Mechanism of Arene Hydroxylation by Vanadium Picolinato Peroxo Complexes

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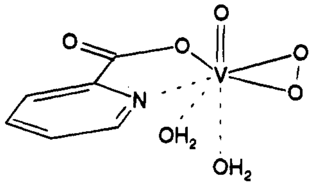
The mechanism of the reaction of $VO(O_2)PIC(H_2O)_2$ (PIC = picolinic acid anion) with benzene and substituted benzenes in CH_3CN, affording the corresponding phenols together with dioxygen, has been further investigated. The reaction is a radical chain process whose initiation produces the actual oxidant which may be described as a radical anion derived from the peroxovanadium complex, possessing, however, a marked electrophilic character. In the propagation steps such species react either with the original peroxo complex yielding dioxygen or with the aromatic substrates affording phenols via the formation of an intermediate.

Introduction

Peroxovanadium complexes are synthetically useful oxidants of organic substrates.[1,2] Depending on the nature of the ligands coordinated to the metal and on the experimental conditions, they act either as electrophilic oxygen transfer reagents[3,4] or as radical oxidants.[1,2,5-7] Typical electrophilic processes are the oxidation of thioethers[4,8,9] and of tertiary amines[10] and the epoxidation of allylic alcohols[3,4,11] or isolated alkenes.[11-13] The oxidation of alcohols[14] and the hydroxylation of aliphatic and aromatic hydrocarbons[5,6] are examples of homolytic reactivity. $VO(O_2)PIC(H_2O)_2$ (**1**) has been reported to be particularly effective in benzene and substituted benzene hydroxylation.[5,6,15,16]



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The picolinato bidendate ligand inhibits the electrophilic reactivity and enhances the homolytic one.[7,17] Accordingly, **1** smoothly oxidizes benzene to phenol in CH_3CN at room temperature.[5,6] The reaction proceeds also under catalytic conditions by employing H_2O_2 to restore the peroxo complex.[15,16]

The mechanism of the hydroxylation of aromatics by **1** is still a matter of debate.[5,6] The original proposal[5] of a simple two-step process in which the vanadium(IV) species, resulting from the homolytic cleavage of the metal-peroxide oxygen bond, i.e., $VO(PIC)(H_2O)_2OO^•$, attacks the aromatic ring forming an intermediate which then collapses to the product does not account for all the available facts. As an example, we have recently investigated the spontaneous decomposition of **1** in CH_3CN in the absence of organic substrates.[18] We found that the reaction proceeds fairly rapidly yielding dioxygen together with a vanadium(V) dimeric oxo species. The kinetic profile is typical of a chain process. A mechanism has been proposed involving several intermediates.[18] Among these, the formal radical anion of **1** has been shown to be the chain carrier.[18] In the presence of an excess of benzene, the decomposition reaction is not suppressed but phenol is also formed.[5,6] Dioxygen evolution and substrate oxidation are related reactions since the ratio of the two products depends on the substrate concentration;[6,15,16] i.e., the production of phenol is maximized when large excesses of benzene are used. Also in this case a sigmoid shaped curve for the disappearance of the oxidant is observed.

On the basis of these studies,[6,15,16] we proposed a simple mechanism[6] in which the active species formed during the initiation process can react either with the peroxometal precursor yielding dioxygen or with the aromatic hydrocarbon forming phenol.[6,18] However, when we extended our investigation to a series of monosubstituted benzenes,[16] we realized that such a simple hypothesis does not account for all the chemistry observed.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1994.

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Table 1. Oxidation of XC_6H_5 (20 mmol) by 1 (0.04 mmol) in CH_3CN (10 mL) at 20 °C. Effect of the Substituent on the Selectivity of the Reaction

no.	X	total yield[a] (%)	nucleus/side chain oxidation	% distribn isomeric phenols
1	$(CH_3)_2CH$	75	1.2[b]	o:(m + p) = 76:24
2	CH_3	64	10.5[c]	o:m:p = 58:19:23
3	H	70		
4	Br	55		o:(m + p) = 51:49
5	F	65		o:(m + p) = 48:52
6	NO_2	31		o:m:p = 21:55:24

[a] Yields based on the peroxo complex initially added. [b] 55% isomeric phenols, 45% $C_6H_5C(CH_3)_2OH$. [c] 91% isomeric cresols, 3% benzyl alcohol, 5% benzaldehyde.

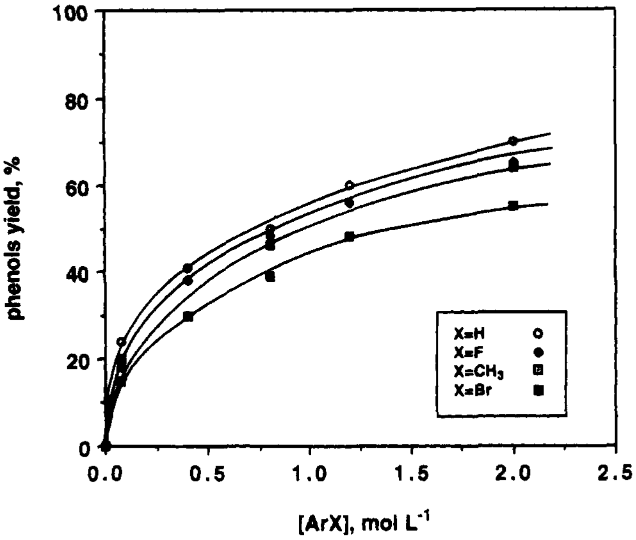

Figure 1. Oxidation of XC_6H_5 by 1 (0.004 mol L^{-1}) in CH_3CN at 20 °C. Dependence of phenol formation on initial concentration of the substrate.

In this paper we present a modification of our previous mechanistic proposal[6] by suggesting the formation of an intermediate between the chain carrier and the aromatic substrate.

Results

An important evidence that the mechanism of benzene hydroxylation by 1 is more complicated than previously thought[5,6,18] is provided by the data of Table 1 and of Figure 1 in which the yields of some monophenols are plotted as a function of the concentration of hydrocarbon added. In all the experiments the sum of phenols and dioxygen evolved accounts, within the experimental error, for the amount of 1 consumed. The yields of monophenols tend to a limiting value at large substrate concentration ranging from 31% for p-$NO_2C_6H_4OH$ to 70% for C_6H_5OH. The factor of ca. 2 observed between these two extremes might indicate a scarce substrate selectivity. However, further data presented in Table 1 lead to an opposite conclusion. From the values of product distribution determined in the oxidation of alkyl-substituted benzenes it is observed that the oxidant preferentially attacks the aromatic ring instead of the alkyl group. Nucleus hydroxylation is the predominant reaction in toluene oxidation, and it is the major process also in the oxidation of cumene whose α-hydrogen is particularly prone to radical abstraction[19] (entries 1 and 2 in Table 1).

It has been reported that the polar character of a radical is an importat factor in controlling the relative rates of hydrogen abstraction versus nucleus addition.[20] In particular, nucleophilic radicals tend to abstract hydrogens, whereas electrophilic radicals tend to add to unsaturated systems.[21-23] Accordingly, these data may be taken as evidence that the oxidant is rather electrophilic in character.

The distribution of isomeric phenols, completely determined in the oxidation of toluene and nitrobenzene (entries 2 and 5 in Table 1), confirms that phenol formation is carried out by a radical possessing an electrophilic character. The percentage of ortho-hydroxylated products, which is rather large as expected for activated benzenes, decreases for substituted benzenes in the order isopropyl > methyl > Br > F > NO_2. The amount of meta isomer found in the oxidation of nitrobenzene is again rather strong evidence of the polar character, and of the selectivity, of the oxidant. Also, the isomeric distribution obtained in toluene hydroxylation closely resembles that reported for other electrophilic radical oxidations.[24,25]

Clearly, the results presented so far are rather contradictory. Some of them suggest that the oxidant is rather selective. Not only does it discriminate between aliphatic and aromatic C—H bonds in toluene and cumene, but also it leads to an isomeric distribution typical of electrophilic radicals. On the other hand, on the basis of the relatively scarce dependence of the hydroxylation yields on the nature of the substrate, one could reach the opposite conclusion. To solve this contradiction we have studied the effect of the substituents in the aromatic ring by using competitive conditions (see the Experimental Section for details). In particular, we have carried out experiments where benzene and substituted benzenes are pitted together to compete against each other with the oxidant and we have determined the product ratios. When the logarithm of such product ratios are correlated in a Hammett plot with the appropriate σ values, the straight line shown in Figure 2 is obtained. The slope of such a line, i.e., the ϱ value -1.24, strongly supports the anticipation that the radical reaction exhibits a remarkable sensitivity to the nature of the substrate and that the oxidant is electrophilic in nature.

Finally, we have studied the modifications of the reaction profile caused by the nature of the substrate. As shown in Figure 3, both the induction time and the slope of the propagation part are affected by the presence of benzene and toluene compared with the simple decomposition. The effect is particularly detectable in the length of the induction time, which increases. We shall discuss the information provided by this feature in the appropriate section of the paper.

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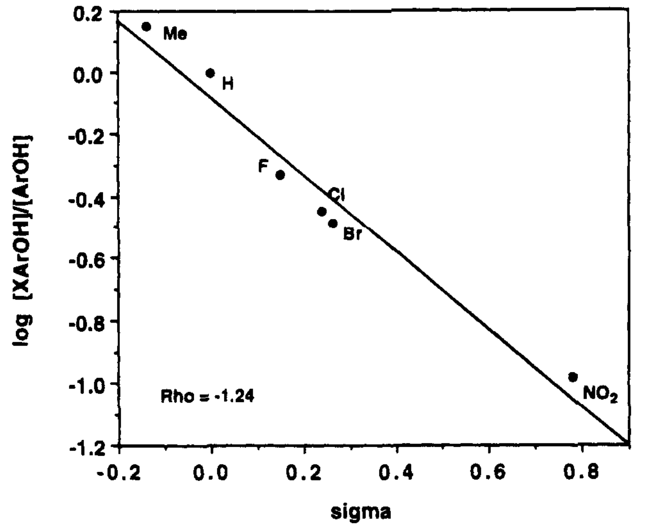


Figure 2. Hammett plot for the hydroxylation of XC_6H_5 by **1** (0.004 mol L^{-1}). ϱ value -1.24 ± 0.11 ($r = 0.98$). The data are obtained from competitive experiments ($[C_6H_6] = [XC_6H_5] = 1$ mol L^{-1}) in CH_3CN at 20 °C. Relative reactivities are as follows: NO_2, 0.104; Br, 0.328; Cl, 0.357; F, 0.472; H, 1; CH_3, 1.408.

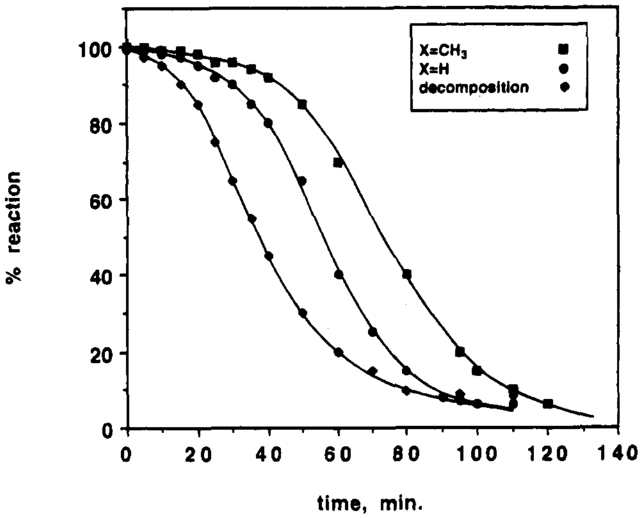
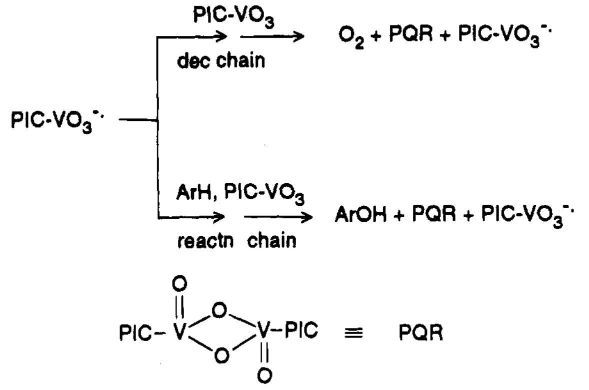


Figure 3. Profile of decomposition reaction of **1** (0.004 mol L^{-1}) and hydroxylation of XC_6H_5 (2 mol L^{-1}) by **1** (0.004 mol L^{-1}) in CH_3CN at 20 °C. Reaction profiles determined by following the decrease of absorbance of **1** at 450 nm ($A_o = 1.8$, $A_{inf} = 0.9$).

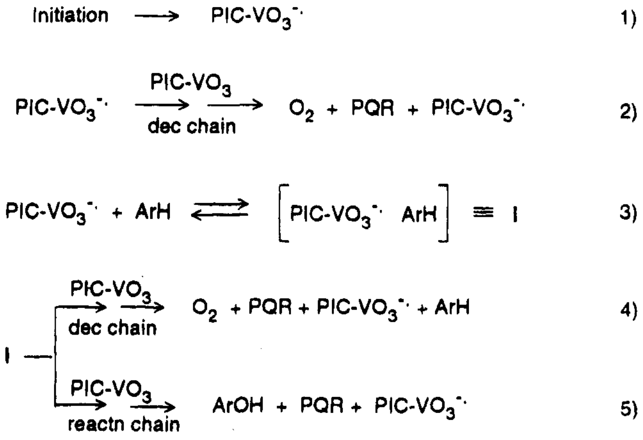
Discussion

The study previously carried out on the decomposition of **1** in CH_3CN, particularly on the initiation process,[18] led us to propose that the chain carrier, which is the oxidant in solution, is the product of the monoreduction of **1**, which, for the sake of simplicity we write as the radical anion, $[PIC-VO_3^{\bullet-}]$ neglecting further reactions involving such species, e.g., the cleavage of the peroxidic bond.[26] The reaction, according to our first proposal,[6] should proceed as shown in Scheme 1. Such a proposal implies that (1) at large, mathematically infinite, concentration of the substrate, dioxygen evolution should be totally suppressed, besides the presumably small amount generated in the initiation process, and (2) a rather different selectivity, measured as the ratio dioxygen/phenol, is expected for different substrates. In particular, the more reactive the substrate is the more phenol should be obtained.

Scheme 1



Scheme 2



The results presented above do not fulfill the predictions. Figure 1 shows that the yields of phenol increase with the concentration of the substrate, tending, however, to a plateau. This does not fit with point 1 unless the unlikely assumption is made that the amount of reagent converted to dioxygen in the initiation process is large. Moreover, the dependence of the limiting yields on the substituent of the benzene ring is not in line with the prediction of point 2. The ϱ value -1.24 measured from competitive experiments allows us to predict that benzene should be at least 10-fold more reactive than *p*-nitrobenzene whereas we find that the yield of phenol is only ca. 2-fold that of *p*-nitrophenol.

Therefore, we suggest the occurrence of a further intermediate, **I**, which may evolve to give either molecular oxygen or hydroxylated products, as shown in Scheme 2. In the schemes for the sake of simplicity, the stoichiometric coefficients of the various species have been omitted.

In the case of the competitive reactions, when two different aromatic substrates, ArH and Ar′H, are present in the system, eqs 3′–5′ and equilibrium 6 must also be added (Scheme 3).

In the absence of substrate, all the dioxygen comes from reaction 2. In the presence of ArH dioxygen is formed from reaction 2 and reaction 4, and ArOH comes from eq 5 via intermediate **I** (eq 3).

By increasing the concentration of aromatic hydrocarbon ArH, the concentration of free $[PIC-VO_3^{\bullet-}]$, according

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[26] Bonchio, M.; Conte, V.; Di Furia, F.; Modena, G.; Moro, S.; Carofiglio, T.; Magno, F.; Pastore, P. *Inorg. Chem.* **1993**, *32*, 5797.

Scheme 3

$$\text{PIC-VO}_3^{\cdot-} + \text{Ar'H} \rightleftharpoons \left[\text{PIC-VO}_3^{\cdot-}\cdot\text{Ar'H}\right] \equiv \text{I}' \qquad 3')$$

$$\text{I}' \xrightarrow[\text{dec chain}]{\text{PIC-VO}_3} \text{O}_2 + \text{PQR} + \text{PIC-VO}_3^{\cdot-} + \text{Ar'H} \qquad 4')$$

$$\text{I}' \xrightarrow[\text{reactn chain}]{\text{PIC-VO}_3} \text{Ar'OH} + \text{PQR} + \text{PIC-VO}_3^{\cdot-} \qquad 5')$$

$$\text{I}' + \text{ArH} \rightleftharpoons \text{I} + \text{Ar'H} \qquad 6)$$

to Scheme 2, decreases and the contribution to the production of dioxygen of reaction 2 also decreases, being eventually suppressed at infinite concentration of ArH. Under these conditions all dioxygen derives from reaction 4, and the ratio between the two products depends only on the ratio of the rate constants of reactions 4 and 5 (k_4/k_5). Both rate constants in turn depend on the nature of ArH.

When two substrates are present in large excess, again the contribution to dioxygen production by reaction 2 is negligibly small. Under these conditions most (all, as a first approximation) of the dioxygen evolved comes from reactions 4 and 4′. Its rate of formation is provided by the sum

$$d(\text{O}_2)/dt = k_4(\text{I}) + k_{4'}(\text{I}') \qquad (7)$$

These considerations rationalize on a simple mathematical basis why, when only one substrate is present, dioxygen evolution and yield of phenol reach a limiting value which does not depend much on the nature of the substrate. Such limiting value depends only on the ratio k_4/k_5. Since both constants depend on the nature of the substrate, it is not unlikely that their ratio is similar for different substrates. In fact, according to Scheme 2, **I** may react with PIC-$\text{VO}_3^{\cdot-}$, forming either phenol or dioxygen. Therefore, different **I** may have different properties without major consequences on the balance between the two competing processes.

This is not true for the ratio $k_4(\text{I})/k_{4'}(\text{I}')$ which is largely influenced by the properties of the two intermediates. Therefore, the proposed formation of intermediates **I** provides a rationale of the experimental results obtained. As a further support[27] to this novel mechanism we have considered the two alternative pathways deriving the appropriate sets of equations and calculating the corresponding behaviors. In the previous one, **I** is not formed so that dioxygen evolution and phenol production derive from two parallel processes. The reaction in the absence of substrate had been previously studied.[18] Phenol production may be described by eq 11. The combination of the two processes leads to Scheme 4. By applying the Bulirch–Stoer method[18,28] it may be observed in Figure 4 that neither phenol production nor peroxide disappearance fits with the calculated curves b and a. By contrast, if the occurrence of intermediate **I** is considered, by substituting eq 11 in Scheme 4 by eqs 15–17, shown in Scheme 5, a nice fitting of the experimental with the calculated curves is observed.[29] Although this is again an indirect evidence of the occurrence of **I**, it indicates at least that the simple picture of the two parallel reactions does not rationalize the results.

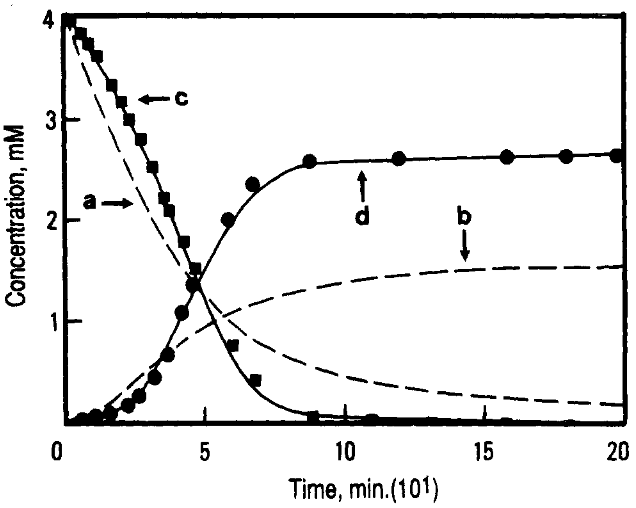

Figure 4. Calculated curves describing the formation of phenol and the disappearance of **1** in CH_3CN at 20 °C, [**1**] = 0.004 mol L^{-1}, [C_6H_6] = 2 mol L^{-1}, under the hypothesis that the phenol production and decomposition of **1** are parallel processes (curves a and b) or that intermediate **I** (see text) is formed (curves c and d). Circles and squares are experimental points.

A further crucial point of Schemes 2 and 3 is the proposal that the aromatic compound can form a radical molecular pair with the radical anion through a fast equilibrium (eqs 3 and 3′). There are several precedents for this kind of intermediates, though in different reactions which involve the attack of a radical, e.g., Cl, to aromatic substrates.[30] We shall examine this point in more details later on in the paper.

As far as the role of the picolinato ligand is concerned, we have addressed this aspect by examining the behavior of peroxovanadium complexes containing other ligands structurally similar to picolinic acid. These data are reported in Chart 1.

It may be observed that the general characteristics observed with picolinic acid are preserved with these ligands (compounds **1**–**3**). On the other hand, relatively minor structural variations (compounds **4** and **5**) cause dramatic changes in the selectivity of the oxidation. It seems likely, therefore, that the ligand exerts its effect by modulating the electronic character of the complex. Such a property is in turn related to the ability of the oxidant to act as a one-electron acceptor.[26]

Returning now to the proposed mechanistic scheme, a direct evidence of the formation of the aromatic radical pair **I**, very likely present in concentrations too low to be detected, is not available. However, there is an indirect evidence which is consistent with its occurrence.

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[27] We thank one of the reviewers for drawing our attention to this aspect.

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[29] The scheme requires that both in the absence or in the presence of benzene an overall quadratic order in vanadium must be observed. This has been confirmed by direct kinetic experiments carried out as previously reported.[18] Note that the decomposition mechanism shown in Scheme 4 differs from that of our previous paper.[18] In particular, in eq 12 [PIC-$\text{VO}_3^{\cdot-}$] is considered to act as an oxidant toward the peroxo complex. This also implies a change in the termination steps. Although both alternatives fit the experimental data, we favor now the possibility for [PIC-$\text{VO}_3^{\cdot-}$] to act as a one-electron acceptor instead of a one-electron donor[18] in the light of its efficiency as electrophilic oxidant revealed by this work.

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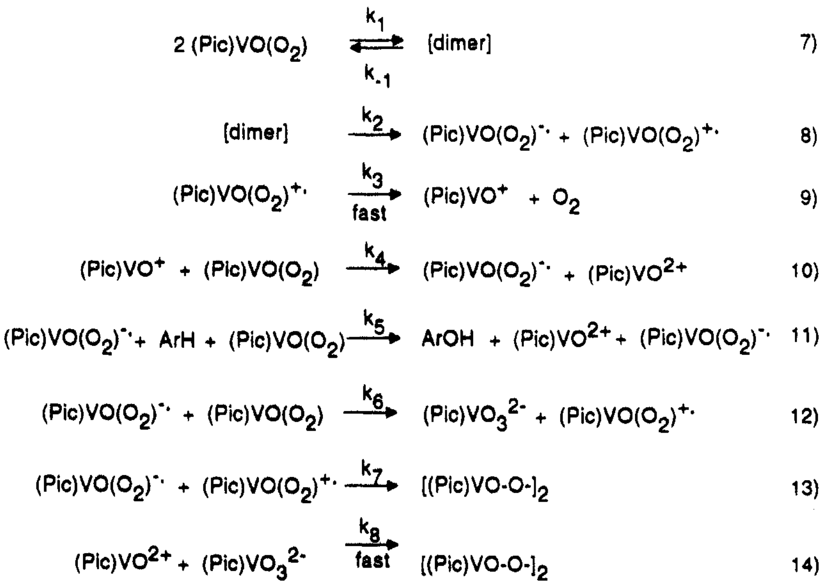
Scheme 4



Scheme 5

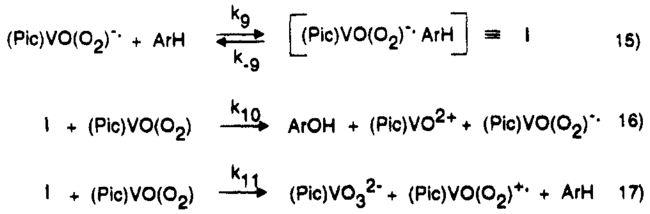
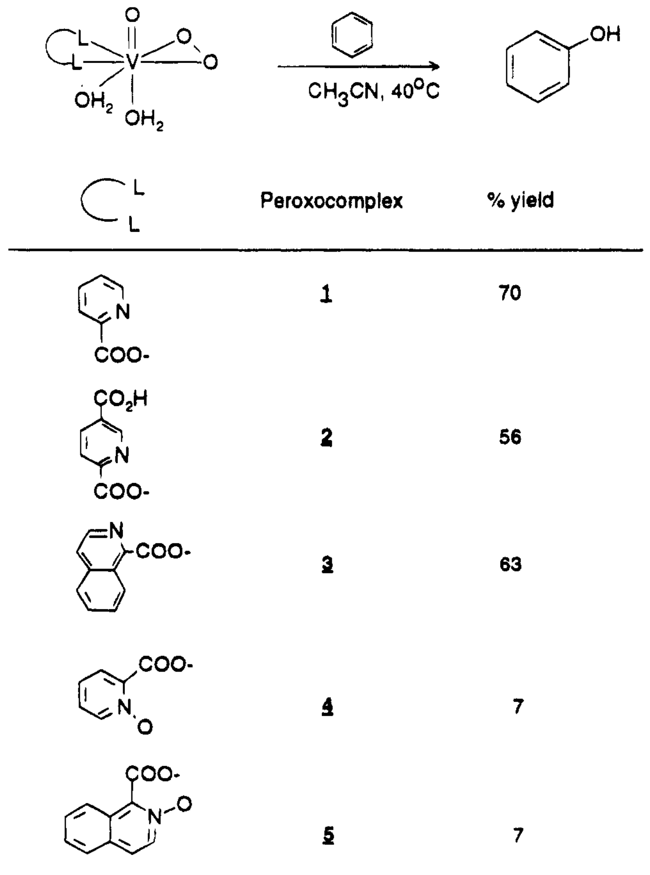


Chart 1



This comes from the increase of the induction time caused by the presence of the substrate. Bearing in mind that the steady-state concentration of [PIC-VO$_3^{\bullet-}$] is reached during the induction period, it is clear that in the absence of aromatic substrates the length of such a period depends only on the ratio between the rate of formation of [PIC-VO$_3^{\bullet-}$] and that of its destruction. When aromatic substrates are present, the species **I** is formed, so that there are now two vanadium-containing active species:

$$[\text{PIC}-\text{VO}_3^{\bullet-}]_{\text{SS}} = [\text{PIC}-\text{VO}_3^{\bullet-}] + (\text{I}) \qquad (8)$$

The association of [PIC-VO$_3^{\bullet-}$] to the substrate leads to the formation of an intermediate **I** more stable than [PIC-VO$_3^{\bullet-}$]. As a consequence, the rates of the propagation steps slow down and the induction time increases (Figure 3).

Accordingly, the induction time is longer in the presence of aromatic substrates than in their absence, and it is also longer when the donor character of Ar, and hence, its ability to form the intermediate **I** with the electrophilic radical, is larger.

Further studies are clearly needed in order to confirm these conclusions, but it is rewarding that the experimental finding is in agreement with the prediction.

Experimental Section

Materials. The aromatic substrates and the solvent used, all commercially available materials, were purified according to standard procedures and stored over 4 Å molecular sieves. All other chemicals, reagent grade (Aldrich), were used without further purification. H_2O_2, 70% w/v (Interox), was used as such.

Complex **1** was synthesized according to a slightly modified literature method.[5] Compounds **2**–**5**, prepared by similar procedures, were characterized by spectroscopic (UV–vis, IR, ^{1}H) analyses, and their purity (98%), measured as active oxygen content, was checked by potentiometric titration.

Apparatus. UV–vis spectra were recorded on a Lambda 5 Perkin-Elmer spectrophotometer, using 1 cm cells, and NMR spectra on a Bruker WP-200 instrument. The GC analyses were performed on a Varian 3700 gas chromatograph equipped with a Varian CDS 401 integrator. GC–MS analyses were performed on a Hewlett-Packard 5890 gas chromatograph connected with a 5970 mass selective detector using a 15 m OV-17 capillary column, 0.25 mm i.d. The potentiometric titrations were carried out with a Metrohm 605 potentiometer. The amount of dioxygen evolved in the reactions was determined by means of a 10 mL maximum capacity gas-buret, thermostated at the desired temperature.

Oxidation Procedures and Product Analyses. The oxidation of aromatics was carried out in a jacketed glass reactor with temperature control better than ±0.05 °C. In a typical run, the peroxovanadium complex (0.04 mmol) was dissolved in 10 mL of CH_3CN containing the aromatic substrate (20 mmol). In competitive experiments 10 mmol of each aromatic hydrocarbon were utilized. The oxidation reactions were followed by monitoring the decrease of the absorbance of the peroxovanadium complex at 450 nm. The amount of dioxygen evolved was measured by using a 100 mL reaction volume. Typically, 0.4 mmol of $VO(O_2)PIC(H_2O)_2$ was reacted with 200 mmol of benzene. At the end of the reaction 0.06 mmol (1.5 mL at 298 K) of O_2 (30% yield) were measured together with 0.28 mmol of phenol (70% yield). Yields are based on the initial amount of peroxo complexes.

The oxidation products were identified by GC–MS comparison with authentic samples, and the yields were determined by quantitative GC analysis (error ± 3%): the columns used were (a) a glass column FFAP 3% on Chromosorb WAW DMCS 50 cm for the oxidation products of benzene and cumene (benzophenone internal standard), (b) a glass column FFAP 3% on Chromosorb WAW DMCS 150 cm for chloro- and fluorophenols (acetophenone and benzophenone as internal standards), and (c) a fused silica capillary column, 20 m, FFAP i.d. 0.25 mm for isomeric cresols and nitrophenols (benzophenone as internal standards).

Mathematical Treatment. Mathematical treatment leading to the calculated curves of Figure 4 involves simultaneous integration of the set of equations of Scheme 4 and of that obtained by substituting eq 11 with those of Scheme 5, with the Burlich–Stoer method.[28] The mean square difference between the calculated and the experimental data has been minimized with the Simplex procedure.[31]

CAUTION. Care should be exercised in handling concentrated solutions of hydrogen peroxide and of complex **1**.

Acknowledgment. Financial support from Progetto Finalizzato Chimica Fine II and MURST is gratefully acknowledged.

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[31] Nash, J. C. *Compact Numerical Methods for computers*; Adam Hilger Ltd.: Bristol, England, 1980; Chapter 14.2.