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FORMATION OF ALKYL PEROXIDES IN OXIDATION OF ALKANES BY
 H_2O_2 CATALYZED BY TRANSITION METAL COMPLEXES

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Some reactions between alkanes and H_2O_2 in the presence of transition metal compounds, e.g. Cr(VI), V(V), Mn(III), Pd(II), Fe(II), yield alkyl hydroperoxides as main products.

Некоторые реакции алканов с H_2O_2 в присутствии соединений переходных металлов, например, Cr(VI), V(V), Mn(III), Pd(II), Fe(II), приводят к образованию алкилгидропероксидов в качестве основных продуктов.

In our previous publications we have shown that photooxygenations of alkanes by atmospheric oxygen catalyzed by transition metal complexes yield alkyl hydroperoxides [1-5]. In some cases peroxide was found [6, 7] to be the main or even the sole product of the photoreaction. The suggested route toward peroxide includes the abstraction of a hydrogen atom from the alkane RH by a photoexcited catalyst species to produce radical R \cdot then rapidly reacting with O_2 to yield radical ROO \cdot . The latter can easily be transformed into alkyl hydroperoxide ROOH either by the abstraction of a hydrogen atom from the donor or by consecutive reduction and proton addition.

Recently, we have found that alkanes can be efficiently

oxidized in dark reactions by H_2O_2 in CH_3CN when the system Bu_4NVO_3 -pyrazine-2-carboxylic acid is used as a catalyst [8, 9]. Alkyl peroxides are the main products of this reaction. Alcohols and carbonyl compounds that are also formed seem to be products of peroxide decomposition.

The results of the present study show that some other reactions of alkane oxidation by H_2O_2 also yield large concentrations of alkyl peroxides determined by the following method. Upon injecting the cyclohexane oxidation solution into a gas-liquid chromatograph equipped with stainless steel columns approximately equal amounts of cyclohexanol and cyclohexanone are detected. But if the reaction solution is treated with excess triphenylphosphine for a few minutes before the injection, the cyclohexanol concentration rises, whereas that of cyclohexanone decreases. It is known that cyclohexyl hydroperoxide is readily decomposed in stainless steel columns to yield approximately equal amounts of cyclohexanol and cyclohexanone [10]. Phosphine reduces alkyl hydroperoxide to the corresponding alcohol [10]. Thus it is possible to estimate the amounts of peroxide, alcohol and ketone at each moment of the reaction of the reaction if the GLC analysis of the reaction solution is carried out before and after phosphine reduction.

This method shows that the oxidation of cyclohexane by H_2O_2 in CH_3COOH catalyzed by Bu_4NVO_3 [11] yields cyclohexyl hydroperoxide as the initial product (Fig. 1). The shapes of kinetic curves indicate that the peroxide is gradually decomposed to produce cyclohexanol and cyclohexanone. Oxidation of n-hexane and 3-methylhexane also yields considerable amounts of isomeric hydroperoxides.

The reaction of cyclohexane with H_2O_2 in CH_3CN catalyzed by $Pd(OCOFCF_3)_2$ at $40^\circ C$ yields approximately equal amounts of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone (Fig. 2). As has been found previously [13], the oxidation of cyclohexane by a peroxo-complex of Pd(II) also yields cyclohexyl hydroperoxide.

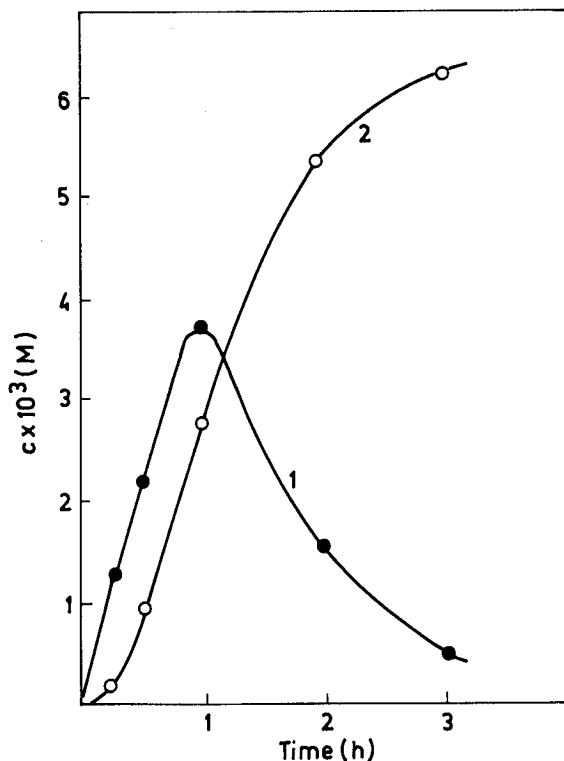


Fig. 1. Kinetics of cyclohexane (0.76 M) oxygenation in CH_3COOH solution by H_2O_2 (0.53 M) catalyzed by BuNVO_3 (0.1 mM) at 50°C .

1 - cyclohexyl hydroperoxide

2 - sum of cyclohexanol and cyclohexanone

After a one day oxidation of cyclohexane (0.61 M) by H_2O_2 (0.42 M) in CH_3CN catalyzed by CrO_3 (0.1 mM) at room temperature [12], cyclohexyl hydroperoxide (1.1 mM), cyclohexanol and cyclohexanone (total 0.8 mM) are formed.

Cyclohexyl hydroperoxide is the main product (0.26 mM with a total concentration of cyclohexanol and cyclohexanone of only 0.04 mM) of the oxidation of cyclohexane (0.12 M) by H_2O_2 (0.42 M) in $\text{CH}_3\text{-CN-CH}_2\text{Cl}_2$ (1:1 v/v) in the presence of LMnCl

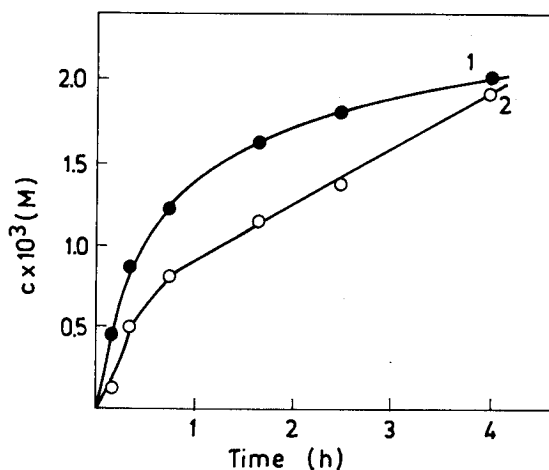


Fig. 2. Kinetics of cyclohexane (0.61 M) oxygenation by H_2O_2 (0.42 M) in CH_3CN at 40°C catalyzed by $\text{Pd}(\text{OCOCF}_3)_2$ (1.0 mM).
 1 - cyclohexyl hydroperoxide,
 2 - sum of cyclohexanol and cyclohexanone

(L : tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrinate) (1 mM) and of imidazole (24 mM) at room temperature (1 day). A similar reaction has been described previously in Ref. [14], but the authors present no data about peroxide production there.

We have also found that the Fenton reactant oxidizes cyclohexane at room temperature predominantly to alkyl hydroperoxide. After intensive stirring of 5 ml solution of cyclohexane (0.3 M), H_2O_2 (0.21 M) and H_2SO_4 (50 mM) in $\text{CH}_3\text{-CN-H}_2\text{O}$ (4 : 1 v/v, total volume 5 ml) with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 mmol, the salt is partly insoluble) for 0.5 h, a mixture of cyclohexyl hydroperoxide (0.26 mM), and cyclohexanol and cyclohexanone (total 0.08 mM) is produced. It should be noted that recently the formation of cyclohexyl hydroperoxide has been detected in oxidation by the Gif-type systems [15].

Thus the results suggest that some reactions of alkane oxidation by H_2O_2 in the presence of transition metal compounds yield high concentrations of alkyl hydroperoxides. Hydroxyl radicals (or other radical-like species) produced from H_2O_2 , abstract a hydrogen atom from alkane RH to form the radical R \cdot then rapidly reacting with O_2 [16-18]. As is seen from Table 1,

Table 1
Selectivity in oxidation of hydrocarbons^a

System	Oxidation	
	n-hexane C(1):C(2):C(3)	3-methylhexane 1°:2°:3°
$H_2O_2 - h\nu$ in CH_3CN	1:10:7	1:6:30 ^b
$H_2O_2 - h\nu$ in CH_3COOH		1:6:26
$H_2O_2 - VO_3^-$ - pyrazine- -2-carboxylic acid in CH_3CN	1:8:7	1:14:64
$H_2O_2 - VO_3^-$ in CH_3COOH		1:8:40
$H_2O_2 - Pd(OCOCF_3)_2$ in CH_3CN	1:3:5	1:7:22

^a Relative reactivities of hydrogen atoms at carbons 1, 2 and 3 of the chain of n-hexane and at primary, secondary and tertiary carbons 1°, 2° and 3° of 3-methylhexane are calculated taking into account the number of hydrogen atoms at each carbon.

^b The selectivity 1°:2°:3°=1:4:12 was found for this reaction in [9].

selectivities of some of the above catalyzed reactions are similar to those found in photochemical reactions with H_2O_2 where hydroxyl radicals are believed to take part.

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