Oxidation of benzene by molecular oxygen catalysed by vanadium

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Abstract

Vanadium compounds can efficiently catalyse the oxidation of benzene to phenol with molecular oxygen. The reaction is truly catalytic only in the presence of a reducing agent able to recycle the oxidised catalyst. Among the reducing agents tested, ascorbate afforded the highest selectivity and reactivity to phenol. With other reductants, such as dithioalcohols, high selectivity (>96%) was obtained toward more oxidised products (i.e. hydroquinone). The reactions were performed in the two-phase system formed by mixing water/acetonitrile/benzene which allows a good separation between reactant and product. The reaction rate and product selectivity depend upon the type of ligand interacting with vanadium as well as upon the ascorbate/V molar ratio. ESR measurements confirmed that V^{IV} species is rapidly formed in the reaction medium after the initial addition of $V^{III}Cl_3$. Moreover, the observed initial induction period of benzene oxidation can be related to the formation of oligomeric V^{IV} species, as assessed by ESR analysis, rather than to the slow formation of V–ascorbate complex.
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1. Introduction

The activation of molecular oxygen by biological systems has always been a source of inspiration for the chemists to develop redox chemical reactions for the synthesis of useful compounds. A catalytic system for the oxidation of aromatics to produce phenols, cathecols and epoxides with molecular oxygen by using the complex Fe/EDTA/ascorbate in aqueous solution was first reported by Udenfriend et al. [1]. This reaction has been well studied because of its similarity to that catalysed by enzymes such as mononuclear monooxygenases (for example, cytochrome P_{450}). The reaction is characterised by the 'activation' of the oxygen molecule by the iron catalysts which generates a ferric ion and by the presence of a reductant species, i.e. ascorbate, which reduces the ferric ion back to the ferrous form, closing the catalytic cycle. EDTA is not necessary at low pH, at which Fe^{II} is soluble [2] or, conversely, may be replaced by a suitable ligand to modulate redox potential as a function of the reaction efficiency. Also ascorbic acid can be substituted, although not so easily [1], by other hydrogen donors [3], including typical biological cofactors [4].

In view of the important role on oxidative reaction in biological system played by vanadium complexes [5,6] for the detoxification of the organism, it was interesting to verify whether iron could be efficiently replaced by vanadium in the oxidative hydroxylation of aromatics. Vanadium compounds do successfully oxidise benzene but most of the reactions reported in the literature used H_2O_2 as primary oxidant [7–9]. Only few studies have been carried on with oxygen as oxidant. For example, Ishida et al. [10] used Udenfriend

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conditions with a supported vanadium catalyst, obtaining good turnover numbers (TNs), although the catalyst was partially released from the support. Hata et al. [11] used crotonaldehyde instead of ascorbic acid as reductant for benzene oxidation, but the catalytic efficiency and selectivity were low.

High reaction yields were claimed by Barnhard and Hughes by using vanadium complexes as catalyst and substituted hydroquinones as reducing agents [12]. However, the concentration of hydroquinones required was comparable or even higher than that of the substrate (benzene) and, consequently, yields with respect to the reductant were low.

It is interesting to note that Fe was substituted by other metals, such as Cu [13] or Ru [14], to oxidise aromatics under strict Udenfriend's conditions, but hydroxylated products were detected only in low yields.

The reaction media have a strong influence on the reactivity of the catalyst. It was found that the double phase system composed by water–acetonitrile–benzene is an efficient solvent system for the hydroxylation of the benzene itself [15]. The iron catalyst is dissolved in the water phase, whereas the substrate and the product (phenol) are mainly confined in the organic phase. This situation is aimed to optimise the separation between the product (phenol) and the catalyst in order to improve selectivity by avoiding the formation of multioxygenated products (cathecols and other polyhydroxylated derivatives).

In this report, vanadium catalysts were successfully used to oxidise benzene in a two-phases reaction system under Udenfriend-like conditions. Relative high turnover numbers (TNs) were found under optimised conditions. Moreover, the selectivity could be modulated to afford phenol or hydroquinone with high selectivity depending upon the type of reductant used.

2. Experimental

All chemicals were reagent grade and were used as purchased. VCl_3 (Aldrich) was stored under N_2. Pyrazine-3-carboxylic acid N-oxide was synthesised as described in the literature [16].

The reactions were carried out in the two-phase system formed when benzene was added to the mixture composed by water and acetonitrile 1:1 by volume (typically 4.5 ml water, 4.5 ml acetonitrile and 1 ml

benzene). The two phases have approximately the same volume. The upper phase is almost completely organic, formed mainly by the benzene–acetonitrile mixture. The reactions were carried out at 50 °C for 17 h (overnight) under 100% oxygen atmosphere. Each reaction mixture was then diluted five times with CH_3CN in order to obtain a homogeneous solution which was analysed by HPLC. A RP-C18 column (250 mm × 4 mm × 5 μm, Merck) was eluted with an aqueous solution of phosphoric acid 10 mM and CH_3CN 60:40 at 1 ml/min, 40 °C. The detection was at 212 nm. In these conditions, phenol, cathecol, p-quinone, hydroquinone and benzene were eluted at 3.5, 3.9, 2.9 and 14 min, respectively.

The ESR spectra were recorded on an ESP-300E spectrometer, operating at X-band frequency and 100 kHz field modulation, equipped with a sample holder dewar flask filled with liquid nitrogen. The modulation amplitude was set to 3 G and microwave power to 1 mW. For quantitative measurements, the first derivative spectra were integrated twice and the areas of the absorption were compared to that of a standard sample of $VO(acac)_2$ ([V] = 1.42 mM) in ethanol.
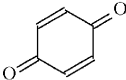
In order to avoid variation in the reagent concentration caused by sample drawing, six different reaction mixtures were warmed in oxygen atmosphere (1 bar pressure) at 50 °C under stirring, stopped at different time intervals and diluted five times with acetonitrile in order to obtain a homogeneous solution (the final H_2O/MeCN ratio was 5/95%, v/v). An aliquot was drawn form each sample, injected in an ESR tube and frozen at liquid nitrogen temperature. The final V concentration was 1 mM.

3. Results and discussion

3.1. Optimisation of the benzene oxidation

A screening of possible metal catalysts for benzene oxidation with dioxygen as primary oxidant was initially assayed in non-optimised conditions. The results are presented in Table 1. In these preliminary experiments, no other reductant was used but finely ground Fe/Cr (60:30) metallic powder was added to the reaction mixture in order to improve reactivity, as suggested in the literature [17]. As shown in Table 1, Cu

Table 1

Benzene oxidation with O_2 catalysed by chloride metal salts[a]

Catalyst	OH	OH OH	OH HO	O O	Conversion (%)	Selectivity[b] (%)
$CuCl_2$	0.7	0.3	0.7	4.1	0.052	70 (pq)
$FeCl_3$	2.0	0.6	0.2	0.3	0.028	64 (phe)
$CrCl_3$	0.7	0.4	0.4		0.013	
$AgCl_2$		0.4			0.003	
VCl_3	2.6	0.1		0.3	0.026	86 (phe)
$TiCl_3$	0.2	0.1			0.002	
$ZrCl_4$	Traces	Traces				
$PdCl_2$		0.4	0.2		0.004	
$CdCl_2$	Traces	Traces				
$RhCl_3$	0.1	0.1	0.3	3.3	0.033	87 (pq)
$RuCl_3$		Traces		Traces		
$CoCl_2$				0.4	0.003	
$NiCl_2$	Traces	Traces				
$ZnCl_2$	0.5		0.1		0.004	

[a] Catalyst: 40 μmol. Fe/Cr powder (1:10 by moles with respect to the metal salt), 50 °C, 17 h, benzene 1 ml (11.3 mmol), two-phase system (water/CH_3CN/benzene = 4.5:4.5:1 ml). Results are expressed in μmol.

[b] Percentage with respect to the compound within parenthesis (abbreviations: pq: *p*-quinone; phe: phenol).
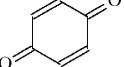
was the most reactive catalyst affording the highest conversion, *p*-quinone being the main product. Also V, Fe and Rh showed a good reactivity although lower than Cu. However, since V had by far the best selectivity with respect to phenol, it was chosen for further optimisation of the reaction parameters.

The effect of the presence of the metal powder on the reaction was assayed with VCl_3 as main catalyst. The results are presented in Table 2. Note that the catalyst–metal powder ratio was increased 10 times (1:1 by moles) with respect to the data showed in Table 1 which brought about an increase of the reac-

tivity by a factor of 10. By changing Fe/Cr with Zn powder the reaction yield did not improve, whereas powdered Cu enhanced the reactivity by a factor of 3 although the selectivity decreases sharply. However, VCl_3 maintained a good selectivity, even enhanced (see Table 1), also in the absence of the ground metal which, therefore, was not used in the following experiments anymore.

In order to optimise the amount of acetonitrile present in the solvent mixture, the reaction was performed as a function of acetonitrile concentration with and without reducing agent. The results are

Table 2

Benzene oxidation with O_2 catalysed by VCl_3 in the presence of metal powder[a]

Catalyst[b]	OH	OH OH	OH HO	O O	Conversion (%)	Selectivity[c] (%)
VCl_3 + Fe/Cr[a]	17.0	1.9	4.6	1.3	0.22	68
VCl_3 + Zn[a]	21.0	1.8		5.0	0.24	75
VCl_3 + Cu[a]	40.0	2.5		43.0	0.75	46
VCl_3	23.1	2.7	9.0	1.0	0.31	65

[a] Finely ground powdered metal, 1:1 by moles with respect to VCl_3.

[b] Catalyst: 40 μmol, 50 °C, 17 h, benzene 1 ml (11.3 mmol) in two-phase system (water/CH_3CN/benzene = 4.5:4.5:1 ml). Results are expressed in μmol.
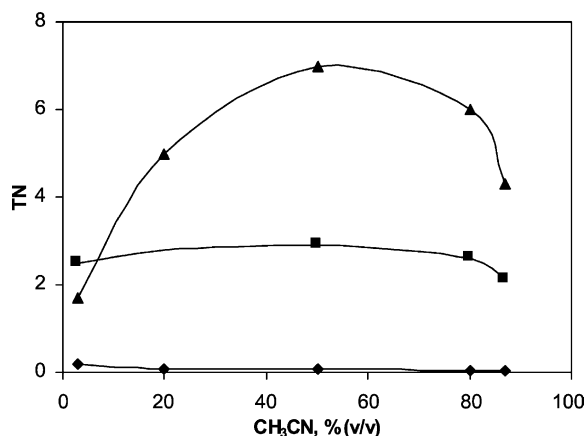
[c] With respect to phenol.

Fig. 1. Effect of the solvent composition as a function of acetonitrile concentration. The turnover number (TN) is defined as the molar ratio of all the oxigenated products (phenol, cathecol, quinones) to the catalyst. Double oxygenated products are considered twice. VCl_3 (40 µmol), 50 °C, 17 h, benzene 1 ml (11.3 mmol), under oxygen atmosphere. Reducing agent: dithiothreitol (▲) and ascorbate (■) 400 µmol (10× VCl_3); without reducing agent (◆).

summarised in Fig. 1 where TNs are plotted as a function of acetonitrile concentration. TN is defined as the products (all the oxygenated products) to catalyst molar ratio. The best results were obtained with the double phase composed by 50% acetonitrile (with either dithiothreitol or ascorbate as reducing agent). It should be noted that, in the presence of a suitable reductant, the activity of the system raised significantly above the stoichiometric level and became truly catalytic.

The efficiency of the reaction is related to the ability of the reductant to reduce V, without being inactivated by the presence of oxygen. As a matter of fact, ascorbate undergoes autooxidation catalysed by metal ions [18] in the presence of oxygen. However, V ions (i.e. vanadyl) are less active than other metal ions, such as Fe^{3+} and Cu^{2+} [19]. Moreover, the ascorbate autooxidation rate decreases in the presence of a substrate to be oxidised.

Several reducing agents were tested in order to find a substitute for ascorbate. The results are shown in Fig. 2. Among all the compounds assayed, ascorbate was still the best reductant, affording the highest TN. Dithiothreitol was a good reducing agent but not as effective as ascorbate. It is interesting to note that thiocompounds support a good catalytic activity in this double phase water–acetonitrile–benzene system, whereas in other solvent (i.e. acetic acid/water) [20] could not efficiently substitute ascorbate. Moreover, under classic Udenfriend conditions, with Fe as
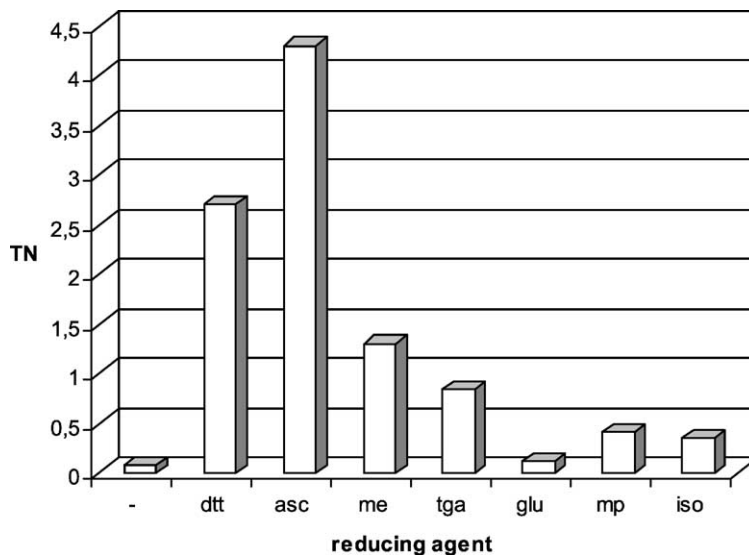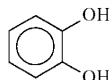

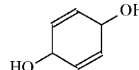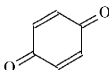Fig. 2. Effect of the reducing agent on the benzene oxidation. VCl_3 (100 µmol), 50 °C, 17 h, benzene 1 ml (11.3 mmol), under atmosphere of oxygen. Reducing agent (1000 µmol): dithiothreitol (dtt), ascorbate (asc), mercaptoethanol (me), thioglycolic acid (tga), glutathione (glu), mercaptopyridine (mp), isopropanol (iso).

Table 3
Effect of the reducing agent on the selectivity of benzene oxidation

Reducing agent (mol of V:mol)	$\begin{array}{c}\text{OH}\end{array}$	$\begin{array}{c}\text{OH}\\\text{OH}\end{array}$	$\begin{array}{c}\text{OH}\\\text{HO}\end{array}$	$\begin{array}{c}\text{O}\\\text{O}\end{array}$	Conversion (%)	Selectivity[a] (%)	TN
Ascorbate (1:10)	274.0	3.2	4.5	0.4	2.5	97.1 (phe)	7.3
Ascorbate (1:20)	397.0	3.0	4.1	0.4	3.6	98.1 (phe)	10.4
Dithiothreitol (1:10)	4.2	0.09	58.6	0.05	0.57	93.0 (hq)	2.9
Dithiothreitol (1:20)	3.2	0.05	76.8	0.04	0.72	95.9 (hq)	3.7
2-Mercaptoethanol (1:10)	2.2	1.3	34.1	0.03	0.33	91.0 (hq)	1.8
Dithiothreitol:Cu[b] (1:10:1)	0.5	0.02	74.5	0.02	0.66	99.0 (hq)	3.7

$50\,^{\circ}$C, 17 h, VCl$_3$ 40 μmol, O$_2$ 1 atm, benzene 1 ml (11.3 mmol) in 50% water/CH$_3$CN two-phase system. Results are expressed in μmol.
[a] hq = hydroquinone, phe = phenol.
[b] Cu as powder.

catalyst, no activity was observed with glutathione or thioglycolic acid [1] as reductants replacing ascorbate.

The selectivity of the reaction changed completely as a function of the type of reducing agents, as it is shown in Table 3. The effect is striking: with ascorbate the main product (97% selectivity) was phenol, whereas with dithiothreitol (and other thiocompounds) benzene was mostly converted into hydroquinone (selectivity almost 96%). Thioreducing agents seem to favour the double oxidation of the aromatic ring of benzene, whereas ascorbate selectively favours the introduction of only one oxygen. This may related to the 'complexing' capacity of the reducing agent: it is well known that ascorbate (only in the reduced form) is able to interact as a chelating agent with several metal ions, including vanadyl (VO^{2+}) or metavanadate (VO$_3{}^+$) [18,19]. This 'binding' ability may result in a restriction of substrate accessibility towards the metal ion which inhibits further oxidation of the substrate. Conversely, dithiols close up to form an internal S–S bond in the oxidised state, decreasing the probability of interactions with the metal ions and increasing substrate accessibility.

It is interesting to note that the exploitation of the reducing capacity of the system is remarkable. As it is shown in Table 3, the efficiency of ascorbate consumption to yield the desired product (i.e. moles of product formed with respect to moles of reductant) is as high as almost 70%, affording a TN higher than 7 (V/ascorbate ratio 1/10).

The results presented in Table 3 also suggest that reaction yield depends upon the amount of ascorbate present or, more precisely, upon the ascorbate/V molar ratio. In Fig. 3, TN are plotted as a function of molar ratio ascorbate/V for different initial concentration of VCl$_3$. TNs increase by raising the amount of ascorbate but also by decreasing the initial catalyst concentration. At ascorbate/V molar ratio of 30/1, a TN as high as 16 ± 1 was observed. To our knowledge, this is the highest TN obtained under Udenfriend conditions (that is, in the presence of oxygen as oxidant at atmospheric pressure, and using ascorbate as reductant, in aqueous solution. In our double phase system, catalysis occurs only in the aqueous polar phase, for the couple catalyst-reductant is actually dissolved only in the water rich phase). By pushing further these

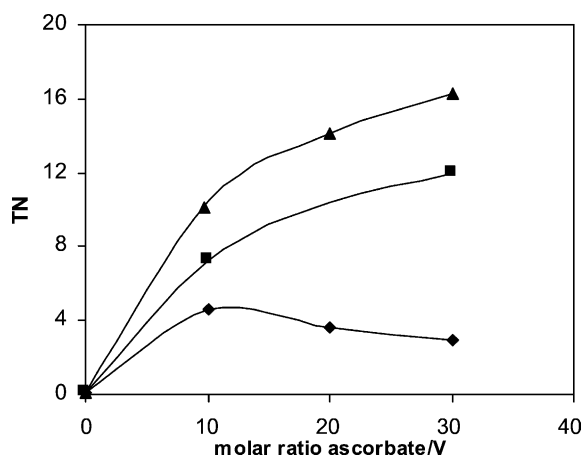Fig. 3. Turnover numbers of benzene oxidation as a function of ascorbate:V molar ratio. Experimental conditions: $50\,^{\circ}$C, 17 h, benzene 1 ml (11.3 mmol), under atmospheric pressure of oxygen. V concentration: 20 μmol (▲), 40 μmol (■), 100 μmol (◆).
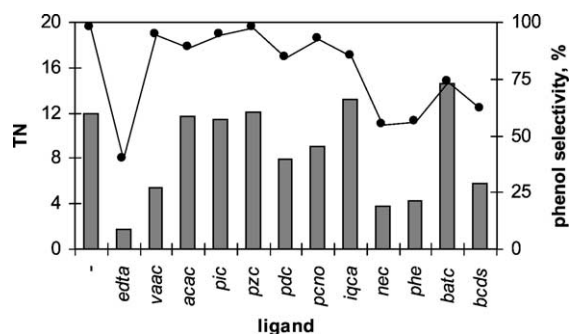
Fig. 4. Turnover numbers (TNs) and phenol selectivity of benzene oxidation catalysed by vanadium in the presence of possible ligands. VCl$_3$ (40 μmol), 50 °C, 17 h, benzene 1 ml (11.3 mmol), under O$_2$ atmosphere. Reducing agent: ascorbate (1200 μmol, 30× V). Complexing agent: 200 μmol. Broken line: phenol selectivity. Ligand: ethylenediaminetetraacetic acid (edta), vanadyl^{IV} acetylacetonate (vaac), acetylacetonate (acac), picolinic acid (pic), 2-pyrazinecarboxylic acid (pzc), 2,6-pyridinedicarboxylic acid (pdc), pyrazine-3-carboxylic acid N-oxide (pcno), 1-isoquinoline carboxylic acid (iqca), neocuproine (nec), phenanthroline (phe), bathocuproine (batc), bathocuproinedisulfonic acid (bcds).

conditions, it is possible to obtain higher TN: for example, decreasing the VCl$_3$ concentration and increasing ascorbate concentration up to a molar ratio of about 750, a TN of 130 was observed (in standard conditions: 50 °C, after 17 h). However, this result was achieved at the expenses of ascorbate utilisation which dropped below 15%.

In order to improve the reaction performance, the effect of the presence of a 'complexing' agent which was able to interact with V ions was studied. The rate of benzene oxidation was then measured in the presence of different compounds which are known to form complexes with metal ions. The results are presented in Fig. 4. Besides phenol, in all the reactions the main sideproduct was hydroquinone. The addition of oxygen containing ligands decreased the TN, except in the case of acetylacetonate. Also nitrogen ligands (i.e. 1,10-phenanthroline and derivatives) had a detrimental effect on both activity and phenol selectivity. The only exception is bathocuproine, which enhances reactivity but lowers selectivity. This is a highly hydrophobic compound (more hydrophobic than phenanthroline) and probably changes the partition of V between the two phases, enhancing the substrate–catalyst contact

probability. The best 'ligands' are those containing the couple O–N as possible site for the binding interaction with V. Both pyrazinecarboxylic and picolinic acid gave a high TN accompanied by the best selectivity with respect to phenol. It seems, however, that even the best ligand induced only a relatively small increment of the reaction performance with respect to that obtained in the absence of ligands. By using Fe (as FeCl$_3$) instead of V, with no ligand, a 30% decrease of the activity was observed.

3.2. Kinetics of benzene oxidation

The time dependence of benzene oxidation is shown in Fig. 5 (ascorbate/V molar ratio equal to 30). The reaction started slowly since a lag period was present at the beginning of the reaction. As a matter of fact, during the first few hours the rate was quite low and then the reaction onset gradually took place. After 18–20 h, the oxidation rate slowed down approaching a plateau value probably because the reserve of reduced ascorbate was almost over. In fact, after 71 h, the ascorbate converted into products was 98%. Since the phenol selectivity in these conditions was 97, 95% of ascorbate has been used to produce phenol. This result implied that the autoxidation rate catalysed by V ions in the presence of oxygen was very low since almost all the ascorbate present was available to reduce V.
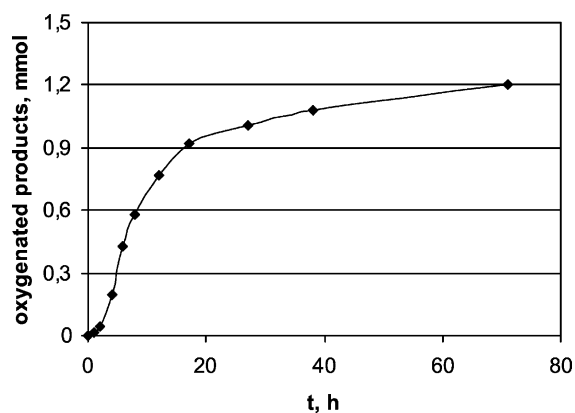

Fig. 5. Time dependence of the benzene oxidation. VCl$_3$ (40 μmol), 50 °C, benzene 1 ml (11.3 mmol), under atmosphere of oxygen, ascorbate (1220 μmol, 30× V) in 50% water/CH$_3$CN two-phase system.

3.3. V–V and V–ascorbate interactions

What is the origin of the initial lag phase? Does the reaction rate take off only after the retarded formation of some kind of 'true' catalytic species? What is the nature of the actual catalyst? These questions may naturally arise by inspection of the time dependence curve presented in Fig. 5. It is possible that the lag period is due to: (a) a change in the oxidation state of V, (b) the formation of the ascorbate–V complex, (c) a slow 'oligomerisation' of some kind of V^{IV} species.

The hypothesis (a) can be ruled out on the basis of ESR spectrum. When the catalyst, $V^{III}Cl_3$, was added to the reaction medium, a brownish solution was formed in aqueous solution. After the beginning of the reaction the solution turned to a pale green–blue colour within 1 h. This is the typical colour of a V^{IV} species. The conclusions based on the visual inspection are confirmed by the ESR analysis. The ESR spectra of the reaction solutions are presented in Fig. 6 at time zero and after 6 h of reaction, respectively. The observed eight-line spectrum is characteristic of vanadyl $V^{IV}O$ species (^{51}V, $I = 7/2$), and in particular, it can be assigned to the $VOCl_2$ species [21]. Note that V^{III} and V^V ions are ESR silent. Whereas the spectrum at time zero is completely resolved, it is clear

from Fig. 6b that after 6 h of reaction a broad unresolved component appeared, underlying the resolved eight-peak counterpart.

The time dependence of the ESR signal (expressed as percentage of the total V present) is shown in Fig. 7. As it can be seen, at time zero, even though only a few minutes elapsed between sample preparation and ESR measurements, almost 20% of the V^{III} initial concentration (which is ESR silent) was already transformed into V^{IV} (ESR active). The conversion was completed within 50–60 min as the light blue colour development. Therefore, the much longer lag period (5–6 h) of the onset of the oxidation reaction does not overlap the observed time dependence of the oxidation state change of V from V^{III} to V^{IV}.

Let us now consider the hypothesis (b). The resolved component of ESR spectrum of the reaction solution (containing ascorbate) after 6 h is still superimposable to that of vanadyl chloride prepared by the direct oxidation of $V^{III}Cl_3$ in the presence of O_2 but without ascorbate in the same solvent conditions. Since ascorbate does not alter significantly the ESR spectrum of the $V^{IV}O$ species (present as vanadyl chloride) as one would expect if some kind of 'complex' were formed, it is possible to conclude that a 'true' complex between vanadyl chloride and ascorbate does not take
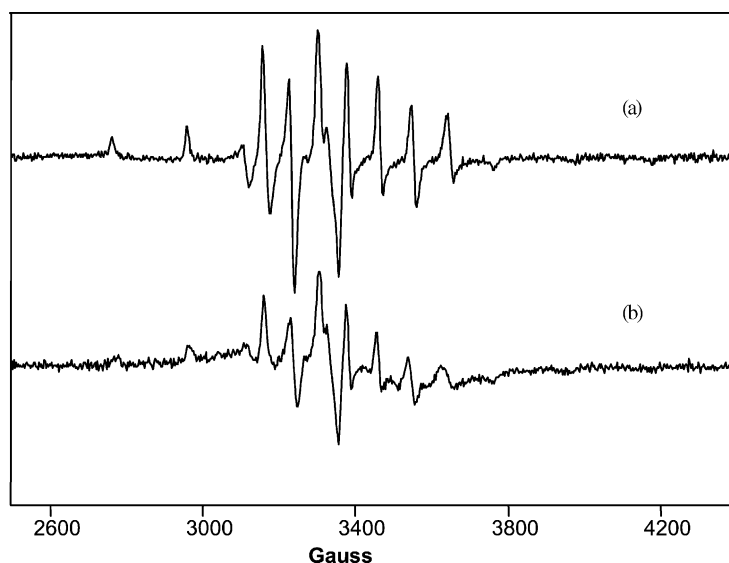

Fig. 6. ESR spectra registered at 80 K. ESR spectra recorded on the reaction mixture (a) immediately after contact of the reagents and after 6 h at 50 °C (b) ([V]/ascorbate/benzene = 1:30:3000, [V] = 1.0 mM; solvent: water/acetonitrile 5:95, temperature 80 K).
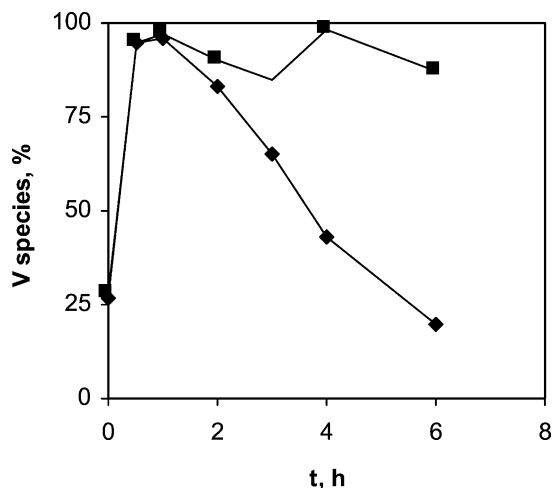
Fig. 7. ESR analysis of V^{IV} species as a function of time during benzene oxidation. Concentration of V^{IV} species as measured by ESR and expressed as a percent fraction of total V (water/CH_3CN 5/95%, v/v, after dilution of the water/acetonitrile/benzene two-phase system): (■) total concentration of the V^{IV} species; (◆) concentration of isolated V^{IV} species. Reagents concentrations as in Fig. 5.

place. This suggests that chloride atoms are not displaced by the O atoms of ascorbate to form a strong O–V interaction pair.

What is the origin then of the observed lag phase? A possible explanation may be suggested by further analysis of the ESR results. As it is shown in Fig. 6, at the beginning of the reaction the spectrum is characteristic of a well resolved ESR signal of the vanadyl V^{IV} ion, whereas as the time proceeds, the presence of an unresolved component becomes more and more present. In general, the loss of resolution in a frozen solution is a consequence of the interactions among the magnetic species. Dimeric V ions were indeed observed in acid solution [23] and a pH-dependent aggregation does occur as a function of concentration [19]. Therefore, it is conceivable to assign the ESR unresolved component, as a first approximation, to the formation of some kind of oligomeric or aggregated vanadyl species (hypothesis c). Since the magnetic parameters of these species are not measurable because of the broadness of the signal, it is not possible to get some insight about the actual ligands of V^{IV}. However, if a change of the pristine chlorine ligands have had occurred, it should have been immediately followed
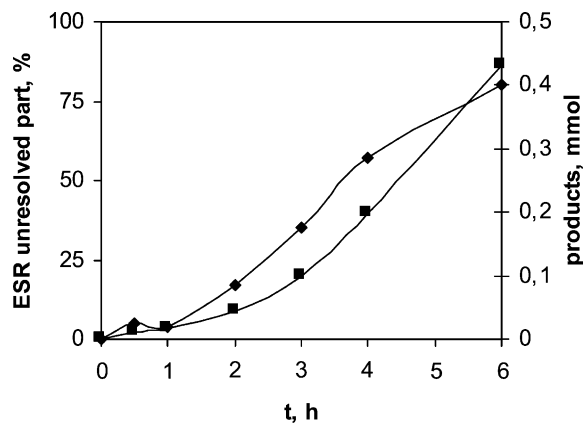

Fig. 8. Time dependence of the unresolved ESR spectra and products formation. Concentration of non isolated V^{IV} species (◆) as a function of time. Data are recalculated from Fig. 7 as the difference between total V^{IV} concentration and the concentration of isolated V^{IV} species. Concentration is expressed as a percent fraction of total vanadium. Reaction products (data from Fig. 5) (■).

by aggregation, otherwise it would have showed up in a change of the magnetic parameters of the isolated species in the resolved part of the spectrum (see hypothesis b). The amount of V^{IV} in the 'aggregated' state, calculated from the ESR data, as a function of time is plotted in Fig. 8. It is clear that 'aggregation' of V^{IV} is a process that slowly grows up in our experimental conditions. Its onset is concurrent to the increase of benzene oxidation rate after the initial lag zone.

As shown in Fig. 7, vanadyl concentration tends to slowly decreases as the benzene oxidation reaction rate increases, generating V^V ions. V^V, which is ESR silent, is readily reduced back to V^{IV} by ascorbate [22], upon rapid complexion. V^V tends to increase as a function of time because of the settlement of the steady state conditions. This suggests that V reduction is not kinetically fast enough to switch back V^V to V^{IV} as soon as it is formed.

4. Conclusions

Vanadium is an efficient alternative to Fe as catalyst under modified Udenfriend conditions for the oxidation of benzene. Relatively high TN were obtained as the reductant–V molar ratio was increased. High selectivity to phenol production was achieved by

using ascorbate as reducing agent, whereas the use of a different reductant (dithiocompounds) changes completely the selectivity toward more oxidised products (i.e. hydroquinone). The study of the V ions electronic state gave some insight of the nature of the V–ascorbate interactions, suggesting that the interaction between vanadyl chloride ion and ascorbate, if any, should be a labile one. The formation of some kind of oligomeric V-species, as inferred by ESR measurements, is concurrent with the induction period at the beginning of the reaction. Studies are in progress to confirm the performance of the reaction system with other aromatic substrates.

References

[1] S. Udenfriend, C.T. Clark, J. Axelrod, B.B. Brodie, J. Biol. Chem. 208 (1954) 731.

[2] G.A. Hamilton, Adv. Enzymol. 32 (1969) 55.

[3] H. Mimoun, I. Seree de Roch, Tetrahedron 31 (1975) 777.

[4] R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981, p. 254.

[5] A. Butler, J.N. Carter, M.T. Simpson, in: I. Bertini, A. Sigel, H. Sigel (Eds.), Handbook of Metalloproteins, Marcel Dekker, New York, 2001, p. 153 (Chapter 6).

[6] H.J. Kramer, G. Krampitz, A. Bäcker, H. Meyer-Lehnert, Clin. Exp. Hypertens. 20 (1998) 557.

[7] H. Minoun, L. Saussine, E. Daire, M. Postel, J. Fisher, R. Weiss, J. Am. Chem. Soc. 105 (1983) 3101.

[8] M. Bonchio, V. Conte, F. Di Furia, G. Modena, J. Org. Chem. 54 (1989) 4368.

[9] G.B. Shul'pin, G. Süss-Fink, J. Chem. Soc. Perkin Trans. 2 (1995) 1459.

[10] M.-a. Ishida, Y. Masumoto, R. Hamada, S. Nishiyama, S. Tsuruya, M. Masai, J. Chem. Soc. Perkin Trans. 2 (1999) 847.

[11] E. Hata, T. Takai, T. Yamada, T. Mukaiyama, Chem. Lett. (1994) 1849.

[12] T.M. Barnhard, A.W. Hughes, US Patent 5,912,391 (1999).

[13] H. Orita, T. Hayakawa, M. Shimizu, K. Takehira, J. Mol. Catal. 42 (1987) 99.

[14] M.M. Taqui Khan, R.S. Shukla, J. Mol. Catal. 45 (1988) 25.

[15] D. Bianchi, R. Bortolo, R. Tassinari, M. Ricci, R. Vignola, Angew. Chem. Int. Ed. 39 (2000) 4321.

[16] C. Venturello, R. D'Aloisio, EP 201934 (1986); Chem. Abstr. 106 (1987) 67349.

[17] J.-M. Maissant, C. Bouchoule, M. Blanchard, J. Mol. Catal. 14 (1982) 333.

[18] M.B. Davies, Polyhedron 11 (1992) 285.

[19] M.M. Taqui Khan, A.E. Martell, J. Am. Chem. Soc. 90 (1968) 6011.

[20] Y.-K. Masumoto, R. Hamada, K. Yokota, S. Nishiyama, S. Tsuruya, J. Mol. Catal. A 184 (2002) 215.

[21] B.A. Goodman, J.B. Raynor, in: H.J. Emeleus, A.G. Sharpe (Eds.), Advances in Inorganic Chemistry and Radiochemistry, vol. 13, Academic Press, New York, 1970, p. 135.

[22] K. Kustin, D.L. Toppen, Inorg. Chem. 12 (1973) 1404.

[23] F.J.C. Rossotti, H.S. Rossotti, Acta Chem. Scand. 9 (1955) 1177.