



## Oxidations by the Reagent $O_2 - H_2O_2 - Vanadium\ complex - Pyrazine-2-carboxylic\ acid$

### Part 7. Hydroperoxidation of Higher Alkanes

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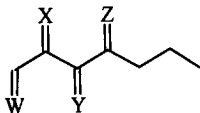
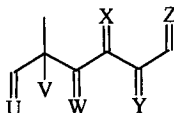
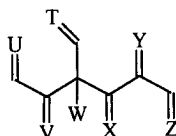
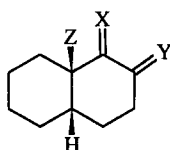
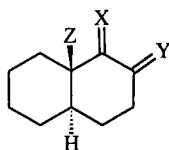
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**Abstract:** Alkanes (*n*-heptane, 2- and 3-methylhexane, *cis*- and *trans*-decalin) are readily oxidized under air in acetonitrile by the  $O_2 - H_2O_2 - PCA - VO_3^-$  reagent at room temperature to produce alkyl hydroperoxides as main products as well as minor amounts of the corresponding alcohols and carbonyl compounds. The site selectivities of the reactions are very similar to those observed with hydroxylation of the alkanes with hydrogen peroxide under UV irradiation. The proposed mechanism involves the catalytic formation of hydroxyl radicals from hydrogen peroxide which abstract hydrogen atoms from the alkanes. The alkyl radicals react rapidly with molecular oxygen to produce peroxy radicals which are transformed mainly into the hydroperoxides. Copyright © 1996 Elsevier Science Ltd

**Key words:** Aerobic oxidation, alkanes, hydrogen peroxide, alkyl hydroperoxides, alcohols, ketones, vanadium complex.

Relatively unstable organic peroxides are valuable substances both for academic laboratories and for industry.<sup>1</sup> Oxidation of organic compounds containing C-H bonds, by molecular oxygen and/or hydrogen peroxide catalyzed by metal complexes,<sup>2</sup> can be a convenient method for preparing such peroxides.

Earlier we have demonstrated that hydrogen peroxide efficiently oxidizes various organic compounds (*e.g.*, aromatic and saturated hydrocarbons, alcohols) in acetonitrile under air and in the presence of catalytic amounts of vanadate anion and pyrazine-2-carboxylic acid ( $PCA-VO_3^-$ ).<sup>3</sup> The oxidation of alkanes does not proceed in the absence of air or either of the two catalyst components. Cyclohexane oxidation under an  $^{18}O_2$  atmosphere unambiguously showed a high degree of  $^{18}O$  incorporation into the oxygenated products.<sup>4</sup> Thus it may be concluded that in alkane oxidation hydrogen peroxide plays the role of a promoter while atmospheric oxygen is the true oxidant. At low temperatures, alkanes are transformed predominantly into alkyl hydroperoxides and only relatively small amounts of the corresponding alcohols and ketones are formed.<sup>3d</sup>

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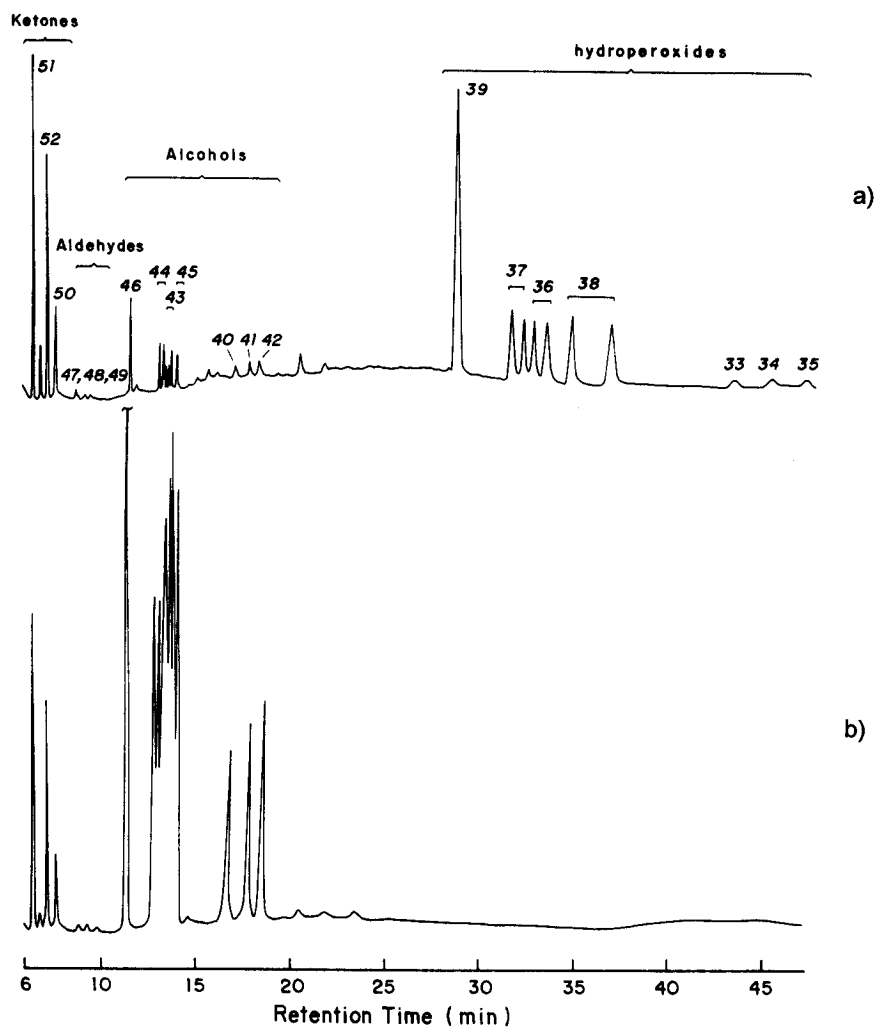
Not much is known, however, about the site and stereo selectivity of the oxidation by the  $PCA-VO_3^-$  system. We wish to report here our results on the oxidation of several higher hydrocarbons which not only allow determination of these selectivities but also show that the true oxidant is the  $HO\cdot$  radical.

## RESULTS AND DISCUSSION

The principal products obtained in the oxidation of higher alkanes are alkylhydroperoxides. Using a quartz lined injector and a fused silica capillary column, the hydroperoxides can be directly determined by gas chromatography. As shown in Figure 1 for the hydroxylation of 3-methylhexane (**32**), the seven possible peroxides are seen as different peaks (compounds **33-39**; for **36-38** the different epimers are also well separated). However, some decomposition of the hydroperoxides in the gas chromatograph may occur (see the small peaks between the alcohols and the hydroperoxides). It is, therefore, safer to determine the hydroperoxides indirectly by integration of the alcohol peaks before and after (Figure 1a and 1b, respectively) addition of an excess of solid triphenylphosphine 20-30 min before the gas chromatographic analysis. The triphenylphosphine reduces the hydroperoxides selectively to the alcohols,<sup>5</sup> thus not increasing the area of the corresponding carbonyl compounds.

n-Heptane (**1**) was oxidized with aqueous 30% and anhydrous hydrogen peroxide in acetonitrile for 3 and 24 h (Table 1). With aqueous hydrogen peroxide the peroxides **2-5** are obtained after 24 h with 86% selectivity and do not decompose under reaction conditions. The alcohols **6-9** and carbonyls **10-13** are formed with 4% and 10% selectivity, respectively. The total turnover number is 282 but the conversion of n-heptane is only 6%. Using anhydrous hydrogen peroxide, conversion of n-heptane increases to 13.5% and the selectivity for the hydroperoxides is reduced to 71%. The turnover number is as high as 623. The site selectivity C(1):C(2):C(3):C(4) of both systems (taking into account the number of hydrogen atoms at carbon atoms 1, 2, 3 and 4) is approximately 1:3:3:3 at the beginning of the reaction, which corresponds to the site selectivity of the UV hydroxylation of n-heptane with aqueous hydrogen peroxide (254 nm) under the same conditions for 1 h. During the reaction course the ratio changes to approximately 1:4:4:4 for aqueous and 1:5:5:5 for anhydrous hydrogen peroxide, showing an increase in preference for the oxidation of secondary carbon atoms. A kinetic study of the oxidation of n-heptane with aqueous 30% hydrogen peroxide (Figure 2) shows a steady increase for the concentration of all compounds (**2-13**) during 48 h, indicating that the alcohols and ketones are formed independently of the hydroperoxides.

The oxidation of 2-methylhexane (**14**) and 3-methylhexane (**32**) gives similar results to those obtained in the oxidation of n-heptane (Table 2 and 3). With aqueous 30% hydrogen peroxide, more than 90% of the



**Fig. 1.** Chromatograms of the reaction mixture obtained in the oxidation of 3-methylhexane by  $O_2 - H_2O_2 - PCA - VO_3^-$  in MeCN at 23 °C (3 h). a) before reduction with  $PPh_3$ ; b) after reduction with  $PPh_3$ .

products formed are the hydroperoxides while with anhydrous hydrogen peroxide up to 32% of alcohols and carbonyl compounds are formed. The turnover numbers are higher for anhydrous hydrogen peroxide, but in the same range as observed for *n*-heptane. As the number of isomers formed in the oxidations is much higher, we calculated the selectivity for primary, secondary and tertiary carbon atoms, normalized for the numbers of hydrogen atoms. Interestingly, we found that the selectivity for the tertiary carbon atoms is higher for aqueous 30% than for anhydrous hydrogen peroxide. In the oxidation of 14 the selectivity for secondary and tertiary

**Table 1.** Oxidation of *n*-Heptane (1) by  $O_2-H_2O_2-VO_3^-$ -PCA in MeCN at 23 °C.<sup>a</sup>

Time [h]	Alkyl hydroperoxides [mmolL <sup>-1</sup> ]				Alcohols [mmolL <sup>-1</sup> ]				Carbonyls [mmolL <sup>-1</sup> ]				TON <sup>b</sup>	Selectivity <sup>c</sup> C(1):C(2):C(3):C(4)
	2	3	4	5	6	7	8	9	10	11	12	13		
3 <sup>d</sup>	0.45	1.57	1.49	0.72	0.02	0.05	0.05	0.02	0.32	0.10	0.11	0.05	50	1.0 : 3.3 : 3.1 : 3.0
24	2.24	9.19	8.63	4.27	0.15	0.34	0.39	0.19	1.23	0.65	0.64	0.29	282	1.0 : 4.2 : 4.0 : 4.0
3 <sup>e</sup>	1.32	6.25	5.89	2.56	0.14	0.34	0.42	0.23	1.59	0.81	0.95	0.43	209	1.0 : 3.6 : 3.5 : 3.2
24	3.02	17.63	15.82	7.86	0.49	0.98	1.63	0.98	2.88	4.20	4.60	2.25	623	1.0 : 5.3 : 5.2 : 5.2

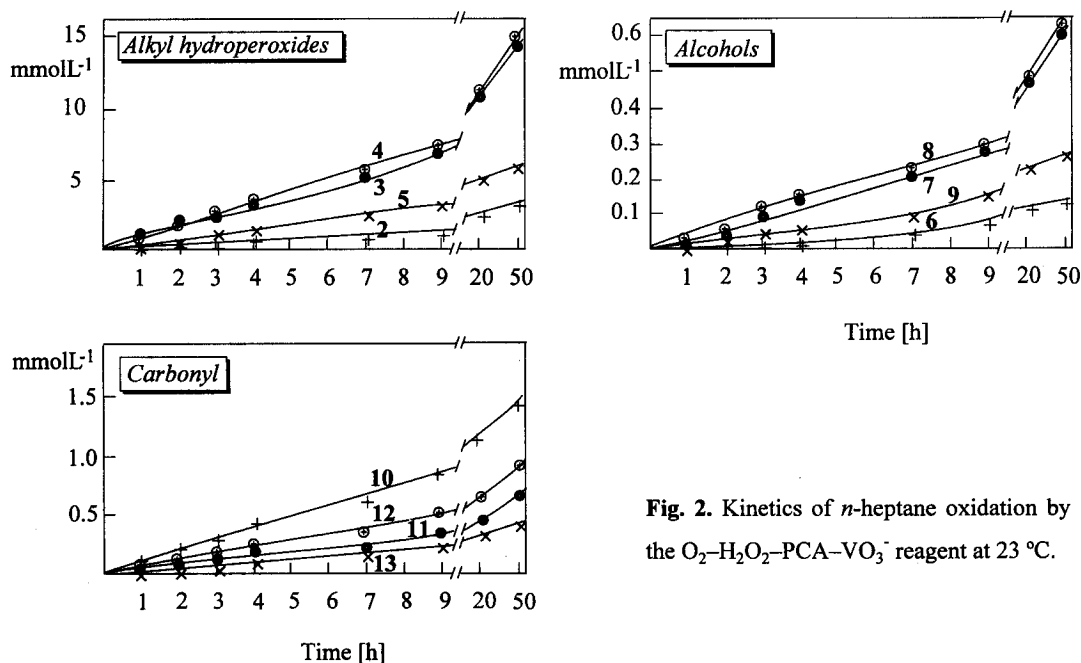
a See experimental for concentrations of starting compounds.

b Turnover number in mmol of all products per mmol of  $VO_3^-$ .

c Normalized for numbers of hydrogen atoms at carbon atoms 1, 2, 3 and 4.

d Aqueous 30%  $H_2O_2$ .

e Anhydrous  $H_2O_2$  in acetonitrile



**Fig. 2.** Kinetics of *n*-heptane oxidation by the  $O_2-H_2O_2-PCA-VO_3^-$  reagent at 23 °C.

carbon atom increases during the reaction course while for the oxidation of 32 a non-uniform behavior is observed. The selectivity found for the hydroxylation of 14 and 32 with aqueous hydrogen peroxide under UV irradiation for 1h was 1:4:19 and 1:5:15.5, respectively, which is very similar to the values observed in the

**Table 2.** Oxidation of 2-Methylhexane (14) by  $O_2 - H_2O_2 - VO_3^- - PCA$  in MeCN at 23 °C<sup>a</sup>.

$H_2O_2$	Time [h]	Alkyl hydroperoxides [mmolL <sup>-1</sup> ]			Alcohols [mmolL <sup>-1</sup> ]			Carbonyls [mmolL <sup>-1</sup> ]			TON <sup>b</sup>	Selectivity <sup>c</sup>						
		15	16	17	18+19	20	21	22	23	24+25			26	27	28	29	30	31
Aqueous	3	0.85	0.54	2.00	3.35	2.93	0.11	0.02	0.02	0.11	0.04	0.37	0.18	0.08	0.12	0.05	108	1.0 : 4.2 : 12.9
	24	3.69	2.08	8.25	13.28	10.97	0.08	0.06	0.08	0.23	0.10	0.35	0.17	0.08	0.12	0.06		
Anhydr.	3	1.26	0.93	4.18	6.09	6.62	0.20	0.11	0.27	0.76	0.16	2.40	1.20	0.59	0.71	0.46	259	1.0 : 3.2 : 10.0
	24	1.77	1.19	7.75	9.52	13.30	0.65	0.30	0.69	2.18	0.56	3.94	1.92	1.82	2.67	1.34		

**Table 3.** Oxidation of 3-Methylhexane (32) by  $O_2 - H_2O_2 - VO_3^- - PCA$  in MeCN at 23 °C<sup>a</sup>.

$H_2O_2$	Time [h]	Alkyl hydroperoxides [mmolL <sup>-1</sup> ]			Alcohols [mmolL <sup>-1</sup> ]			Carbonyls [mmolL <sup>-1</sup> ]			TON <sup>b</sup>	Selectivity <sup>c</sup>									
		33	34	35	36	37	38	39	40	41			42	43	44	45	46	47-49	50	51	52
Aqueous	3	0.18	0.20	0.23	0.55	0.70	0.69	2.71	0.02	0.02	0.03	0.05	0.07	0.06	0.17	0.10	0.11	0.27	0.23	64	1.0 : 5.4 : 11.1
	24	0.88	1.07	1.26	3.63	3.93	4.68	7.86	0.11	0.05	0.05	0.17	0.21	0.21	0.25	0.11	0.21	0.67	0.55	259	1.0 : 6.0 : 7.0
Anhydr.	3	0.56	0.70	0.79	3.22	3.05	1.68	6.28	0.05	0.06	0.07	0.14	0.22	0.15	0.28	1.26	0.19	0.70	0.87	191	1.0 : 4.4 : 5.7
	24	1.26	1.51	1.72	3.29	7.03	7.03	16.08	0.22	0.25	0.30	0.93	0.51	0.73	0.93	3.29	0.86	3.62	2.88	524	1.0 : 4.7 : 6.0

<sup>a</sup> See experimental for concentrations of starting compounds.<sup>b</sup> Turnover number in mmol of all products per mmol of  $VO_3^-$ .<sup>c</sup> Normalized for numbers of hydrogen atoms at primary, secondary and tertiary (1°, 2°, 3°) carbon atoms.

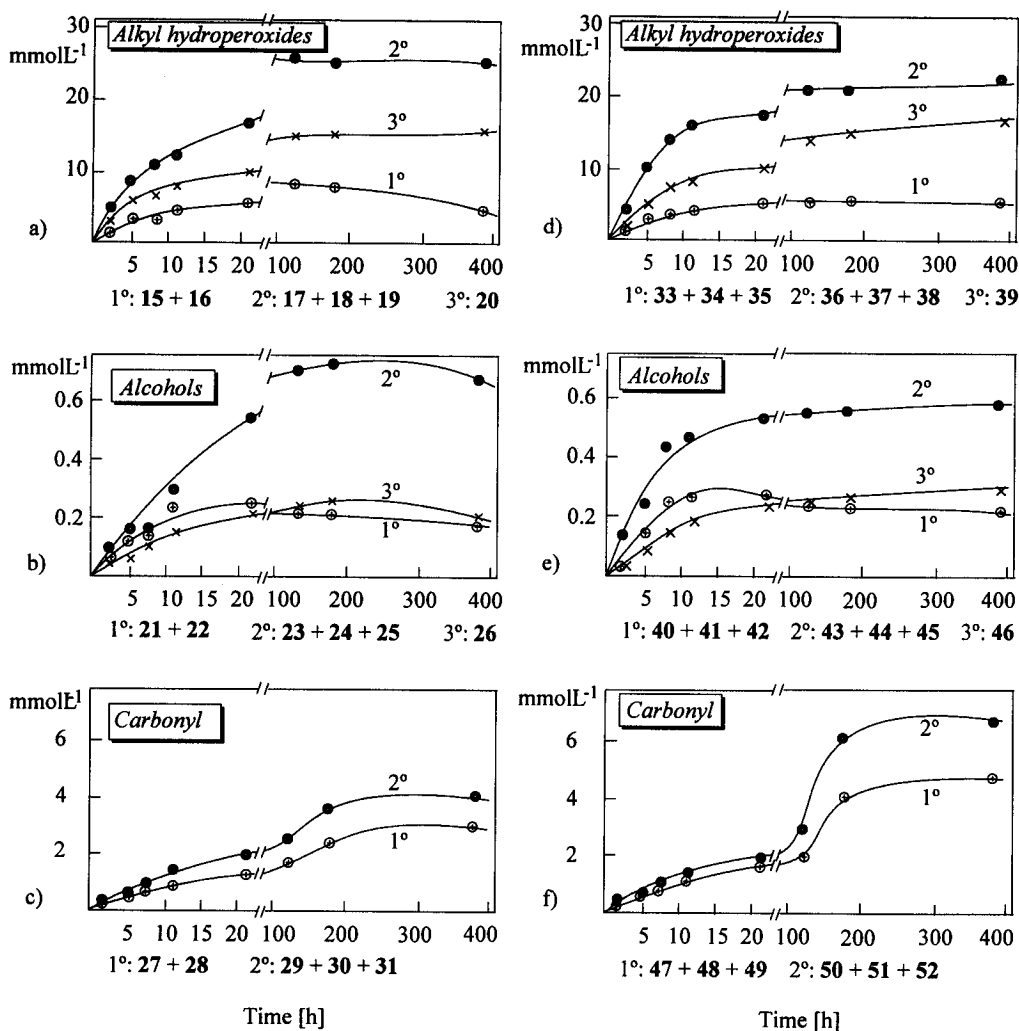
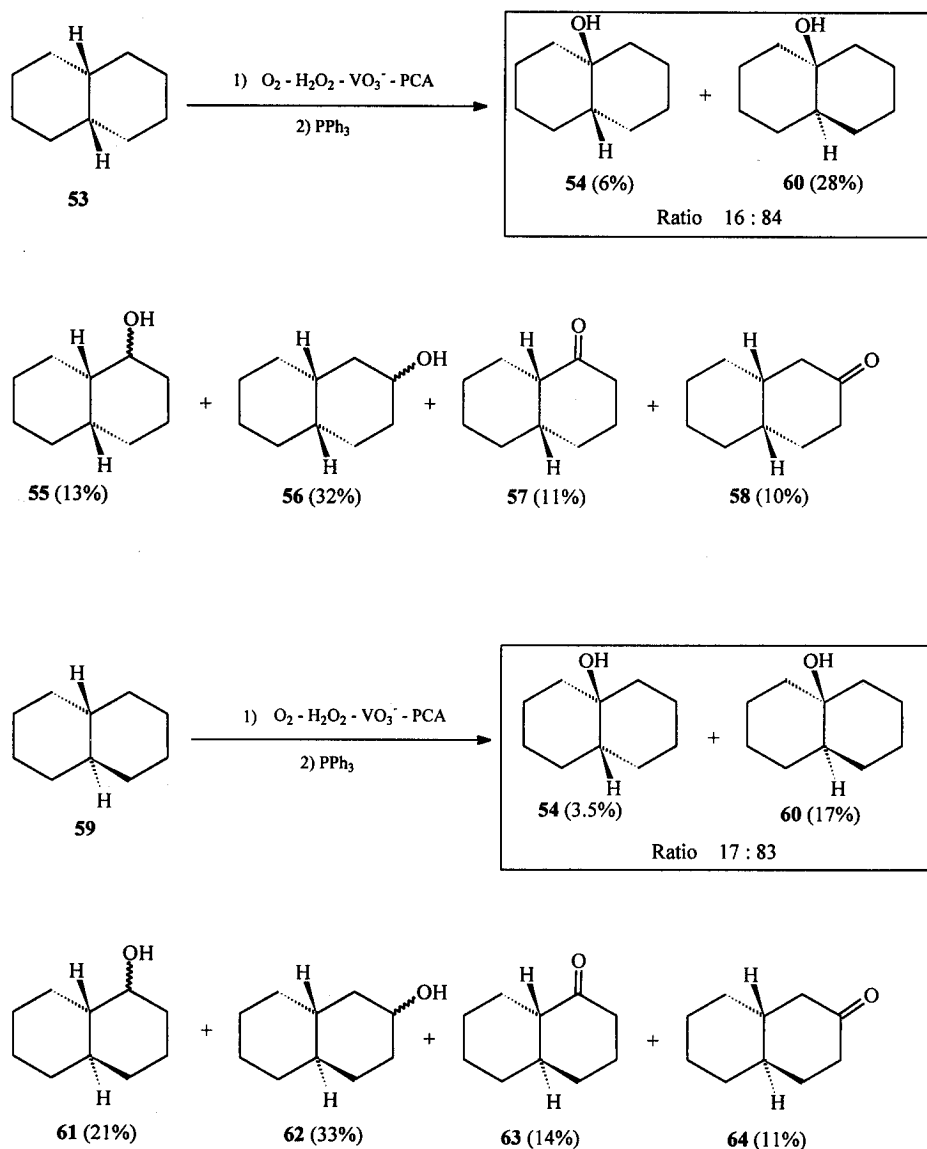


Fig. 3. Kinetics of 2-methylhexane (14) oxidation (a-c) and 3-methylhexane (32) oxidation (d-f) by the  $O_2-H_2O_2-PCA-VO_3^-$  reagent at 23 °C (Oxidation at primary, secondary and tertiary carbon atoms are shown as 1°, 2° and 3°).

oxidations with the catalytic system. The kinetic studies (Figure 3) show that the concentrations of the alkylhydroperoxides, alcohols and carbonyls increase steadily during the same time interval studied for n-heptane oxidation. However, after 120 h the primary hydroperoxides and alcohols slowly react giving carbonyl compounds while the secondary and tertiary hydroperoxides and alcohols seem to be stable under these conditions.

In order to understand the stereoselectivity of the catalytic system, we studied the oxidation of *cis*-decalin (53) and *trans*-decalin (59) separately. The percentages of the products formed with aqueous 30%

hydrogen peroxide after 330 h are shown in Figure 4. The ratio for secondary to tertiary carbon oxidation is



**Fig. 4.** Oxidation of *cis*- and *trans*-decalin by the  $O_2-H_2O_2-PCA-VO_3^-$  reagent at 23 °C for 330h.

lower for **53** (1:4.1), which is less hindered, than for **59** (1:2.1). However, the ratio of *cis*-1-hydroxydecalin (**54**) to *trans*-1-hydroxydecalin (**60**), formed in the oxidation, is the same for both substrates (1:4.8), suggesting that during the oxidation of **53** and **59** the same intermediate is formed. Furthermore, the same



ratio of **54** to **60** is observed if **53** or **59** are irradiated by UV light in the presence of aqueous hydrogen peroxide, confirming that the reaction has the same intermediate. This *cis-trans* isomerization of the C(1)-C(6) bridge is only observed if the hydrocarbon is oxidized at tertiary carbons. The products formed by oxidation of the secondary carbons of **53** maintain the *cis* configuration at the bridge, while the products formed by oxidation of the secondary carbons of **59** maintain the *trans* configuration at the bridge. Due to steric reasons the C(2) carbons of **53** and **59** are not as easily oxidized as the C(3) carbons. No *cis-trans* isomerization of C(1)-C(6) bridge was observed in the oxidation of the secondary carbons of **53** and **59** under UV irradiation.

#### Mechanism

For all hydrocarbons studied and using aqueous 30% hydrogen peroxide, the  $PCA-VO_3^-$  catalyzed reaction gave the same site selectivity as observed in the UV irradiated reaction. It seems, therefore, very probable that both systems form the same active species which attacks the hydrocarbon. The active species formed from aqueous hydrogen peroxide under UV irradiation is the  $HO^\bullet$  radical.<sup>6</sup> We, therefore, propose that the  $O_2-H_2O_2-PCA-VO_3^-$  reagent also produces the  $HO^\bullet$  radical with turnover numbers of 500 and more, which is in contrast to the Fenton system, where normally a  $Fe^{II}/H_2O_2$  ratio of 1:1 is employed.<sup>7</sup> For the catalytic formation of this radical we propose the cycle shown in Figure 5. In this cycle  $PCA-V^V$  is reduced by hydrogen peroxide to  $PCA-V^{IV}$ . The superoxide  $HO_2^\bullet$  disproportionates to hydrogen peroxide and  $O_2$ .<sup>7</sup>

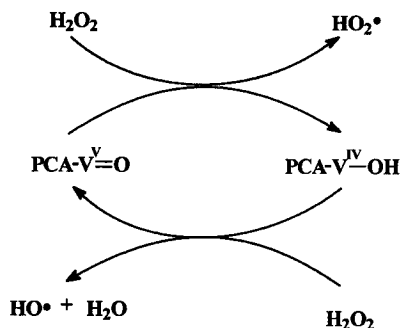
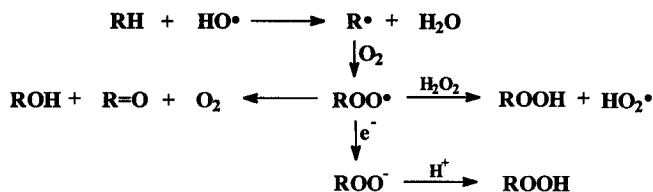


Fig. 5. Catalytic cycle for the formation of  $HO^\bullet$  radicals from  $H_2O_2$  using the  $PCA-VO_3^-$  reagent.

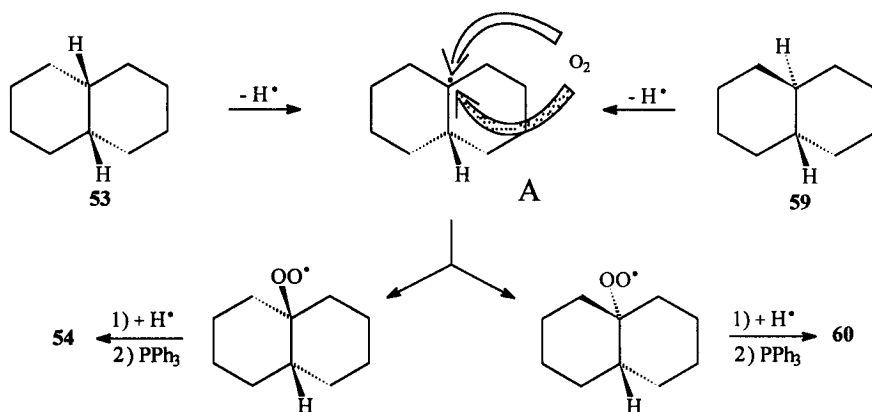
The  $PCA-V^{IV}$  then reacts with hydrogen peroxide to form the  $HO^\bullet$  radical and  $PCA-V^V$ . The  $HO^\bullet$  radical reacts with the hydrocarbon  $R-H$  (Figure 6) to form the alkyl radical  $R^\bullet$  which reacts with  $O_2$  to form the alkylperoxy radical  $ROO^\bullet$ . The  $ROO^\bullet$  radical may either disproportionate in a Russell-type termination to alcohol and ketone<sup>8</sup> or react with further hydrogen peroxide to form the hydroperoxide and superoxide  $HO_2^\bullet$ ,

which again disproportionates to hydrogen peroxide and  $O_2$ . Reduction and posterior protonation of the peroxy radical to form the hydroperoxide is also possible.



**Fig. 6.** Possible routes to form the different oxidation products from alkylperoxy radicals.

The same ratio of *cis*- (**54**) and *trans*-hydroxydecalin (**60**) formed in the reaction of **53** and **59** in the presence of the oxidation reagent or by UV irradiation suggests that the only function of the catalyst is the formation of the  $HO^\bullet$  radical from aqueous hydrogen peroxide. The 3° decaliny radical (A), formed by the reaction of **53** or **59** with  $HO^\bullet$ , is planar<sup>9</sup> and may be attacked by  $O_2$  from both sides (Figure 7). The ratio of the *cis*- and *trans*-peroxy radical thus formed, as well as of the tertiary alcohols **54** and **60**, only depends on the steric hindrance of the  $O_2$  approach at the decaliny radical A. This proposal opens a new perspective for the radical oxidation of hydrocarbons as it is now possible to produce  $HO^\bullet$  radicals with high turnover numbers. The PCA ligand is necessary to achieve a high activity of the  $V^V$  complex. We believe that the PCA ligand facilitates the reduction of the  $V^V$  complex by hydrogen peroxide, thus increasing the amount of  $PCA^{IV}$  species and consequently the rate of formation of  $HO^\bullet$  radicals.



**Fig. 7.** Different modes of  $O_2$  addition to the tertiary decaliny radical.

## EXPERIMENTAL

*n*-Heptane (Aldrich, 99.5%), 2-methylhexane (Carlo Erba, 99%), 3-methylhexane (Carlo Erba, 99%), *cis*-decalin (Aldrich, 99%), *trans*-decalin (Aldrich, 99%), hydrogen peroxide (Merck, 30%), pyrazine-2-carboxylic acid (Fluka, 99%), triphenylphosphine (Merck, 98%) and acetonitrile (EM Science, 99.99%) were used as purchased. Anhydrous hydrogen peroxide was prepared from 20 mL of commercial 30% hydrogen peroxide (Merck) which was concentrated under vacuum to 82.6%. 2.77 g of the concentrated hydrogen peroxide were dissolved in 63.6 mL of acetonitrile and 3g of anhydrous  $MgSO_4$  (Riedel-de Haën, 99.5%) were added. After 3 h the solution was filtered and used in the oxidations.

All reactions were carried out under air in an open thermostated 20 mL cylindrical flask equipped with a magnetic stirrer and a condenser. Into the reaction flask, 0.1  $\mu$ mol of *n*-Bu<sub>4</sub>NVO<sub>3</sub>, 0.4  $\mu$ mol of PCA and 4.6 mmol of the hydrocarbon were introduced and the total volume adjusted with acetonitrile to 9.8 mL. The reaction was started by the addition of 0.2 mL (2 mmol) of 30% aqueous hydrogen peroxide. When anhydrous hydrogen peroxide was used, the total volume was adjusted with acetonitrile to 8.0 mL before addition of 2 mL of the solution of anhydrous hydrogen peroxide in acetonitrile. In the experiments performed with UV irradiation 4.6 mmol of the hydrocarbon were dissolved in acetonitrile to give a total of 9.8 mL. 0.2 mL (2 mmol) of aqueous hydrogen peroxide were added and the reaction mixture directly irradiated for 1 h with a beam of UV light (254 nm) obtained from a 200 W mercury lamp.

After the predetermined time interval, 0.35 mL of the reaction mixture were taken for quantitative analysis. The samples were analyzed before and 20 to 30 min after addition of excess of triphenylphosphine. For the analysis, a Hewlett Packard 5890 Series II chromatograph equipped with a FID and outfitted with a Carbowax 20M (25 m  $\times$  0.2 mm  $\times$  0.2  $\mu$ m) column was used. The carrier gas was helium at 0.25 ms<sup>-1</sup>. The temperature was first held at 55°C for 7 min, then increased at a rate 40°Cmin<sup>-1</sup> to 100°C. The decalins and their products were isothermally analyzed at 120°C. The signals were integrated by a Shimadzu CR3A integrator. For quantitative analysis of the reaction products the external calibration technique was used, which consists of injecting 5  $\mu$ L of a standard solution of 4-heptanone, 1-heptanol and heptanal, followed by injection of 5  $\mu$ L of the unknown sample. The compounds were identified by gas chromatography coupled to a mass spectrometer, using a Shimadzu GC-17A/QP5000 instrument under the same analysis conditions used in the gas chromatographic analysis. All compounds were attributed by comparison of their mass-spectra with those from a Wiley Library Class-5000. The alkyl hydroperoxides were identified by comparison of their mass spectra with the fragmentation patterns of the corresponding alcohols.

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