

Composition and Stability of Peroxide Products of Liquid-Phase Cyclohexanol Oxidation¹

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Abstract—The kinetics of accumulation of peroxide compounds during noncatalytic cyclohexanol oxidation at 130°C is studied. The oxidation of cyclohexanol at the CH bond in the 1-position yields hydrogen peroxide and 1-hydroxycyclohexyl hydroperoxide along with peroxides resulting from the oxidation of the CH bonds of the alcohol in the 2-, 3-, and 4-positions, namely, *cis*- and *trans*-2-, -3-, and -4-hydroxycyclohexyl hydroperoxides. Product accumulation curves and the variation of the proportions of *cis*- and *trans*-2-, -3-, and -4-hydroxycyclohexyl hydroperoxides as a function of cyclohexanol conversion indicate that these hydroperoxides have different stabilities during oxidation. The highest stability is inherent in *cis*-2-, *trans*-2-, and *cis*-3-hydroxycyclohexyl hydroperoxides, while *cis*-4-, *trans*-4-, and *trans*-3-hydroxycyclohexyl hydroperoxides are characterized by the lowest stability. This fact is explained by the stabilization of the first three isomers by an intramolecular hydrogen bond, which prevents their decomposition involving substrate molecules.

INTRODUCTION

Secondary alcohols along with ketones result from the liquid-phase oxidation of aliphatic and alicyclic hydrocarbons at the secondary hydroperoxide decomposition stage [1–3]. Their further conversion is usually believed to be due to free-radical chain oxidation at the activated α -CH bond resulting in 1-hydroxyhydroperoxide or ketone and hydrogen peroxide [2–4]. The possibility of oxidation of secondary alcohols at more remote CH bonds is usually ignored, and the properties of isomeric hydroxyhydroperoxides formed in these processes are not studied. This is due to the facts that hydroxyhydroperoxides with a β - or a more remote hydroxyl group form at a lower rate than their counterparts with an α -hydroxyl [4, 5] and that there are no reliable synthetic methods for these peroxides [6, 7]. The purpose of this work is to study the formation and conversion of hydrogen peroxide and isomeric hydroxyhydroperoxides using cyclohexanol oxidation as an example.

EXPERIMENTAL

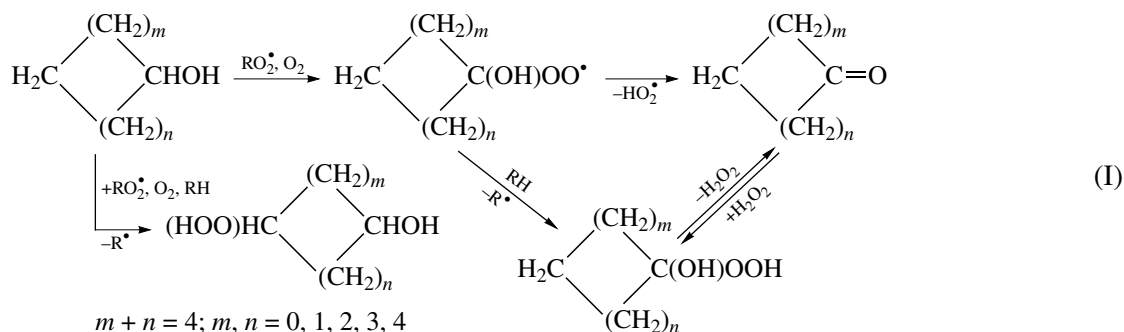
Cyclohexanol (analytical grade) was purified to remove cyclohexanone and ethers using a published procedure [4, 5]. According to GLC data, the cyclohexanol content of the purified substance was at least $99.5 \pm 0.1\%$.

Cyclohexanol was oxidized with dioxygen in the absence of a solvent in a glass bubbler at 130°C.

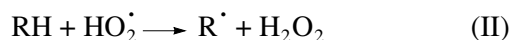
Hydrogen peroxide and organic hydroperoxides were determined separately by iodometric titration using catalase [8]. *Cis*- and *trans*-2-, -3-, and -4-hydroxycyclohexyl hydroperoxides were determined by GLC after the corresponding diols were converted into diacetates by reduction followed by acetylation [4, 5].

RESULTS AND DISCUSSION

In the absence of initiating agents, cyclohexanol is oxidized with dioxygen by a degenerate-branching chain mechanism [2], yielding hydroperoxides with different structures:



¹ Based on a report at the XI International Conference on the Chemistry of Organic and Organoelement Peroxides (Moscow, June 24–26, 2003)



Under these conditions, the process rate can be expressed as follows [9]:

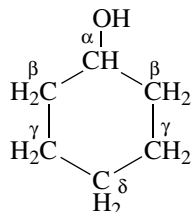
$$w_{\text{rc}} = k_{\text{pr}}^{\text{br}} (k_t)^{-0.5} [\text{R}_2\text{CHOH}] (w_{\text{in}})^{0.5},$$

where $k_{\text{pr}}^{\text{br}}$ and k_t are the apparent rate constants of chain propagation and termination, respectively; $[\text{R}_2\text{CHOH}]$ is the substrate concentration; and w_{in} is the overall initiation rate.

It is shown [5] that, at 130°C, the propagation of the oxidation chain is mainly due to the HO_2^\cdot radical; that is, type (II) reactions are main chain propagation reactions. Therefore, we can accept that $k_{\text{pr}}^{\text{br}}$ is equal to the sum of partial rate constants for the interaction between hydroperoxyl radicals (HO_2^\cdot) and different types of CH bond in cyclohexanol, taking into account the numbers (n_i) of these bonds:

$$k_{\text{pr}}^{\text{br}} = \sum n_i k^{\text{H}}.$$

An electron-withdrawing hydroxyl group activates the α -CH bonds, deactivates the β - and γ -CH bonds, and has no appreciable effect on the δ -CH bonds of cyclohexanol in the reaction with either the *tert*-butylperoxy or the HO_2^\cdot radical (Table 1). This results in a low yield of hydroxyhydroperoxides with functional groups in β - or more widely separated positions.



To solve the problem stated, we studied the kinetics of accumulation of peroxides resulting from cyclohex-

anol oxidation: hydrogen peroxide; 1-hydroxycyclohexyl hydroperoxide; and *cis*- and *trans*-2-, -3-, and -4-hydroxycyclohexyl hydroperoxides (Fig. 1).

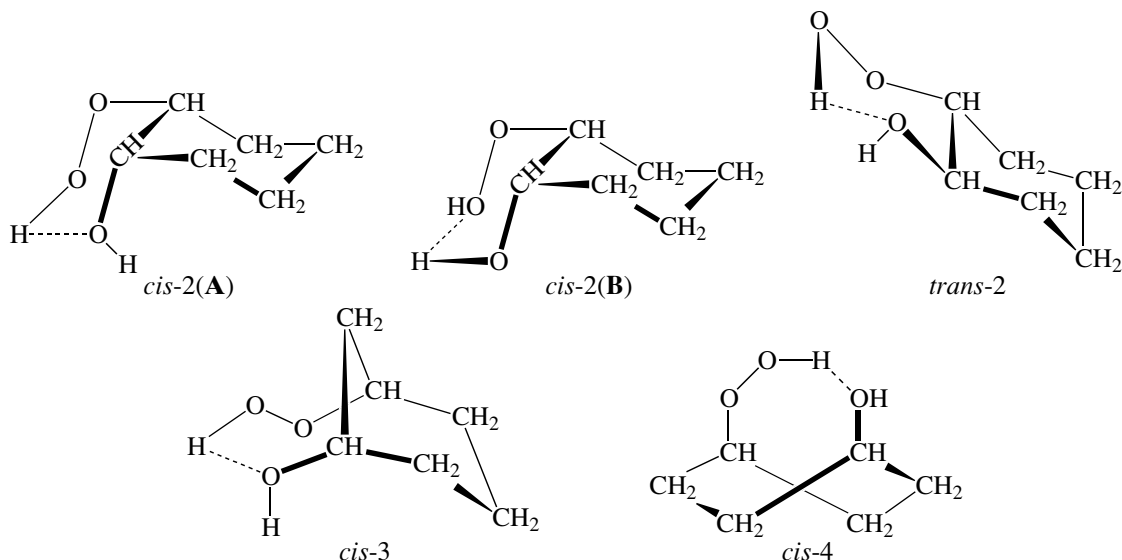
Hydrogen peroxide begins to accumulate earlier than 1-hydroxycyclohexyl hydroperoxide (Fig. 1). The ratio of the former to the latter decreases due to the reversible nucleophilic addition of H_2O_2 to ketone [4].

Cis- and *trans*-2-, -3-, and -4-hydroxycyclohexyl hydroperoxides result from cyclohexanol oxidation at the β -, γ -, and δ -CH bonds, and the ratio between the resulting geometric isomers differs from unity (Fig. 2, Table 2).

For 2- and 4-hydroxycyclohexyl hydroperoxides, the predominant formation of *trans* isomers can be explained by their thermodynamic stability. It is well known that the heats of formation of *trans*-1,2- and *trans*-1,4-dimethylcyclohexanes are lower by 8 kJ/mol than those of the corresponding *cis* isomers [10]. This explanation is not valid for 3-hydroxycyclohexyl hydroperoxide because *cis*-1,3-dimethylcyclohexane is more stable than its *trans* counterpart [10].

As alcohol conversion increases, the proportion of *cis*-2-, *trans*-2-, and *cis*-3-hydroxycyclohexyl hydroperoxides in the total amount of hydroxyhydroperoxides grows and the proportion of *cis*-4-, *trans*-4-, and *trans*-3-hydroxycyclohexyl hydroperoxides decreases (Fig. 2). This is in agreement with kinetic data presented in Fig. 1 and is evidently due to the different stabilities of the hydroxycyclohexyl hydroperoxide (HCHHP) isomers. As a consequence, the *trans/cis* ratio decreases (Fig. 2, Table 2).

It can be seen from the data presented in Table 2 and Fig. 2 that the stability of hydroxycyclohexyl hydroperoxides decreases in the order *cis*-2 \geq *trans*-2 > *cis*-3 > *trans*-3 \geq *cis*-4 > *trans*-4. This order agrees well with the ability of hydroxycyclohexyl hydroperoxides to form intramolecular hydrogen bonds.



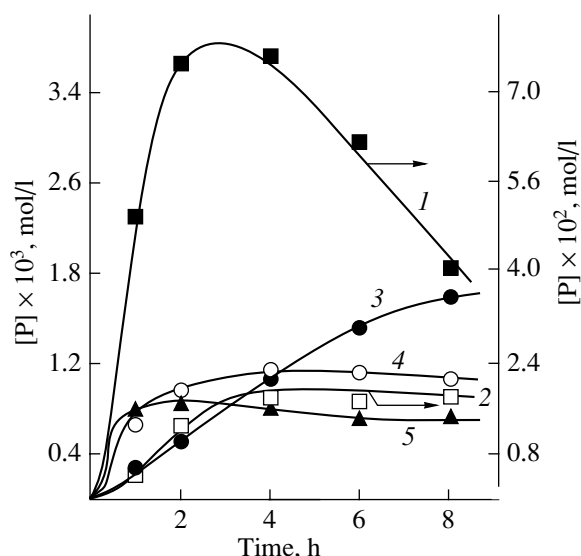


Fig. 1. Peroxide (P) accumulation kinetics for cyclohexanol oxidation at 130°C: (1) hydrogen peroxide, (2) 1-HCHHP, (3) *cis*- and *trans*-2-HCHHP, (4) *cis*- and *trans*-3-HCHHP, and (5) *cis*- and *trans*-4-HCHHP.

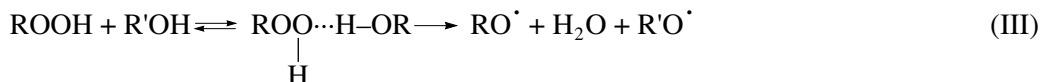
1-Hydroxycyclohexyl hydroperoxide is known to form a strong intramolecular hydrogen bond [11]. Since the formation of such a bond in a six- and, especially, seven-membered reaction cycle is energetically more favorable [12], the assumption that there is a

strong hydrogen bond in the *cis*-2(A), *cis*-2(B), *trans*-2, and *cis*-3 compounds seems to be well grounded.

Hydroxyhydroperoxides with different structures can theoretically form two types of intramolecular hydrogen bond, involving the hydrogen atom of either the hydroperoxy or the hydroxyl group [2, 11]. Due to the more acidic character of the hydrogen atom of the OO-H bond as compared to the hydrogen atom of the O-H bond, the *cis*-2(A) structure is more likely than the *cis*-2(B) structure. At the same time, although the *trans*-2 structure must be more stable than the *cis*-2(A) structure on account of the totality of steric factors (as in the case of *cis*- and *trans*-decalins [10]), the mutual influence of the polar groups of hydroxycyclohexyl hydroperoxides and the solvation effects of the substrate can diminish the difference in stability between these compounds.

The formation of an intramolecular hydrogen bond in *cis*-4-hydroxycyclohexyl hydroperoxide is less probable than the formation of the same bond in 2- and 3-hydroxyhydroperoxides because it would lead to a more strained configuration [13]. For the *trans*-3 and *trans*-4 isomers, the formation of an intramolecular hydrogen bond resulting in a six-membered ring is impossible and the formation of larger rings is problematic.

A strong intramolecular hydrogen bond in hydroxycyclohexyl hydroperoxides must prevent the formation of linear hydroperoxide-substrate associates:



These associates decompose at a higher rate than free hydroperoxides [2, 14].

An oxygen-containing functional group (in particular, a hydroxyl group) introduced into a hydroperoxide molecule is known [2, 3, 6, 7] to decrease the thermal stability of this molecule, including through a polarizing (*-I*) effect on the O-O bond. It was, therefore,

expected that hydroxyhydroperoxides with neighboring functional groups would be less stable than hydroxyhydroperoxides with more widely spaced ones. In fact, our results indicate that 2-hydroxyhydroperoxides are more stable than 3- or 4-hydroxyhydroperoxides. Evidently, the rates of intramolecular and intermolecular associative interactions are most significant in this

Table 1. Relative reactivity of the CH bonds of cyclohexanol in the reactions with the HO_2^\bullet and *tert*-butylperoxy radicals

Type of CH bond	Relative reactivity of CH bonds	
	HO_2^\bullet [4]	$(\text{CH}_3)_3\text{COO}^\bullet$ [5]
α	215	88.6
β	0.22	0.064
γ	0.3	0.082
δ	1.00	1.00

Table 2. Ratio of *cis* isomers to *trans* isomers ($C_{\text{trans}}/C_{\text{cis}}$) for 2-, 3-, and 4-hydroxycyclohexyl hydroperoxides (HCHHPs) in cyclohexanol oxidation at 130°C

Hydroperoxide	Cyclohexanol conversion, %			
	5	10	15	20
2-HCHHP	1.87	1.90	1.46	1.20
3-HCHHP	2.0	1.60	1.20	1.00
4-HCHHP	1.60	1.45	1.30	1.00

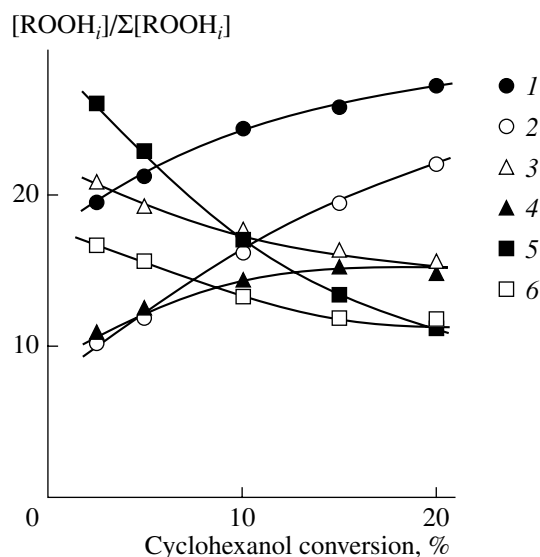


Fig. 2. Fraction of *cis*- and *trans*-2-, -3-, and -4-hydroxycyclohexyl hydroperoxides (ROOH_i) in their total amount (ΣROOH_i) during cyclohexanol oxidation at 130°C : (1) *cis*-2-HCHHP, (2) *trans*-2-HCHHP, (3) *trans*-3-HCHHP, (4) *cis*-3-HCHHP, (5) *trans*-4-HCHHP, and (6) *cis*-4-HCHHP.

case. It is these interactions that determine the stability of hydroxyhydroperoxide isomers.

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