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Liquid-Phase Oxidation of Alkyl-Substituted Cyclohexylbenzenes

G. N. Koshel', E. A. Kurganova, E. V. Smirnova, S. G. Koshel',
V. V. Plakhtinskii, and M. S. Belysheva

Yaroslavl State Technical University, Moskovskii pr. 88, Yaroslavl, 150023 Russia
e-mail: koshelgn@ystu.ru

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Abstract—The reactivity of alkyl-substituted cyclohexylbenzenes in liquid-phase oxidation was estimated by the $k_2/\sqrt{k_6}$ value which considerably decreased as the number of methyl groups in the substrate molecule increased. The observed difference in the reactivity of the title compounds was attributed to the degree of coplanarity of intermediate radical species.

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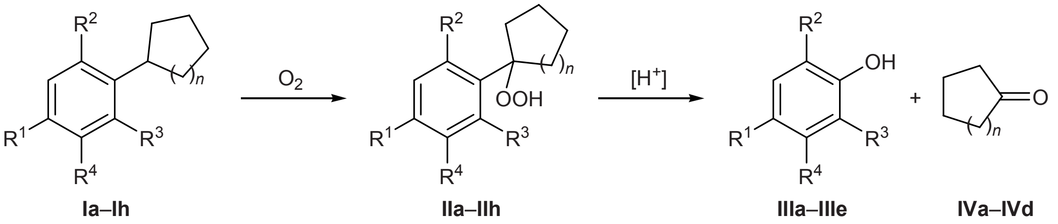
Hydroperoxide oxidation of cycloalkylbenzenes **Ia**–**Ih** (Scheme 1) follows an analogous pattern to the oxidation of cumene (**Va**) and cymene (**Vb**) (Scheme 2) [1]; these reaction underlie procedures for the joint synthesis of alkylphenols **IIIa**–**IIIe** and cycloalkanones **IVa**–**IVd**. The reactivity of cycloalkylbenzenes **Ia**–**Ih** in the oxidation process attracts certain interest from both theoretical and practical viewpoints.

We previously found [2] that the rate of oxidation and the conversion of cycloalkylbenzenes **Ia**, **Ib**, **Ig**, and **Ih** containing 5 to 12 carbon atoms in the cycloalkyl group strongly depend on the size of the latter. The observed relation was interpreted in terms of specific structure of substrates **Ia**, **Ib**, **Ig**, and **Ih**, which is contributed by the following factors: (1) degree of σ,π-conjugation between the tertiary C–H bond in the carbocycle and π-electron system of the benzene ring; (2) coplanarity of intermediate radical species; and (3) steric hindrances to attack by oxygen (radical) on the C–H bond at the tertiary carbon atom. On the other hand, the reactivity of alkyl-substituted cyclohexylbenzenes **Ic**–**If** (that are potential starting materials for the joint preparation of alkylphenols and cyclohexanone) in liquid-phase oxidation was not studied.

The rates of oxidation of hydrocarbons **Ib**, **Ic**, **Ie**, and **If** (Fig. 1, plot *1*) and accumulation of the corresponding hydroperoxide (Fig. 1, plot *2*) were different despite similar conditions and the same reaction direction (in all cases, the oxidation involved the tertiary C–H bond). Increase in the number of methyl groups in the benzene ring of compounds **Ib**, **Ic**, **Ie**, and **If** was accompanied by decrease in the reaction rate. However, the rate of oxidation of cumene (**Va**) and cymene (**Vb**) that are structural analogs of cyclohexylbenzene (**Ib**) and *p*-cyclohexyltoluene (**Ic**) was considerably higher. *p*-Cyclohexylcumene (**Id**) was characterized by the highest rates of oxidation and accumulation of the corresponding hydroperoxide.

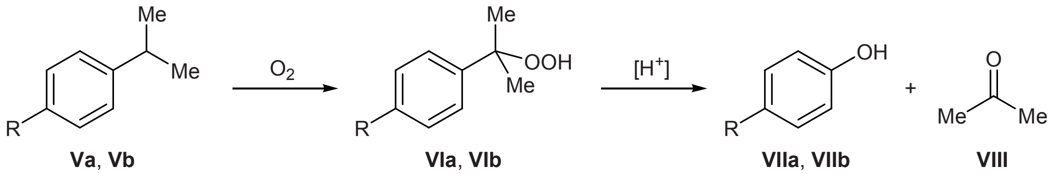
The reactivity of compounds **Ib**–**If** in liquid-phase oxidation was estimated by the ratio of the rate constants for chain propagation and chain termination $k_2/\sqrt{k_6}$ (so-called oxidizability parameter). To exclude

Scheme 1.



I, **II**, $R^1 = R^2 = R^3 = R^4 = H$, $n = 1$ (**a**), 2 (**b**), 4 (**g**), 8 (**h**); $n = 2$, $R^2 = R^3 = R^4 = H$, $R^1 = Me$ (**c**), Me_2CH (**d**), $R^1 = R^3 = H$, $R^2 = R^4 = Me$ (**e**), $R^1 = R^2 = R^3 = Me$, $R^4 = H$ (**f**); **III**, $R^1 = R^2 = R^3 = R^4 = H$ (**a**), $R^2 = R^3 = R^4 = H$, $R^1 = Me$ (**b**), Me_2CH (**c**), $R^1 = R^3 = H$, $R^2 = R^4 = Me$ (**d**), $R^1 = R^2 = R^3 = Me$, $R^4 = H$ (**e**); **IV**, $n = 1$ (**a**), 2 (**b**), 4 (**c**), 8 (**d**).

Scheme 2.



R = H (**a**), Me (**b**).

possible errors, the kinetics of AIBN-initiated oxidation of hydrocarbons **Ib**–**If**, **Va**, and **Vb** were studied using the same setup. The kinetic parameters ($k_2/\sqrt{k_6}$ ratios, $E_2 - 1/2E_6$ values, and logarithms of the preexponential factors log$A$ in the Arrhenius equation) for the examined transformations of cyclohexylbenzenes **Ib**–**If** are collected in Table 1. It is seen from Fig. 2 that the character of variation of the rate of initiated oxidation (W_{io}) and $k_2/\sqrt{k_6}$ is analogous to the character of variation of the corresponding parameters in the "gross" oxidation (Fig. 1).

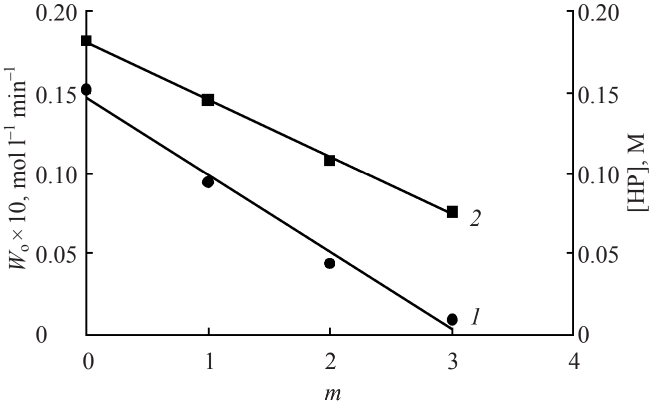


Fig. 1. Plots of (*1*) the rate of oxidation of cyclohexylbenzenes **Ib**, **Ic**, **Ie**, and **If** and (*2*) accumulation of the corresponding hydroperoxides ([HP]) at high substrate conversions versus the number of methyl groups in their molecules (*m*); temperature 120°C, reaction time 2 h.

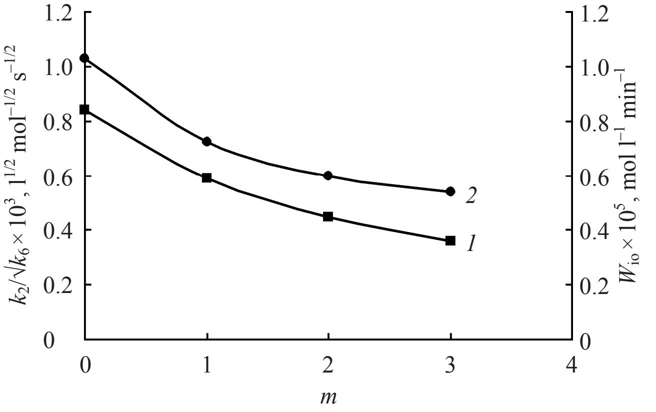


Fig. 2. Plots of (*1*) $k_2/\sqrt{k_6}$ and (*2*) rates of AIBN-initiated oxidation of cyclohexylbenzenes **Ib**, **Ic**, **Ie**, and **If** versus the number of methyl groups in their molecules (*m*); temperature 70°C, AIBN concentration 0.063 M, reaction time 10 min.

The observed differences in the reactivity in the series of cyclohexylbenzenes **Ib**–**If**, as well as between hydrocarbons **Ib**–**If** and compounds **Va** and **Vb**, may be attributed to different structures of the substrates and radical species derived therefrom. It is known that the formation of radical from cumene molecule is accompanied by transformation of the tertiary carbon atom from sp^3- to sp^2-hybrid state, and the bond angles at that atom change to 120°. As a result, the α- and β-carbon atoms and the benzene ring appear in one plane, and the radical thus formed is stabilized by conjugation between the unpaired p electron and π electrons in the benzene ring [3, 4].

The three C–C bonds at the α-carbon atom in molecule **Va** can readily be arranged in the benzene ring plane, so that isopropyl radical is a coplanar system. Unlike cumene (**Va**), carbon atoms in the cyclohexyl fragment of compound **Ib** are located in different planes, and no coplanar system is formed in the radicals derived therefrom (only a part of carbon atoms, namely C^α, C^β, and C_{arom}, can be arranged in one plane; flattening of the cyclohexane ring should be accompanied by appearance of considerable steric strains). Presumably, just that factor is responsible for the lower reactivity of radicals derived from cyclohexylbenzene (**Ib**) and hence for the lower reactivity of **Ib** as compared to cumene (**Va**). Reactions of phenylcyclohexyl radicals with hydrocarbon molecules having nonplanar structure involve steric hindrances, i.e., mutual orientation of the reactants must be more rigorous than in reactions with planar radicals. The effect of coplanarity in liquid-phase oxidation of alkylaromatic hydrocarbons (such as isopropylxylenes and isopropylnaphthalenes) was demonstrated in [5].

The presence of alkyl groups in the benzene ring of compounds **Ic**–**If** is likely to reinforce noncoplanarity of their molecules and radicals, thus reducing their reactivity as compared to cyclohexylbenzene (**Ib**) and cumene (**Va**). It was found that the calculated (AM1) ionization potentials (*I*) of the initial molecular sys-

Table 1. Ratios of rate constants for chain propagation and chain termination and activation parameters of liquid-phase oxidation of cycloalkylbenzenes **Ib**–**If** and alkylbenzenes **Va** and **Vb**

Compound no.	Temperature, °C				$E_2 - 1/2 E_6$, kJ/mol	$\log A$	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta G^{\neq}$, kJ/mol
	60	65	70	75				
	$k_2/\sqrt{k_6} \times 10^3$, l$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$							
Ib	0.58	0.75	1.03	1.20	47.70	4.25	436.42	–87.00
Ic	0.36	0.53	0.71	0.97	63.05	6.44	486.51	–104.22
Id	4.51	5.28	6.10	7.01	28.16	2.07	363.34	–98.31
Ie	0.35	0.43	0.62	0.77	52.62	4.78	454.94	–105.51
If	0.34	0.44	0.54	0.66	41.13	2.99	425.87	–107.70
Va	3.79	4.50	5.07	5.71	35.36	3.10	385.98	–99.88
Vb	2.39	3.20	3.85	4.66	42.01	3.82	408.08	–101.10

tems (Table 2) are related to $\log(k_2/\sqrt{k_6})$ values through Eq. (1):

$$\log(k_2/\sqrt{k_6}) = (-4.26 \pm 0.54) + (0.565 \pm 0.061)I; \quad (1)$$
$$r = 0.989,\ s = 0.0223\ (7.9\%).$$

The greater the ionization potential I, the higher the reactivity. An analogous relation was found in [6] for the oxidation of phenyl- and vinylphenylmethanes.

We performed AM1 semiempirical calculations of the localization energies $\Delta\Delta H$ for the stage of formation of radicals from cyclohexylbenzenes **Ib**, **Ic**, **Ie**, and **If**; the $\Delta\Delta H$ values were calculated as the difference between the energies of formation ΔH_f of the radicals and parent molecular systems (Table 2). The reactivity parameters $\log(k_2/\sqrt{k_6})$ of hydrocarbons **Ib**, **Ic**, **Ie**, and **If** showed a good correlation with the calculated $\Delta\Delta H$ values [Eq. (2)] and Gibbs energies $\Delta G^{\neq}$ (Table 1; Eq. (3)].

$$\log(k_2/\sqrt{k_6}) = (1.64 \pm 0.16) + (0.0179 \pm 0.0024)\Delta\Delta H^{\neq}; \quad (2)$$
$$r = 0.982,\ s = 0.0276\ (9.8\%);$$

$$\log(k_2/\sqrt{k_6}) = (1.11 \pm 0.16) + (0.0126 \pm 0.0015)\Delta G^{\neq}; \quad (3)$$
$$r = 0.985,\ s = 0.0258\ (9.2\%).$$

Thus the linear free energy relationship principle is obeyed. The examined reaction series is isokinetic: a linear relation exists between the enthalpy of activation $\Delta H^{\neq}$ and entropy of activation $\Delta S^{\neq}$. Our results provide an additional support to the fact that increase in the number of methyl groups in the benzene ring in the series of hydrocarbons **Ib**, **Ic**, **Ie**, and **If** is accompanied by increase if the entropy contribution, which affects the rates of the chain propagation and chain termination steps.

The rate of oxidation of compound **Id** considerably exceeds those found for the other examined hydrocarbons. The $k_2/\sqrt{k_6}$ value for **Id** is approximately equal to the sum of the $k_2/\sqrt{k_6}$ values for **Va** and **Ib**. This means that hydrocarbon **Id** can be oxidized at the C–H bonds in both isopropyl and cyclohexyl fragments simultaneously.

EXPERIMENTAL

Cyclohexylbenzene (**Ib**), *p*-cyclohexyltoluene (**Ic**), *p*-cyclohexylcumene (**Id**), 2-cyclohexyl-1,4-dimethylbenzene (**Ie**), and cyclohexylmesitylene (**If**) were synthesized by alkylation of toluene, isopropylbenzene, *p*-xylene, and mesitylene, respectively, with cyclohexanol in the presence of sulfuric acid [7]. The purity of hydrocarbons **Ib**–**If** was checked by GLC. The oxidation of compounds **Ib**–**If** was performed on a kinetic setup ensuring variation of the oxygen absorption rate from 7×10^{-6} to 4×10^{-5} mol l^{-1} s^{-1} with a conversion of 0.05 to 0.5% [8]. The experimental error did not exceed 5%. The reactions were carried out at 65 to 80°C to avoid degenerate chain branching (initiation

Table 2. Calculated (AM1) ionization potentials I, localization energies $\Delta\Delta H$, and energies of formation of hydrocarbons **Ib**, **Ic**, **Ie**, and **If** [ΔH_f(RH)] and radicals derived therefrom [$\Delta H_f(R^{\cdot})$]

Compound no.	I, eV	ΔH_f(RH), kJ/mol	$\Delta H_f(R^{\cdot})$, kJ/mol	$\Delta\Delta H$, kJ/mol
Ib	9.318	–37.221	38.365	75.586
Ic	9.055	–62.281	5.469	67.750
Ie	8.941	–61.628	2.789	64.427
If	8.821	–90.926	–31.116	59.810

occurred only as a result of decomposition of the initiator); azobis(isobutyronitrile) was used as initiator. The $k_2/\sqrt{k_6}$ values were calculated by Eq. (4) [9]:

$$W = k_2/\sqrt{k_6}\,[\mathrm{RH}]\,\sqrt{W_\mathrm{i}}. \qquad (4)$$

Here, W is the rate of oxidation (mol l^{-1} s^{-1}), W_i is the rate of initiation (mol l^{-1} s^{-1}), and [RH] is the substrate concentration. The rates of initiation were calculated according to formula (5):

$$W_\mathrm{i} = k_\mathrm{i}[\mathrm{AIBN}], \qquad (5)$$

where k_i is the initiation rate constant (s^{-1}).

The oxidation of hydrocarbons **Ib**–**If** with higher conversions was performed using a kinetic setup described in [10]. The concentration of hydroperoxides was determined by iodometric titration.

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