Chapter 21

MOLECULAR DESIGN AND REACTIVITY OF THE 1-HYDROXYCYCLOHEXYL HYDROPEROXIDE - ALK₄NBR COMPLEXES

N.A. Turovskij[qq,1], E.V. Raksha[1], E.N. Pasternak[1], I.A. Opeida[2], and G.E. Zaikov[rr,3]

[1]Donetsk National University, Donetsk, Ukraine
Ukrainian-American Laboratory of Computational Chemistry, Kharkov,
Ukraine, Jackson, U.S.A.
[2]Institute of Physico-Organic and Coal Chemistry of the National Academy of Sciences
of Ukraine, R. Luxemburg 70, 83114 Donetsk, Ukraine
[3]Institute of Biochemical Physics, Russian Academy of Sciences,
Moscow, Russian Federation

ABSTRACT

Chemically activated 1-hydroxycyclohexyl hydroperoxide decomposition in the presence of ammonium salts is proposed to proceed through the complexation stage. Complex structure and reactivity have been investigated by molecular modelling methods. Kinetics of the chemically activated hydroperoxide decomposition in the presence of quaternary ammonium salts (Et₄NBr, Pr₄NBr, Bu₄NBr, and Hex₄NBr) has been studied. The correlation between reactivity and structural characteristics of ammonium cations was found.

Keywords: *molecular modelling, cyclohehanone hydroperoxides, quaternary ammonium salts, chemical activation, complexation.*

[qq]Universitetskaya str. 24, 83055, Ukraine E-mail: turov@dongu.donetsk.ua;
[rr]4 Kosygina, 117334 Moscow, Russian Federation, E-mail: chembio@sky.chph.ras.ru.

INTRODUCTION

Peroxides and hydroperoxides are widely used as initiators as well as components of binary initiating systems in the processes of vinyl monomers polymerization, polymers modification [1-3], and oxidation of organic substances by molecular oxygen [4, 5]. Initiating systems on the base of quaternary ammonium bromides were found to be the most effective in the case of the liquid phase oxidation of isopropyl benzene by O_2 [5]. 1-hydroxycyclohexyl hydroperoxide - Et_4NBr system initiates the reaction of liquid phase isopropyl benzene oxidation at 308–340 K [6] while the hydrocarbon oxidation in the presence of only one component of the binary system did not occur. The present work presents the study of 1-hydroxycyclohexyl hydroperoxide decomposition activated by the tetraalkylammonium bromides to investigate the role of ammonium salt cation in the process of chemical activation of peroxide bond.

EXPERIMENTAL

1-hydroxycyclohexyl hydroperoxide has been prepared from cyclohexanone and H_2O_2 in anhydrous ether according with [7]. Tetraalkylammonium bromides (Et_4NBr, Pr_4NBr, and Bu_4NBr) were recrystallized from the saturated acetonitrile solution by addition of diethyl ether excess. The solvent (acetonitrile) purity was controlled by electrical conductivity value, which was within $(8.5 \pm 0.2) \cdot 10^{-6}$ Om^{-1} sm^{-1} at 303 K. Reactions were carried out in the glass-soldered ampoules in argon atmosphere. Hydroperoxide kinetic concentration was controlled by the iodometric titration with potentiometric fixation of the equivalent point.

CALCULATION METHODS

Quantum chemical calculations of hydroperoxides molecules and corresponding radicals were carried out by AM1 semiempirical method implemented in MOPAC package [8]. The RHF method was applied to the calculation of the wave function. Optimization of structure parameters of hydroperoxide and hydroperoxide complexes was carried out by Eigenvector Following procedure. The molecular geometry parameters were calculated with boundary gradient norm 0.01. Solvent effect was considered in COSMO approximation [9].

RESULTS AND DISCUSSION

It was shown recently that cyclohexanone peroxides decomposition in the presence of Et_4NBr proceeds with lower activation barrier as compared with thermolysis. This fact can be explained by the complexation in the studied system [6]. We assume that the activation extent of the peroxide bond in the complex correlates with hydroperoxide reactivity in the reaction of radical decomposition. Thus we investigated the molecular design and reactivity of the complexes in the system 1-hydroxycyclohexyl hydroperoxide – Alk_4NBr.

Molecular Design of the 1-Hydroxycyclohexyl Hydroperoxide - Alk₄NBr Complex

To obtain the structure information the molecular modelling of the ROOH-Alk$_4$NBr ion-molecular complexes has been carried out for the case of Et$_4$NBr. In contrast to the aralkyl hydroperoxides (like isopropylbenzene hydroperoxide) the molecule of 1-hydroxycyclohexyl hydroperoxide does not contain the aromatic ring but there is the hydroxide group OH in their structure that also can participate in the intermolecular hydrogen bonds formation. We assume the model of complex formation with combined action of cation and anion (Figure 1) such as previously proposed model of substrate separated ion pair (SubSIP) [10, 11].

Formation of such type associate is accompanied by considerable conformation changes of the hydroperoxide fragment. Association between hydroperoxide molecule and the salt ions occurs by the intermolecular hydrogen bonds formation. It is confirmed by charge increasing on the hydrogen atoms of the corresponding bonds C-H$_3$, O-H$_1$, and O-H$_2$ and elongation of these bonds from 1.11 Å to 1.17 Å and from 0.96 Å to 1.08 Å correspondingly. Calculations in COSMO approximation show that the electron density transfer from bromide-anion to the hydroperoxide fragment is lower in the case of solvent effect taken into account (Table 1).

Stage determining the rate of the hydroperoxide decomposition is that of O-O bond cleavage. Thus the reaction activation energy will be determined by the energy of peroxide bond homolytic decomposition. Some possible elementary stages of the complex decomposition with the free radical formation are listed in Table 2.
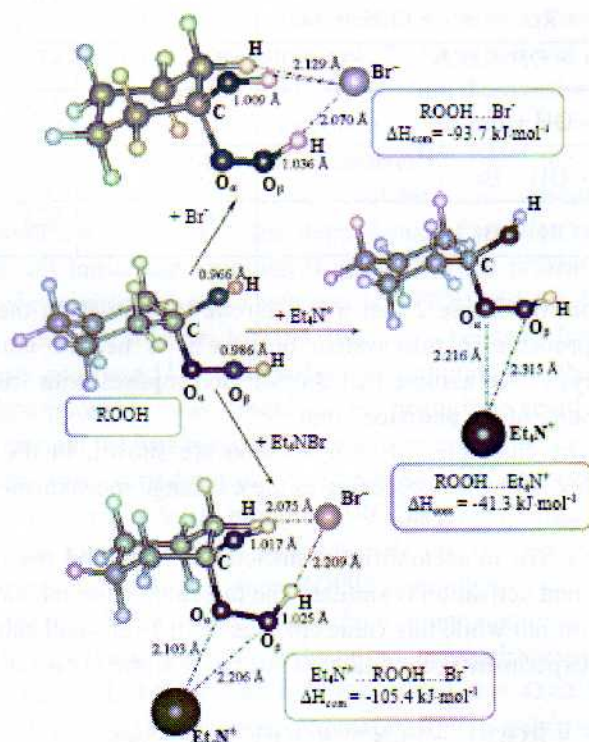

Figure 1. Complexes of 1-hydroxycyclohexyl hydroperoxide with tetraethylammonium bromide.

Table 1. Electron and stereochemical characteristics of COOH-fragment in ROOH – Et$_4$NBr complexes

parameters	ROOH	Et$_4$N$^+$...ROOH...Br$^-$	ROOH...Br$^-$	ROOH...
$q_{O\alpha}$, e	- 0.18	- 0.24	- 0.18	- 0.20
$q_{O\beta}$, e	- 0.20	- 0.26	- 0.29	- 0.23
q_{H1}, e	0.20	0.25	0.25	0.22
q_{H2}, e	0.22	0.27	0.27	0.04
q_{H3}, e	0.10	0.17	0.11	0.10
$\angle CO_\alpha O_\beta H$	90.8	33.4	68.3	77.5
q_{Br}^-	-	- 0.81	- 0.85	-

Table 2. Heats of some elementary stages of ROOH – Et$_4$NBr complex decomposition

Reaction	ΔH^0, kJ mol^{-1}	
	gas phase	acetonitrile
ROOH → RO$^\cdot$ + $^\cdot$OH	148	151
Et$_4$N$^+$...ROOH...Br$^-$ → RO$^\cdot$ + $^\cdot$OH + Et$_4$N$^+$ + Br$^-$	481	239
Et$_4$N$^+$...ROOH...Br$^-$ → RO$^\cdot$ + $^\cdot$OH + Et$_4$NBr	65	108
Et$_4$N$^+$...ROOH...Br$^-$ → RO$^-$ + $^\cdot$OH + Et$_4$N$^+$ + Br$^\cdot$	615	354
Et$_4$N$^+$...ROOH...Br$^-$ → RO$^\cdot$ + OH$^-$ + Et$_4$N$^+$ + Br$^\cdot$	435	249
ROOH...Et$_4$N$^+$ → RO$^\cdot$ + $^\cdot$OH + Et$_4$N$^+$	192	179
ROOH...Br$^-$ → RO$^\cdot$ + $^\cdot$OH + Br$^-$	242	208
ROOH...Br$^-$ → RO$^-$ + $^\cdot$OH + Br$^\cdot$	188	219
ROOH...Br$^-$ → RO$^\cdot$ + OH$^-$ + Br$^\cdot$	376	323

It can be seen from the Table 2 that the electrone transfer from the bromide ion to the peroxide bond is improbable in this system because it is needed more energy inputs as compared with homolysis. We assume that SubSIP decomposes with free radicals formation due to homolytical rupture of the peroxide bond.

On the Figure 1 the enthalpies of complexation are shown. In the case of SubSIP we assume that the complex is formed according to the exchange mechanism (1) while possibility of the threemolecular reaction (2) is low.

Solubility of the Et$_4$NBr in acetonitrile is sufficiently high, and reactivity of the ions and ion pairs in peroxide bond activation is similar. The threemolecular reaction (2) determines the second reaction order on salt while this value changes from 1 (at small salt concentrations) to 0 (at salt abundance) in experimental conditions. Thus the reaction (1) is rather preferable.

$$Et_4N^+...Solv...Br^- + ROOH \rightarrow Et_4N^+...ROOH...Br^- + Solv \qquad (1)$$

$$(\Delta H_{r(2)} = - 53.7 \text{ kJ·mol}^{-1}) \qquad (2)$$

$$Et_4N^+ + ROOH + Br^- \rightarrow Et_4N^+...ROOH...Br$$

$$(\Delta H_{r(3)} = -88.1 \text{ kJ·mol}^{-1})$$

Corresponding models like $Et_4N^+...ROOH...Br^-$ were obtained for tetraalkylammonium salts (Pr_4NBr, Bu_4NBr, и Hex_4NBr). Changes in peroxide bond energy (i.e. total of electronic and nuclear energies of two-center term O-O atom pair) can be suggested as extent of the peroxide bond activation. Stable peroxide structure has the lowest O-O bond energy (-12.08 eV for free hydroperoxide) and less stable (or activated) peroxide conformation has the highest one (-11.78 eV for complex $Et_4N^+...ROOH...Br^-$). Difference between energy of stable and activated peroxide structure increases in the catalyst row: Hex_4NBr, Bu_4NBr, Pr_4NBr, and Et_4NBr indicating weakening of the O-O bond in the ROOH-Alk_4NBr complex. From this point of view the O-O bond activation in the case of $Et_4N^+...ROOH...Br^-$ is the highest and in complex with Hex_4NBr is the lowest. This suggestion is in correspondence with experimental data.

Kinetic Features of the Activated Hydroperoxide Decomposition

Reaction of 1-hydroxycyclohexyl hydroperoxide (ROOH) decomposition activated by the tetraalkylammonium bromides (Alk_4NBr) has been investigated at 323 – 353 K under conditions of ammonium salts abundance ($[ROOH]_0 = 5·10^{-3}$ mol·dm^{-3}, $[Alk_4NBr]_0 = 2.5·10^{-2} – 1·10^{-1}$ mol·dm^{-3}). Kinetics of ROOH activated decomposition on these conditions could be described by the first order reaction proceedings low. The reaction was carried out up to 50 % hydroperoxide conversion and the products did not effect on the reaction proceeding as kinetic curves anamorphouses are linear in the corresponding first order coordinates. The effective rate constant (k_{ef}, sec^{-1}) was found to be independent from the hydroperoxide initial concentration within $[ROOH]_0 = 2.5·10^{-3} – 1·10^{-2}$ mol·dm^{-3} and constant amount of Alk_4NBr ($5·10^{-2}$ mol·dm^{-3}). Nonlinear character of the dependence of reaction rate effective constants from the ammonium salt initial concentration (Figure 2) in the present conditions points out onto the occurrence of complexation stage between the ROOH and Alk_4NBr. These facts are in an agreement with reaction scheme for the isopropyl benzene hydroperoxide activated decomposition recently proposed [12]. Thermolysis contribution into the total reaction rate the ROOH activated decomposition was found to be negligibly small because the thermal decomposition rate constant [6] was two orders lower then corresponding k_{ef} values.

Some experiments were carried out under conditions of ROOH excess as compared with salts concentration ($[Alk_4NBr]_0 = 5·10^{-3}$ mol·dm^{-3}, $[ROOH]_0 = 5·10^{-2}$ mol·dm^{-3}) at 323 K. Even at present concentration ratio of ROOH and Alk_4NBr the rate of hydroperoxide activated decomposition is several orders higher then ROOH thermolysis rate. The Br$^-$ concentration during reaction proceeding is unaltered. These facts point out onto catalytic character of Alk_4NBr action in the process. Catalytic scheme of the hydroperoxide decomposition is supported also in works [13, 14] in which it was noted that O-O bond cleavage in the hydroperoxide – catalyst complex proceeds homolytically, catalyst is not consumed and deactivated in the system.
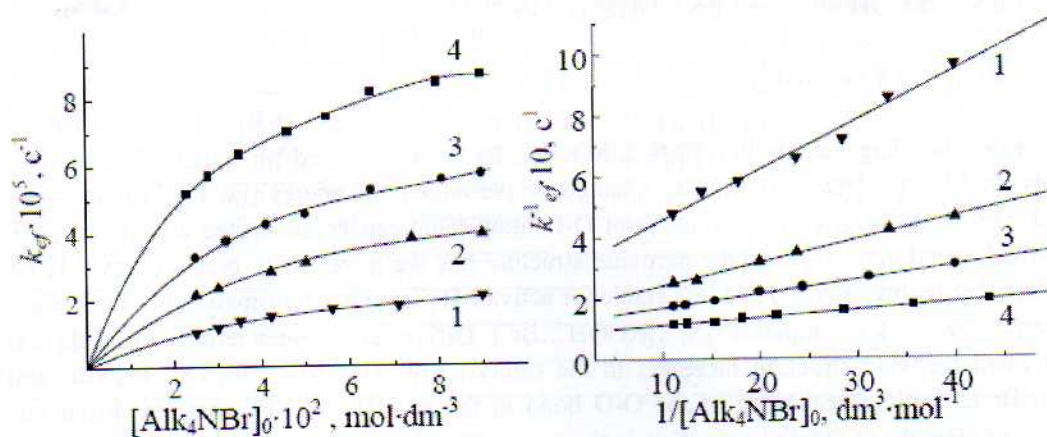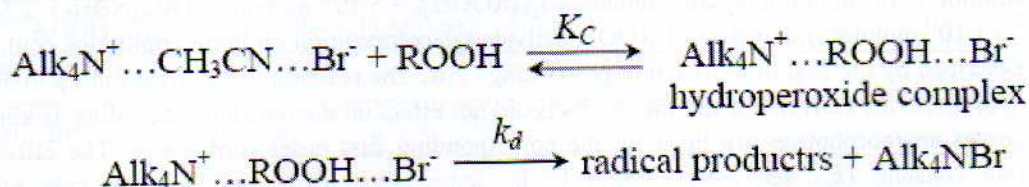
Figure 2. Dependence of k_{ef} from the catalyst initial concentration in the direct (a) and inverse (b) coordinates. [ROOH]0 = 5.0·10-3 mol·dm-3, 333 K, 1 – Hex4N+, 2 – Bu4N+, 3 – Pr4N+, 4 – Et4N+.

The kinetic scheme is proposed for the chemically activated ROOH decomposition. It includes the complexation stage between ROOH and salts ions as well as stage of the complex-bonded hydroperoxide decomposition with catalyst regeneration:

k_{ef} dependence on the salt concentration can be expressed by the relationship (3):

$$Alk_4N^+...CH_3CN...Br^- + ROOH \xrightleftharpoons{K_C} Alk_4N^+...ROOH...Br^-$$
hydroperoxide complex

$$Alk_4N^+...ROOH...Br^- \xrightarrow{k_d} radical\ productrs + Alk_4NBr$$

$$\frac{1}{k_{ef}} = \frac{1}{k_d K_C [Alk_4NBr]} + \frac{1}{k_d} \qquad (3)$$

The dependence of k_{ef} on Alk4NBr concentration is linear in double inverse coordinates (Figure 2). It is in the agreement with the proposed kinetic scheme. The values of rate constants of complex-bonded peroxide decomposition (k_d) obtained for the investigated salts decrease in the following order: $Et_4N^+ > Pr_4N^+ > Bu_4N^+ > Hex_4N^+$. The values of equilibrium constants of complexation between ROOH and Alk4NBr ions change similarly (Table 3).

Isokinetic relationship between complexation parameters in the system leads to the insignificant changes in free energy of complexation for different alkyl substituent in ammonium cation. Considering the intermolecular bonds energy the strongest complex is formed between hydroperoxide and Et4NBr, the weakest - in the case of Hex4NBr (see the corresponding ΔH_{com} values in Table 3). The reactivity of complex-bonded ROOH also decreases with increasing of alkyl substituent size. Isokinetic relationship for the obtained

activation parameters points out upon the unified mechanism of ROOH - Alk$_4$NBr complex decomposition.

Table 3. Kinetic parameters of 1-hydroxycyclohexyl hydroperoxide decomposition in the presence of tetraalkylammonium bromides

parameters	T, K	ROOH + Et$_4$NBr	ROOH + Pr$_4$NBr	ROOH + Bu$_4$NBr	ROOH + Hex$_4$NBr
$k_d \cdot 10^4$, sec^{-1}	333	1.14 ± 0.04	0.8 ± 0.1	0.59 ± 0.06	0.34 ± 0.01
	343	2.5 ± 0.1	1.80 ± 0.09	1.51 ± 0.04	0.97 ± 0.02
	353	5.1 ± 0.2	4.20 ± 0.09	3.48 ± 0.08	2.40 ± 0.06
K_C, dm^{3}mol^{-1}	333	36 ± 2	28 ± 3	23 ± 2	18 ± 3
	343	29 ± 2	24 ± 1	20 ± 1	16 ± 2
	353	23 ± 1	20 ± 1	18 ± 2	15 ± 2
E_a, kJmol^{-1}	333-353	73 ± 1	81 ± 2	87 ± 3	96 ± 2
lg$A$, (A, c^{-1})		7.5 ± 0.6	8.6 ± 0.3	9.4 ± 0.2	10.5 ± 0.3
ΔH_{com}, kJmol^{-1}		-20 ± 1	-16 ± 2	-12 ± 2	-9 ± 1
ΔS_{com}, Jmol^{-1}K^{-1}		-30 ± 4	-21 ± 5	-10 ± 4	-3 ± 3

Changes of the peroxide bond activation in the complex in the case of different ammonium cations point out the role of steric factor at the stage of complex formation as well as at the formation of their decomposition transition state. In the simplest case the own volume of the investigated cations could describe the steric effect. A good correlation between activation parameters of the complex decomposition and calculated values of Van-der-Waals volumes of cations has been obtained (Figure 3). V_{VDW} values for the tetraalkylammonium cations were calculated in HyperChem package. Calculated values are in agreement with corresponding own volumes of cations listed in [15]. Linear relationship has been observed between the complex heat of formation - ΔH^0_f and experimental activation parameters - $\Delta H^{\neq}$ (Figure 4).

Obtained experimental facts have shown that the salt cation participates both in complexation stage and in stage of complex ROOH - Alk$_4$NBr decomposition. Ammonium cation has the regulating action upon the catalytic reactivity of the halide-anion in the reaction of catalytic decomposition of the 1-hydroxycyclohexyl hydroperoxide in the presence of Alk$_4$NBr. Thus the cation structure influences on the reactivity of the hydroperoxide complex and on the extent of peroxide bond activation. The molecular modeling of the hydroperoxide-catalyst reactive complex can be used to preliminarily predict the reactivity of the system.
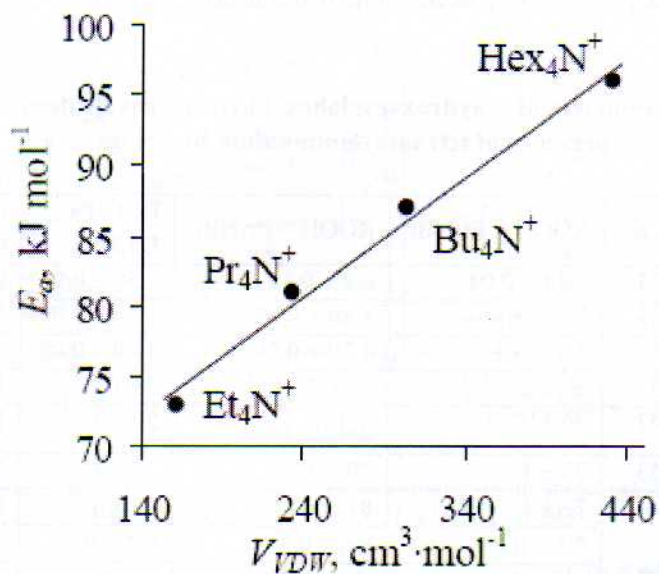
Figure 3. Relationship between activation parameters of the complex decomposition and Van-der-Waals volume of the tetraalkylammonium cations.
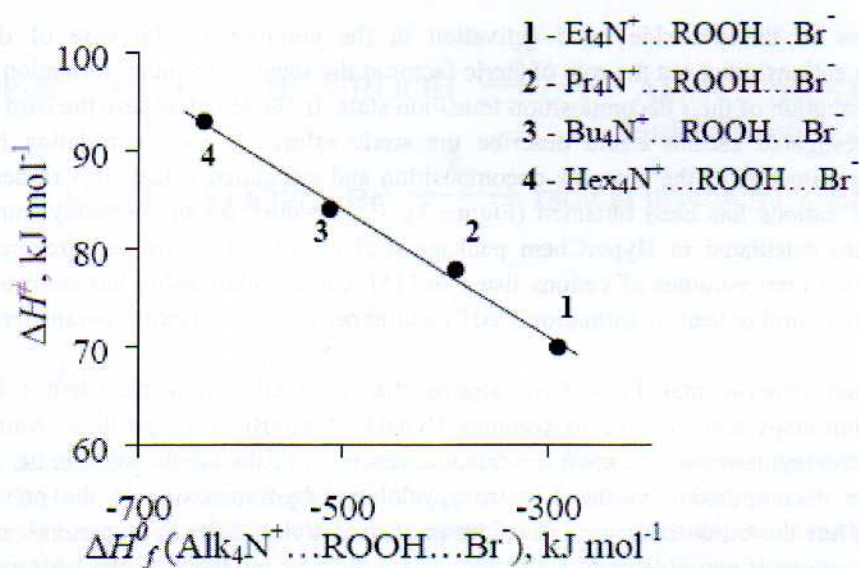

1 - $Et_4N^+...ROOH...Br^-$
2 - $Pr_4N^+...ROOH...Br^-$
3 - $Bu_4N^+...ROOH...Br^-$
4 - $Hex_4N^+...ROOH...Br^-$

Figure 4. Relationship between the complex heat of formation ($\Delta H0f$) and experimental activation parameters ($\Delta H\neq$).

CONCLUSIONS

Summarizing, obtained experimental facts have shown that the chemical activation of the peroxide bond is observed in the presence of Alk_4NBr. The kinetic parameters of the hydroperoxide catalytic decomposition have been obtained for the Et_4NBr, Pr_4NBr, Bu_4NBr, and Hex_4NBr. Catalysis of the 1-hydroxycyclohexyl hydroperoxide decomposition has been shown to occur through accompanied action of the ammonium salt cation and anion.

REFERENCES

[1] E.T. Denisov, T.G. Denisova, T.S. Pokidova. *Handbook of Free Radical Initiators*. John Wiley and Sons Inc.: Hoboken, New Jersey, 2003. - 879 p.

[2] N.A. Turovskij, I.O. Opeida, O.V. Kush, E.L. Baranovskij. *J. Appl. Chem.* 77, 1887 (2004).

[3] C.J. Perez, E.M. Valles, M.D. Failla. *Polymer,* 46, 725 (2005).

[4] I.A. Opeida, N.M. Zalevskaya, E.N. Turovskaya. *Kinetika i Kataliz,* 45, 776 (2004).

[5] I.A. Opeida, N.M. Zalevskaya, E.N. Turovskaya, U.I. Sobka, *Petroleum Chemistry,* 42, № 6. 460 (2002).

[6] M.A. Turovskyj, I.A. Opeida, E.N. Turovskaya, O.V. Raksha, N.O. Kuznetsova, G.E. Zaikov. *Oxid. Commun.,* 29, 249 (2006).

[7] N.A. Milas, S.A. Harris, P.C. Panagiotacos. *J.Am.Chem.Soc.,* 61, No 9 2430 (1939).

[8] J.J.P. Stewart. *MOPAC 2000.00 Manual;* Fujitsu Limited: Tokyo: Japan, 1999.

[9] A.Klamt. *J.Chem. Soc. Perkin Trans.,* №2 799 (1993).

[10] M.A. Turovskyj, I.O. Opeida O.M. Turovskaya, O.V. Raksha, N.O. Kuznetsova, and G.E. Zaikov. *Order and Disorder in Polymer Reactivity*. Howell New York: Nova Science Publishers, Inc.-2006. - pp. 37-51.

[11] N.A. Turovskij, S.Yu. Tselinskij, Yu.E. Shapiro, A.R. Kal'uskij. *Teor. Eksp. Khim.,* 28, №4. 320 (1992).

[12] M.A. Turovskyj, A.M. Nikolayevskyj, I.A. Opeida, V.N. Shufletuk. *Ukrainian Chem. Bull.,* 8, 151 (2000).

[13] L.M. Pisarenko, O.T. Kasaikina. *Russ Chem Bull*, 3, 419 (2002).

[14] L.M. Pisarenko, V.G. Kondratovich, O.T. Kasaikina. *Russ Chem Bull*, 10, 2110 (2004).

[15] Y.Marcus. *Ion salvation*. Chichester, etc.: Wiley. – 1985. – 306p.

Chapter 21

MOLECULAR DESIGN AND REACTIVITY OF THE 1-HYDROXYCYCLOHEXYL HYDROPEROXIDE - ALK₄NBR COMPLEXES

N.A. Turovskij[qq,1], E.V. Raksha[1], E.N. Pasternak[1], I.A. Opeida[2], and G.E. Zaikov[rr,3]

[1]Donetsk National University, Donetsk, Ukraine
Ukrainian-American Laboratory of Computational Chemistry, Kharkov,
Ukraine, Jackson, U.S.A.
[2]Institute of Physico-Organic and Coal Chemistry of the National Academy of Sciences
of Ukraine, R. Luxemburg 70, 83114 Donetsk, Ukraine
[3]Institute of Biochemical Physics, Russian Academy of Sciences,
Moscow, Russian Federation

ABSTRACT

Chemically activated 1-hydroxycyclohexyl hydroperoxide decomposition in the presence of ammonium salts is proposed to proceed through the complexation stage. Complex structure and reactivity have been investigated by molecular modelling methods. Kinetics of the chemically activated hydroperoxide decomposition in the presence of quaternary ammonium salts (Et₄NBr, Pr₄NBr, Bu₄NBr, and Hex₄NBr) has been studied. The correlation between reactivity and structural characteristics of ammonium cations was found.

Keywords: *molecular modelling, cyclohehanone hydroperoxides, quaternary ammonium salts, chemical activation, complexation.*

[qq]Universitetskaya str. 24, 83055, Ukraine E-mail: turov@dongu.donetsk.ua;
[rr]4 Kosygina, 117334 Moscow, Russian Federation, E-mail: chembio@sky.chph.ras.ru.

INTRODUCTION

Peroxides and hydroperoxides are widely used as initiators as well as components of binary initiating systems in the processes of vinyl monomers polymerization, polymers modification [1-3], and oxidation of organic substances by molecular oxygen [4, 5]. Initiating systems on the base of quaternary ammonium bromides were found to be the most effective in the case of the liquid phase oxidation of isopropyl benzene by O_2 [5]. 1-hydroxycyclohexyl hydroperoxide - Et_4NBr system initiates the reaction of liquid phase isopropyl benzene oxidation at 308–340 K [6] while the hydrocarbon oxidation in the presence of only one component of the binary system did not occur. The present work presents the study of 1-hydroxycyclohexyl hydroperoxide decomposition activated by the tetraalkylammonium bromides to investigate the role of ammonium salt cation in the process of chemical activation of peroxide bond.

EXPERIMENTAL

1-hydroxycyclohexyl hydroperoxide has been prepared from cyclohexanone and H_2O_2 in anhydrous ether according with [7]. Tetraalkylammonium bromides (Et_4NBr, Pr_4NBr, and Bu_4NBr) were recrystallized from the saturated acetonitrile solution by addition of diethyl ether excess. The solvent (acetonitrile) purity was controlled by electrical conductivity value, which was within $(8.5 \pm 0.2) \cdot 10^{-6}$ Om^{-1} sm^{-1} at 303 K. Reactions were carried out in the glass-soldered ampoules in argon atmosphere. Hydroperoxide kinetic concentration was controlled by the iodometric titration with potentiometric fixation of the equivalent point.

CALCULATION METHODS

Quantum chemical calculations of hydroperoxides molecules and corresponding radicals were carried out by AM1 semiempirical method implemented in MOPAC package [8]. The RHF method was applied to the calculation of the wave function. Optimization of structure parameters of hydroperoxide and hydroperoxide complexes was carried out by Eigenvector Following procedure. The molecular geometry parameters were calculated with boundary gradient norm 0.01. Solvent effect was considered in COSMO approximation [9].

RESULTS AND DISCUSSION

It was shown recently that cyclohexanone peroxides decomposition in the presence of Et_4NBr proceeds with lower activation barrier as compared with thermolysis. This fact can be explained by the complexation in the studied system [6]. We assume that the activation extent of the peroxide bond in the complex correlates with hydroperoxide reactivity in the reaction of radical decomposition. Thus we investigated the molecular design and reactivity of the complexes in the system 1-hydroxycyclohexyl hydroperoxide – Alk_4NBr.

Molecular Design of the 1-Hydroxycyclohexyl Hydroperoxide - Alk$_4$NBr Complex

To obtain the structure information the molecular modelling of the ROOH-Alk$_4$NBr ion-molecular complexes has been carried out for the case of Et$_4$NBr. In contrast to the aralkyl hydroperoxides (like isopropylbenzene hydroperoxide) the molecule of 1-hydroxycyclohexyl hydroperoxide does not contain the aromatic ring but there is the hydroxide group OH in their structure that also can participate in the intermolecular hydrogen bonds formation. We assume the model of complex formation with combined action of cation and anion (Figure 1) such as previously proposed model of substrate separated ion pair (SubSIP) [10, 11].

Formation of such type associate is accompanied by considerable conformation changes of the hydroperoxide fragment. Association between hydroperoxide molecule and the salt ions occurs by the intermolecular hydrogen bonds formation. It is confirmed by charge increasing on the hydrogen atoms of the corresponding bonds C-H$_3$, O-H$_1$, and O-H$_2$ and elongation of these bonds from 1.11 Å to 1.17 Å and from 0.96 Å to 1.08 Å correspondingly. Calculations in COSMO approximation show that the electron density transfer from bromide-anion to the hydroperoxide fragment is lower in the case of solvent effect taken into account (Table 1).

Stage determining the rate of the hydroperoxide decomposition is that of O-O bond cleavage. Thus the reaction activation energy will be determined by the energy of peroxide bond homolytic decomposition. Some possible elementary stages of the complex decomposition with the free radical formation are listed in Table 2.
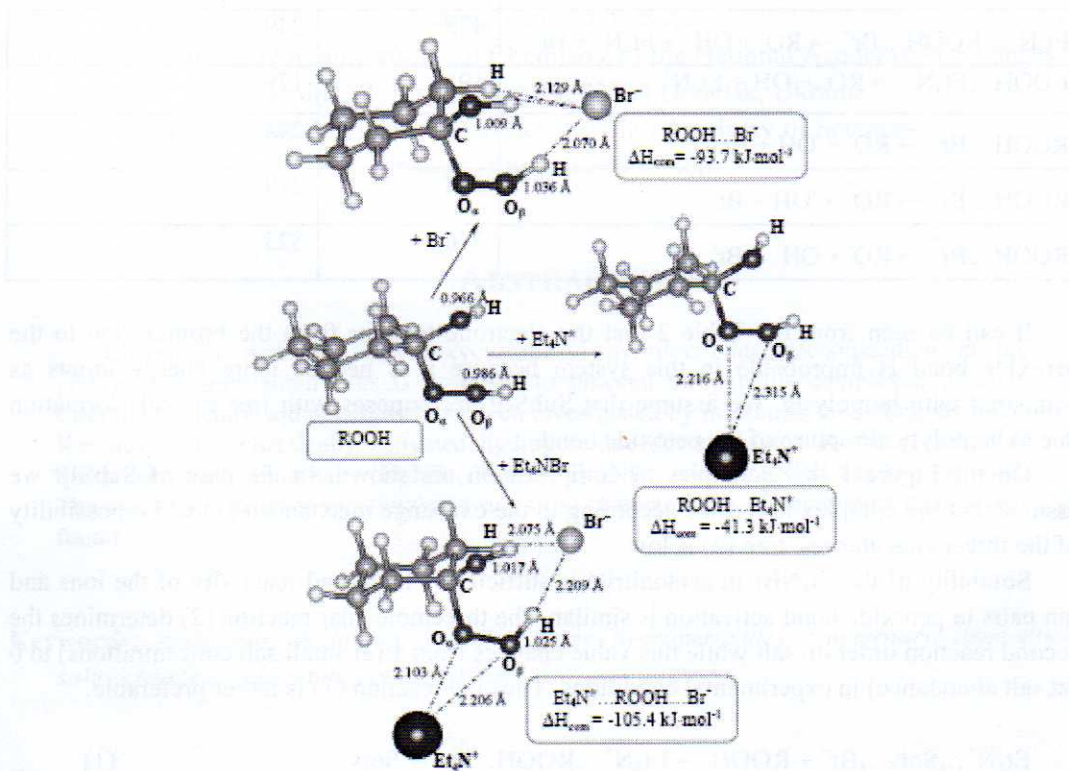

Figure 1. Complexes of 1-hydroxycyclohexyl hydroperoxide with tetraethylammonium bromide.

Table 1. Electron and stereochemical characteristics of COOH-fragment in ROOH – Et_4NBr complexes

parameters	ROOH	$Et_4N^+...ROOH...Br^-$	$ROOH...Br^-$	ROOH...
$q_{O\alpha}$, e	- 0.18	- 0.24	- 0.18	- 0.20
$q_{O\beta}$, e	- 0.20	- 0.26	- 0.29	- 0.23
q_{H1}, e	0.20	0.25	0.25	0.22
q_{H2}, e	0.22	0.27	0.27	0.04
q_{H3}, e	0.10	0.17	0.11	0.10
$\angle CO_\alpha O_\beta H$	90.8	33.4	68.3	77.5
q_{Br}^-	-	- 0.81	- 0.85	-

Table 2. Heats of some elementary stages of ROOH – Et_4NBr complex decomposition

Reaction	ΔH^0, kJ mol^{-1}	
	gas phase	acetonitrile
$ROOH \rightarrow RO^\cdot + {}^\cdot OH$	148	151
$Et_4N^+...ROOH...Br^- \rightarrow RO^\cdot + {}^\cdot OH + Et_4N^+ + Br^-$	481	239
$Et_4N^+...ROOH...Br^- \rightarrow RO^\cdot + {}^\cdot OH + Et_4NBr$	65	108
$Et_4N^+...ROOH...Br^- \rightarrow RO^- + {}^\cdot OH + Et_4N^+ + Br^\cdot$	615	354
$Et_4N^+...ROOH...Br^- \rightarrow RO^\cdot + OH^- + Et_4N^+ + Br^\cdot$	435	249
$ROOH...Et_4N^+ \rightarrow RO^\cdot + {}^\cdot OH + Et_4N^+$	192	179
$ROOH...Br^- \rightarrow RO^\cdot + {}^\cdot OH + Br^-$	242	208
$ROOH...Br^- \rightarrow RO^- + {}^\cdot OH + Br^\cdot$	188	219
$ROOH...Br^- \rightarrow RO^\cdot + OH^- + Br^\cdot$	376	323

It can be seen from the Table 2 that the electrone transfer from the bromide ion to the peroxide bond is improbable in this system because it is needed more energy inputs as compared with homolysis. We assume that SubSIP decomposes with free radicals formation due to homolytical rupture of the peroxide bond.

On the Figure 1 the enthalpies of complexation are shown. In the case of SubSIP we assume that the complex is formed according to the exchange mechanism (1) while possibility of the threemolecular reaction (2) is low.

Solubility of the Et_4NBr in acetonitrile is sufficiently high, and reactivity of the ions and ion pairs in peroxide bond activation is similar. The threemolecular reaction (2) determines the second reaction order on salt while this value changes from 1 (at small salt concentrations) to 0 (at salt abundance) in experimental conditions. Thus the reaction (1) is rather preferable.

$$Et_4N^+...Solv...Br^- + ROOH \rightarrow Et_4N^+...ROOH...Br^- + Solv \qquad (1)$$

$$(\Delta H_{r(2)} = - 53.7 \text{ kJ} \cdot \text{mol}^{-1}) \qquad (2)$$

$$Et_4N^+ + ROOH + Br^- \rightarrow Et_4N^+...ROOH...Br$$

$$(\Delta H_{r(3)} = -88.1 \text{ kJ·mol}^{-1})$$

Corresponding models like $Et_4N^+...ROOH...Br^-$ were obtained for tetraalkylammonium salts (Pr_4NBr, Bu_4NBr, и Hex_4NBr). Changes in peroxide bond energy (i.e. total of electronic and nuclear energies of two-center term O-O atom pair) can be suggested as extent of the peroxide bond activation. Stable peroxide structure has the lowest O-O bond energy (-12.08 eV for free hydroperoxide) and less stable (or activated) peroxide conformation has the highest one (-11.78 eV for complex $Et_4N^+...ROOH...Br^-$). Difference between energy of stable and activated peroxide structure increases in the catalyst row: Hex_4NBr, Bu_4NBr, Pr_4NBr, and Et_4NBr indicating weakening of the O-O bond in the ROOH-Alk_4NBr complex. From this point of view the O-O bond activation in the case of $Et_4N^+...ROOH...Br^-$ is the highest and in complex with Hex_4NBr is the lowest. This suggestion is in correspondence with experimental data.

Kinetic Features of the Activated Hydroperoxide Decomposition

Reaction of 1-hydroxycyclohexyl hydroperoxide (ROOH) decomposition activated by the tetraalkylammonium bromides (Alk_4NBr) has been investigated at 323 – 353 K under conditions of ammonium salts abundance ($[ROOH]_0 = 5·10^{-3}$ mol·dm^{-3}, $[Alk_4NBr]_0 = 2.5·10^{-2} – 1·10^{-1}$ mol·dm^{-3}). Kinetics of ROOH activated decomposition on these conditions could be described by the first order reaction proceedings low. The reaction was carried out up to 50 % hydroperoxide conversion and the products did not effect on the reaction proceeding as kinetic curves anamorphouses are linear in the corresponding first order coordinates. The effective rate constant (k_{ef}, sec^{-1}) was found to be independent from the hydroperoxide initial concentration within $[ROOH]_0 = 2.5·10^{-3} – 1·10^{-2}$ mol·dm^{-3} and constant amount of Alk_4NBr ($5·10^{-2}$ mol·dm^{-3}). Nonlinear character of the dependence of reaction rate effective constants from the ammonium salt initial concentration (Figure 2) in the present conditions points out onto the occurrence of complexation stage between the ROOH and Alk_4NBr. These facts are in an agreement with reaction scheme for the isopropyl benzene hydroperoxide activated decomposition recently proposed [12]. Thermolysis contribution into the total reaction rate the ROOH activated decomposition was found to be negligibly small because the thermal decomposition rate constant [6] was two orders lower then corresponding k_{ef} values.

Some experiments were carried out under conditions of ROOH excess as compared with salts concentration ($[Alk_4NBr]_0 = 5·10^{-3}$ mol·dm^{-3}, $[ROOH]_0 = 5·10^{-2}$ mol·dm^{-3}) at 323 K. Even at present concentration ratio of ROOH and Alk_4NBr the rate of hydroperoxide activated decomposition is several orders higher then ROOH thermolysis rate. The Br$^-$ concentration during reaction proceeding is unaltered. These facts point out onto catalytic character of Alk_4NBr action in the process. Catalytic scheme of the hydroperoxide decomposition is supported also in works [13, 14] in which it was noted that O-O bond cleavage in the hydroperoxide – catalyst complex proceeds homolytically, catalyst is not consumed and deactivated in the system.

activation parameters points out upon the unified mechanism of ROOH - Alk_4NBr complex decomposition.

Table 3. Kinetic parameters of 1-hydroxycyclohexyl hydroperoxide decomposition in the presence of tetraalkylammonium bromides

parameters	T, K	ROOH + Et_4NBr	ROOH + Pr_4NBr	ROOH + Bu_4NBr	ROOH + Hex_4NBr
$k_d \cdot 10^4$, sec^{-1}	333	1.14 ± 0.04	0.8 ± 0.1	0.59 ± 0.06	0.34 ± 0.01
	343	2.5 ± 0.1	1.80 ± 0.09	1.51 ± 0.04	0.97 ± 0.02
	353	5.1 ± 0.2	4.20 ± 0.09	3.48 ± 0.08	2.40 ± 0.06
K_C, dm^{3}mol^{-1}	333	36 ± 2	28 ± 3	23 ± 2	18 ± 3
	343	29 ± 2	24 ± 1	20 ± 1	16 ± 2
	353	23 ± 1	20 ± 1	18 ± 2	15 ± 2
E_a, kJmol^{-1}	333-353	73 ± 1	81 ± 2	87 ± 3	96 ± 2
lg$A$, (A, c^{-1})		7.5 ± 0.6	8.6 ± 0.3	9.4 ± 0.2	10.5 ± 0.3
ΔH_{com}, kJmol^{-1}		-20 ± 1	-16 ± 2	-12 ± 2	-9 ± 1
ΔS_{com}, Jmol^{-1}K^{-1}		-30 ± 4	-21 ± 5	-10 ± 4	-3 ± 3

Changes of the peroxide bond activation in the complex in the case of different ammonium cations point out the role of steric factor at the stage of complex formation as well as at the formation of their decomposition transition state. In the simplest case the own volume of the investigated cations could describe the steric effect. A good correlation between activation parameters of the complex decomposition and calculated values of Van-der-Waals volumes of cations has been obtained (Figure 3). V_{VDW} values for the tetraalkylammonium cations were calculated in HyperChem package. Calculated values are in agreement with corresponding own volumes of cations listed in [15]. Linear relationship has been observed between the complex heat of formation - ΔH^0_f and experimental activation parameters - $\Delta H^{\neq}$ (Figure 4).

Obtained experimental facts have shown that the salt cation participates both in complexation stage and in stage of complex ROOH - Alk_4NBr decomposition. Ammonium cation has the regulating action upon the catalytic reactivity of the halide-anion in the reaction of catalytic decomposition of the 1-hydroxycyclohexyl hydroperoxide in the presence of Alk_4NBr. Thus the cation structure influences on the reactivity of the hydroperoxide complex and on the extent of peroxide bond activation. The molecular modeling of the hydroperoxide-catalyst reactive complex can be used to preliminarily predict the reactivity of the system.
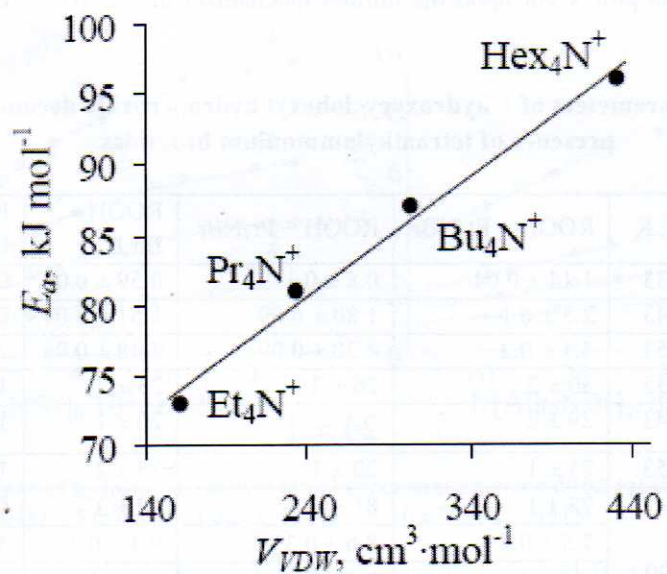
Figure 3. Relationship between activation parameters of the complex decomposition and Van-der-Waals volume of the tetraalkylammonium cations.
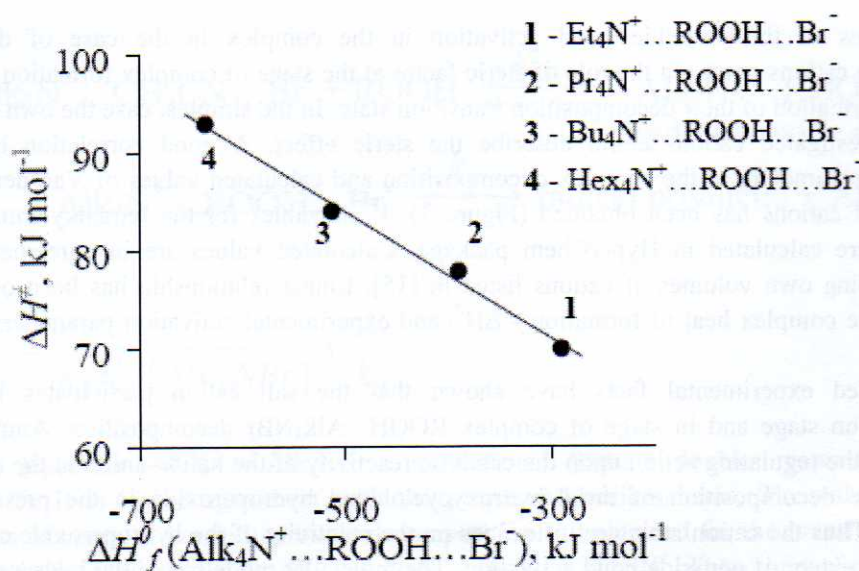

Figure 4. Relationship between the complex heat of formation ($\Delta H0f$) and experimental activation parameters ($\Delta H\neq$).

CONCLUSIONS

Summarizing, obtained experimental facts have shown that the chemical activation of the peroxide bond is observed in the presence of Alk_4NBr. The kinetic parameters of the hydroperoxide catalytic decomposition have been obtained for the Et_4NBr, Pr_4NBr, Bu_4NBr, and Hex_4NBr. Catalysis of the 1-hydroxycyclohexyl hydroperoxide decomposition has been shown to occur through accompanied action of the ammonium salt cation and anion.

REFERENCES

[1]   E.T. Denisov, T.G. Denisova, T.S. Pokidova. *Handbook of Free Radical Initiators*. John Wiley and Sons Inc.: Hoboken, New Jersey, 2003. - 879 p.

[2]   N.A. Turovskij, I.O. Opeida, O.V. Kush, E.L. Baranovskij. *J. Appl. Chem.* 77, 1887 (2004).

[3]   C.J. Perez, E.M. Valles, M.D. Failla. *Polymer,* 46, 725 (2005).

[4]   I.A. Opeida, N.M. Zalevskaya, E.N. Turovskaya. *Kinetika i Kataliz,* 45, 776 (2004).

[5]   I.A. Opeida, N.M. Zalevskaya, E.N. Turovskaya, U.I. Sobka, *Petroleum Chemistry*, 42, № 6. 460 (2002).

[6]   M.A. Turovskyj, I.A. Opeida, E.N. Turovskaya, O.V. Raksha, N.O. Kuznetsova, G.E. Zaikov. *Oxid. Commun.,* 29, 249 (2006).·

[7]   N.A. Milas, S.A. Harris, P.C. Panagiotacos. *J.Am.Chem.Soc.,* 61, No 9 2430 (1939).

[8]   J.J.P. Stewart. *MOPAC 2000.00 Manual;* Fujitsu Limited: Tokyo: Japan, 1999.

[9]   A.Klamt. *J.Chem. Soc. Perkin Trans.,* №2 799 (1993).

[10]   M.A. Turovskyj, I.O. Opeida O.M. Turovskaya, O.V. Raksha, N.O. Kuznetsova, and G.E. Zaikov. *Order and Disorder in Polymer Reactivity*. Howell New York: Nova Science Publishers, Inc.-2006. - pp. 37-51.

[11]   N.A. Turovskij, S.Yu. Tselinskij, Yu.E. Shapiro, A.R. Kal'uskij. *Teor. Eksp. Khim.,* 28, №4. 320 (1992).

[12]   M.A. Turovskyj, A.M. Nikolayevskyj, I.A. Opeida, V.N. Shufletuk. *Ukrainian Chem. Bull.,* 8, 151 (2000).

[13]   L.M. Pisarenko, O.T. Kasaikina. *Russ Chem Bull*, 3, 419 (2002).

[14]   L.M. Pisarenko, V.G. Kondratovich, O.T. Kasaikina. *Russ Chem Bull*, 10, 2110 (2004).

[15]   Y.Marcus. *Ion salvation*. Chichester, etc.: Wiley. – 1985. – 306p.

Chapter 21

MOLECULAR DESIGN AND REACTIVITY OF THE 1-HYDROXYCYCLOHEXYL HYDROPEROXIDE - ALK4NBR COMPLEXES

N.A. Turovskij[qq,1], E.V. Raksha[1], E.N. Pasternak[1], I.A. Opeida[2], and G.E. Zaikov[rn,3]

[1]Donetsk National University, Donetsk, Ukraine
Ukrainian-American Laboratory of Computational Chemistry, Kharkov, Ukraine, Jackson, U.S.A.
[2]Institute of Physico-Organic and Coal Chemistry of the National Academy of Sciences of Ukraine, R. Luxemburg 70, 83114 Donetsk, Ukraine
[3]Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russian Federation

ABSTRACT

Chemically activated 1-hydroxycyclohexyl hydroperoxide decomposition in the presence of ammonium salts is proposed to proceed through the complexation stage. Complex structure and reactivity have been investigated by molecular modelling methods. Kinetics of the chemically activated hydroperoxide decomposition in the presence of quaternary ammonium salts (Et4NBr, Pr4NBr, Bu4NBr, and Hex4NBr) has been studied. The correlation between reactivity and structural characteristics of ammonium cations was found.

Keywords: *molecular modelling, cyclohehanone hydroperoxides, quaternary ammonium salts, chemical activation, complexation.*

[qq]Universitetskaya str. 24, 83055, Ukraine E-mail: turov@dongu.donetsk.ua;
[rn]4 Kosygina, 117334 Moscow, Russian Federation, E-mail: chembio@sky.chph.ras.ru.

INTRODUCTION

Peroxides and hydroperoxides are widely used as initiators as well as components of binary initiating systems in the processes of vinyl monomers polymerization, polymers modification [1-3], and oxidation of organic substances by molecular oxygen [4, 5]. Initiating systems on the base of quaternary ammonium bromides were found to be the most effective in the case of the liquid phase oxidation of isopropyl benzene by O_2 [5]. 1-hydroxycyclohexyl hydroperoxide - Et_4NBr system initiates the reaction of liquid phase isopropyl benzene oxidation at 308–340 K [6] while the hydrocarbon oxidation in the presence of only one component of the binary system did not occur. The present work presents the study of 1-hydroxycyclohexyl hydroperoxide decomposition activated by the tetraalkylammonium bromides to investigate the role of ammonium salt cation in the process of chemical activation of peroxide bond.

EXPERIMENTAL

1-hydroxycyclohexyl hydroperoxide has been prepared from cyclohexanone and H_2O_2 in anhydrous ether according with [7]. Tetraalkylammonium bromides (Et_4NBr, Pr_4NBr, and Bu_4NBr) were recrystallized from the saturated acetonitrile solution by addition of diethyl ether excess. The solvent (acetonitrile) purity was controlled by electrical conductivity value, which was within $(8.5 \pm 0.2) \cdot 10^{-6}$ Om^{-1} sm^{-1} at 303 K. Reactions were carried out in the glass-soldered ampoules in argon atmosphere. Hydroperoxide kinetic concentration was controlled by the iodometric titration with potentiometric fixation of the equivalent point.

CALCULATION METHODS

Quantum chemical calculations of hydroperoxides molecules and corresponding radicals were carried out by AM1 semiempirical method implemented in MOPAC package [8]. The RHF method was applied to the calculation of the wave function. Optimization of structure parameters of hydroperoxide and hydroperoxide complexes was carried out by Eigenvector Following procedure. The molecular geometry parameters were calculated with boundary gradient norm 0.01. Solvent effect was considered in COSMO approximation [9].

RESULTS AND DISCUSSION

It was shown recently that cyclohexanone peroxides decomposition in the presence of Et_4NBr proceeds with lower activation barrier as compared with thermolysis. This fact can be explained by the complexation in the studied system [6]. We assume that the activation extent of the peroxide bond in the complex correlates with hydroperoxide reactivity in the reaction of radical decomposition. Thus we investigated the molecular design and reactivity of the complexes in the system 1-hydroxycyclohexyl hydroperoxide – Alk_4NBr.

Molecular Design of the 1-Hydroxycyclohexyl Hydroperoxide - Alk$_4$NBr Complex

To obtain the structure information the molecular modelling of the ROOH-Alk$_4$NBr ion-molecular complexes has been carried out for the case of Et$_4$NBr. In contrast to the aralkyl hydroperoxides (like isopropylbenzene hydroperoxide) the molecule of 1-hydroxycyclohexyl hydroperoxide does not contain the aromatic ring but there is the hydroxide group OH in their structure that also can participate in the intermolecular hydrogen bonds formation. We assume the model of complex formation with combined action of cation and anion (Figure 1) such as previously proposed model of substrate separated ion pair (SubSIP) [10, 11].

Formation of such type associate is accompanied by considerable conformation changes of the hydroperoxide fragment. Association between hydroperoxide molecule and the salt ions occurs by the intermolecular hydrogen bonds formation. It is confirmed by charge increasing on the hydrogen atoms of the corresponding bonds C-H$_3$, O-H$_1$, and O-H$_2$ and elongation of these bonds from 1.11 Å to 1.17 Å and from 0.96 Å to 1.08 Å correspondingly. Calculations in COSMO approximation show that the electron density transfer from bromide-anion to the hydroperoxide fragment is lower in the case of solvent effect taken into account (Table 1).

Stage determining the rate of the hydroperoxide decomposition is that of O-O bond cleavage. Thus the reaction activation energy will be determined by the energy of peroxide bond homolytic decomposition. Some possible elementary stages of the complex decomposition with the free radical formation are listed in Table 2.
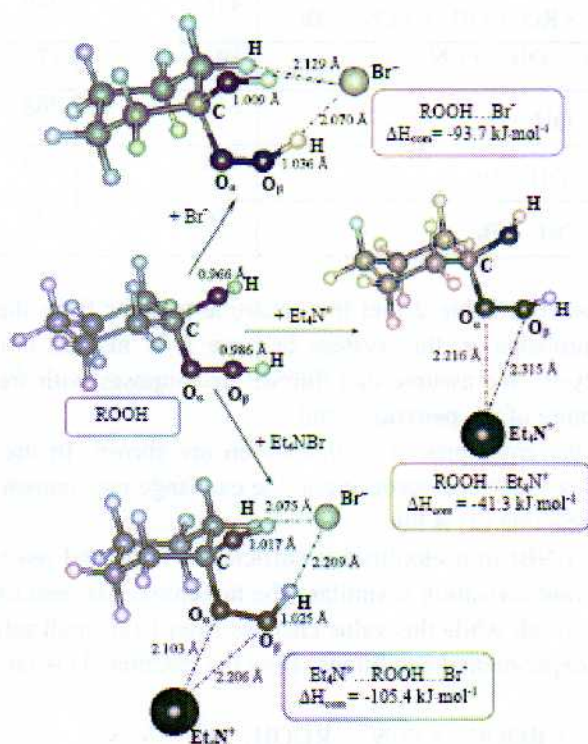

Figure 1. Complexes of 1-hydroxycyclohexyl hydroperoxide with tetraethylammonium bromide.

Table 1. Electron and stereochemical characteristics of COOH-fragment in ROOH – Et₄NBr complexes

parameters	ROOH	$Et_4N^+...ROOH...Br^-$	$ROOH...Br^-$	ROOH...
$q_{O\alpha}$, e	- 0.18	- 0.24	- 0.18	- 0.20
$q_{O\beta}$, e	- 0.20	- 0.26	- 0.29	- 0.23
q_{H1}, e	0.20	0.25	0.25	0.22
q_{H2}, e	0.22	0.27	0.27	0.04
q_{H3}, e	0.10	0.17	0.11	0.10
$\angle CO_\alpha O_\beta H$	90.8	33.4	68.3	77.5
q_{Br}^-	-	- 0.81	- 0.85	-

Table 2. Heats of some elementary stages of ROOH – Et₄NBr complex decomposition

Reaction	ΔH^0, kJ mol^{-1}	
	gas phase	acetonitrile
$ROOH \rightarrow RO^· + ^·OH$	148	151
$Et_4N^+...ROOH...Br^- \rightarrow RO^· + ^·OH + Et_4N^+ + Br^-$	481	239
$Et_4N^+...ROOH...Br^- \rightarrow RO^· + ^·OH + Et_4NBr$	65	108
$Et_4N^+...ROOH...Br^- \rightarrow RO^- + ^·OH + Et_4N^+ + Br^·$	615	354
$Et_4N^+...ROOH...Br^- \rightarrow RO^· + OH^- + Et_4N^+ + Br^·$	435	249
$ROOH...Et_4N^+ \rightarrow RO^· + ^·OH + Et_4N^+$	192	179
$ROOH...Br^- \rightarrow RO^· + ^·OH + Br^-$	242	208
$ROOH...Br^- \rightarrow RO^- + ^·OH + Br^·$	188	219
$ROOH...Br^- \rightarrow RO^· + OH^- + Br^·$	376	323

It can be seen from the Table 2 that the electrone transfer from the bromide ion to the peroxide bond is improbable in this system because it is needed more energy inputs as compared with homolysis. We assume that SubSIP decomposes with free radicals formation due to homolytical rupture of the peroxide bond.

On the Figure 1 the enthalpies of complexation are shown. In the case of SubSIP we assume that the complex is formed according to the exchange mechanism (1) while possibility of the threemolecular reaction (2) is low.

Solubility of the Et₄NBr in acetonitrile is sufficiently high, and reactivity of the ions and ion pairs in peroxide bond activation is similar. The threemolecular reaction (2) determines the second reaction order on salt while this value changes from 1 (at small salt concentrations) to 0 (at salt abundance) in experimental conditions. Thus the reaction (1) is rather preferable.

$$Et_4N^+...Solv...Br^- + ROOH \rightarrow Et_4N^+...ROOH...Br^- + Solv \qquad (1)$$

$$(\Delta H_{r(2)} = - 53.7 \, kJ \cdot mol^{-1}) \qquad (2)$$

$$Et_4N^+ + ROOH + Br^- \rightarrow Et_4N^+...ROOH...Br$$

$$(\Delta H_{r(3)} = -88.1 \text{ kJ}\cdot\text{mol}^{-1})$$

Corresponding models like $Et_4N^+...ROOH...Br^-$ were obtained for tetraalkylammonium salts (Pr_4NBr, Bu_4NBr, и Hex_4NBr). Changes in peroxide bond energy (i.e. total of electronic and nuclear energies of two-center term O-O atom pair) can be suggested as extent of the peroxide bond activation. Stable peroxide structure has the lowest O-O bond energy (-12.08 eV for free hydroperoxide) and less stable (or activated) peroxide conformation has the highest one (-11.78 eV for complex $Et_4N^+...ROOH...Br^-$). Difference between energy of stable and activated peroxide structure increases in the catalyst row: Hex_4NBr, Bu_4NBr, Pr_4NBr, and Et_4NBr indicating weakening of the O-O bond in the ROOH-Alk_4NBr complex. From this point of view the O-O bond activation in the case of $Et_4N^+...ROOH...Br^-$ is the highest and in complex with Hex_4NBr is the lowest. This suggestion is in correspondence with experimental data.

Kinetic Features of the Activated Hydroperoxide Decomposition

Reaction of 1-hydroxycyclohexyl hydroperoxide (ROOH) decomposition activated by the tetraalkylammonium bromides (Alk_4NBr) has been investigated at $323 - 353$ K under conditions of ammonium salts abundance ($[ROOH]_0 = 5\cdot10^{-3}$ mol·dm^{-3}, $[Alk_4NBr]_0 = 2.5\cdot10^{-2} - 1\cdot10^{-1}$ mol·dm^{-3}). Kinetics of ROOH activated decomposition on these conditions could be described by the first order reaction proceedings low. The reaction was carried out up to 50 % hydroperoxide conversion and the products did not effect on the reaction proceeding as kinetic curves anamorphouses are linear in the corresponding first order coordinates. The effective rate constant (k_{ef}, sec^{-1}) was found to be independent from the hydroperoxide initial concentration within $[ROOH]_0 = 2.5\cdot10^{-3} - 1\cdot10^{-2}$ mol·dm^{-3} and constant amount of Alk_4NBr ($5\cdot10^{-2}$ mol·dm^{-3}). Nonlinear character of the dependence of reaction rate effective constants from the ammonium salt initial concentration (Figure 2) in the present conditions points out onto the occurrence of complexation stage between the ROOH and Alk_4NBr. These facts are in an agreement with reaction scheme for the isopropyl benzene hydroperoxide activated decomposition recently proposed [12]. Thermolysis contribution into the total reaction rate the ROOH activated decomposition was found to be negligibly small because the thermal decomposition rate constant [6] was two orders lower then corresponding k_{ef} values.

Some experiments were carried out under conditions of ROOH excess as compared with salts concentration ($[Alk_4NBr]_0 = 5\cdot10^{-3}$ mol·dm^{-3}, $[ROOH]_0 = 5\cdot10^{-2}$ mol·dm^{-3}) at 323 K. Even at present concentration ratio of ROOH and Alk_4NBr the rate of hydroperoxide activated decomposition is several orders higher then ROOH thermolysis rate. The Br$^-$ concentration during reaction proceeding is unaltered. These facts point out onto catalytic character of Alk_4NBr action in the process. Catalytic scheme of the hydroperoxide decomposition is supported also in works [13, 14] in which it was noted that O-O bond cleavage in the hydroperoxide – catalyst complex proceeds homolytically, catalyst is not consumed and deactivated in the system.
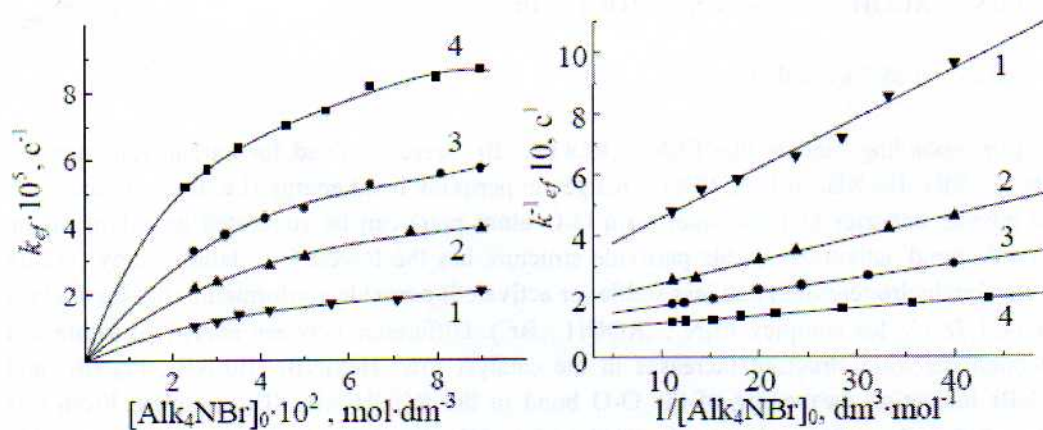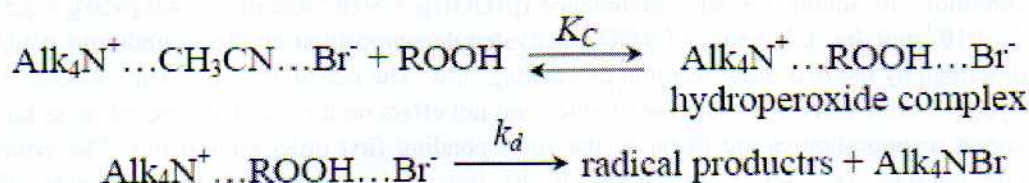
Figure 2. Dependence of k_{ef} from the catalyst initial concentration in the direct (a) and inverse (b) coordinates. [ROOH]0 = 5.0·10-3 mol·dm-3, 333 K, 1 – Hex4N+, 2 – Bu4N+, 3 – Pr4N+, 4 – Et4N+.

The kinetic scheme is proposed for the chemically activated ROOH decomposition. It includes the complexation stage between ROOH and salts ions as well as stage of the complex-bonded hydroperoxide decomposition with catalyst regeneration:

k_{ef} dependence on the salt concentration can be expressed by the relationship (3):

$$Alk_4N^+...CH_3CN...Br^- + ROOH \underset{}{\overset{K_C}{\rightleftharpoons}} \quad Alk_4N^+...ROOH...Br^-$$
$$\text{hydroperoxide complex}$$

$$Alk_4N^+...ROOH...Br^- \xrightarrow{k_d} \text{radical productrs} + Alk_4NBr$$

$$\frac{1}{k_{ef}} = \frac{1}{k_d K_C [Alk_4NBr]} + \frac{1}{k_d} \tag{3}$$

The dependence of k_{ef} on Alk4NBr concentration is linear in double inverse coordinates (Figure 2). It is in the agreement with the proposed kinetic scheme. The values of rate constants of complex-bonded peroxide decomposition (k_d) obtained for the investigated salts decrease in the following order: $Et_4N^+ > Pr_4N^+ > Bu_4N^+ > Hex_4N^+$. The values of equilibrium constants of complexation between ROOH and Alk4NBr ions change similarly (Table 3).

Isokinetic relationship between complexation parameters in the system leads to the insignificant changes in free energy of complexation for different alkyl substituent in ammonium cation. Considering the intermolecular bonds energy the strongest complex is formed between hydroperoxide and Et4NBr, the weakest - in the case of Hex4NBr (see the corresponding ΔH_{com} values in Table 3). The reactivity of complex-bonded ROOH also decreases with increasing of alkyl substituent size. Isokinetic relationship for the obtained

activation parameters points out upon the unified mechanism of ROOH - Alk$_4$NBr complex decomposition.

Table 3. Kinetic parameters of 1-hydroxycyclohexyl hydroperoxide decomposition in the presence of tetraalkylammonium bromides

parameters	T, K	ROOH + Et$_4$NBr	ROOH + Pr$_4$NBr	ROOH + Bu$_4$NBr	ROOH + Hex$_4$NBr
$k_d \cdot 10^4$, sec^{-1}	333	1.14 ± 0.04	0.8 ± 0.1	0.59 ± 0.06	0.34 ± 0.01
	343	2.5 ± 0.1	1.80 ± 0.09	1.51 ± 0.04	0.97 ± 0.02
	353	5.1 ± 0.2	4.20 ± 0.09	3.48 ± 0.08	2.40 ± 0.06
K_C, dm^{3}mol^{-1}	333	36 ± 2	28 ± 3	23 ± 2	18 ± 3
	343	29 ± 2	24 ± 1	20 ± 1	16 ± 2
	353	23 ± 1	20 ± 1	18 ± 2	15 ± 2
E_a, kJmol^{-1}	333- 353	73 ± 1	81 ± 2	87 ± 3	96 ± 2
lg$A$, (A, c^{-1})		7.5 ± 0.6	8.6 ± 0.3	9.4 ± 0.2	10.5 ± 0.3
ΔH_{com}, kJmol^{-1}		-20 ± 1	-16 ± 2	-12 ± 2	-9 ±1
ΔS_{com}, Jmol^{-1}K^{-1}		-30 ± 4	-21 ± 5	-10 ± 4	-3 ± 3

Changes of the peroxide bond activation in the complex in the case of different ammonium cations point out the role of steric factor at the stage of complex formation as well as at the formation of their decomposition transition state. In the simplest case the own volume of the investigated cations could describe the steric effect. A good correlation between activation parameters of the complex decomposition and calculated values of Van-der-Waals volumes of cations has been obtained (Figure 3). V_{VDW} values for the tetraalkylammonium cations were calculated in HyperChem package. Calculated values are in agreement with corresponding own volumes of cations listed in [15]. Linear relationship has been observed between the complex heat of formation - ΔH^0_f and experimental activation parameters - $\Delta H^{\neq}$ (Figure 4).

Obtained experimental facts have shown that the salt cation participates both in complexation stage and in stage of complex ROOH - Alk$_4$NBr decomposition. Ammonium cation has the regulating action upon the catalytic reactivity of the halide-anion in the reaction of catalytic decomposition of the 1-hydroxycyclohexyl hydroperoxide in the presence of Alk$_4$NBr. Thus the cation structure influences on the reactivity of the hydroperoxide complex and on the extent of peroxide bond activation. The molecular modeling of the hydroperoxide-catalyst reactive complex can be used to preliminarily predict the reactivity of the system.
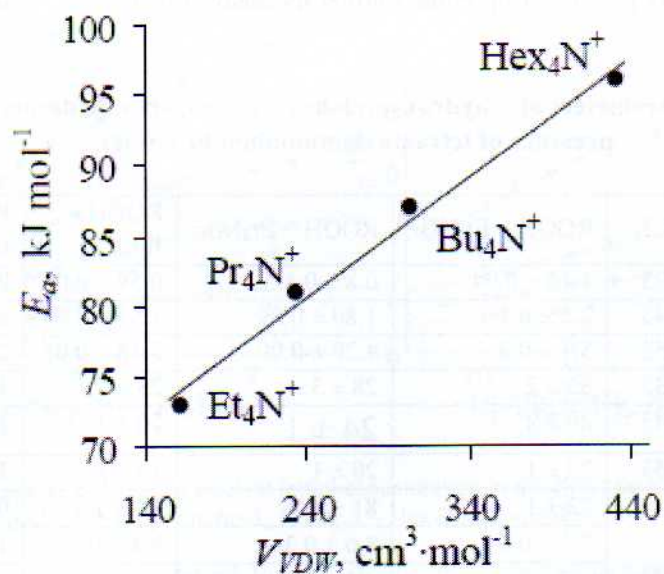
Figure 3. Relationship between activation parameters of the complex decomposition and Van-der-Waals volume of the tetraalkylammonium cations.
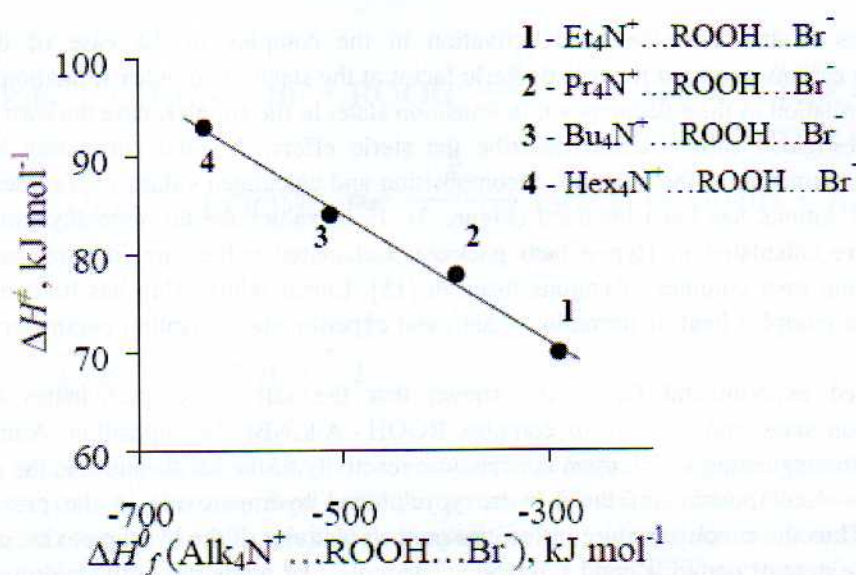

Figure 4. Relationship between the complex heat of formation ($\Delta H0f$) and experimental activation parameters ($\Delta H\neq$).

CONCLUSIONS

Summarizing, obtained experimental facts have shown that the chemical activation of the peroxide bond is observed in the presence of Alk_4NBr. The kinetic parameters of the hydroperoxide catalytic decomposition have been obtained for the Et_4NBr, Pr_4NBr, Bu_4NBr, and Hex_4NBr. Catalysis of the 1-hydroxycyclohexyl hydroperoxide decomposition has been shown to occur through accompanied action of the ammonium salt cation and anion.

REFERENCES

[1]   E.T. Denisov, T.G. Denisova, T.S. Pokidova. *Handbook of Free Radical Initiators*. John Wiley and Sons Inc.: Hoboken, New Jersey, 2003. - 879 p.

[2]   N.A. Turovskij, I.O. Opeida, O.V. Kush, E.L. Baranovskij. *J. Appl. Chem.* 77, 1887 (2004).

[3]   C.J. Perez, E.M. Valles, M.D. Failla. *Polymer,* 46, 725 (2005).

[4]   I.A. Opeida, N.M. Zalevskaya, E.N. Turovskaya. *Kinetika i Kataliz,* 45, 776 (2004).

[5]   I.A. Opeida, N.M. Zalevskaya, E.N. Turovskaya, U.I. Sobka, *Petroleum Chemistry*, 42, № 6. 460 (2002).

[6]   M.A. Turovskyj, I.A. Opeida, E.N. Turovskaya, O.V. Raksha, N.O. Kuznetsova, G.E. Zaikov. *Oxid. Commun.,* 29, 249 (2006).

[7]   N.A. Milas, S.A. Harris, P.C. Panagiotacos. *J.Am.Chem.Soc.,* 61, No 9 2430 (1939).

[8]   J.J.P. Stewart. *MOPAC 2000.00 Manual;* Fujitsu Limited: Tokyo: Japan, 1999.

[9]   A.Klamt. *J.Chem. Soc. Perkin Trans.,* №2 799 (1993).

[10]   M.A. Turovskyj, I.O. Opeida O.M. Turovskaya, O.V. Raksha, N.O. Kuznetsova, and G.E. Zaikov. *Order and Disorder in Polymer Reactivity.* Howell New York: Nova Science Publishers, Inc.-2006. - pp. 37-51.

[11]   N.A. Turovskij, S.Yu. Tselinskij, Yu.E. Shapiro, A.R. Kal'uskij. *Teor. Eksp. Khim.,* 28, №4. 320 (1992).

[12]   M.A. Turovskyj, A.M. Nikolayevskyj, I.A. Opeida, V.N. Shufletuk. *Ukrainian Chem. Bull.,* 8, 151 (2000).

[13]   L.M. Pisarenko, O.T. Kasaikina. *Russ Chem Bull*, 3, 419 (2002).

[14]   L.M. Pisarenko, V.G. Kondratovich, O.T. Kasaikina. *Russ Chem Bull*, 10, 2110 (2004).

[15]   Y.Marcus. *Ion salvation.* Chichester, etc.: Wiley. – 1985. – 306p.