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## CONFORMATIONAL ASPECTS OF THE REACTION PRODUCTS OF OXIDATIVE HYDROXYHALOGENATION OF ALKYL CYCLOHEXENES

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**Abstract:** The kinetic patterns of the reaction oxidative hydroxyhalogenated alkylcyclohexenes involving hydrogen peroxide and hydrogen halide acids in the liquid phase are considered. The reaction is reversible and has a second order in the forward and reverse directions. The speed of both stages of the process is correlated with the conformational effects of the substituents. The optimal reaction conditions were established and the isomeric and conformational composition of the obtained products was determined. The results of the kinetic studies and the study of stereochemistry and conformational equilibrium of the obtained adducts suggest that this reaction proceeds according to the electrophilic mechanism with the formation of trans-addition products. It was found that in the equilibrium mixture of reaction adducts, there are mainly conformers with an axial arrangement of a halogen atom and a hydroxyl group with an equatorial position of the substituents. Based on kinetic and spectral data, a probable reaction mechanism and conformer structure are proposed.

**Keywords:** conformers, hydroxyhalogenation, products, alkylcyclohexenes, hydrogen peroxide, hydrohalic acids.

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### Introduction

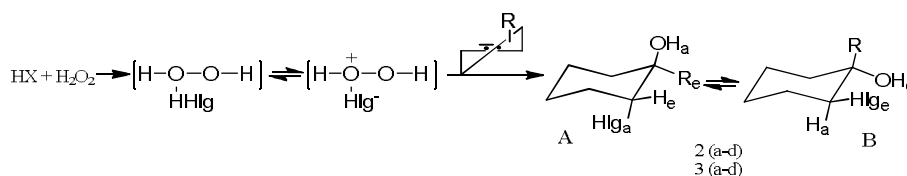
Cyclohexene and its derivatives exist mainly in the conformation of the half-chair and the substituents located close to the plane of the double bond in the C<sub>3</sub> and C<sub>6</sub> orientations are sterically extremely disadvantageous and especially, if they are present at the olefin carbon atom [1,2]. For 2,3-disubstituted cyclohexenes with chlorine or bromine atoms and some oxygen containing functional groups (OH, OCH<sub>3</sub>, OOCCH<sub>3</sub>, etc.), the pseudo-axial orientation is preferable, and this, according to the authors [3], is due to both spatial factors and hyperconjugation.

Information about the conformation of the products of oxidative hydroxyhalogenation of 1-, 3-alkyl, 1-acyl- and 4-alkenylcyclohexenes is practically absent in the literature.

This paper presents the results of studies on the synthesis and study of the

configuration of hydroxychloro(bromo)ide 1,3-methyl-, 1-acetyl- and 4-ethenyl cyclohexenes in *in situ* mode of addition of electrophilic reagents formed in the HX-H<sub>2</sub>O<sub>2</sub>-cycloolefin system. The task of these studies also included study of the influence of the nature of various substitutions located close to the plane or near the double bond, in order to interpret the stepwise addition of electrophilic intermediates under the combined conditions of the reagents.

Hydroxychloro(bromo)ide acid of these cyclo-olefins are obtained by the previously developed method [4,5]. In this case, the synthesis process is carried out sequentially in several stages, with the formation of hydroxychloro-2 (a-d) and hydroxybromide-3 (a-d) according to the scheme:



Where, Hlg=Cl (2); Br (3); R=1-CH<sub>3</sub> (a), 3-CH<sub>3</sub> (b), 1-CH<sub>3</sub>OC- (c), 4-CH=CH<sub>2</sub> (d)

### Scheme 1

### Experimental

Experiments have shown that the selectivity of the process and the yield of the target product depend on the nature of the alkyl radical, temperature, the concentration of hydrohalic acids and the intensity of mixing of the reaction mass. In the case of using 11-15% HCl solutions and 8-10% HBr, the highest yields of active oxyhalide intermediate and reaction products are achieved. When the temperature rises to 20-50°C, the yield of hydroxyhalides increases and reaches 72-80.5% for hydroxychlorides and 64-75% for hydroxybromides. It should be noted that carrying out the reaction at a temperature above 50°C and increasing the concentration of Hlg is impractical because the decomposition rate of hydrogen peroxide and the active electrophilic intermediate increases,

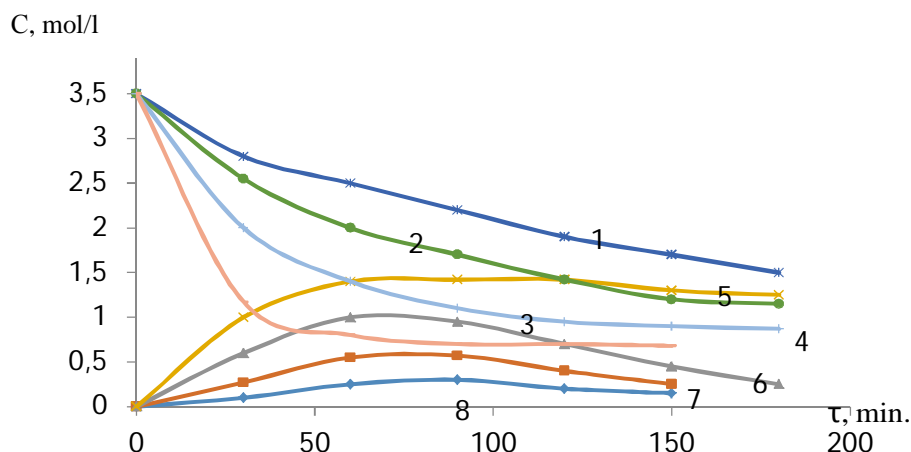
and with the formation of molecular oxygen chlorine (or bromine) in the reaction products, along with hydroxyhalides, it accumulates up to 15-25% dichloro(bromo)derivatives of cycloolefins.

The reaction of the hydroxyhalogenation of substrates in *in situ* mode proceeds through the steps of generating the intermediate [Hlg<sup>+</sup>OH<sup>-</sup>] in the aqueous phase, with the subsequent attack of the double bond of the substrates in the organic phase. An increase in the stirring rate (200-400 rev/min) of the reaction mass removes all diffusion factors. As a result, the transition of the active oxyhalide intermediate from the aqueous phase to the organic phase is facilitated, which have positive effects on the process and the yield of reaction products.

### Results and discussion

The study of the influence of the nature of the alkyl group on the yield of the target product in the optimal conditions found showed that, with changes in the size and nature of the alkyl radicals near the multiple bond plane, the hydroxyhalide yields are: 80.5% for 2-Cl-1-CH<sub>3</sub>- and 72.3% for 2-Br-1-CH<sub>3</sub>-cyclohexenols, 72.6% for 1-(1-Cl-2-OH-) and 69.5% for 1-(1-Br-2-OH-cyclohexyl)ethanones, 74.3% for 2-Cl-3-CH<sub>3</sub>

and 68.3% for 2-Br-3-CH<sub>3</sub>-cyclohexanols, 67.4% for 2-Cl-4-ethenyl- and 64.8% for 2-Br-4-ethenylcyclohexan-1-ols, respectively. From the above data it follows that in the case of more bulky (1-acyl- and 4-ethenyl-) radicals, the yield of the target product is 7-10% lower. This is probably due to the spatial difficulties created by the shielding of the double bond by these radicals.

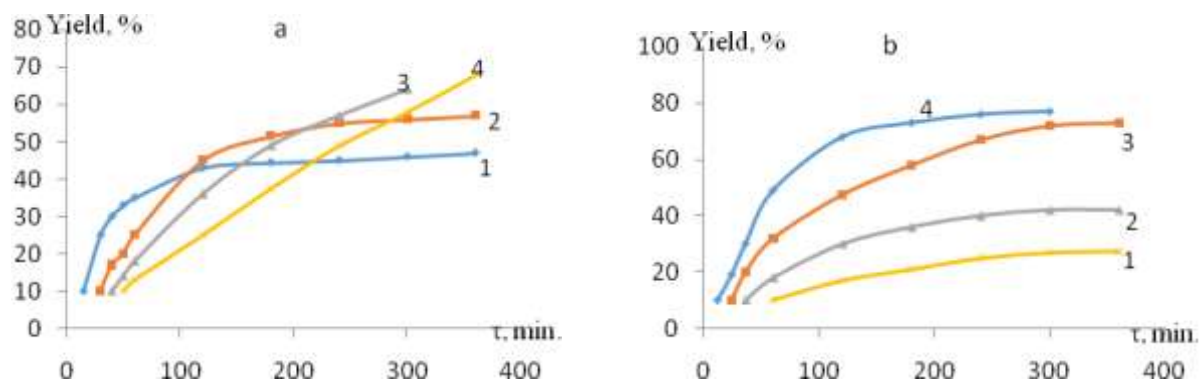


**Fig. 1.** Kinetic curves of consumption of H<sub>2</sub>O<sub>2</sub> (1-4) and accumulation of HOCl (5-8) at various temperatures, 1 and 8- 20°C, 2 and 7- 30°C, 3 and 6- 40°C, 4 and 5- 50°C. (molar relative: 4-ECH:HCl:H<sub>2</sub>O<sub>2</sub>=1:1.5:1.5)

Investigation of the effect of temperature and molar amount of hydrogen peroxide on the rate of the oxidative hydroxyhalogenation reaction  $C_6$  cycloolefins shows that with an increase in temperature from 20°C to 50°C and a molar amount of  $H_2O_2$  from 1.0 to 2.5 mole, the rate of  $H_2O_2$  consumption increases from  $4.45 \cdot 10^{-4}$  to  $29.12 \cdot 10^{-4} \text{ mole} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$  (fig.1 and tab.1).

With a decrease in the concentration of HCl in the range 36–10% and HBr acid in the range 35–5%, the rate of reaction of their consumption and the rate of formation of hydroxychloro- (fig.2a) and hydroxybromo-4-vinylcyclohexene (fig.2b) increase from 3.58

to  $18.6 \cdot 10^{-5} \text{ mole} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$  and from 1.52 to  $14.72 \cdot 10^{-5} \text{ mole} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$ , respectively. A decrease in the reaction rate and yield of hydroxyhalides at high concentrations of hydrohalic acids is possibly due to the fact that it contributes to an increase in the yield of molecular halogens and dihalogen derivatives in the reaction medium. With a decrease in the concentration of hydrohalic acids, the mobility of halogen ions increases greatly, which contributes to a shift in the equilibrium to the formation of an electrophilic intermediate and its increase in concentration in the reaction medium, which positively affects the yield and selectivity of the target product.



**Fig. 2.** The effect of the concentration of HHLg acid (a-HCl, b-HBr) on the yield of 4-ethenylcyclohexene hydroxyhalides (for HCl: 1-36%, 2-26%, 3-16%, 4-10% and HBr: 1-35%, 2-25%, 3-5%, 4-8%; (molar ratio: 4-ECH:HHlg: $H_2O_2$ =1:1.5:1.5, T, 30°C)

**Table 1.** The results of the influence of temperature, concentration of HHLg and  $H_2O_2$  on the reaction rate of oxidative hydroxyhalogenation of 4-ethenylcyclohexene (molar ratio: 4-ECH = HHLg).

$C_{4\text{-vCH}}$ , mole/l	HCl,* %	T, °C	HBr, %	$H_2O_2$ , mole/l	$W \cdot 10^{-5}$ *, mole/l/s	$W \cdot 10^{-5}$ mole/l/s
1.0	36	30	35	1.5	3.58	1.52
1.0	26	30	25	1.5	4.52	5.05
1.5	16	30	15	2.0	5.54	4.67
2.0	16	30	8.0	2.2	6.36	5.32
2.5	26	30	5.0	2.2	6.55	4.28
1.0	16	30	5.0	1.5	18.60	9.80
1.0	10	20	8.0	1.5	11.42	12.45
1.0	10	40	8.0	1.5	16.10	13.65
1.0	10	50	8.0	1.5	29.12	14.72

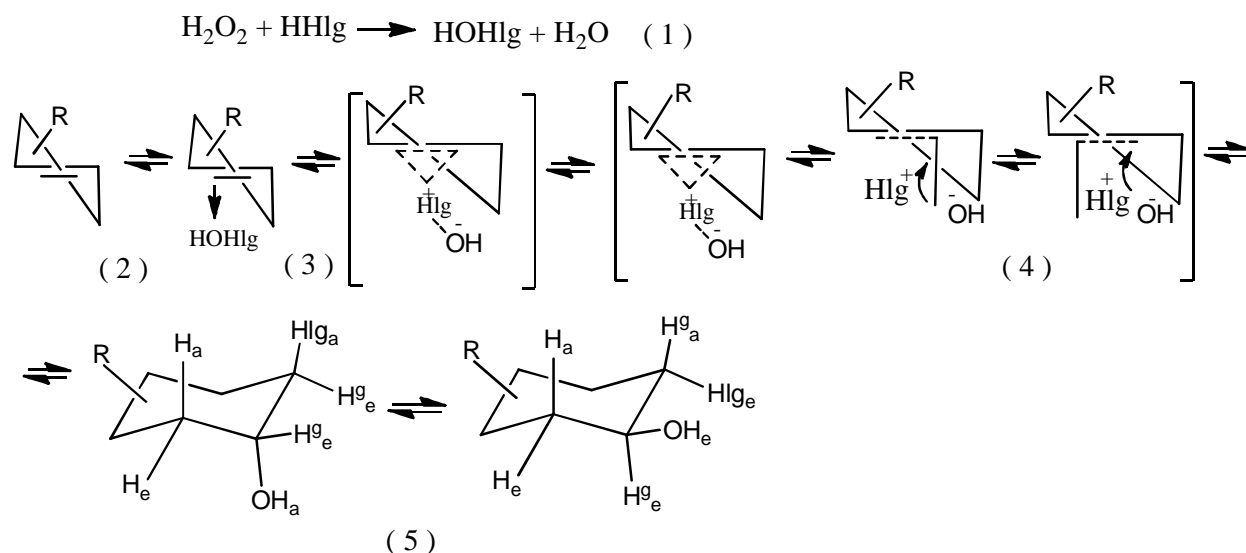
With a further increase in temperature and a molar amount of an oxidizing agent, side

reactions - decomposition of  $H_2O_2$  and electrophilic intermediate HlgOH (Hlg= Cl or

Br) or halogenation of the double bond of the substrate - occur, that negatively affects the selectivity of the reaction.

The reaction studied is described by a second-order kinetic equation. First order in the substrate (cycloolefin) and first order in the

electrophilic and intermediates (HlgOH). The value of activation energy  $E = 43.8$  kJ/mol was calculated. According to the data of [4, 5] and our results, we can present the following probable reaction mechanism for the hydroxyhalogenation of  $C_{12}$  cycloolefins:



**Scheme 2**

The proposed reaction mechanism is explained by a series of kinetic data. The observed induction period on the kinetic curves (fig. 2) of formation and expenditure hydroxhalogen is apparently related to the accumulation by oxidation of the oxidatively generated electrophilic intermediate HlgOH to certain concentrations in the initial stages. From the nature of the curves, it is obvious that after the stage of hydroxyhalogenation of the substrates, an unproductive decomposition of  $H_2O_2$  and HlgOH is observed.

Figure 2 shows that the initial rate of formation of hydroxychloro-alkylcyclohexanes (2a) is greater than the initial rate of formation of hydroxybromo alkylcyclohexanes of the latter (2b). This is due to the fact that in the initial period, oxidatively generated HlgOH form a  $\pi$ -complex (3) with a double bond, alkylcyclohexenes, which then turns into an activated transition state (4) with an internal ion pair. Then this complex regroups into reaction products (5).

It should be noted that a direct determination of the rates of formation and decomposition of intermediate unstable intermediates and compounds was not carried out. Using IR,  $^1H$  and  $^{13}C$  NMR spectroscopy, it was possible to identify the structures of the conformers 2-chloro(bromo)-4-methylcyclohexan-1-ol and 1-[1-chloro(bromo)-2-hydroxycyclohexyl]ethan-1-ones, which determine the direction of addition of HlgOH intermediate intermediates to alkylcyclohexenes and stereochemistry of the final conformers.

The study of the conformational equilibrium of the synthesized hydroxyhalogen derivatives of alkyl- and acetylcyclohexanols was carried out according to the known method [2]. According to the half-width ( $W_{1/2}$ ) of the signal observed and calculated from the data of the constants of the spin-spin interaction of the signal ( $H_g$ ), the position of 2 conformers having a chemical shift of 4.51 ppm for 1e-CH<sub>3</sub>-2a-trans-Cl-, 4.80 ppm

for 1e-CH<sub>3</sub>-2a-trans-Br-cyclohexanols and 3.79 ppm for 1e-acetyl-trans-2a-Cl- and 1e-acetyl-trans-2a-Br-cyclohexanols, 4.4 ppm for 4e-ethenyl-trans-2a-Cl- and 4e-ethenyl-trans-2a-Br-cyclohexanols was established. Based on the half-width ( $W_{1/2}$ ) of the signal ( $H_g$ ) observed and calculated according to the data of the spin-spin coupling constants, the position of 2 conformers having a chemical shift of 4.51 ppm was established.

As a result of the spin-spin interaction of a germinal proton of a relative chlorine (or bromine) atom ( $H_g$  of the second C atom) with the axial and equatorial and vicinal protons at the C<sub>3</sub> atom (based on the values of the spin-spin interaction constants  $J_{aa}$ ,  $J_{ae}$  and  $J_{ee}$  [2, 6-8] conformers) calculated  $W_{1/2}$   $H_g$ , respectively. Using the calculated and observed values of  $W_{1/2}$  according to the well-known formula [2] we determined  $W_{1/2} = P_{ae}(J_{ee}-J_{ae})+(1-P_{aa})(J_{aa}-J_{ae})$ , where  $W_{1/2}$  is the observed half-width of the signal  $H_g$ ;  $P_{aa}$  is the molar fraction of the diaxial conformer in the equilibrium mixture;  $J_{aa}$ ,  $J_{ae}$  and  $J_{ee}$  –CSSC of the germinal equatorial H, with vicinal, equatorial, axial H with the vicinal and axial equatorial protons. The conformational equilibrium constant (K) was calculated using

the well-known formula [6]:  $K = (1-P_{aa})/P_{aa}=P_{ee}/P_{aa}$ . Based on the K value, the difference between the conservative energy  $\Delta E(\Delta G)=-4.576T \lg K$  (where T is the absolute temperature) is calculated. The structure and conformation of the synthesized compounds 2 (a-d) and 3 (a-d) were studied by IR [6] and NMR spectroscopy methods [8].

Based on the spectral data of table 2, it was found that the products of oxidative hydroxyhalogenation of alkylcyclohexenes consist of two final conformers, which are formed as a result of trans-addition of the HlgOH intermediate to a multiple C=C bond of substrates.

The conformational equilibrium of the obtained conformers was carried out according to the width ( $W_{1/2}$ ) of the signal of the H<sup>+</sup> proton located at position 2 observed and calculated according to the spin-spin coupling constants with a chemical shift of 4.46 ppm. As a result of the spin-spin interaction of H<sup>+</sup> with axial and equatorial vicinal protons at the C<sup>3</sup> atom (CSSC)  $J_{aa}$ -11.8 Hz,  $J_{ae}$ -3.6 and  $J_{ee}$ -2.8 Hz for conformers 4-methyl and  $J_{aa}$ -12.2 Hz,  $J_{ee}$ -4.2 and  $J_{ee}$ -3.3 Hz for conformers of 1-acetyl derivatives [8] for conformers (5) are respectively  $\approx 7$  and 16 Hz.

**Table 2.** Conformation and IR and NMR parameters of the species of the oxidative hydroxyhalogenation of 1-CH<sub>3</sub>-, 3-CH<sub>3</sub>, 1-acyl and 4-etenyl-trans-2-Cl (or Br) –cyclohexanols

№	IR spectroscopy, $\nu$ , cm <sup>-1</sup>									
	CH <sub>3</sub>	C-OH C-O*	CH	C-Cl	C-Br	CH= CH <sub>2</sub>	C=O* CO-Ac	$\Delta G(ee-aa)$ J·mole <sup>-1</sup>	$C_{aa}$ , %	K
2a	2870	3486 1115 *992-1031 (a) *1032-1041 (e)	2876	780 (a) *643-728 (a) *734-853 (e) 760 (e)				2785	74	0.23
2b	2875	3480 1110	2880	780 (a) 760 (e)				2780	73	0.226
2c	2855	3465 1115	2870 2950	750 (a) 610, 625 688, 726 720 (e)			1731* 1720* 1011-1020 (a) 1023-1030 (e)	2820	77	0.293
2d		3485 3360 1125 1095	2950	780 (a) 760 (e)		3080 3050		2830	78	0.295

3a	2870	3495 1115	2876		610 (a) 538-686 (a) 680-830 (e) 550 (e)			2783	72	0.223
3b	2872	3485 1115	2880		610 (a) 578 (e)			2781	73	0.22
3c	2845	3488 978	2875 1349		615 (a) 585 (e)		1730 1725 1717	2780	71	0.29
3d		3486 3360 1125	2950		720 670 620 525	3082 3055		2835	78	0.296

Continuation Table 2

№	NMR spectroscopy, $\delta$ , ppm				
	CH <sub>3</sub>	CH=CH <sub>2</sub>	CH <sub>2</sub> cycle	H <sub>g</sub>	W <sub>1/2</sub> , Hz
2a	1.32		1.78	4.49	10.9
2b	0.98		1.78 1.67	3.49	7.8 9.2
2c	2.3		1.75	3.73	10.2
2d		5.8; J 16.8, 10.2, 6.3 Hz 5.0; J 16.9, 2.2 Hz 4.95; J 10.2, 2.2 Hz	1.78	3.51	7.8 10.3
3a	1.32		1.72	4.78	11.3
3b	0.98		1.78 1.67	3.46	8.2 9.6
3c	2.3		1.76	3.69	10.6
3d		5.78; J 16.7, 10.1, 6.3 Hz 5.0; J 16.9, 2.2 Hz 4.95; J 10.2, 2.2 Hz	1.75	3.46	7.9 10.2

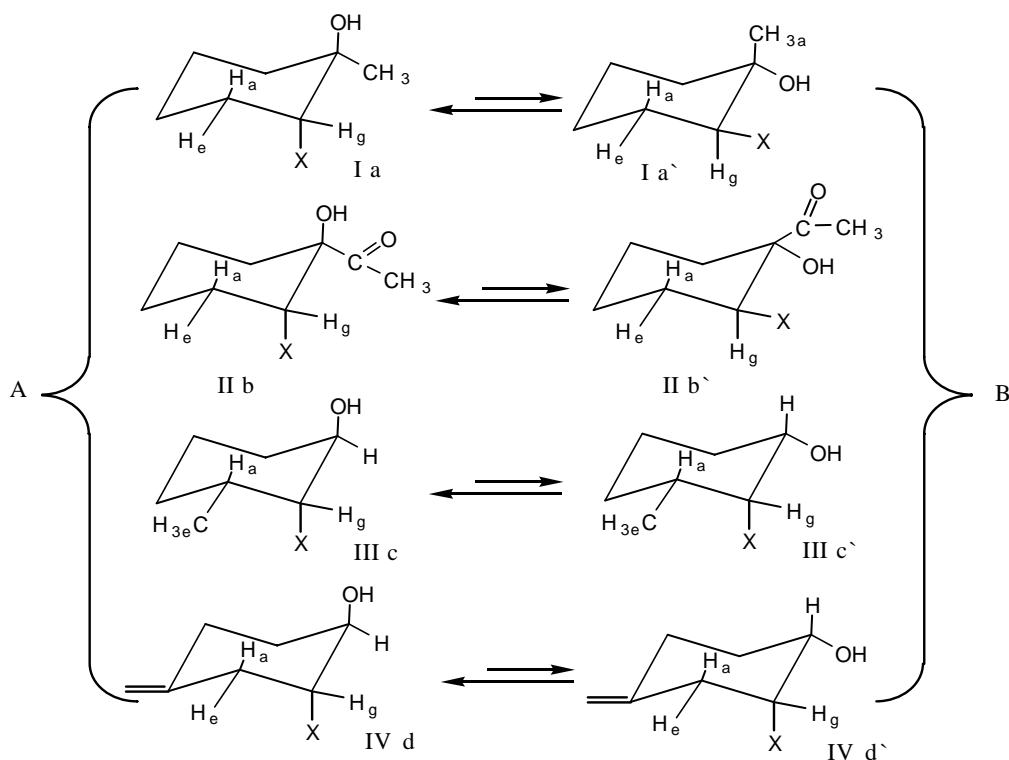
The position of conformational equilibrium, the difference in conformational energies, the conformational equilibrium constant (K), and the diaxial and diequatorial contents of the halogen atom (Cl, Br) and the hydroxyl group of the C<sub>aa</sub> and C<sub>ee</sub> conformers in equilibrium with 2-chloro(bromo)-4-methylcyclohexanes were determined and 1-[1-chloro(bromo)-2-hydroxycyclohexyl]ethan-1-ones and established the spatial position of the methyl and acetyl groups relative to the C-H<sub>g</sub> and C-OH bond cycle.

It was revealed that conformers with a diaxial spatial position of halogen atoms and a hydroxyl group (85-93%) (5) and an equatorial position of the methyl-ethenyl and acyl groups, where the carbonyl bond penetrates the transoidal configuration relative to C-H<sub>g</sub>

in the ring are predominant in the equilibrium mixture [6].

The results of kinetic studies of the oxidative hydroxyhalogenation of alkylcyclohexenes and the study of the stereochemistry and conformational equilibrium of the obtained conformers suggest that this reaction proceeds according to the electrophilic mechanism with the formation of products of the transaddition of HlgOH intermediates.

Thus, it was found that the preferred in the equilibrium mixture of hydroxygenides of alkyl-, acyl- and alkenyl-cyclohexanes mixture are the converters with the axial spatial arrangements of the halogen atom and hydroxyl group and the equatorial position of alkyl radicals:



Scheme 3

NMR and IR spectra of hydroxyhalides have enough information to determine their isomeric composition and each isomer. The presence of a band at about  $1010\text{--}987\text{ cm}^{-1}$  in the IR spectra of compounds indicates the axial position of OH (which is in good agreement with the results of NMR spectroscopy); in the absorption region of the equatorial OH group ( $1068\text{ cm}^{-1}$ ) there are no bands of any significant intensity. In the IR spectra of the compounds, intense bands are observed in the region of the axial tertiary and secondary C-Cl bond ( $610, 625, 688, 726\text{ cm}^{-1}$ ) and C-Br bond ( $526, 623, 675, 715\text{ cm}^{-1}$ ). In compounds 2c and 3c, by mixing the  $\nu$  band (C=O) of the relative “normal” value ( $1720\text{ cm}^{-1}$ ), one can judge the spatial arrangement of the atoms of the functional groups (H<sub>1</sub>lg and OH) located in the  $\alpha$ -position to the alkyl group, which indicates on the anti-arrangement of halogen atoms or the.

In the NMR spectrum of compounds 2 (a-d) and 3 (a-d), 2 signals are observed that correspond in total intensity to one proton:  $\delta$  3.81 and 4.10 ppm. 2 (a-d), 3.93 and 4.4 ppm. 3 (a-d). These signals can be attributed to the H<sup>g</sup> proton, which is in the geminal position [7].

According to the data of [6, 8], the chemical shift of a proton geminally located with chlorine atoms is greater than the chemical shift of a proton geminally located with OH group. Therefore, the signal is 4.51 ppm. observations in the spectrum of compounds 2 (a-d), can be attributed to the proton in the group of HCl, and 3.85 ppm - to the HCOH. In the spectra of the compounds, the signal is 4.10 ppm. refers to the HCB<sub>r</sub> proton, and the signal 3.95 ppm- to the HCOH proton. The half-width ( $W_{1/2}$ ) of the proton signals HCHlg and HCOH is 7.2 Hz, which indicates their equatorial position, which means that the substituents Cl, Br and OH are axially arranged. For axial H<sup>g</sup>, expecting an allowed multiplet signal with a half-width between the extreme peaks of 15.89–16.2 Hz. It means that the synthesized hydroxyhalides in the oxidizing system consist of a mixture of approximately equal amounts of 1e(3e,4e)-alkyl-trans-2a-Hlg-1a-cyclohexanol (A) and 1e(3e,4e)-alkyl-trans-1a-Hlg-2a-cyclohexanol (B).

Calculations of the spin-spin coupling constants of the proton H<sup>g</sup> with the protons H<sub>a</sub> and H<sub>e</sub> in position 3 of the conformers 2 (a, d,

c) and 3 (a, d, c) ( $^3J_{ea}$  2.2,  $^3J_{ee}$  3.2 Hz [9]) showed that the  $H^g$  signals should be triplet with a distance between extreme peaks (or half width  $W_{1/2}$ ) of 7.2 Hz and an intensity ratio of  $\sim 1:2:1$ . As can be seen, the characteristic parameters of the observed  $CH_2$ ,  $CH_3$  and  $OH$  for both compounds are at 1.52-1.78, 2.27-2.32 and 3.35-3.52 ppm. respectively.

The number of isomers of alkylcyclohexene hydroxyhalides was determined from the values of the integrated intensities of the proton signals  $H^g$  in the NMR

spectra. The mixture consists of approximately equal A and B. The results are in good agreement with the results of the hydroxyhalogenation of unsaturated compounds with one or more electron-withdrawing and electron-donating substituents at the  $\alpha$ - and  $\beta$ - positions. A decrease in the proportion of the products of electrophilic addition of  $HHlg^+OH^-$  is observed according to the Markovnikov's rule as the number and strength of electron-acceptor substituents increase.

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## ALKİLSİKLOHEKSENLERİN OKSIDLƏŞDİRİCİ HİDROKSİHALOGENLƏŞMƏ REAKSİYA MƏHSULLARININ KONFORMASİYON ASPEKTİ

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Maye fazada hidrogen peroksid və hidrogen-halogenid turşuları iştirakı ilə alkilsikloheksenlərin oksidləşdirici hidrosihalogenləşdirilməsinin kinetik qanunauyğunluqları nəzərdən keçirilmişdir. Reaksiya dönərdir, düz və əks istiqamətlərdə ikinci bir nizama malikdir. Prosesin hər iki mərhələsinin sürəti əvəzedicilərin konformasiya effektləri ilə əlaqələndirilir. Optimal reaksiya şəraiti tapılmış, alınan məhsulların izomer və konformasiya tərkibi müəyyən edilmişdir. Kinetik tədqiqatların nəticələri və alınan adduktların stereokimya və uyğunluq tarazlığının öyrənilməsi bu reaksiyanın trans-qoşulma məhsullarının meydana gəlməsi ilə elektrofilik mexanizmə uyğun getdiyini göstərir. Reaksiya adduktlarının tarazlıq qarışığında əsasən bir halogen atomunun oxlu tənzimlənməsi və əvəzedicilərin ekvator mövqeyi olan bir hidrosil qrupu olduğu aşkar edilmişdir. Kinetik və spektral məlumatlara əsasən ehtimal olunan reaksiya mexanizmi və konformasiya quruluşu təklif olunmuşdur.

**Açar sözlər:** oksidləşdirici hidrosihalogenləşdirilmə, alkilsikloheksenlər, hidrogen peroksid, hidrogen-halogenid turşuları



**КОНФОРМАЦИОННЫЕ АСПЕКТЫ ПРОДУКТОВ РЕАКЦИИ  
ОКИСЛИТЕЛЬНОГО ГИДРОКСИГАЛОГЕНИРОВАНИЯ АЛКИЛЦИКЛОГЕКСЕНОВ****Ш.И. Исмаилова**

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*Рассмотрены кинетические закономерности реакции окислительного гидроксигалогенирования алкилциклогексенов с участием пероксида водорода и галогено-водородных кислот в жидкой фазе. Реакция обратима и имеет второй порядок в прямом и обратном направлениях. Скорость обеих стадий процесса коррелируется конформационными эффектами заместителей. Установлены оптимальные условия реакции и определен изомерный и конформационный состав полученных продуктов. Результаты проведенных кинетических исследований и изучение стереохимии и конформационных равновесий полученных аддуктов позволяют предположить, что данная реакция протекает по электрофильному механизму с образованием продуктов транс-присоединения. Обнаружено, что в равновесной смеси аддуктов реакции присутствуют, в основном конформеры с аксиальным расположением атома галогена и гидроксильной группы с экваториальным положением заместителей. На основе кинетических и спектральных данных предложен вероятный механизм реакции и структура конформеров.*

**Ключевые слова:** окислительное гидроксигалогенирование, алкилциклогексены, пероксид водорода, галогено-водородные кислоты