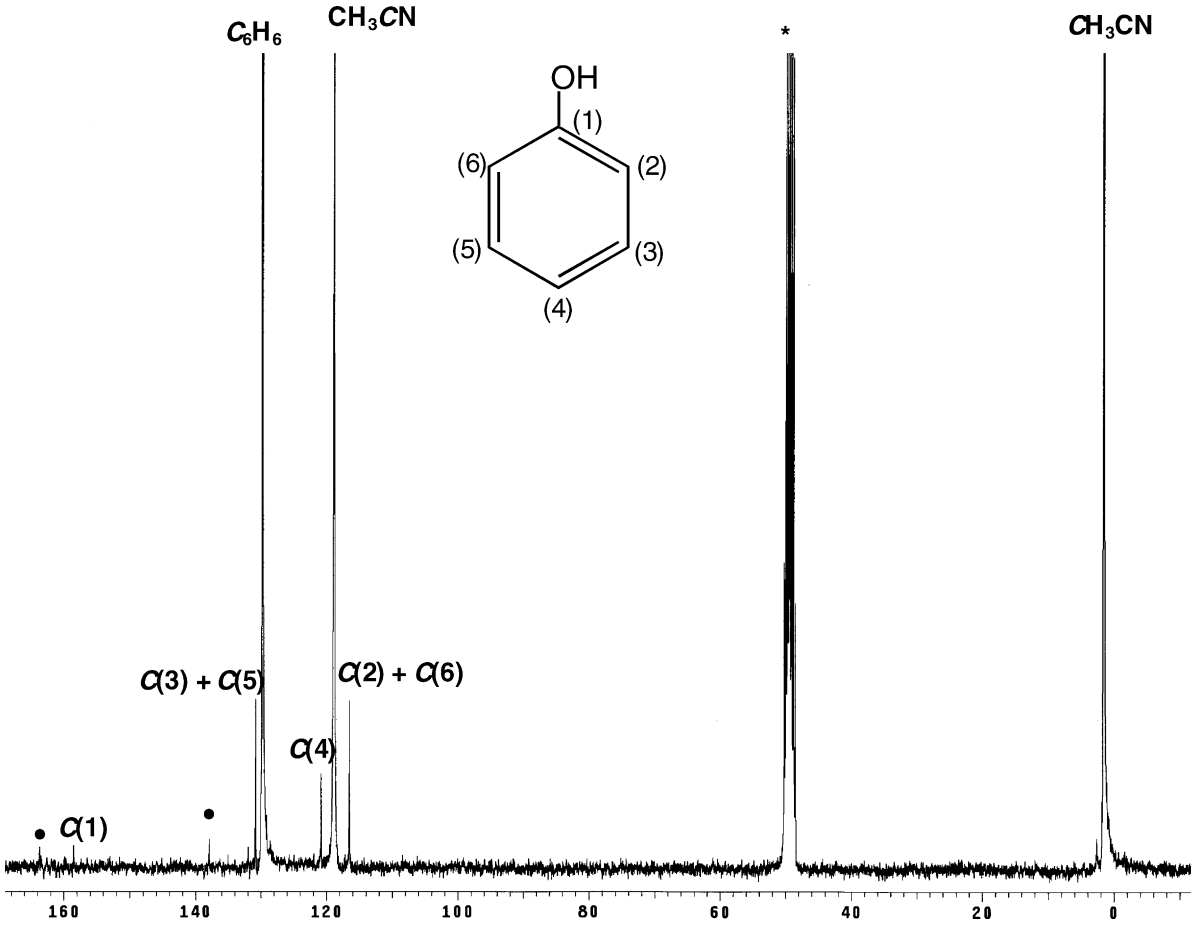


Fig. 1. $^{13}C-\{^1H\}$ NMR of the reaction solution of benzene with H_2O_2 and HNO_3 in CH_3CN using the catalyst $Ca[V(hida)_2]$ (entry 15, Table 1), run in CD_3OD. (*) Solvent; (●) unidentified.

solved in 2.5 mL CH_3CN with stirring. Then aqueous hydrogen peroxide (30%), nitric acid (65%) and substrate (5 mmol) were added. After 6 h of reaction at the desired temperature, the organic phase was extracted with 6.5 mL of diethyl ether and 90 μL of internal standard (cyclopentanone) were added. The reaction products, phenol and 3,5-dimethylbenzaldehyde, were quantitatively analyzed by GC (1 μL samples) using calibration curves based on the relative peak areas of samples with known amounts of those compounds and of cyclopentanone. They were also identified by GC–MS and ^{13}C–$\{^1H\}$ NMR (CD_3OD) of the final reaction organic phase. NMR shifts (δ): C_6H_5OH – 116.5 ($C_2 + C_6$); 120.8 (C_4), 130.8 ($C_3 + C_5$), 158.5 (C_1) (see Fig. 1); $C_6H_3(CH_3\text{-}3,5)_2CHO$ – 21.6 (CH_3), 125.7 ($C_2 + C_6$), 126.1 (C_4), 128.7 (C_1), 131.2 ($C_3 + C_5$).

The catalytic turnover number (TON) and the yield were estimated as the molar ratio of product/V catalyst precursor and the molar ratio (%) of product/substrate, respectively.

3. Results and discussion

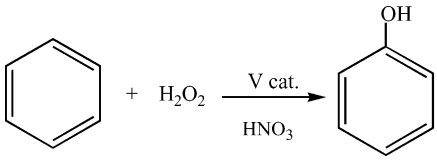
The catalyst precursors used are V^V or V^{IV} complexes with polydentate *N,O*-donor ligands: the oxo-vanadium(V) complex $[VO\{N(CH_2CH_2O)_3\}]$ with triethanolamine (basic form); the vanadium(IV) complexes (Amavadine models) with basic forms of *N*-hydroxyiminodicarboxylic acids, $Ca[V(hida)_2]$ [hida = $^-ON(CH_2COO^-)_2$] and $Ca[V(hidpa)_2]$ [hidpa = $^-ON(CHCH_3COO^-)_2$], or with the basic forms of other iminodiacetic acids, $[VO(ada)(H_2O)]$ [ada = $(H_2NCOCH_2)N(CH_2COO^-)_2$] and $[VO(Hheida)(H_2O)]$ [Hheida = $(HOCH_2CH_2)N(CH_2COO^-)_2$]. Vanadium oxides and vanadyl sulphate were also tested for comparative purposes.

The reactions occur typically by treatment of an acetonitrile solution of the vanadium complex, in the presence of aqueous H_2O_2 (30%) and HNO_3, with the substrate (benzene or mesitylene). They proceed in liquid medium and the analysis of the product (by GC and GC–MS of the diethyl ether extract from the final reaction solution, and by ^{13}C–$\{^1H\}$ NMR of the final reaction organic phase) is usually performed after 6 h reaction at room temperature (however, different reaction temperatures have also been tested, for comparison).

3.1. Benzene hydroxylation

The above vanadium systems proved to be active for the peroxidative hydroxylation of benzene to phenol (reaction 1), in acidic medium, at room temperature (ca. 20 °C). The results are summarized in Table 1 and blank tests (entries 1 and 2) have shown that no product was obtained without both the V compound and the hydrogen peroxide.

The systems appear to have a high selectivity since phenol was the only product detected by GC and GC–MS, whereas only traces of unidentified species were detected by ^{13}C–$\{^1H\}$ NMR of the final reaction organic phase (Fig. 1).



(1)

The most active complex, which can give TONs over 16 with yields over 3%, is the Amavadine model $Ca[V(hida)_2]$ (entry 15, Table 1), followed by $[VO\{N(CH_2CH_2O)_3\}]$. However, in the latter complex, replacement of the ligand by iminodiacetates in $[VO(ada)(H_2O)]$ and $[VO(Hheida)(H_2O)]$, i.e. replacement of the three or two alkoxide arms of the ligand by carboxylates or acetamide, results in loss of the catalytic activity (entries 22 and 23), showing a marked influence of the type of ligand used. Vanadium oxides, mainly V_2O_5 [20] and, less effective, V_2O_4, and vanadyl sulphate, also catalyse the reaction (entries 24–26) under identical experimental conditions, but with a lower activity per V atom than the $Ca[V(hida)_2]$ and $[VO\{N(CH_2CH_2O)_3\}]$ complexes.

The effect on the TON of the amount of H_2O_2 is shown in Fig. 2 for the $Ca[V(hida)_2]$ and $[VO\{N(CH_2CH_2O)_3\}]$ catalysts (for a constant HNO_3/V molar ratio of 72): the catalytic activity increases with the amount of peroxide up to a maximum level (for H_2O_2/V ca. 450 or 900, respectively), beyond which the TON starts to decrease slightly.

As depicted in Fig. 3, the addition of acid also promotes the formation of phenol, up to a HNO_3/V molar ratio of ca.

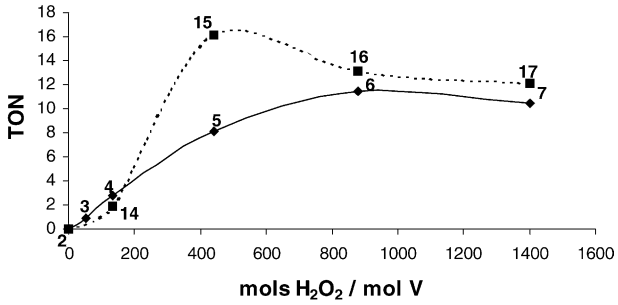


Fig. 2. Effect of H_2O_2 amount (H_2O_2/V catalyst molar ratio) on the TON, using $[VO\{N(CH_2CH_2O)_3\}]$ (♦) or $Ca[V(hida)_2]$ (■) as catalyst, for the peroxidative hydroxylation of benzene (for a constant HNO_3/V catalyst molar ratio of 72). Point numbers correspond to those of entries in Table 1.

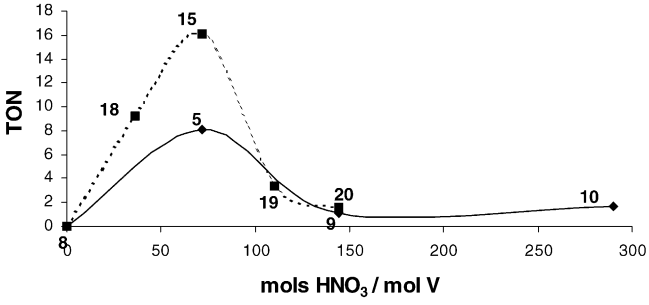


Fig. 3. Effect of the HNO_3 amount (HNO_3/V catalyst molar ratio) on the TON, using $[VO\{N(CH_2CH_2O)_3\}]$ (♦) or $Ca[V(hida)_2]$ (■) as catalyst, for the peroxidative hydroxylation of benzene (for constant H_2O_2/V catalyst molar ratio of 440). Point numbers correspond to those of entries in Table 1.

Table 1
Peroxidative hydroxylation of benzene by some vanadium(IV and V) catalysts[a]

Entry	Catalyst	H_2O_2/catalyst (molar ratio)	HNO_3/catalyst (molar ratio)	T (°C)	TON[b]	Yield[c] (%)
1	–	440	72	20	–	–
2	$[VO\{N(CH_2CH_2O)_3\}]$	–	72	20	–	–
3		54	72	20	0.9	0.2
4		134	72	20	2.8	0.6
5		440	72	20	8.1	1.6
6		880	72	20	11.5	2.3
7		1400	72	20	10.5	2.1
8		440	–	20	–	–
9		440	144	20	1.1	0.2
10		440	290	20	1.7	0.3
11		54	72	50	–	–
12		134	72	0	0.6	0.1
13		134	72	50	–	–
14	$Ca[V(hida)_2]$[d]	134	72	20	1.9	0.4
15		440	72	20	16.1	3.2
16		880	72	20	13.1	2.6
17		1400	72	20	12.1	2.4
18		440	36	20	9.2	1.8
19		440	110	20	3.4	0.6
20		440	144	20	1.6	0.3
21	$Ca[V(hidpa)_2]$[e]	440	72	20	5.8	1.2
22	$[VO(ada)(H_2O)]$[f]	440	72	20	–	–
23	$[VO(Hheida)(H_2O)]$[g]	440	72	20	–	–
24	V_2O_5	440	72	20	17.4 (8.7)[h]	3.5
25	$VOSO_4.5H_2O$	440	72	20	10.5	2.1
26	V_2O_4	440	72	20	4.9 (2.5)[h]	1.0

[a] Conditions: 0.010 mmol catalyst, 2.5 mL CH_3CN, 0.45 mL benzene, benzene/catalyst molar ratio of 500, reaction time 6 h.
[b] TON = moles product/mol catalyst.
[c] Yield (%) = moles product/mol substrate × 100.
[d] hida = basic form of 2,2′-(hydroxyimino)diacetic acid, $HON(CH_2COOH)_2$ (also with the loss of the HON proton).
[e] hidpa = basic form of 2,2′-(hydroxyimino)dipropionic acid, $HON(CHCH_3COOH)_2$ (also with the loss of the HON proton).
[f] ada = basic form of *N*-(2-acetamido)iminodiacetic acid $(H_2NCOCH_2)N(CH_2COOH)_2$.
[g] Hheida = dibasic form of *N*-(2-hydroxyethyl)iminodiacetic acid $(HOCH_2CH_2)N(CH_2COOH)_2$.
[h] Moles product/mol V.

70 (corresponding to a HNO_3/benzene molar ratio of 0.14), for both $Ca[V(hida)_2]$ and $[VO\{N(CH_2CH_2O)_3\}]$ catalysts. The enhancing activity effect of HNO_3 conceivably concerns the acid promotion of the reductive cleavage of the O–O bond in the peroxide (or hydroperoxide) intermediates leading to H_2O and an oxo-metal species (see, in particular, the known mechanism of hydroxylation reactions catalysed by cytochrome P-450 and, in general, the overall reactions of monooxygenases which catalyse the transfer of one oxygen atom from O_2 whereas the other one is reduced to O^{2-} forming H_2O [38–40]).

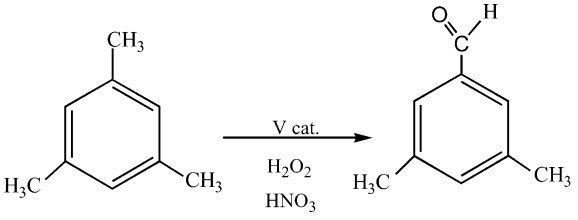
For an higher acid excess, the activity decreases abruptly, probably as a consequence of decomposition of the catalyst.

Another important factor is the temperature (°C) (see entries 3, 11 and 4, 12, 13, Table 1). Heating to a temperature of 50 °C or cooling to 0 °C essentially results in loss of activity, former effect conceivably resulting from decomposition of intermediates.

3.2. Mesitylene oxidation

Mesitylene reaches a higher oxidation level than benzene since, under identical conditions, in the presence of a V catalyst, undergoes peroxidative oxidation to an aldehyde, 3,5-dimethylbenzaldehyde (reaction 2, Table 2). The oxidation of a methyl group thus occurs preferentially to that of the benzene ring. No other oxidation product was detected by GC or GC–MS.

Oxidation to the aldehyde as the main product (although with a low selectivity and with a lower TON than in our systems) has been recognized [35] for some heteropoly vanadomolybdate and vanadium substituted silicate catalysts in the presence of hydrogen peroxide, in acetonitrile without addition of acid, whereas a different product, mesitol (2,4,6-trimethylphenol), has been reported [11] to be formed in a non-catalytic way when the peroxo-complex $[VO(O_2)(Pic)]\cdot 2H_2O$ (Pic = basic form of picolinic acid) in CH_3CN, no acid having been added.



(2)

Table 2
Peroxidative oxidation of mesitylene by some vanadium(IV and V) catalysts[a]

Entry	Catalyst	H_2O_2/catalyst (molar ratio)	HNO_3/catalyst (molar ratio)	T (°C)	TON[b]	Yield[c] (%)
1	–	440	72	20	–	–
2	$[VO\{N(CH_2CH_2O)_3\}]$	–	72	20	–	–
3		54	–	20	1.0	0.2
4		880	–	20	1.3	0.3
5		54	72	20	5.5	1.1
6		134	72	20	10.1	2.0
7		220	72	20	10.3	2.1
8		440	72	20	12.0	2.4
9		880	72	20	14.2	2.8
10		1320	72	20	10.9	2.2
11		134	144	20	6.5	1.3
12		880	144	20	16.0	3.2
13		880	290	20	10.1	2.0
14		134	72	50	15.4	3.1
15		134	72	75	24.1	3.8
16		440	72	70	32.7	6.5
17		440	72	80	37.9	7.6
18	$Ca[V(hida)_2]$[d]	54	72	20	2.0	0.4
19		134	72	20	5.2	1.0
20		220	72	20	12.1	2.4
21		880	72	20	17.1	3.4
22		1320	72	20	6.7	1.3
23		134	72	50	7.4	1.5
24		134	72	75	7.8	1.6
25		440	72	50	29.7	5.9
26		440	72	80	35.1	7.0
27	$Ca[V(hidpa)_2]$[e]	440	72	20	3.6	0.7
28	$[VO(ada)(H_2O)]$[f]	440	72	80	37.3	7.5
29	$[VO(Hheida)(H_2O)]$[g]	440	72	80	40.2	8.0
30	V_2O_5	440	72	80	36.4 (18.2)[h]	7.3
31	$VOSO_4.5H_2O$	440	72	80	38.5	7.7
32	V_2O_4	440	72	80	37.1 (18.6)[h]	7.4

[a] Conditions: 0.010 mmol catalyst, 2.5 mL CH_3CN, 0.70 mL mesitylene, mesitylene/catalyst molar ratio of 500, reaction time 6 h. The other footnotes (b–h) of Table 1 also apply to this table.

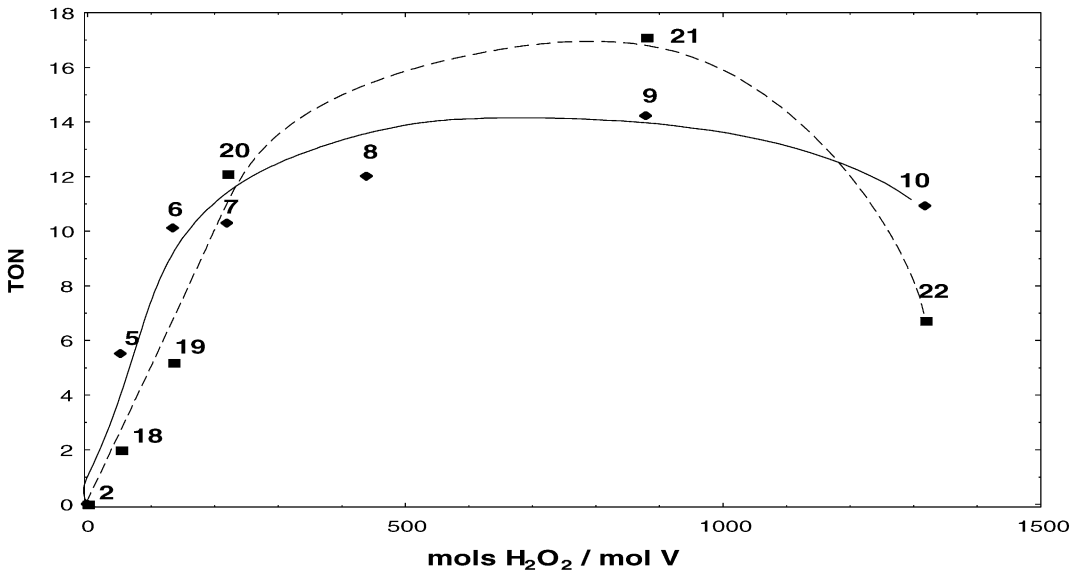


Fig. 4. Effect of the H_2O_2 amount (H_2O_2/V catalyst molar ratio) on the TON, using $[VO\{N(CH_2CH_2O)_3\}]$ (♦) or $Ca[V(hida)_2]$ (■) as the catalyst, for the peroxidative oxidation of mesitylene (for a constant HNO_3/V catalyst molar ratio of 72). Point numbers correspond to entries in Table 2.

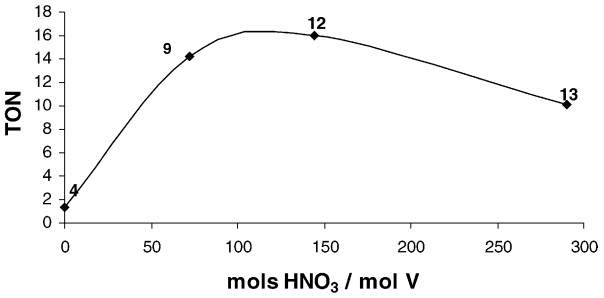


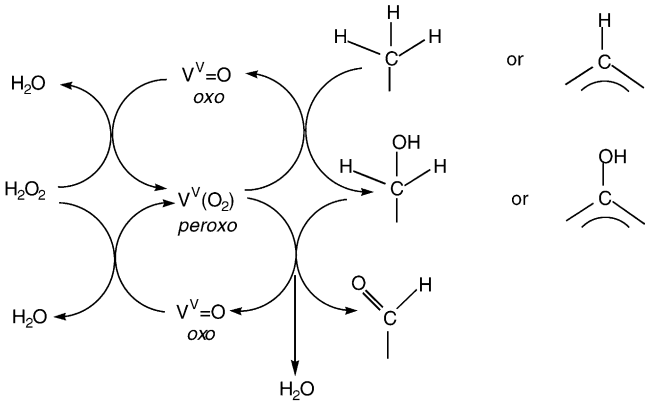
Fig. 5. Effect of the HNO_3 amount (HNO_3/V catalyst molar ratio) on the TON, using [VO{N(CH_2CH_2O)$_3$}] as the catalyst, for the peroxidative oxidation of mesitylene (for a constant H_2O_2/V catalyst molar ratio of 880). Point numbers correspond to the entries of Table 2.

As in the case of benzene, without addition of hydrogen peroxide or the vanadium catalyst, no product is obtained (entries 1 and 2, Table 2). Maximum TONs of ca. 35–40 and yields of ca. 7–8% are reached by all the V complex catalysts, except Ca[V(hidpa)$_2$]. These values are higher than those observed for the hydroxylation of benzene and, in contrast to the latter reaction, do not depend markedly on the type of ligand of the V complex. The oxides V_2O_5 and V_2O_4, as well as $VOSO_4$, display activities (entries 30–32) that approach those of the other V catalysts.

The increase of H_2O_2 promotes the formation of 3,5-dimethylbenzaldehyde up to a H_2O_2/V molar ratio of ca. 900. Beyond this value, the TON and yield begin to decrease (Fig. 4). The amount of acid and the temperature are also factors of noticeable relevance.

In contrast with the hydroxylation of benzene, we observe even without addition of acid the formation of a small amount of the aldehyde product (entries 3 and 4, Table 2). However, the addition of HNO_3 promotes the reaction (Fig. 5) as in the case of the hydroxylation of benzene, and beyond a HNO_3/V molar ratio of ca. 100, for [VO{N(CH_2CH_2O)$_3$}], the TON and yield decrease, perhaps due to the decomposition of the catalyst.

The TONs and yields for the formation of 3,5-dimethylbenzaldehyde increase with the temperature, until ca. 80 °C (the boiling point of the solution) for [VO{N(CH_2CH_2O)$_3$}], in contrast with the formation of phenol from benzene which is inhibited by heating above the room temperature.



Scheme 1. .

4. Conclusions

The peroxidative hydroxylation of benzene and oxidation of mesitylene by the above vanadium complexes with *N*,*O*-ligands proceed smoothly at room temperature, under relatively moderate conditions, and appear to exhibit a marked selectivity towards the formation of a main single product, i.e. phenol and 3,5-dimethylbenzaldehyde, respectively. Hence, mesitylene undergoes oxygenation preferably at a methyl group than at an aromatic carbon and reaches with higher yields and TONs, a higher oxidation level (aldehyde) than benzene (conversion to phenol).

The catalytic activity is very dependent on the type of *N*,*O*-ligand in the case of the former reaction where replacement of the three or two of the ligating alkoxide arms by carboxylates or acetamide groups has an inhibitory effect. Increasing amounts of both H_2O_2 and HNO_3 promote the reactions, but only up to certain values beyond which an inhibition also results. The 3,5-dimethylbenzaldehyde yield is enhanced by increasing the temperature, but not that of phenol.

Although the isolation and full characterization of intermediates have not yet been achieved and the mechanism of the reactions is still unknown, we suggest the involvement of active peroxo-vanadium complexes as it has been proposed [7–20,36–38] for a number of V-catalyzed peroxidative oxidations hydrocarbons. In our vanadium(IV) systems, namely $[V(hida)_2]^{2-}$ and $[V(hidpa)_2]^{2-}$, H_2O_2 oxidizes the metal to V^V [29,41] and since the hydroxyimine(1−) groups η^2–O–N of the ligands in these complexes are electron-donors identical to peroxide(2−), the oxidized complexes relate to *bis*(peroxo)-vanadium(V) species. The overall catalytic processes can conceivably be accounted for by the Scheme 1 in which a peroxo-vanadium species can act as the oxygenating agent of a benzene carbon or of a methyl group of mesitylene.

The aldehyde is conceivably formed from further oxidation of the intermediate alcohol derived from the initial oxidation of mesitylene. In fact, by using 3,5-dimethylbenzyl alcohol as the substrate, instead of mesitylene, under identical conditions to those of entry 21 (Table 2), the same product, i.e., 3,5-dimethylbenzaldehyde was obtained with higher values of yield (6.3% versus 3.4%) and TON (31.7 versus 17.1), thus providing some supporting testimony to the proposed mechanism. Attempts for isolation of other intermediates and extension of the study to other aromatics and alkyl-substituted aromatic compounds, are under way in our laboratory.

The work also provides further support for a possible biological role of *Amavadine* as a peroxidase towards aromatic substrates. Alkanes [29,30] and thiols [42] are other

substrates we have previously found for such a biological complex whose function still remains unknown.

Acknowledgements

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References

[1] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879.
[2] R.H. Crabtree, J. Chem. Soc., Dalton Trans. (2001) 2437.
[3] G.B. Shul'pin e, G.S. Fink, J. Chem. Soc., Perkin Trans. 2 (1995) 1459.
[4] E.G. Derouane, J. Haber, F. Lemos, F. Ramôa Ribeiro, M. Guinet (Eds.), Catalytic Activation and Functionalisation of Light Alkanes, NATO ASI Series, vol. 44, Kluwer Academic Publishers, Dordrecht, 1998.
[5] W. Jordan, H.V. Barneveld, O. Gerlich, M.K. Boymann, J. Ullrich, Phenol, Ullmann's-Encyclopedia of Industrial Chemistry, VCH, 1989.
[6] T. Miyake, M. Hamada, H. Niwa, M. Nishizuka, M. Oguri, J. Mol. Catal. A 178 (2002) 199.
[7] A. Butler, M.J. Clague, G.E. Meister, Chem. Rev. 94 (1994) 625.
[8] M. Bianchi, M. Bonchio, V. Conte, F. Coppa, F. Di Furia, G. Modena, S. Moro, S. Standen, J. Mol. Catal. 83 (1993) 107.
[9] K. Nomiya, H. Yanagibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu, Y. Shimizu, J. Mol. Catal. A 114 (1996) 181.
[10] M. Bonchio, V. Conte, F. Coppa, F. Di Furia, G. Modena, J. Org. Chem. 54 (1989) 4368.
[11] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, R. Weiss, J. Am. Chem. Soc. 105 (1983) 3101.
[12] M. Bonchio, V. Conte, F. Di Furia, G. Modena, S. Mouro, J. Org. Chem. 59 (1994) 6262.
[13] G.B. Shul'pin, D. Attanasio e, L. Suber, Russ. Chem. Bull. 42 (1993) 55.
[14] G.B. Shul'pin, D. Attanasio e, L. Suber, J. Catal. 142 (1993) 147.
[15] N. Kitajima, M. Ito, H. Fukui, Y. Moro-oka, J. Chem. Soc., Chem. Commun. (1991) 102.
[16] H. Mimoun, P. Chaumette, M. Mignard, L. Saussine, Nouv. J. Chim. 7 (1983) 467.
[17] V. Conte, F. Di Furia, S. Moro, J. Mol. Catal. A 117 (1997) 139.
[18] K. Nomiya, S. Matsuoka, T. Hasegawa, Y. Nemoto, J. Mol. Catal. A 156 (2000) 143.
[19] G.B. Shul'pin, J. Mol. Catal. A 189 (2002) 39.
[20] N.A. Milas, J. Am. Chem. Soc. 59 (1937) 2342.
[21] D. Bianchi, R. Bortolo, R. Tassinari, M. Ricci, R. Vignola, Angew. Chem. 112 (2000) 4491;
D. Bianchi, R. Bortolo, R. Tassinari, M. Ricci, R. Vignola, Angew. Chem. Int. Ed. 39 (2000) 4321.
[22] D. Bianchi, M. Bertoli, R. Tassinari, M. Ricci, R. Vignola, J. Mol. Catal. A 200 (2003) 111.
[23] D. Bianchi, M. Bertoli, R. Tassinari, M. Ricci, R. Vignola, J. Mol. Catal. A 204/205 (2003) 419.
[24] A. Bhaumik, P. Mukherjee, R. Kumar, J. Catal. 178 (1998) 101.
[25] U. Schuchardt, D. Mandelli, G.B. Shul'pin, Tetrahedron Lett. 37 (1996) 6487.
[26] J.F. Jia, K.S. Pillai, W.M.H. Sachtler, J. Catal. 221 (2004) 119.
[27] A.A. Ivanov, U.S. Chernyavsky, M.J. Gross, A.S. Kharitonov, A.K. Uriarte, G.I. Panov, Appl. Catal. A-Gen. 249 (2003) 327.
[28] R. Hamada, Y. Shibota, S. Nishiyamas, S. Tsuruya, Phys. Chem. Chem. Phys. 5 (2003) 956.
[29] P.M. Reis, J.A.L. Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, Chem. Commun. (2000) 1845.
[30] P.M. Reis, J.A.L. Silva, A.F. Palavra, J.J.R. Fraústo da Silva, T. Kitamura, Y. Fujiwara, A.J.L. Pombeiro, Angew. Chem. 115 (2003) 845;
P.M. Reis, J.A.L. Silva, A.F. Palavra, J.J.R. Fraústo da Silva, T. Kitamura, Y. Fujiwara, A.J.L. Pombeiro, Angew. Chem. Int. Ed. 42 (2003) 821.
[31] C.A. Root, J.D. Hoeschele, C.R. Cornman, J.W. Kampf, V.L. Pecoraro, Inorg. Chem. 32 (1993) 3855.
[32] D.C. Crans, H. Chen, O.P. Anderson, M.M. Miller, J. Am. Chem. Soc. 115 (1993) 6769.
[33] R.E. Berry, E.M. Armstrong, R.L. Beddoes, D. Collison, S.N. Ertok, M. Helliwell, C.D. Garner, Angew. Chem. 111 (1999) 871;
R.E. Berry, E.M. Armstrong, R.L. Beddoes, D. Collison, S.N. Ertok, M. Helliwell, C.D. Garner, Angew. Chem. Int. Ed. 38 (1999) 795.
[34] B.J. Hamstra, A.L.P. Houseman, G.J. Colpas, J.W. Kampf, R. LoBrutto, W.D. Frasch, V.L. Pecoraro, Inorg. Chem. 36 (1997) 4866.
[35] Athilakshmi, B. Viswanathan, React. Kinet. Catal. Lett. 1 (1998) 193.
[36] A.S. Tracey, D.C. Crans (Eds.), Vanadium Compounds, ACS Symposium Series no. 711, ACS, Washington, 1998.
[37] H. Siegel, A. Siegel (Eds.), Metal Ions in Biological Systems, vol. 31, Marcel Dekker Inc., New York, 1995.
[38] J.J.R. Fraústo da Silva, R.J.P. Williams, The Biological Chemistry of the Elements, 2nd ed., Clarendon Press, Oxford, 2001.
[39] S.J. Lippard, J.M. Berg, Principles of Bioinorganic Chemistry, University Science Books, Mill Valley, CA, 1994.
[40] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, Wiley, Chichester, 1994.
[41] C.M.M. Matoso, A.J.L. Pombeiro, J.J.R. Fraústo da Silva, M.F.C. Guedes da Silva, J.A.L. da Silva, J.L. Baptista-Ferreira, F. Pinho-Almeida, in: A.C. Tracey, D.C. Crans (Eds.), Vanadium Compounds – Chemistry, Biochemistry and Therapeutic Applications, American Chemical Society Symposium Series, no. 711, Oxford University Press, 1998, pp. 241–247 (Chapter 18).
[42] M.F.C. Guedes da Silva, J.A.L. da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, C. Amatore, J.N. Verpeaux, J. Am. Chem. Soc. 118 (1996) 7658.