

## Metal Catalysis in Oxidation by Peroxides. 31.<sup>1</sup> The Hydroxylation of Benzene by VO(O<sub>2</sub>)(PIC)(H<sub>2</sub>O)<sub>2</sub>: Mechanistic and Synthetic Aspects

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The oxidation of benzene to phenol by the vanadium(V) peroxy complex VO(O<sub>2</sub>)(PIC)(H<sub>2</sub>O)<sub>2</sub> (1) has been investigated in various solvents and in the presence of both one-electron donors and radical traps. The hypothesis is advanced that the active oxidizing species is a vanadium complex resulting from the monoreduction of 1, i.e., formally a radical-anion derivative. Such a process readily occurs in noncoordinating solvents (CH<sub>3</sub>NO<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, and also CH<sub>3</sub>CN) whereas it is almost suppressed in coordinating ones (CH<sub>3</sub>OH and DMF). The PIC ligand plays a role, likely in stabilizing the active species, which, however, may be formed also from simple peroxy complexes such as VO(O<sub>2</sub>)(OR). As far as the synthetic applications of 1 are concerned, preliminary data indicate that by running the oxidation in a two-phase system the main drawback of the process, i.e., the fast decomposition of the oxidant, may be, at least in part, overcome.

### Introduction

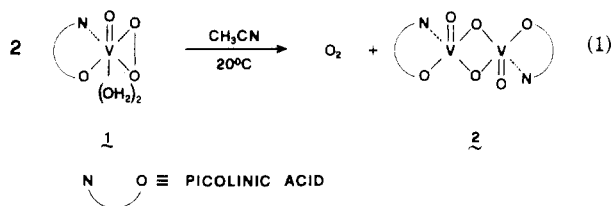
Transition-metal peroxy complexes are attracting renewed attention in context with the oxidation of organic substrates.<sup>2</sup> It has been shown, for example, that V(V) and Mo(VI) peroxy complexes, aside from their classical reactivity as oxygen transfer reagents toward nucleophiles<sup>2</sup> such as alkenes or thioethers, display other interesting oxidative capabilities. Thus [MoO(O<sub>2</sub>)<sub>2</sub>(PIC)]<sup>-</sup>Bu<sub>4</sub>N<sup>+</sup> and [MoO(O<sub>2</sub>)<sub>2</sub>(PICO)]<sup>-</sup>Bu<sub>4</sub>N<sup>+</sup> (PIC = picolinic acid; PICO = picolinic acid *N*-oxide) oxidize primary and secondary alcohols to aldehydes and ketones, respectively.<sup>3</sup> By contrast, V(V) peroxy complexes also containing the PIC ligand, e.g., VO(O<sub>2</sub>)(PIC)(H<sub>2</sub>O)<sub>2</sub> (1), have been found to hydroxylate aliphatic and aromatic hydrocarbons.<sup>4</sup>

As part of our continuing efforts directed toward the elucidation of the mechanistic details of oxidations by peroxy complexes,<sup>5</sup> we have further<sup>4</sup> explored the behavior of complex 1 in a model reaction, i.e., the hydroxylation of benzene. We present here the results of our study aimed at enlarging both the understanding and the scope of this synthetically convenient reaction and of related transformations.

### Results

The red complex 1 was prepared from V<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>O<sub>2</sub>, and picolinic acid by a reported procedure<sup>4</sup> and its identity confirmed by spectroscopic (IR, UV-visible, <sup>1</sup>H and <sup>13</sup>C NMR) and potentiometric measurements.

Earlier work by Mimoun et al.<sup>4</sup> has established that complex 1 decomposes in CH<sub>3</sub>CN according to the stoichiometry



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(4) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fisher, J.; Weiss, R. *J. Am. Chem. Soc.* 1983, 105, 3101-10.

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Such a decomposition reaction may be conveniently followed by monitoring the decrease of the absorbance at 450 nm.<sup>4</sup> As shown in Figure 1 (curve A), a sigmoid-shaped curve is obtained, typical of radical chain reactions.<sup>6</sup> When benzene is allowed to react with 1 in CH<sub>3</sub>CN at 25 °C (curves B and C), together with the dioxygen evolution phenol is also formed, as revealed by GC analysis of the reaction mixtures, whose yield increases with increasing concentration of benzene (see Figure 1 caption). On the other hand, the sigmoid shape of the curves of Figure 1 is maintained and also the overall rate of disappearance of 1 is not greatly modified.

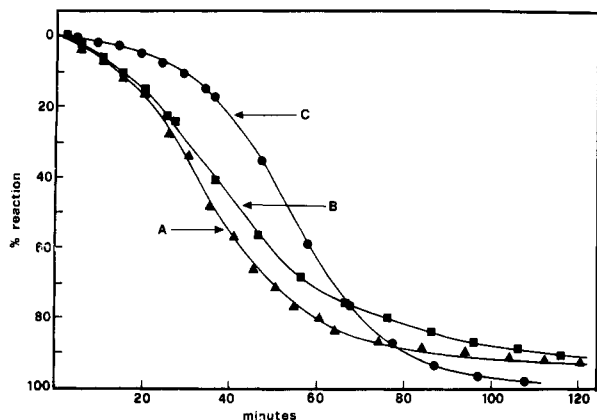
It has been reported<sup>4</sup> that methanolic solutions of 1 are fairly stable and that in such a medium no hydroxylation of benzene takes place. We have confirmed this observation and also found that solutions of 1 in DMF are equally stable so that oxidation of benzene in such a medium does not occur. Clearly both the decomposition reaction and benzene oxidation are rather sensitive to the nature of the solvent. Therefore this aspect has been investigated in some more detail.

When 1 (0.4 mmol in 100 mL) is dissolved in CH<sub>3</sub>NO<sub>2</sub>, where it is sparingly soluble, a prompt decomposition takes place. Moreover, if benzene is added, formation of phenol is observed, whose yield depends on the initial excess of the substrate, ranging from 30% (20-fold excess) to 50% (500-fold excess). Similarly, if 1 (0.04 mmol in 100 mL) is suspended in benzene with stirring, again decomposition to complex 2 occurs together with dioxygen evolution and phenol formation. The yields of phenol are enhanced from 40 to 60% when the temperature is raised from 20 to 80 °C.

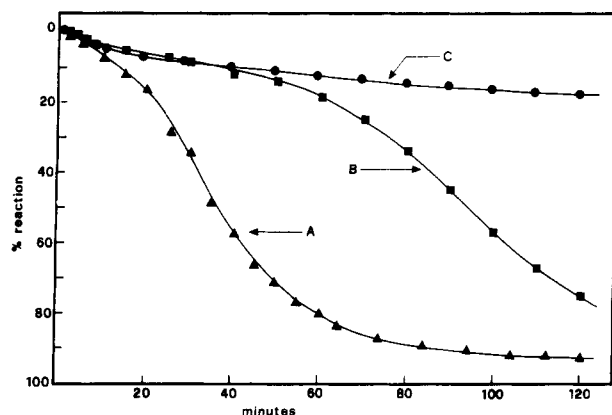
In Figure 2 is shown the effect of the addition of DMF to solutions of complex 1 (0.4 mmol in 100 mL) in CH<sub>3</sub>CN in the presence of added benzene (200 mmol). It may be seen that DMF significantly slows down the reaction and, at sufficiently high concentration, also decreases the yield of phenol, which drops to 5% when 65 mmol of DMF is present. In agreement with a radical nature of the process, we observed that promoters or inhibitors of radical reactions remarkably affect the overall rate of hydroxylation of benzene without major variations of the yields of phenol. The effects of Co<sup>2+</sup> and Bu<sup>n</sup>S, which might act as one-electron donors,<sup>2,7</sup> and of di-*tert*-butyl-*p*-cresol (DTPC),

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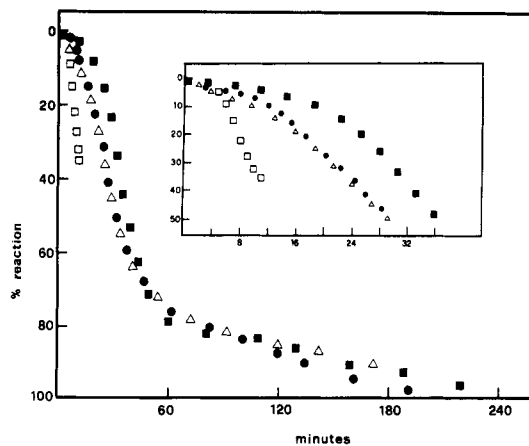
**Figure 1.** Hydroxylation of benzene at 20 °C by complex 1, 0.4 mmol, in  $\text{CH}_3\text{CN}$  (100 mL) as followed by the decrease of the absorbance at 450 nm ( $A_0 = 1.85$ ,  $A_\infty = 0.94$ ). Curve A: benzene, 0 mmol;  $\text{O}_2$  evolved, 0.2 mmol (100% yield). Curve B: benzene, 8 mmol;  $\text{O}_2$  evolved, 0.14 mmol (70%); phenol formed, 0.12 mmol (30%). Curve C: benzene, 200 mmol;  $\text{O}_2$  evolved, 0.06 mmol (30%); phenol formed, 0.28 mmol (70%).



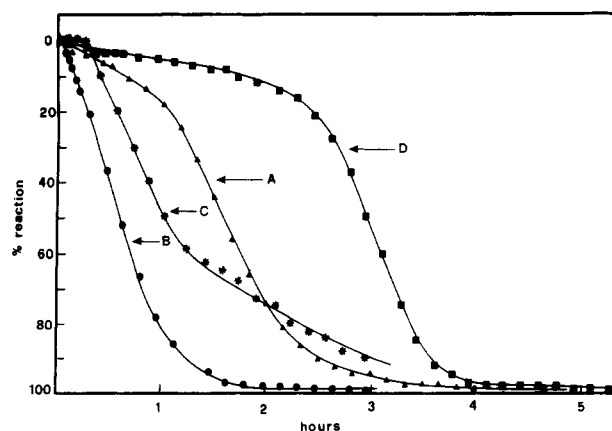
**Figure 2.** Hydroxylation of benzene (200 mmol) at 20 °C by complex 1, 0.4 mmol, in  $\text{CH}_3\text{CN}$  (100 mL) as followed by the decrease of the absorbance at 450 nm ( $A_0 = 1.85$ ,  $A_\infty = 0.94$ ), in the presence of added DMF. Curve A: DMF, 0 mmol; phenol formed, 0.28 mmol (70%). Curve B: DMF, 0.4 mmol; phenol formed, 0.27 mmol (67%). Curve C: DMF, 65 mmol; phenol formed, 0.2 mmol (5%).

an efficient radical trap,<sup>8</sup> have been studied in the reaction of benzene (200 mmol in 100 mL) with complex 1 either in  $\text{CH}_3\text{CN}$  or in  $\text{CH}_3\text{CN}$ -DMF (0.4 mmol) solvents. The results obtained are shown in Figures 3 and 4. Both  $\text{Co}^{2+}$  and  $\text{Bu}^n_2\text{S}$ , particularly in  $\text{CH}_3\text{CN}$ /DMF, accelerate the first slow part of the reaction. The effect in  $\text{CH}_3\text{CN}$  (also because the overall rates are faster) is less evident but still detectable for  $\text{Co}^{2+}$ . By contrast, if 0.04 mmol of DTPC is added, no reaction takes place for about 2 h. After this time, the reaction starts proceeding as in the absence of the inhibitor.

Since sulfides are known to behave mostly as nonradical reductants toward transition-metal peroxo complexes,<sup>9</sup> including V(V) derivatives,<sup>10</sup> the reaction of 1 (0.4 mmol in 100 mL) with  $\text{Bu}^n_2\text{S}$  has been further investigated.  $\text{Bu}^n_2\text{S}$  in slight excess (0.48 mmol) over the oxidant rapidly reacts with 1 in  $\text{CH}_3\text{CN}$ , and the initial slow reaction is



**Figure 3.** Hydroxylation of benzene (200 mmol) at 20 °C by complex 1, 0.4 mmol, in  $\text{CH}_3\text{CN}$  (100 mL) as followed by the decrease of the absorbance at 450 nm ( $A_0 = 1.85$ ,  $A_\infty = 0.94$ ), at two different time scales. (●): no additives present (see curve C, Figure 1). (Δ):  $\text{Bu}^n_2\text{S}$ , 0.04 mmol; phenol formed, 0.22 mmol (55%). (□):  $\text{Co}^{II}$ , 0.04 mmol; phenol formed, 0.20 mmol (51%), after 11-min precipitation occurs. (■): DTPC, 0.04 mmol; phenol formed, 0.23 mmol (57%).



**Figure 4.** Hydroxylation of benzene (200 mmol) at 20 °C by complex 1, 0.4 mmol, in  $\text{CH}_3\text{CN}$  (100 mL) as followed by the decrease of the absorbance at 450 nm ( $A_0 = 1.85$ ,  $A_\infty = 0.94$ ), in the presence of DMF, 0.4 mmol. Curve A: no additives present (see curve B, Figure 2). Curve B:  $\text{Bu}^n_2\text{S}$ , 0.04 mmol; phenol formed, 0.24 mmol (60%). Curve C:  $\text{Co}^{II}$ , 0.04 mmol; phenol formed, 0.24 mmol (60%). Curve D: DTPC, 0.04 mmol; phenol formed, 0.26 mmol (65%).

suppressed. However, poor yields of sulfoxide (0.11 mmol, 27% based on the oxidant) and sulfone (0.04 mmol, 20%) are obtained. Dioxygen evolved (0.12 mmol, 30%) provides for the remaining active oxygen. An increase in the ratio sulfide:oxidant to 2 leads to an enhanced yield of sulfoxide (44%) whereas the yield of sulfone decreases (11%). Even when the initial sulfide concentration is 20-fold that of the oxidant, the yield of sulfoxide is only 87%. Under these conditions no sulfone is formed.

As mentioned above, peroxovanadium complexes not containing the PIC ligand behave as electrophilic oxidants, e.g., in the epoxidation of allylic alcohols.<sup>11</sup> Since in complex 1 several pieces of evidence indicate a radical mechanism, it was considered of interest to evaluate the effect of the ligand on the reactivity of V(V) peroxo species. Therefore, the behavior of the system  $\text{VO}(\text{O}i\text{Pr})_3/\text{H}_2\text{O}_2/\text{picolinic acid}$  has been examined. When a slight excess (1.2-fold) of  $\text{H}_2\text{O}_2$  (from 70% w/v commercial solution in

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Table I. Benzene Hydroxylation in a Two-Phase System,<sup>a</sup> at 40 °C

V <sub>2</sub> O <sub>5</sub> , mmol	H <sub>2</sub> O <sub>2</sub> , mmol	ligand		t, h	H <sub>2</sub> O <sub>2</sub> consmd, %	phenol, mmol	turnover no. <sup>b</sup>	yield, <sup>c</sup> %
		type	mmol					
0.050	5			22	68	0.09	1.8	3
0.050	5	PIC	0.07	22	71	0.13	2.6	4
0.050	5	HPCA	0.07	22	70	0.24	4.8	7
0.050	1	HPCA	0.07	6	100	0.29	5.8	29
0.050	1	HPCA	0.04	24	40	0.13	6.5	32
0.025 <sup>d</sup>	5	HPCA	0.04	94	90	0.31	12.1	7

<sup>a</sup> Benzene (5 mL)/H<sub>2</sub>O (2 mL). See the Experimental Section for details. <sup>b</sup> Based on V<sub>2</sub>O<sub>5</sub>. <sup>c</sup> Based on the hydrogen peroxide consumed. <sup>d</sup> Benzene (10 mL)/H<sub>2</sub>O (2 mL).

water) is added to a solution of VO(OiPr)<sub>3</sub> (0.48 mmol in 100 mL) in CH<sub>3</sub>CN, the typical red color of the vanadium monoperoxo compounds<sup>12,13</sup> is observed, followed by a fast decomposition affording a green solution (likely due to the formation of V<sup>4+</sup> derivatives). If benzene (200 mmol) is present, some phenol is formed but in lower yield (0.07 mmol, 15%) than with complex 1 at the same concentration of V(V). On the other hand, if 1 equiv of picolinic acid is added to the acetonitrile solution of VO(OiPr)<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, the UV-visible spectrum obtained is practically indistinguishable from that of complex 1. Under these conditions, if benzene is added, the yields of phenol are comparable (0.33 mmol, 70%) with those obtained with the isolated complex.

Addition of larger excesses of H<sub>2</sub>O<sub>2</sub> to the vanadium precursor, either in the presence or in the absence of picolinic acid, does not lead to an increase in the amount of phenol formed. In particular, with a 1.2 ratio of picolinic acid:V(V) (0.48 mmol of V(V) in 100 mL) and in the presence of 200 mmol of benzene, upon addition of 2.5, 5, and 10 equiv of hydrogen peroxide, the amount of phenol obtained (ranging from 0.35 to 0.49 mmol) does not significantly increase, thus indicating that the excess of oxidant undergoes a fast decomposition.

However, if the complex 1, formed from its components, i.e., VO(OiPr)<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/PIC, in CH<sub>3</sub>CN, is allowed to react with benzene to produce phenol, addition of a subsequent portion of H<sub>2</sub>O<sub>2</sub> after complete consumption of the peroxide leads to further oxidation of benzene, producing about the same amount of phenol. This procedure can be repeated several times even though the yields of phenol gradually decrease, likely because of the effect of water either added together with H<sub>2</sub>O<sub>2</sub> or formed in the reaction.

A way to circumvent this problem is provided by the two-phase procedure already developed for Mo- and W-catalyzed oxidations.<sup>14</sup> This involves the formation of a peroxovanadium complex in the aqueous phase by addition of hydrogen peroxide to V<sub>2</sub>O<sub>5</sub> and then its extraction by a lipophilic ligand into an organic phase where benzene is present.

Preliminary experiments aimed at evaluating the applicability of the two-phase procedure to benzene hydroxylation have been carried out, and the pertinent results are reported in Table I. PIC and the more lipophilic 4-(3-heptyl)pyridine-2-carboxylic acid (HPCA) have been used as extracting agents. In both cases, phenol is formed and the calculated turnover numbers, based on the amount of V(V) present, indicate that a catalytic process is indeed taking place. As it might have been expected, HPCA provides better results than PIC, likely owing to its higher

extracting ability. On the other hand, it is observed that the yields of phenol, based on the amount of hydrogen peroxide initially present in the aqueous phase, are still rather low for both ligands, thus confirming that also in the two-phase system the decomposition of hydrogen peroxide significantly competes with benzene hydroxylation.

### Discussion

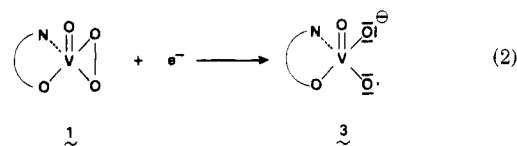
Mimoun et al. had already suggested<sup>4</sup> that the reaction of 1 with aromatic or aliphatic substrates in CH<sub>3</sub>CN is radical in nature. In fact, the sigmoid-shaped curves are evidence of chain-mechanism processes.<sup>6</sup>

Our experiments provide more information on the general features of the reaction. The effect of one-electron donors such as Co<sup>2+</sup> and sulfides strongly suggests that the radical may be formed by one-electron reduction of the vanadium peroxo complex. The picolinato ligand does have an effect on this process, but its presence is not a necessary requisite, as the data with VO(OiPr)<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> indicate.

The inhibitory effect of the DTTC confirms the hypothesis of a chain reaction which may be inhibited by the presence of a one-electron acceptor.

It is noteworthy that even a dialkyl sulfide which usually reacts with peroxides via a two-electron process<sup>10</sup> may act as a one-electron donor. This is confirmed by comparing the results obtained here with those reported on the electrophilic oxidation of sulfides by peroxo metal complexes.<sup>10</sup> In the latter processes, quantitative yields of sulfoxide are obtained and no presence of sulfone is detected when relatively small excesses of the substrate over the oxidant are used.

Also, the fast decomposition of H<sub>2</sub>O<sub>2</sub> in excess over the complex is in agreement with the presence of a radical species which may give rise to a radical chain reaction. The simplest formulation, which however at this time is only tentative, of such a radical may be



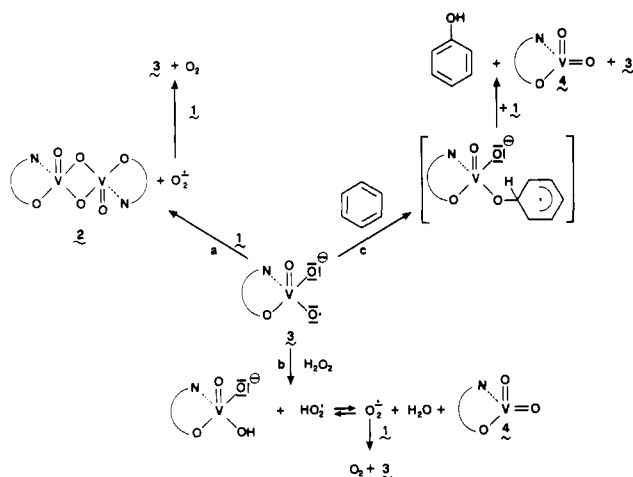
How 3 may be formed from 1 in the absence of a one-electron donor is not yet clear. However, the identical behavior in the presence or in the absence of initiator shown by the steep part of the decomposition reaction and of the oxidation of benzene suggests that the same species should be formed. Moreover, the solvent effect found indicates that the peroxo compound 1 and likely also the radical species 3 are stabilized by coordinating solvents, such as DMF or CH<sub>3</sub>OH, so that no decomposition nor benzene oxidation takes place. Accordingly, solvents like CH<sub>3</sub>CN, CH<sub>3</sub>NO<sub>2</sub>, and benzene are not able to stabilize 1 or 3 and hence the decomposition, eventually leading to the same radical species, takes place.

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Scheme I



Assuming that the radical carrier is always 3, independently of how it is formed, the main reactions observed, i.e., decomposition, benzene hydroxylation, and  $H_2O_2$  oxidation (when it is present), may be outlined as shown in Scheme I.

Complex 4, produced in paths b and c, is simply the monomeric precursor of the dimeric complex 2, i.e., the identified product of the reaction.<sup>4</sup>

It must be stressed that the reactions reported above, though accounting for the experimental data obtained, are somewhat speculative and, very likely, an oversimplified picture of the system.

The experiments reported here also indicate that the rate constants of the reaction of the vanadium radical with the peroxovanadium complex, path a, and with  $H_2O_2$ , path b, are larger than that with benzene, path c, and even with  $Bu^n_2S$ , the reaction with  $H_2O_2$  being the fastest so far observed. This appears to be a major problem as far as synthetic applications are concerned. However, the finding that a two-phase procedure may be applied to the system allows for a possible development of a catalytic oxidation.

### Conclusion

The results presented in this paper provide some further insight into the reaction and may open its synthetic utilization. Although a detailed mechanistic description of the system is not yet possible, our data point to a reaction pathway different from that previously proposed,<sup>4</sup> particularly as far as the nature of the active species in the hydroxylation of benzene by 1 is concerned.

Further studies are now in progress in both directions.

### Experimental Section

**Materials.** Benzene, thiophene free (Baker), was purified according to standard procedure and stored over 4-Å molecular sieves. Commercial  $Bu^n_2S$  (Aldrich) was purified by distillation. All the solvents used were purified, by following standard procedure, from highly pure commercial samples. All other chemicals, reagent grade (Aldrich), were used without further purification.  $H_2O_2$ , 70% w/v (Interlox), was used as such. Complex 1 was synthesized by following a published procedure.<sup>4</sup> HPCA was prepared according to literature methods<sup>15</sup> and its identity confirmed by spectral data (IR,  $^1H$  and  $^{13}C$  NMR, and MS).  $VO(OiPr)_3$  was prepared according to a literature procedure.<sup>16</sup>

**Apparatus.** UV-visible spectra were recorded on a Lambda 5 Perkin-Elmer spectrophotometer, using 1-cm cells, and NMR spectra on a Bruker WP200 instrument. The GC analyses were performed with a Varian 3700 gas chromatograph equipped with a Varian CDS 401 integrator. The potentiometric titrations were carried out with a Metrohm 605 potentiometer. GC-MS analyses were performed on a Hewlett-Packard 5890 gas chromatograph connected with a 5970 mass selective detector using a 15-m OV17 capillary column, 0.25-mm i.d. The dioxygen evolved in the reactions was measured by a gas buret.

**Oxidation Procedures and Product Analysis.** The oxidation reactions were followed either by monitoring the decrease of the absorbance of complex 1 at 450 nm or by quantitative GC analysis (acetophenone internal standard) of the oxidized products at various time intervals. The temperature control was always better than  $\pm 0.1$  °C. The glass column used was a 3% FFAP on Chromosorb WAW DMCS (50 cm). The oxygenated products were identified by GC-MS comparison with authentic samples. The oxidation of benzene in the two-phase system was carried out at 40 °C in a double-jacketed glass flask. In a typical run, 2 mL of water containing 0.05 mmol of  $V_2O_5$  and 1 mmol of  $H_2O_2$  were added to 5 mL of benzene containing 0.07 mmol of ligand with vigorous stirring until the red organic phase turned to a blue color. Then the two phases were separated, and the amount of unreacted  $H_2O_2$  was determined in the aqueous phase by standard iodometric titration, whereas the phenol yield was obtained by quantitative GC analysis of the organic phase.

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

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