

Kinetics and Thermodynamics of the Exchange Reactions of Peroxy Radicals with Hydroperoxides

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Abstract—The enthalpies and equilibrium constants of the exchange reactions of peroxy radicals with hydroperoxides of various structures are calculated. The experimental data on the reactions of hydrogen atom abstraction by the peroxy radicals from the hydroperoxides are analyzed, and the kinetic parameters characterizing these reactions are calculated using the intersecting parabolas method. The activation energies and rate constants for nine reactions of H atom abstraction by a peroxy radical from the OOH group of a peroxide are calculated using the above parameters. The geometric parameters of the transition states for the reactions are calculated. The low triplet repulsion plays an important role in the fast occurrence of the reactions. The polar interaction in the transition state is manifested in the reactions of the peroxy radicals with hydroperoxides containing a polar group.

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INTRODUCTION

The exchange reactions between a peroxy radical RO_2^\bullet and a hydroperoxide $\text{R}'\text{OOH}$ with a different structure,



occur rapidly during the cooxidation of organic compounds [1]. These reactions play an important role in the measurements of the rate constants of the reactions of the RO_2^\bullet radical of a given structure with various hydrocarbons $\text{R}'\text{H}$, when $\text{R}'\text{H}$ is oxidized in the presence of individual hydroperoxide ROOH [2]. Experimental measurements indicate that these reactions occur rather rapidly. The reaction center in the transition state (TS) of such a reaction is symmetric ($\text{O}\cdots\text{H}\cdots\text{O}$) and, hence, this class of reactions is especially interesting. We have recently estimated the dissociation energies of the O–H bonds in hydroperoxides of various structures [3]. This allowed us to calculate the rate and equilibrium constants for the reactions involving hydroperoxides of various structures. The present article is devoted to an analysis of the experimental data and calculation of the equilibrium and rate constants for the reactions of H atom exchange between the peroxy radical RO_2^\bullet and the hydroperoxide $\text{R}'\text{OOH}$. The intersecting parabolas model (IPM) [4, 5] was used in the calculation of the reaction rate constants. Along with the kinetic characteristics of the reactions, the geometric parameters of the TS were calculated using a recently developed method [6, 7].

CALCULATION PROCEDURE

Enthalpy and Equilibrium Constant of the Exchange Reaction

Equilibrium (I) is rapidly established when the radicals are generated in a binary system of two hydroperoxides [2].

Since the reaction is symmetric, its entropy is almost zero, so the equilibrium constant K is determined by the reaction enthalpy ΔH , and the latter depends only on the dissociation energy of the O–H bonds of the hydroperoxides involved in the equilibrium

$$\Delta H = D_{\text{O-H}}^i - D_{\text{O-H}}, \quad (1)$$

$$K = \exp(-\Delta H/RT). \quad (2)$$

IPM Applied to Reactions of Peroxy Radicals with Hydroperoxides

In the framework of the IPM, the free-radical reaction of H atom transfer is characterized by the following parameters [4, 5, 8]:

(1) The classical enthalpy ΔH_e , which includes the enthalpy of the reaction and the zero-point energies of the reacting bonds. The enthalpy ΔH_e for the class of reactions considered is equal to ΔH because the zero-point energies of the breaking and forming bonds are equal and $\Delta H_e = \Delta H = D_{\text{O-H}}^i - D_{\text{O-H}}$.

(2) The classical potential barrier E_e , which is related to the activation energy of the reaction through the equation [8]

$$E_e \text{ (kJ/mol)} = E + 21.2 - 0.5RT, \quad (3)$$

where R is the universal gas constant, T is absolute temperature, and 21.2 kJ/mol is the zero-point vibrational energy of the O–H bond in the hydroperoxide. The activation energy E is calculated from the experimental reaction rate constant (k) using the Arrhenius formula

$$k = A \exp(-E/RT); \quad (4)$$

(3) The parameters b and b_f ($2b^2$ and $2b_f^2$ are the force constants of the breaking and forming bonds, respectively). For the reaction considered, these force constants are $b = b_f = 46.00 \times 10^{10} \text{ (kJ/mol)}^{1/2} \text{ m}^{-1}$ [8].

(4) The coefficient $\alpha = b/b_f = 1.00$.

(5) The extension of the reacting bonds in the transition state, r_e .

(6) The preexponential factor $A = 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ [8].

The enthalpy ΔH_e and the classical potential barrier E_e are related to α , b , and r_e through the equation

$$br_e = \alpha \sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \quad (5)$$

The parameter br_e derived from experimental data makes it possible to calculate the classical potential barrier of the thermally neutral reaction, $E_{e,0}$ ($\Delta H_e = 0$):

$$E_{e,0} = 0.25(br_e)^2. \quad (6)$$

The activation energy of the reaction can be calculated from the enthalpy of the reaction and br_e :

$$E = \{0.5br_e + \Delta H/2br_e\}^2 - 21.2 + 0.5RT. \quad (7)$$

Next, the reaction rate constant can be calculated using formula (4). Note that formula (7) is valid for reactions whose enthalpy ranges within $\Delta H_{\min} < \Delta H < \Delta H_{\max}$ [4]. For reactions with $\alpha = 1$, $\Delta H_{\min} = -\Delta H_{\max}$ and ΔH_{\max} depends on br_e [4]:

$$\Delta H_{\max} = (br_e)^2 - 2br_e \sqrt{21.2}. \quad (8)$$

For reactions with $|\Delta H| > \Delta H_{\max}$, the preexponential factor A depends on the enthalpy of the reaction [4].

Formulas (4) and (7) were used to calculate the activation energies and rate constants of H atom exchange between peroxy radicals and hydroperoxides. The contribution from the polar interaction ΔE_μ to the activation energy of the reaction was estimated using the formula [7]

$$\Delta E_\mu = 0.25[(br_{e,\mu})^2 - (br_{e,RH})^2], \quad (9)$$

where $br_{e,\mu}$ refers to the reaction of an alkylperoxy radical with a hydroperoxide containing a polar group in a polar solvent and $br_{e,RH} = 13.44 \text{ (kJ/mol)}^{1/2}$ characterizes the reaction of the alkylperoxy radical with the alkyl hydroperoxide in a hydrocarbon solvent.

Estimation of the Geometric Parameters of the TS in Reaction (I)

In terms of the IPM, the interatomic distance $O \cdots H \cdots O$ in the TS of the reaction is the sum consisting of two terms [6, 7]:

$$r^\#(O^i \cdots H \cdots O) = 2r_{OH} + \beta r_e, \quad (10)$$

where r_{OH} is the length of the corresponding bond in the ROOH molecule, r_e is the extension of the two O–H bonds in the TS calculated in terms of the IPM using formula (5), and the coefficient β makes the $r^\#(O^i \cdots H \cdots O)$ distance equal to that obtained by quantum chemical calculations [6]. The coefficient β for the class of reactions considered is 1.49 [6]. Since r_e can be expressed through $E_{e,0}$, $\alpha = 1$, and $b = 46.00 \times 10^{10} \text{ (kJ/mol)}^{1/2} \text{ m}^{-1}$, the following formula is obtained for the calculation of the $r^\#(O^i \cdots H \cdots O)$ distance in the TS of the reaction $RO_2^\bullet + RiOOH$:

$$\begin{aligned} r^\#(O^i \cdots H \cdots O) \times 10^{10} / \text{m} \\ = 2r_{OH} \times 10^{10} + (\alpha + 1)\beta b^{-1} \sqrt{E_{e,0}} \\ = 1.94 + 6.48 \times 10^{-2} \sqrt{E_{e,0}}. \end{aligned} \quad (11)$$

The position of the H atom in the $O^i \cdots H \cdots O$ reaction center of the TS is characterized by the distances $r^\#(O^i \cdots H)$ and $r^\#(O \cdots H)$. These distances depend on the activation energy E_e and the reaction enthalpy ΔH_e . They are expressed through the formulas [7]

$$\begin{aligned} r^\#(O^i \cdots H) \times 10^{10}, \text{ m} \\ = r_{OH} \times 10^{10} + \beta b^{-1} \sqrt{E_e} = 0.97 + 3.24 \times 10^{-2} \sqrt{E_e}, \end{aligned} \quad (12)$$

$$\begin{aligned} r^\#(O \cdots H) \times 10^{10}, \text{ m} \\ = r_{OH} \times 10^{10} + \alpha \beta b^{-1} \sqrt{E_e - \Delta H_e} \\ = 0.97 + 3.24 \times 10^{-2} \sqrt{E_e - \Delta H_e}. \end{aligned} \quad (13)$$

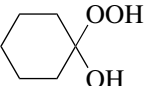
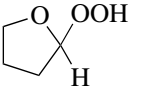
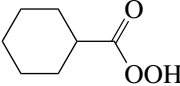
The error of the estimation of these distances is $0.011 \times 10^{-10} \text{ m}$ [6].

RESULTS AND DISCUSSION

Equilibrium in the Exchange Reactions of Peroxy Radicals with Hydroperoxides

The enthalpies of exchange reaction (I) calculated using formula (1) and the equilibrium constants calculated using formula (2) are given in Table 1. The strengths of the O–H bonds of the hydroperoxides are borrowed from [3]. These data show that the enthalpy of this equilibrium varies in a wide range (from –54 to 54 kJ/mol) and the equilibrium constant ranges within 20 orders of magnitude. This wide range of ΔH and, correspondingly, K values is due to the strong dependence of the O–H bond dissociation energy in hydroperoxides on their structure (see the D_{O-H} values in Table 1).

Table 1. Enthalpies and equilibrium constants of the reaction $\text{Me}_3\text{CO}_2^\bullet + \text{R}^i\text{OOH} \rightleftharpoons \text{Me}_3\text{COOH} + \text{R}^i\text{O}_2^\bullet$

R^iOOH	$D_{\text{O-H}}^i$, kJ/mol	ΔH , kJ/mol	K ($T = 300$ K)	K ($T = 350$ K)
HOOH	369.0	10.4	1.55×10^{-2}	2.80×10^{-2}
<i>sec</i> -ROOH	365.5	6.9	6.29×10^{-2}	9.34×10^{-2}
<i>tert</i> -ROOH	358.6	0.0	1.00	1.00
	362.1	3.5	2.46×10^{-1}	3.00×10^{-1}
RPhC(OH)OOH	359.8	1.2	0.62	0.66
ROCH(OOH)R	367.3	8.7	3.06×10^{-2}	5.03×10^{-2}
$\text{R}_2\text{CHOC}(\text{OOH})\text{R}_2$	358.4	-0.2	1.08	1.07×10^{-2}
ROCH(OOH)Ph	374.8	16.2	1.51×10^{-3}	3.82×10^{-3}
	367.6	9.0	2.71×10^{-2}	4.54×10^{-2}
RC(O)OOH	387.1	28.5	1.09×10^{-5}	5.58×10^{-5}
$\text{R}_3\text{CC}(\text{O})\text{OOH}$	376.9	18.3	6.51×10^{-4}	1.86×10^{-3}
	376.9	18.3	6.51×10^{-4}	1.86×10^{-3}
PhC(O)OOH	403.9	45.3	1.30×10^{-8}	1.73×10^{-7}
RC(O)CH(OOH)R	369.8	11.2	1.12×10^{-2}	2.13×10^{-2}
RC(O)CH(OOH)Ph	376.4	17.8	7.06×10^{-4}	2.21×10^{-3}
$\text{CCl}_3\text{CCl}_2\text{OOH}$	413.1	54.5	3.51×10^{-10}	7.35×10^{-8}
$\text{CHCl}_2\text{CCl}_2\text{OOH}$	411.6	53.0	5.92×10^{-10}	1.23×10^{-8}

Note: The strengths of the O–H bonds are borrowed from [3].

As will be demonstrated below, the exchange reaction occurs very rapidly, so the equilibrium constant K determines the composition of the peroxy radicals when a hydrocarbon is oxidized in the presence of two hydroperoxides (ROOH and R^iOOH). In this binary mixture, the ratio of the concentrations of the RO_2^\bullet and $\text{R}^i\text{O}_2^\bullet$ radicals is related to K and the concentrations of the hydroperoxides ROOH and R^iOOH through the simple equation

$$[\text{R}^i\text{O}_2^\bullet] = K \frac{[\text{R}^i\text{OOH}]}{[\text{ROOH}]} [\text{RO}_2^\bullet], \quad (14)$$

from which the following equation is obtained for the fraction of the RO_2^\bullet radicals:

$$\frac{[\text{R}^i\text{O}_2^\bullet]}{[\text{R}^i\text{O}_2^\bullet] + [\text{RO}_2^\bullet]} = \frac{K[\text{R}^i\text{OOH}]}{[\text{ROOH}] + K[\text{R}^i\text{OOH}]}. \quad (15)$$

The dependence of the fraction of the cyclohexyl peroxy radicals on the concentration of cyclohexyl hydroperoxide in its mixture with 1,1-dimethylethyl hydroperoxide calculated using formula (15) is shown in Fig. 1. It can be seen that the cyclohexyl peroxy radicals are almost completely substituted for the 1,1-dimethylethyl peroxy radicals at $[\text{C}_6\text{H}_{11}\text{OOH}] > 5.0$ mol/l.

Kinetic Parameters of the Reactions of Peroxy Radicals with Hydroperoxides

Experimental data and the br_e values calculated from them (formulas (3) and (5)) are given in Table 2. The results of calculation show that the br_e values are similar, so we deal with reactions of the same class, characterized by $br_e = 13.44 \pm 0.31$ (kJ/mol)^{1/2}, a classical potential barrier of $E_{e,0} = 45.2 \pm 2.1$ kJ/mol (formula (6)), and a limiting enthalpy value of $\Delta H_{\text{max}} = 56.8$ kJ/mol (formula (8)). These characteristics were used to calculate the activation energies and rate constants of the reactions. It was found that the following condition is fulfilled for all the reactions considered in the present work: -56.8 kJ/mol $< \Delta H < 56.8$ kJ/mol (Tables 2, 3). For this reason, the activation energy was calculated by formula (7) and the rate constant was calculated using formula (4). The calculation procedure is described above. The results of these calculations are presented in Table 3.

The parameter br_e for the reactions between an alkyl peroxy radical and alkyl hydroperoxide in a hydrocarbon (Table 2) is lower than that for the reactions between RO_2^\bullet and a hydroperoxide containing a polar ether ($\equiv\text{COC}\equiv$) group in the nonpolar solvent [10] (see Table 4).

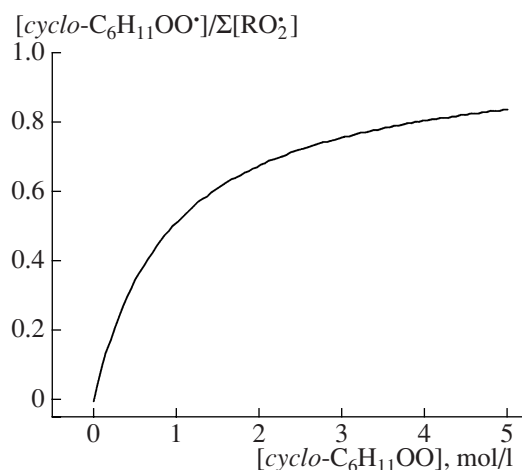


Fig. 1. Fraction of cyclohexyl peroxy radicals versus the concentration of cyclohexyl hydroperoxide in its mixture with 1,1-dimethylethyl hydroperoxide under equilibrium conditions ($[\text{Me}_3\text{COH}]_0 = 0.1 \text{ mol/l}$, $T = 350 \text{ K}$).

The activation energy of these reactions includes the energy of the interaction of the polar group with the polar reaction center of the TS [11–14]. The data in Table 4 show that the polar interaction, which can be characterized by the increment ΔE_μ , increases the activation energy of the exchange reaction by $\Delta E_\mu = 6.9 \pm 0.5 \text{ kJ/mol}$.

Geometric Parameters of the TS for Reaction (I)

The geometry of the TS of the reaction between the hydroperoxy radical and hydrogen peroxide was calculated using density functional theory [6]. In the TS, the $\text{O}\cdots\text{H}\cdots\text{O}$ atoms lie on a straight line. The interatomic distances in the TS, $r^\#(\text{R}^i\text{OO}\cdots\text{H}) = r^\#(\text{O}^i\cdots\text{H})$ and $r^\#(\text{ROO}\cdots\text{H})$, were calculated using formulas (12) and (13). The results of these calculations are presented in Table 3. As can be seen from the data in Table 3, the distance $r^\#(\text{R}^i\text{OO}\cdots\text{H})$ elongates and $r^\#(\text{ROO}\cdots\text{H})$ shortens with an increase in the enthalpy of the reaction. The dependence of $r^\#(\text{R}^i\text{OO}\cdots\text{H})$ on the enthalpy is linear (Fig. 2) and is described by the formula

$$\begin{aligned} r^\#(\text{O}^i\cdots\text{H}) \times 10^{10}/\text{m} \\ = 1.188 + 1.19 \times 10^{-3} \Delta H/\text{kJ/mol}. \end{aligned} \quad (16)$$

Factors Affecting Exchange Reaction (I)

The first factor affecting all radical abstraction reactions is the enthalpy of the reaction [4, 8]. The effect of the enthalpy of the reaction on its activation energy is reflected by the $\Delta E/\Delta H$ ratio, where $\Delta E = E - E_0$ and $E_0 = E(\Delta H = 0)$. The ΔH and E values (in kJ/mol) and the $\Delta E/\Delta H$ ratio for the reactions of H atom abstraction

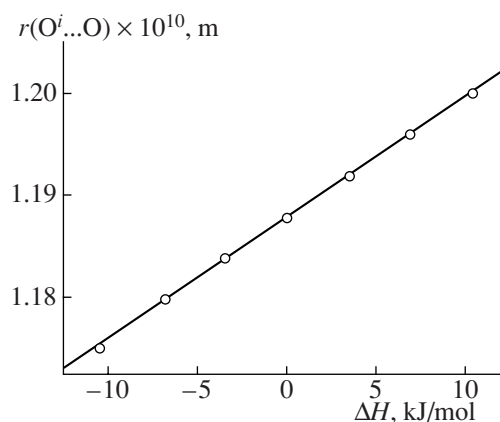


Fig. 2. Interatomic distance in the transition state ($r^\#(\text{R}^i\text{OO}\cdots\text{H})$) versus the enthalpy of reaction (I).

by the 1,1-dimethylethyl peroxy radical from several hydroperoxides R^iOOH are presented below.

R^iOOH	ΔH	E	$\Delta E/\Delta H$
H_2O_2	10.4	30.8	0.51
<i>sec</i> -ROOH	6.9	29.0	0.51
$\text{ROCH}(\text{OOH})\text{Ph}$	16.2	33.9	0.52
$\text{RC}(\text{O})\text{OOH}$	28.5	40.8	0.54
$\text{PhC}(\text{O})\text{OOH}$	45.3	51.0	0.56
$\text{CCl}_3\text{Cl}_2\text{OOH}$	54.5	56.8	0.57

These data show that the contribution from the enthalpy to the activation energy is large and increases with an increase in the reaction enthalpy. This contribution can be expressed in analytical form. By transforming formula (7) and substituting the numerical values of α and br_e , we obtain the following expression for the $\Delta E/\Delta H$ ratio:

$$\Delta E/\Delta H = 0.50 + 1.38 \times 10^{-3} \Delta H (\text{kJ/mol}). \quad (17)$$

Another important factor affecting the activation energy is the triplet repulsion in the TS [4, 5, 8]. For the reactions of oxygen-centered radicals with the O–H bonds of various compounds, the classical potential barriers of thermally neutral reactions ($E_{e,0}$, kJ/mol) are very similar, as can be seen from the examples presented below [8].

TS	$E_{e,0}$, kJ/mol
$\text{ROO}\cdots\text{HOOR}$	45.2
$\text{ROO}\cdots\text{HOAr}$	43.3
$\text{ROO}\cdots\text{HONR}_2$	45.6
$\text{R}_2\text{NO}\cdots\text{HOAr}$	45.8

All the reaction classes considered are characterized by the same classical potential barrier $E_{e,0} = 45.0 \pm 1.0 \text{ kJ/mol}$. However, for the reactions with a $\text{C}\cdots\text{H}\cdots\text{C}$ reaction center, the barrier is much higher, namely, $E_{e,0} =$

Table 2. Enthalpies, activation energies, and br_e values for reactions between a peroxy radical and an alkyl hydroperoxide

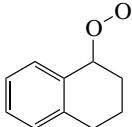
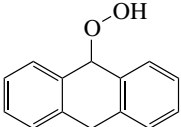
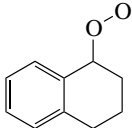
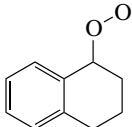
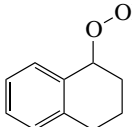
RO_2^\bullet	R^iOOH	ΔH , kJ/mol	T , K	k_{exp} , $\text{l mol}^{-1} \text{s}^{-1}$	E_e , kJ/mol	br_e , (kJ/mol) $^{1/2}$	References
$\text{Me}_3\text{CO}^\bullet$	EtMeCHOOH	6.9	294	4.85×10^2	49.9	13.62	[9]
$\text{Me}_3\text{COO}^\bullet$		6.9	190	11.2	45.3	12.93	[9]
$\text{Me}_3\text{COO}^\bullet$		6.9	294	7.40×10^2	48.9	13.47	[9]
$\text{EtMe}_2\text{COO}^\bullet$		6.9	200	12	46.5	13.11	[9]
$\text{PhMe}_2\text{COO}^\bullet$		6.9	303	600	50.3	13.68	[2]
$\text{PhMe}_2\text{COO}^\bullet$		6.9	329	1.10×10^3	51.2	13.81	[2]
$br_e = 13.44 \pm 0.31$							

Table 3. Enthalpies, activation energies, rate constants, and transition state geometries for reactions between a peroxy radical and a hydroperoxide calculated using formulas (1), (4), (7), (12), and (13)

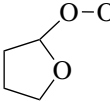
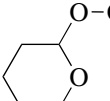
RO_2^\bullet	R^iOOH	ΔH , kJ/mol	E , kJ/mol	k (350 K), $\text{l mol}^{-1} \text{s}^{-1}$	$r^\#(\text{O}^i \cdots \text{H}) \times 10^{10}$, m	$r^\#(\text{O} \cdots \text{H}) \times 10^{10}$, m
HO_2^\bullet	HOOH	0.0	25.5	3.17×10^4	1.188	1.188
HO_2^\bullet	<i>sec</i> -ROOH	-3.5	23.7	2.88×10^4	1.184	1.192
HO_2^\bullet	<i>tert</i> -ROOH	-10.4	20.4	9.00×10^4	1.175	1.200
<i>sec</i> - RO_2^\bullet	HOOH	3.5	27.2	2.83×10^4	1.192	1.184
<i>sec</i> - RO_2^\bullet	<i>sec</i> -ROOH	0.0	25.5	1.59×10^4	1.188	1.188
<i>sec</i> - RO_2^\bullet	<i>tert</i> -ROOH	-6.9	22.1	5.08×10^4	1.180	1.196
<i>tert</i> - RO_2^\bullet	HOOH	10.4	30.8	5.05×10^3	1.200	1.175
<i>tert</i> - RO_2^\bullet	<i>sec</i> -ROOH	6.9	29.0	4.74×10^3	1.196	1.180
<i>tert</i> - RO_2^\bullet	<i>tert</i> -ROOH	0.0	25.5	1.59×10^4	1.188	1.188

68.0 kJ/mol [4]. This large difference is due to the high strength of the C–C bond (370 kJ/mol) and, hence, the strong triplet repulsion. By contrast, the O–O bond in the tetroxide ROO–OOR is weak (only 88 kJ/mol [11]) and, therefore, the triplet repulsion in the TS is also weak [4]. It is this circumstance that is responsible for

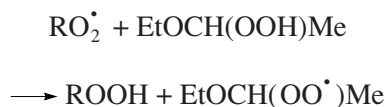
the comparatively high H exchange rates between the peroxy radicals and the hydroperoxides.

The third factor is the polar interaction between the reaction center ($\text{OO} \cdots \text{H} \cdots \text{OO}$) in the TS and the polar group of the reactant [12–14]. As was mentioned when comparing the $E_{e,0}$ values characterizing the reactions

Table 4. Thermodynamic and kinetic parameters of reactions between a peroxy radical and an ether hydroperoxide calculated from experimental data [10] ($T = 303$ K, cumene) using formulas (1), (3)–(5), and (9)

RO_2^\bullet	R^iOOH	ΔH , kJ/mol	E_e , kJ/mol	br_e , (kJ/mol) ^{1/2}	ΔE_μ , kJ/mol
$PhMe_2COO^\bullet$	EtOCH(OOH)Me	8.7	55.8	14.33	6.2
$PhMe_2COO^\bullet$		9.0	57.2	14.50	7.4
$PhMe_2COO^\bullet$		9.0	56.7	14.44	7.0

between an alkyl peroxy radical and an alkyl hydroperoxide in the hydrocarbon solvent and the reactions of alkyl peroxy radicals with hydroperoxides containing a polar group in the nonpolar solvent, the reaction is affected by the polar interaction in the TS. Its contribution to the activation energy of the reaction



is $\Delta E_\mu = 6.9$ kJ/mol (see above).

Thus, the experimental data for the H-exchange reactions between RO_2^\bullet and R^iOOH were analyzed and the kinetic parameters characterizing this class of reactions, equilibrium constants, and the rate constants of some of these reactions were calculated. The following three factors affect the activation energy of the reactions: reaction enthalpy, triplet repulsion, and polar interaction in the TS between the reaction center and the polar group of the reactant. Weak triplet repulsion leads to a low activation energy and a comparatively high reaction rate.

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