POLYMER PRODUCTS and CHEMICAL PROCESSES

Techniques, Analysis and Applications

Editors
Richard A. Pethrick, PhD, DSc
Eli M. Pearce, PhD
Gennady E. Zaikov, DSc

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SECTION II: SUPRAMOLECULAR DECOMPOSITION OF THE ARALKYL HYDROPEROXIDES IN THE PRESENCE OF ET$_4$NBR

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11.1   INTRODUCTION

Kinetics of the aralkyl hydroperoxides decomposition in the presence of tetraethylammonium bromide (Et$_4$NBr) has been investigated. Et$_4$NBr has been shown to reveal the catalytic properties in this reaction. The use of Et$_4$NBr leads to the decrease up to 40 kJ·mol^{-1} of the hydroperoxides decomposition activation energy. The complex formation between hydroperoxides and Et$_4$NBr has been shown by the kinetic and ^{1}H NMR spectroscopy methods. Thermodynamic parameters of the complex formation and kinetic parameters of complex-bonded hydroperoxides have been estimated. The model of the reactive hydroperoxide – catalyst complex structure has been proposed. Complex formation is accompanied with hydroperoxide chemical activation.

Quaternary ammonium salts *exhibit high catalytic activity in* radical-chain reactions *of hydrocarbons liquid phase oxidation by O$_2$* [1, 2]. Tetraalkylammonium halides accelerate radical decomposition of hydroperoxides [3, 4] that are primary molecular products of *hydrocarbons oxidation reaction. Reaction rate of the hydroperoxides decomposition in the presence of* quaternary ammonium salts is determined by the nature of the salt anion [4] as well as cation [5]. The highest reaction rate of the *tert*-butyl hydroperoxide and cumene hydroperoxide decomposition has been observed in the case of iodide anions as compared with bromide and chloride ones [4]. *Among* tetraalkylammonium bromides tetraethylammonium

one possesses the highest reactivity in the reaction of catalytic decomposition of 1-hydroxy-cyclohexyl hydroperoxide [5] and lauroyl peroxide [6]. Benzoyl peroxide – tetraalkylammonium bromide binary systems were found to be the most efficient in the liquid-phase oxidation of isopropylbenzene *although corresponded iodides revealed* the highest reactivity in the reaction of benzoyl peroxide decomposition [1, 7, 8].

Thus, the elucidation of the reaction pathways requires taking into account many parameters and makes the investigation of other peroxide compounds reactivity a justified task. To get more information on the reaction scope and limitations, we studied aralkyl hydroperoxides reactivity in the presence of quaternary ammonium salt. The analysis of the data obtained earlier enabled us to consider tetraethylammonium bromide the *appropriate* catalyst to study aralkyl hydroperoxides reactivity.

The present paper reports on new results of kinetic investigations of aralkyl hydroperoxides catalytic decomposition in the presence of tetraethylammonium bromide as well as the results of AM1/COSMO molecular modeling of hydroperoxide – catalyst interactions. Aralkyl hydroperoxides under consideration are: dimethylbenzylmethyl hydroperoxide ($PhCH_2C(CH_3)_2OOH$), 1,1-dimethyl-3-phenylpropyl hydroperoxide ($Ph(CH_2)_2C(CH_3)_2OOH$), 1,1-dimethyl-3-phenylbutyl hydroperoxide ($PhCH(CH_3)CH_2C(CH_3)_2OOH$), 1,1,3-trimethyl-3-(*p*-methylphenyl)butyl hydroperoxide (p-$CH_3PhC(CH_3)_2CH_2C(CH_3)_2OOH$), *p*-carboxyisopropylbenzene hydroperoxide ((p-COOH)-$phC(CH_3)_2OOH$). *Tert*-butyl hydroperoxide (($CH_3)_3COOH$) and cumene hydroperoxide ($Ph(CH_3)_2COOH$) were also used in spectroscopic investigations.

11.2   EXPERIMENTAL METHODS

Aralkyl hydroperoxides (ROOH) were purified according to Ref. [9]. Their purity (98.9%) was controlled by iodometry method. Tetraalkylammonium bromide (Et_4NBr) was recrystallized from acetonitrile solution by addition of diethyl ether excess. The salt purity (99.6%) was determined by argentum metric titration with potentiometric fixation of the equivalent point. Tetraalkyl ammonium bromide was stored in box dried with P_2O_5. Acetonitrile (CH_3CN) was purified according to Ref. [10]. Its purity was

controlled by electro conductivity χ value, which was within $(8.5 \pm 0.2) \times 10^{-6}$ W^{-1} cm^{-1} at 303 K.

Reactions of the hydroperoxides catalytic decomposition were carried out in glass-soldered ampoules in argon atmosphere. To control the proceeding of hydroperoxides thermolysis and their decomposition in the presence of Et$_4$NBr the iodometric titration with potentiometric fixation of the equivalent point was used.

^{1}H NMR spectroscopy investigations of the aralkyl hydroperoxides and hydroperoxide – Et$_4$NBr solutions were carried out at equimolar components ratio ([ROOH] = [Et$_4$NBr] = 0.1 mol dm^{-3}) in D$_3$CCN at 294 K. The ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) using TMS as an internal standard.

Dimethylbenzylmethyl hydroperoxide (PhCH$_2$C(CH$_3$)$_2$OOH) ^{1}H NMR (400 MHz, acetonitrile-d$_3$): δ = 1.11 (s, 6 H, CH$_3$), 2.84 (s, 2 H, CH$_2$), 7.20–7.31 (m, 5H, H-aryl), 8.88 (s, 1 H, -COOH) ppm.

1,1-dimethyl-3-phenylpropyl hydroperoxide (Ph(CH$_2$)$_2$C(CH$_3$)$_2$OOH) ^{1}H NMR (400 MHz, acetonitrile-d$_3$): δ = 1.22 (s, 6 H, CH$_3$), 1.80 (t, J = 8.0 Hz, 2 H, Ph-CH$_2$CH$_2$-), 2.64 (t, J = 8.0 Hz, 2 H, Ph-CH$_2$CH$_2$-), 7.15–7.30 (m, 5 H, H-aryl), 8.86 (s, 1 H, -COOH) ppm.

1,1,3-trimethyl-3-(p-methylphenyl)butyl hydroperoxide (*p*-CH$_3$PhC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$OOH) ^{1}H NMR (400 MHz, acetonitrile-d$_3$): δ = 0.86 (s, 6 H, -C(CH$_3$)$_2$OOH), 1.34 (s, 6 H, -phC(CH$_3$)$_2$-), 2.03 (s, 2 H, -CH$_2$-), 2.29 (s, 3 H, CH$_{3-}$h-), 7.10 (d, J = 8.0 Hz, 2 H, H-aryl), 7.30 (d, J = 8.0 Hz, 2 H, H-aryl), 8.51 (s, 1 H, -COOH) ppm.

p-carboxyisopropylbenzene hydroperoxide ((*p*-COOH) PhC(CH$_3$)$_2$OOH) ^{1}H NMR (400 MHz, acetonitrile-d$_3$): δ = 1.53 (s, 6 H, -C(CH$_3$)$_2$OOH), 7.57 (d, J = 8.0 Hz, 2 H, H-aryl), 7.98 (d, J = 8.0 Hz, 2 H, H-aryl) ppm. Signals from -COOH and -C(O)OH exchaneable protons were not observed.

Tert-butyl hydroperoxide ((CH$_3$)$_3$COOH) ^{1}H NMR (400 MHz, acetonitrile-d$_3$): δ = 1.18 (s, 6 H, –CH$_3$), 8.80 (s, 1 H, -COOH) ppm.

Cumene hydroperoxide (Ph(CH$_3$)$_2$COOH) ^{1}H NMR (400 MHz, acetonitrile-d$_3$): δ = 1.52 (s, 6 H, -CH$_3$), 7.27 (t, J = 8.0 Hz, 1 H, H-aryl), 7.36 (t, J = 8.0 Hz, 2 H, H-aryl), 7.47 (d, J = 8.0 Hz, 2 H, H-aryl), 8.95 (s, 1 H, -COOH) ppm.

Tetraethylammonium bromide (Et$_4$NBr) ^{1}H NMR (400 MHz, acetonitrile-d$_3$): δ = 1.21 (t, *J* = 8.0 Hz, 12 H, –CH$_3$), 3.22 (q, *J* = 8.0 Hz, 8 H, -CH$_2$) ppm.

Quantum chemical calculations of the equilibrium structures of hydroperoxides molecules and corresponding radicals as well as tetraethylammonium bromide and ROOH – Et$_4$NBr complexes were carried out by AM1 semiempirical method implemented in MOPAC2009™ package [11]. The RHF method was applied to the calculation of the wave function. Optimization of hydroperoxides structure parameters was carried out by Eigenvector following procedure. The molecular geometry parameters were calculated with boundary gradient norm 0.01. The nature of the stationary points obtained was verified by calculating the vibrational frequencies at the same level of theory. Solvent effect in calculations was considered in the COSMO [12] approximation.

11.3   RESULTS AND DISCUSION

Kinetics of the aralkyl hydroperoxides decomposition in the presence of the Et$_4$NBr. Kinetics of the aralkyl hydroperoxides decomposition in the presence of Et$_4$NBr has been studied under conditions of ammonium salts excess in the reaction mixture. Reactions were carried out at 373–393 K, hydroperoxide initial concentration was 5×10^{-3} mol dm^{-3}, Et$_4$NBr concentration in the system was varied within $2 \times 10^{-2} – 1.2 \times 10^{-1}$ mol dm^{-3}. Hydroperoxides decomposition kinetics could be described as the first order one. The reaction was carried out up to 80% hydroperoxide conversion and the products did not affect the reaction proceeding, as the kinetic curves anamorphous were linear in the corresponding first order coordinates.

The reaction effective rate constant (k_{ef}, s^{-1}) was found to be independent on the hydroperoxide initial concentration within [ROOH]$_0$ = 1×10^{-3} – 8×10^{-3} mol dm^{-3} at 383 K, however, Et$_4$NBr amount was kept constant (5×10^{-2} mol dm^{-3}) in these studies. This fact allows one to exclude the simultaneous hydroperoxides reactions in the system under consideration.

Typical nonlinear k_{ef} dependences on Et$_4$NBr concentration at the constant hydroperoxide initial concentration are presented on Fig. 1a. The

nonlinear character of these dependences allows us to assume that an intermediate adduct between ROOH and Et_4NBr is formed in the reaction of ROOH decomposition in the presence of Et_4NBr. These facts conform to the kinetic scheme of activated cumene hydroperoxide and hydroxycyclohexyl hydroperoxide decomposition that has been proposed *previously* [3–5, 13].
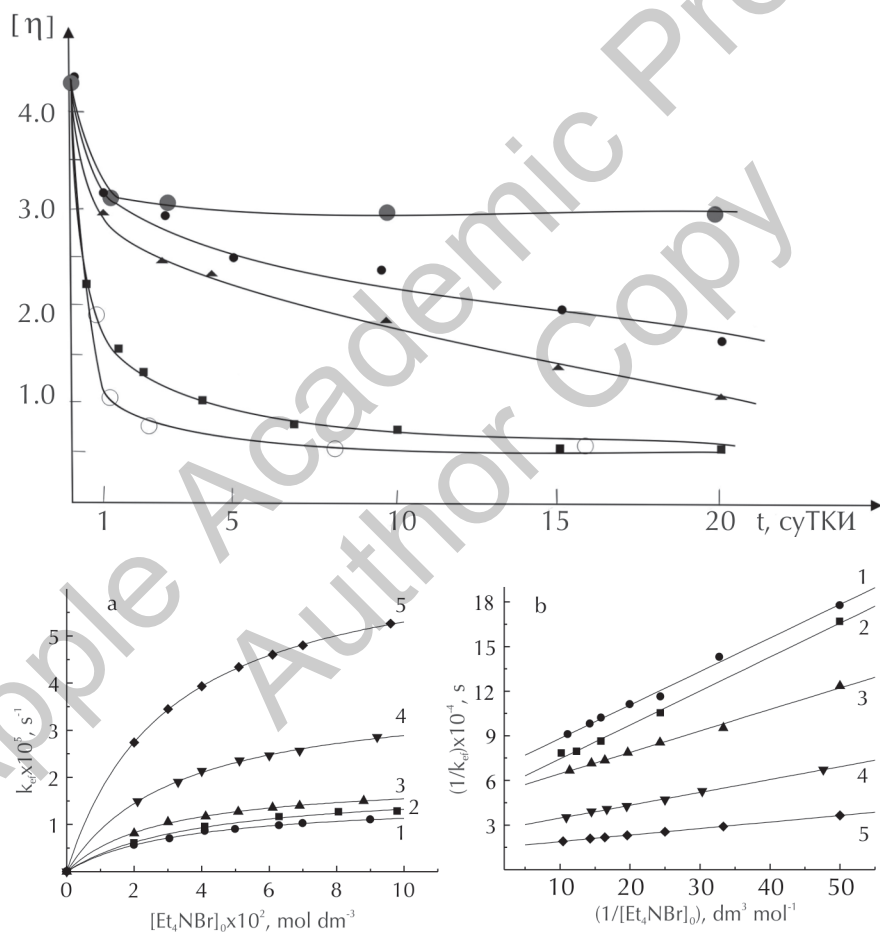
FIGURE 1   Dependence of k_{ef} on the Et_4NBr initial concentration in direct (a) and inverse (b) coordinates ([ROOH]$_0$ = 5.0×10^{-3} mol dm^{-3}, 383 K).
1 – PhCH$_2$C(CH$_3$)$_2$OOH; *2* – Ph(CH$_2$)$_2$C(CH$_3$)$_2$OOH; *3* – PhCH(CH$_3$)CH$_2$C(CH$_3$)$_2$OOH;
4 – *p*-CH$_3$PhC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$OOH; *5* – *p*-HOC(O)PhC(CH$_3$)$_2$OOH

The hydroperoxide – Et_4NBr kinetic mixtures were subjected to ^1H NMR analysis in order to confirm the complex formation between ROOH and Et_4NBr. Experiment was carried out at 298 K when the rates of the hydroperoxides thermolysis as well as activated decomposition were negligibly small. Fig. 2a presents ^1H NMR spectra of the $p\text{-}CH_3PhC(CH_3)_2CH_2C(CH_3)_2OOH$ in CD_3CN. Chemical shift of the hydroperoxide moiety of the compound corresponds to the signal at 8.51 ppm. Addition of the Et_4NBr equivalent amount to the solution causes the dislocation of this signal by 0.51 ppm towards weak *magnetic fields (Fig. 2b)*.
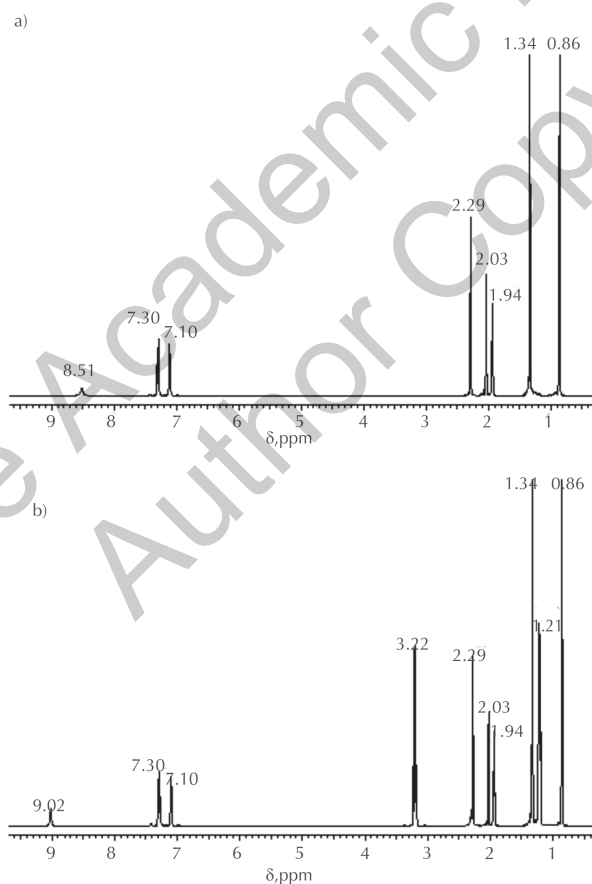
FIGURE 2 ^1H NMR spectra of the $p\text{-}CH_3PhC(CH_3)_2CH_2C(CH_3)_2OOH$ (*a*) and mixture of the $p\text{-}CH_3PhC(CH_3)_2CH_2C(CH_3)_2OOH$ – Et_4NBr (*b*) in CD_3CN at 298 K [ROOH] = [Et_4NBr] = 1.0×10^{-1} mol dm^{-3}.

The similar effect was also observed for the rest investigated hydroper-oxides. Thus presence of the Et_4NBr in the solution causes the downfield shifts of the COOH moiety signal by 0.40–0.76 ppm as compared to the chemical shift of the hydroperoxide (Table 1) depending on the hydroper-oxide structure. This effect is typical for the hydroperoxide complexation processes.

TABLE 1 ^1H NMR spectra parameters of the hydroperoxides and the hydroperoxide – Et_4NBr mixture in D_3CCN at 294 K.

ROOH	δ, ppm (ROO–H)		
	ROOH	**ROOH + Et₄NBr**	**Δδ**
$PhCH_2C(CH_3)_2OOH$	8.88	9.64	0.76
p-$CH_3PhC(CH_3)_2CH_2C(CH_3)_2OOH$	8.51	9.02	0.51
$(CH_3)_3COOH$	8.80	9.20	0.40
$Ph(CH_3)_2COOH$	8.95	9.60	0.65

Chemically activated by Et_4NBr aralkyl hydroperoxides decomposi-tion is suggested to proceed in accordance with following kinetic scheme (1). It includes the stage of a complex formation between the hydroperox-ide molecule and Et_4NBr ions as well as the stage of complex – bonded hydroperoxide decomposition.

$$ROOH + Et_4NBr \xrightleftharpoons{K_C} [complex] \xrightarrow{k_d} products \qquad (1)$$
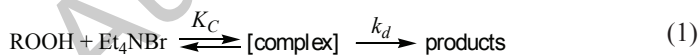
where K_C – *equilibrium* constant of the complex formation ($dm^3\ mol^{-1}$), and k_d – rate constant of the complex decomposition (s^{-1}).

As the kinetic parameters of hydroperoxides decomposition are in-fluenced by the nature of the salt anion [4] as well as cation [5, 6] we assume the model of ROOH-Et_4NBr complex formation with combined action of cation and anion. The hydroperoxides thermolysis *contribution* to the overall reaction rate of the ROOH activated decomposition is neg-ligibly small because thermolysis rate constants [14] are less by an order of magnitude then correspondent k_{ef} values. Using a kinetic model for the generation of active species (Scheme 1) and analyzing this scheme in a

quasi-equilibrium approximation one can obtain the following equation for the k_{ef} dependence on Et_4NBr concentration:

$$k_{ef} = \frac{K_C k_d [Et_4NBr]_0}{1 + K_C [Et_4NBr]_0} \tag{2}$$

To simplify further analysis of the data from Fig. 1a, let us transform Eq. (2) into the following one:

$$\frac{1}{k_{ef}} = \frac{1}{k_d K_C [Et_4NBr]_0} + \frac{1}{k_d} \tag{3}$$

Eq. (3) can be considered as equation of straight line in ($\frac{1}{k_{ef}}$, $\frac{1}{[Et_4NBr]_0}$) coordinates. The k_{ef} dependences on Et_4NBr concentration are linear in double inverse coordinates (Fig. 1b). Thus the experimentally obtained parameters with reasonable accuracy correspond to the proposed kinetic model and are in the quantitative agreement with this model if we assume that K_C and k_d have correspondent values listed in Table 2.

Values of equilibrium constants of complex formation (K_C) between ROOH and Et_4NBr estimated are within 21–34 dm^3 mol^{-1} (at 273–293 K) for the investigated systems. It should be noted that k_d values do not depend on the ROOH and Et_4NBr concentration and correspond to the *ultimate case when all hydroperoxide molecules are complex-bonded and further addition of* Et_4NBr to the reaction mixture will not lead to the increase of the reaction rate.

Estimated values of complex formation reaction enthalpies (ΔH_{com} in Table 2) are within $(-15 \div -22)$ kJ mol^{-1} and correspond to the hydrogen bond energy in weak interactions [15]. Considering the intermolecular bonds energy, the strongest complex is formed between Et_4NBr and hydroperoxide $PhCH(CH_3)CH_2C(CH_3)_2OOH$ (*see* the corresponding ΔH_{com} values in Table 2).
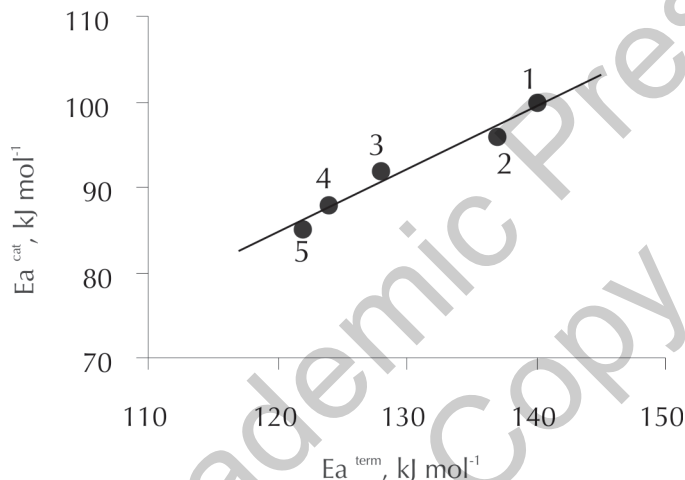
Symbate changes in thermolysis and catalytic decomposition activation energies are observed for considered aralkyl hydroperoxides (Fig. 3). Thus peroxide bond *cleavage causes the activation energy of the complex-bonded hydroperoxide decomposition.*

Hydroperoxide p-HO(O)CPhC(CH$_3$)$_2$OOH in which hydroperoxide moiety is directly connected with aromatic ring shows the highest reactivity. Aliphatic group *occurrence between* hydroperoxide moiety and aromatic ring leads to the *decrease of* hydroperoxide reactivity in the reaction of catalytic decomposition in the presence of Et$_4$NBr. According to the E_a values listed in Table 2 the reactivity of the complex-bonded hydroperoxides increases as follows: phCH$_2$C(CH$_3$)$_2$OOH < Ph(CH$_2$)$_2$C(CH$_3$)$_2$OOH < PhCH(CH$_3$)CH$_2$C(CH$_3$)$_2$OOH < (p-CH$_3$)PhC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$OOH < p-HO(O)CPhC(CH$_3$)$_2$OOH. Using of Et$_4$NBr allows decreasing by 40 kJ mol^{-1} the activation energy of hydroperoxides decomposition in acetonitrile.

TABLE 2 Kinetic parameters of aralkyl hydroperoxides decomposition activated by Et$_4$NBr.

ROOH[1]	T (K)	$k_d \times 10^5$ (s^{-1})	K_C (dm^3 mol^{-1})	E_a (kJ mol^{-1})	ΔH_{com} (kJ mol^{-1})
1	373	0.89 ± 0.04	27 ± 1	100 ± 3	-15 ± 1
	383	1.94 ± 0.09	23 ± 2		
	393	4.6 ± 0.2	21 ± 2		
2	373	1.52 ± 0.09	29 ± 3	96 ± 5	-17 ± 2
	383	3.75 ± 0.08	26 ± 1		
	393	7.3 ± 0.1	22 ± 1		
3	373	2.00 ± 0.06	34 ± 2	92 ± 4	-22 ± 2
	383	4.3 ± 0.1	27 ± 3		
	393	8.5 ± 0.1	24 ± 2		
4	373	3.85 ± 0.07	31 ± 3	88 ± 5	-19 ± 2
	383	9.07 ± 0.09	26 ± 2		
	393	17.3 ± 0.6	23 ± 2		
5	373	3.32 ± 0.06	37 ± 2	85 ± 1	-15 ± 1
	383	6.90 ± 0.05	33 ± 3		
	393	13.4 ± 0.4	29 ± 3		

[1]ROOH: 1 – $PhCH_2C(CH_3)_2OOH$; 2 – $Ph(CH_2)_2C(CH_3)_2OOH$; 3 – $PhCH(CH_3)CH_2C(CH_3)_2OOH$; 4 – $(p\text{-}CH_3)PhC(CH_3)_2CH_2C(CH_3)_2OOH$; 5 – $p\text{-}HO(O)CPhC(CH_3)_2OOH$

FIGURE 3   Symbate changes in thermolysis (E_a^{term}) and catalytic (E_a^{cat}) decomposition activation energies of aralkyl hydroperoxides (E_a^{term} values are listed elsewhere [14]).

Molecular modeling of the Et_4NBr activated hydroperoxides decomposition. On the base of experimental facts mentioned above we consider the salt anion and cation as well as acetonitrile (solvent) molecule participation when model the possible structure of the reactive hydroperoxide – catalyst complex. Model of the substrate separated ion pair (Sub-SIP) is one of the possible realization of join action of the salt anion and cation in hydroperoxide molecule activation. In this complex hydroperoxide molecule is located between cation and anion species. For the symmetric molecules such as benzoyl peroxide [16], lauroyl peroxide [17], and dihydroxydicyclohexyl peroxide [18] attack of salts ions is proposed to be along direction of the peroxide dipole moment and perpendicularly to the peroxide bond. Hydroperoxides are asymmetric systems, that is why different directions of ion's attack are possible. The solvent effect can be considered by means of direct inclusion of the solvent molecule to the complex structure. From the other hand methods of modern computer

chemistry allow estimation the solvent effect in continuum solvation models approximations [12, 19, 20].

Catalytic activity of the Et_4NBr in the reaction of the aralkyl hydroperoxides decomposition can be considered due to chemical activation of the hydroperoxide molecule in the salt presence. Activation of a molecule is the modification of its electronic and nucleus structure that leads to the increase of the molecule reactivity. The SubSIP structural model has been obtained for the complex between hydroperoxide molecule and Et_4NBr (Fig. 4).
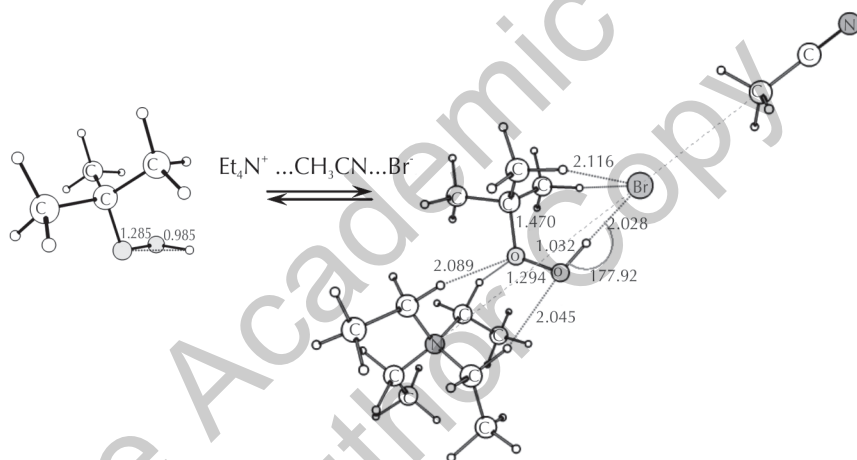
FIGURE 4   Typical structural model of the aralkyl hydroperoxides – Et_4NBr complexes with combined action of the cation, anion and the solvent molecule obtained by AM1/COSMO method.

Investigation of the SubSIP structural model properties for considered aralkyl hydroperoxides has revealed that complex formation was accompanied by following structural effects: (i) peroxide bond elongation on 0.02 Å as compared with nonbonded hydroperoxide molecules; (ii) considerable conformation changes of the hydroperoxide fragment; (iii) O–H bond elongation on 0.07 Å in complex as compared with nonbonded hydroperoxide molecules; (iv) rearrangement of electron density on the hydroperoxide group atoms.

Optimization of complex bonded hydroperoxides in COSMO approximation has shown that solvent did not effect on the character of structural changes in hydroperoxides molecules in the SubSIP complex. Only partial electron density transfer from bromide anion on to peroxide bond is less noticeable in this case.

Hydroperoxide moiety takes part in the formation of hydrogen bond (O)H…Br- in all obtained complexes. In all structures distances (O)H…Br- are within $2.03 \div 2.16$ Å, bond angle O-H…Br- is higher than 90° and within $170° \div 180°$ corresponding from aralkyl moiety in the hydroperoxide molecule. Thus the interaction type of bromide anion with hydroperoxide can be considered as hydrogen bond [15].

Associative interactions of a hydroperoxide molecule with Et_4NBr to the peroxide bond dissociation energy (D_{O-O}) decrease. D_{O-O} value for the aralkyl hydroperoxide was calculated according to Eq. (4) and for the ROOH – Et_4NBr complexes – according to Eq. (5).

$$D_{O-O} = (\Delta_f H°(RO^\bullet) + \Delta_f H°(^\bullet OH)) - \Delta_f H°(ROOH), \tag{4}$$

$$D_{O-O} = (\Delta_f H°(RO^\bullet) + \Delta_f H°(^\bullet OH)) - \Delta_f H°(ROOH_{comp}), \tag{5}$$

where $\Delta_f H°(RO^\bullet)$ – standard heat of formation of the corresponding oxi-radical; $\Delta_f H°(^\bullet OH)$ – standard heat of formation of the $^\bullet OH$ radical; $\Delta_f H°(ROOH)$ – standard heat of formation of the corresponding hydroperoxide molecule; $\Delta_f H°(ROOH_{comp})$ – heat of formation of the hydroperoxide molecule that corresponds to the complex configuration. D_{O-O} value for the hydroperoxide configuration that corresponds to complex one is less than D_{O-O} for the nonbonded hydroperoxide molecule. Difference between bonded and nonbonded hydroperoxide D_{O-O} value is $\Delta D_{O-O} = (43 \pm 5)$ kJ·mol^{-1} (Table 3) and in accordance with experimental activation barrier decreasing in the presence of Et_4NBr: $\Delta E_a = (40 \pm 3)$ kJ·mol^{-1}.

Linear dependence has been obtained between experimental activation energy of the aralkyl hydroperoxide – Et_4NBr complex decomposition and calculated value of ΔD_{O-O} that characterizes the peroxide bond strength decreasing (Fig. 5a). Thus changes in the hydroperoxide moiety configuration during complex formation lead to the destabilization of the peroxide bond, its strength decreasing, and to the increasing of the hydroperoxide molecule reactivity.

TABLE 3 Values of $\Delta_f H°$(ROOH), $\Delta_f H°$(ROOH$_{comp}$), ΔD_{O-O} i $\Delta_r H°$ for the aralkyl hydropero-xides obtained with AM1/COSMO method.

[1]ROOH	$\Delta_f H°$(ROOH), kJ·mol^{-1}	$\Delta_f H°$(ROOH$_{comp}$), kJ·mol^{-1}	ΔD_{O-O}, kJ·mol^{-1}	$\Delta_r H°$, kJ·mol^{-1}
1	−69.3	−31.2	38.1	68.8
2	−99.0	−59.7	39.1	65.9
3	−107.9	−66.9	41.0	62.7
4	−128.7	−84.7	44.0	58.4
5	−409.4	−360.9	48.5	57.5
6	−34.3	13.0	47.3	56.7

[1]ROOH: 1 – PhCH$_2$C(CH$_3$)$_2$OOH; 2 – Ph(CH$_2$)$_2$C(CH$_3$)$_2$OOH; 3 – PhCH(CH$_3$)CH$_2$-C(CH$_3$)$_2$OOH; 4 – (p-CH$_3$)PhC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$OOH; 5 – p-HO(O)CPhC(CH$_3$)$_2$OOH; 6 – Ph(CH$_3$)$_2$COOH.
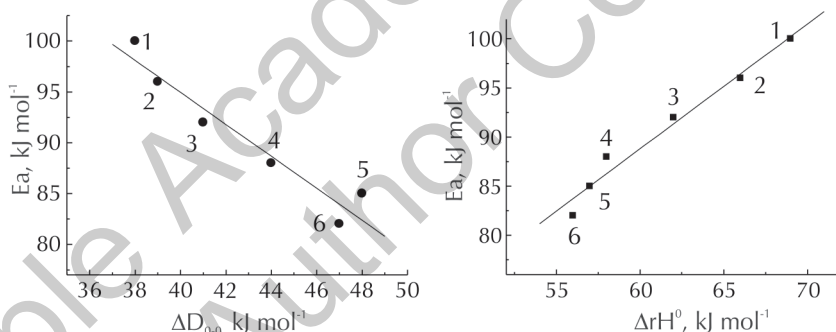
FIGURE 5 Dependence between experimental E_a of the aralkyl hydroperoxides decomposition in the presence of Et$_4$NBr and (a) – calculated ΔD_{O-O} values; (b) – calculated $\Delta_r H°$ values for the reaction (6).

Complex formation with structure of substrate separated ion pair is the exothermal process. Part of the revealed energy can be spent on structural reorganization of the hydroperoxide molecule (structural changes in –COOH group configuration). It leads to the corresponding electron reorganization of the reaction center (peroxide bond). Thus the increase of the hydroperoxide reactivity occurs after complex-bonding of the hydroperoxide molecule. So the chemical activation of the hydroperoxide

molecule is observed as a result of the hydroperoxide interaction with Et$_4$NBr. This activation promotes radical decomposition reaction to proceed in mild conditions.

In the framework of proposed structural model the hydroperoxide molecule is directly bonded in complex with ammonium salt anion and cation. This fact is in accordance with experimental observation of the anion and cation nature effects on the kinetic parameters of the activated hydroperoxide decomposition. Solvated anion approximation allows to directly account the solvent effect on the reactivity of complex bonded aralkyl hydroperoxides.

11.4   CONCLUSIONS

Investigations of kinetics of the aralkyl hydroperoxides decomposition in the presence of Et$_4$NBr have revealed that reaction occurred through the complex formation stage. The complex formation enthalpy value is within $(-10 \div -22)$ kJ·mol^{-1} corresponding from aralkyl substituent in the hydroperoxide structure. Et$_4$NBr addition leads to the hydroperoxide decomposition activation energy decrease on 40 kJ·mol^{-1}. The hydroperoxides reactivity increases in the following way: phCH$_2$C(CH$_3$)$_2$OOH < Ph(CH$_2$)$_2$C(CH$_3$)$_2$OOH < Ph(CH$_3$)CHCH$_2$C(CH$_3$)$_2$OOH < (p-CH$_3$)Ph(CH$_3$)$_2$CCH$_2$C(CH$_3$)$_2$OOH < p-HO(O)CPhC(CH$_3$)$_2$OOH. The structural model of reactive complex was proposed that allowed to account the hydroperoxide nature as well as ammonium salt anion and cation effect, and the solvent one. Formation of the complex with proposed structural features is accompanied with chemical activation of the aralkyl hydroperoxide molecule.

KEYWORDS

- **acetonitrile**
- **aralkyl hydroperoxides**
- **peroxide bond**
- **tetraethylammonium bromide**

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