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Kinetic Parameters of Alkyl, Alkoxy, and Peroxy Radical Isomerization

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Abstract—The parabolic model of radical abstraction reactions is used to analyze experimental data on monomolecular hydrogen-atom transfer in the reactions

$$\mathrm{R\dot{C}H(CH_2)_{\mathit{n}}CH_2R^1 \longrightarrow RCH_2(CH_2)_{\mathit{n}}\dot{C}HR^1}\quad (n = 2, 3, 4),$$

$$\mathrm{RCH(O^{\bullet})(CH_2)_2CH_2R^1 \longrightarrow RCH(OH)(CH_2)_2\dot{C}HR^1},$$

$$\mathrm{RCH(OO^{\bullet})(CH_2)_{\mathit{n}}CH_2R^1 \longrightarrow RCH(OOH)(CH_2)_{\mathit{n}}\dot{C}HR^1}\quad (n = 1, 2).$$

The activation energies and rate constants that specify each class of these reactions are calculated. Alkyl radical isomerization is characterized by the following activation energies of a thermally neutral reaction depending on the cycle size in the transition state (n is the number of atoms in a cycle): $E_{e,0}$ (kJ/mol) = 46.6 ($n = 6$), 59.4 ($n = 5$), and 57.1 ($n = 7$). Alkoxy radicals isomerize with $E_{e,0}$ (kJ/mol) = 53.4 ($n = 6$), whereas peroxy radicals isomerize with $E_{e,0}$ (kJ/mol) = 53.2 ($n = 6$) and $E_{e,0}$ (kJ/mol) = 54.8 ($n = 7$). The $E_{e,0}$ value varies with changes in the cycle size and the strain energy in cycloparaffin C_nH_{2n} in the same manner. The activation energies $E_{e,0}$ for the intra- and intermolecular H-atom abstractions are compared. It is found that $E_{e,0}$ (isomerization) < $E_{e,0}$ ($\mathrm{R^{\bullet} + R^1H}$) for alkyl radicals and that $E_{e,0}$ (isomerization) ≈ $E_{e,0}$ ($\mathrm{RO^{\bullet}\ (RO_2^{\bullet}) + R^1H}$) for alkoxy and peroxy radicals.

INTRODUCTION

Alkyl radical isomerization accompanied by free-valence transfer from one carbon atom to another occurs in the chain cracking and radiolysis of hydrocarbons [1], radical polymerization and oligomerization of monomers [2], and the thermal and thermooxidative destruction of polymers [3, 4]. These reactions affect both the rate of the overall process and the composition of the resulting products. Peroxy radical isomerization during hydrocarbon oxidation results in the formation of bifunctional products (dihydroperoxides, diatomic alcohols, etc.) even at early oxidation stages [5–8]. These reactions are very important in the oxidation of carbochain polymers [4, 8]. The available data on the rates of such reactions are rather scarce. Therefore, the aim of this work was to analyze these data using the parabolic model of a radical abstraction reaction, to obtain parameters describing such reactions, and to calculate the activation energies and the rate constants for these reactions involving radicals of different structure. We also analyzed the competition between the intra- and intermolecular hydrogen-atom abstractions that occur in parallel in the relevant systems (hydrocarbons and polymers).

CALCULATION OF KINETIC PARAMETERS

Within the framework of the parabolic model, free-radical reactions

$$\mathrm{R\dot{C}H(CH_2)_3CH_2R^1 \longrightarrow RCH_2(CH_2)_3\dot{C}HR^1},$$

$$\mathrm{RCH(O^{\bullet})(CH_2)_2CH_2R^1 \longrightarrow RCH(OH)(CH_2)_2\dot{C}HR^1},$$

$$\mathrm{RCH(OO^{\bullet})CH_2CH_2R^1 \longrightarrow RCH(OOH)CH_2\dot{C}HR^1}$$

are considered to be a result of the intersection of the potential curves, which describe the stretching vibrations of the breaking (i) and forming (f) bonds in the coordinates of the potential energy vs. the bond stretching vibration amplitude [9, 10]. The stretching vibration of a bond is considered harmonic. In terms of this model, isomerization is described by the following parameters: the enthalpy ΔH_e, the activation energy E_e, the b_i and b_f coefficients ($2b^2$ is the force constant of a bond), and the sum of the amplitudes of the reacting bond vibrations r_e in the transition state (the distance between the peaks of two parabolas). The reaction enthalpy ΔH_e includes the difference between the zero-point energies of the reacting bonds:

$$\Delta H_e = D_i - D_f + 0.5hN_A(\nu_i - \nu_f), \tag{1}$$

where D_i and D_f are the dissociation energies of the breaking and forming bonds, respectively; ν_i and ν_f are the frequencies of the stretching vibrations of these bonds; and h and N_A are the Planck and Avogadro constants, respectively. The activation energy E_e also includes the zero-point vibration energy of a breaking bond:

$$E_e = E + 0.5(hN_A\nu_i - RT), \tag{2}$$

where E is the activation energy, and $0.5hN_A\nu_i$ is the zero-point vibration energy of a breaking bond. Radical reactions of the same class are characterized by the same preexponential factor per attacked C–H bond [10]. Therefore, the activation energy E was calculated from the reaction rate constant k by the equation:

$$E = -RT\ln(k/n_iA_{C-H}), \tag{3}$$

where n_i is the number of C–H bonds that are equally reactive (n_i = 1, 2, 3), and A_{C-H} is the preexponential factor per one C–H bond. Within the framework of the parabolic model, each radical reaction class is characterized by the parameters $\alpha = b_i/b_f$ and br_e ($b = b_i$). The br_e parameter is calculated for each individual reaction by the following equation [10]:

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \tag{4}$$

Along with the α and br_e parameters, each radical reaction class is characterized by the activation energy of a thermally neutral reaction $E_{e,0}$ and the position of the transition state $r_0^{\neq}$ on the r_e distance at $E_e = E_{e,0}$:

$$\sqrt{E_{e,0}} = \frac{br_e}{1+\alpha}, \tag{5}$$

$$r_0^{\neq}/r_e = \alpha(1+\alpha)^{-1}. \tag{6}$$

Table 1 lists these parameters (α, b_i, $0.5hN_A\nu_i$, and $r_0^{\neq}/r_e$) for the reaction class under consideration.

ALKYL RADICAL ISOMERIZATION

The kinetic parameters for alkyl radical isomerization have been determined for several reactions [11–21]. To calculate the br_e parameter (Table 2), one should know the enthalpy ΔH_e and activation energy of a reaction along with the physical characteristics of the bonds (Table 1). For alkyl radical isomerization involving the cleavage of one C–H bond and the formation of the other C–H bond, we have $\nu_i = \nu_f$ and $\Delta H_e = \Delta H = D_i - D_f$. The dissociation energies for aliphatic C–H bonds were taken from [6], whereas those for chlorine-containing compounds D_{C-H} were estimated as follows. The D_{C-H} values for chlorinated methane are 415.9 kJ/mol for CH_3Cl and 406.7 kJ/mol in CH_2Cl_2 [22], whereas, for methane, D_{C-H} = 440 kJ/mol [6]. Therefore, the introduction of one and two chlorine atoms causes a decrease (ΔD) in the D_{C-H} value of 24.1 and 33.3 kJ/mol, respectively. Using these increments and D_{C-H} = 422 kJ/mol for the CH_3 group [6], we obtain D_{C-H} = 397.9 kJ/mol for RCH_2Cl and D_{C-H} = 388.7 kJ/mol for RCH_2Cl_2. These D_{C-H} values were used to calculate the ΔH parameters for the isomerization of chlorine-containing alkyl radicals (Table 2). The activation energy E was calculated by Eq. (3), and the preexponential factor for the reaction per attacked C–H bond A_{C-H} ($1.0 \times 10^{9 \pm 0.13}$ s^{-1}) was calculated by averaging experimental values (Table 2). Table 2 summarizes the calculated br_e parameters. Alkyl radical isomerization occurs via a cyclic transition state and is characterized by different br_e values and the activation energy of a thermally neutral reaction $E_{e,0}$ depending on the cycle size (Table 3). The six-membered transition state is preferable. Alkyl

Table 1. Physical parameters of bond transformation in radical isomerization

Reaction	α	$b_i \times 10^{-11}$, (kJ/mol)$^{1/2}$	$0.5hN_A\nu_i$, kJ/mol	$0.5hN_A\nu_f$, kJ/mol	$0.5hN_A(\nu_i - \nu_f)$, kJ/mol	$r_0^{\neq}/r_e$
$R^{\bullet} \longrightarrow R^{1\bullet}$	1.000	3.743	17.4	17.4	0	0.50
$C_6H_4^{\bullet}CH_2R \longrightarrow C_6H_5C^{\bullet}HR$	0.945	3.743	17.4	18.4	–1.0	0.49
$RO^{\bullet} \longrightarrow R^{1\bullet}$	0.796	3.743	17.4	21.7	–4.3	0.56
$RO_2^{\bullet} \longrightarrow R^{1\bullet}$	0.814	3.743	17.4	21.2	–3.8	0.45
$R^{1\bullet} \longrightarrow RO_2^{\bullet}$	1.228	4.600	21.2	17.4	3.8	0.55

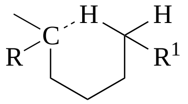
radical isomerization occurring via the formation of a six-membered activated complex is specified by $br_e = 13.66 \pm 0.68$ (kJ/mol)$^{1/2}$ and the activation energy of a thermally neutral reaction $E_{e,0} = 46.6 \pm 4.8$ kJ/mol. In the case of the five ($br_e = 15.41$ (kJ/mol)$^{1/2}$) and seven-membered ($br_e = 15.11$ (kJ/mol)$^{1/2}$) transition states, the $E_{e,0}$ value is higher and equal to 59.4 and 57.1 kJ/mol, respectively.

Let us compare the kinetic parameters for intermolecular H-atom abstraction [10] in radical reactions and intramolecular H-atom transfer via the six-membered activated complex.

Reaction	br_e, (kJ/mol)$^{1/2}$	E_{e0}, kJ/mol	$r_e \times 10^{11}$, m
$R^{\bullet} \longrightarrow R^{1\bullet}$	13.66	46.6	3.65
$R^{\bullet} + R^1H \longrightarrow RH + R^{1\bullet}$	17.30	74.8	4.62

The above comparison suggests that hydrogen-atom abstraction inside the radical is characterized by a slightly lower activation energy $\Delta E_{e,0} = 74.8 - 46.6 = 28.2$ kJ/mol and, hence, by a lower r_e parameter ($\Delta r_e = 9.7 \times 10^{-12}$ m, that is, by a more compact location of the reacting atoms in the reaction center. This can be due to a difference in the transition state configuration. In the bimolecular abstraction reaction, the atoms of the reaction center $C{\cdot\cdot}H{\cdot\cdot}C$ are on a straight line. The most advantageous transition state for isomerization takes the form of a six-membered cycle:

$RC^{\bullet}H(CH_2)_3CH_2R^1 \longrightarrow$



$\longrightarrow RCH_2(CH_2)_3C^{\bullet}HR^1.$

This cyclic transition state also explains the lower value of $A_{C-H} = 10^9$ s^{-1}. Monomolecular decomposition involving the cleavage of one bond is characterized by $A \approx 10^{14}$–10^{15} s^{-1}. Why is the monomolecular isomerization characterized by such a low preexponential factor? The reason is in the cyclic transition state of radical isomerization: by becoming cyclic the radical loses entropy $\Delta S^{\neq}$ during isomerization. This decrease in the entropy can be estimated by comparing the entropy of n-hexane ($S^0 = 388$ J mol^{-1} degree^{-1}) and cyclohexane ($S^0 = 298$ J mol^{-1} degree^{-1}) [23]. We see that $\Delta S = S^0(n\text{-hexane}) - S^0(\text{cyclohexane}) = 90$ J mol^{-1} degree^{-1}. Within the framework of the transition state theory, this decrease in the entropy corresponds to the factor $e^{\Delta S^{\neq}/R} = 2 \times 10^{-5}$. Therefore, one should expect

Table 2. Thermodynamic and kinetic parameters for alkyl radical isomerization*

Radical $R^{\bullet}$	D_i, kJ/mol	D_f, kJ/mol	ΔH_e, kJ/mol	E, kJ/mol	br_e, (kJ/mol)$^{1/2}$	Cycle**	Reference
$C^{\bullet}Cl_2(CH_2)_3(C{-}H)HCl$	397.9	388.7	9.2	43.8	14.83	6	[11, 12]
$C^{\bullet}Cl_2(CH_2)_3(C{-}H)HCH_3$	413.0	388.7	24.3	39.9	13.08	6	[11]
$C^{\bullet}Cl_2(CH_2)_3(C{-}H)HCH_2CH_3$	414.5	388.7	25.8	39.0	12.80	6	[11]
$C^{\bullet}Cl_2(CH_2)_2Si(CH_2CH_3)_2(C{-}H)HCH_3$	413.0	388.7	24.3	44.8	13.82	6	[13, 14]
$C^{\bullet}H_2(CH_2)_3(C{-}H)HC(O)OCH_3$	398.8	422.0	–23.2	25.1	14.42	6	[15]
$(C{-}H)(O)CH_2CH(CMe_3)CH_2C^{\bullet}H_2$	385.6	422.0	–36.4	12.5	13.38	6	[16]
$CH(O)(C{-}H)HCH_2CH{-}(CMe_3)CH_2C^{\bullet}H_2$	397.8	422.0	–24.2	17.1	13.31	6	[16]
$C^{\bullet}H_2(CH_2)_4(C{-}H)HC(O)OCH_3$	398.8	422.0	–23.2	30.2	15.11	7	[15]
$C^{\bullet}H_2(CH_2)_2(C{-}H)HC(O)OCH_3$	398.8	422.0	–23.2	32.4	15.41	5	[15]
$2\text{-}[Me_2C(C{-}H)H_2]\text{-}4,6\text{-}(Me_3C)_2C_6\dot{H}_2$	422.0	474.0	–52.0	19.0	14.72	5	[17–19]
$2\text{-}[Ad{-}H]\text{-}4,6\text{-}Ad_2C_6\dot{H}_2$ ***	408.8	474.0	–65.0	18.0	15.23	5	[17, 19]

Notes: * Experimental activation energies (E); the br_e parameter is calculated by Eq. (4) for $T = 350$ K; and the bonds being attacked are denoted as (C–H).

** A cycle is a number of atoms in the cyclic transition state.

*** Ad—adamantyl.

Table 3. Physical and kinetic parameters for radical isomerization*

Radical	br_e, (kJ/mol)$^{1/2}$	$E_{e,0}$, kJ/mol	$r_e \times 10^{11}$, m	$A_{C–H}$, s^{-1}	$E_{e,0}$(bimol.)**, kJ/mol
$R^{\bullet} \longrightarrow R^{1\bullet}$ (six-membered transition state)					
$RC^{\bullet}H(CH_2)_3(C–H)HY$	13.66	46.6	3.65	10^9	74.8
$RC^{\bullet}H(CH_2)_3(C–H)HPh$	14.16	50.1	3.78	10^8	79.2
$RC^{\bullet}H(CH_2)_3(C–H)HCH{=}CH_2$	14.96	56.0	4.00	10^8	86.5
$R^{\bullet} \longrightarrow R^{1\bullet}$ (five-membered transition state)					
$RC^{\bullet}H(CH_2)_2(C–H)HY$	15.41	59.4	4.12	10^9	74.8
$RC^{\bullet}H(CH_2)_2(C–H)HPh$	15.91	63.3	4.25	10^8	79.2
$RC^{\bullet}H(CH_2)_2(C–H)HCH{=}CH_2$	16.71	69.8	4.46	10^8	86.5
$Ph^{\bullet}C(CH_3)_2CH_2–H$	14.98	59.3	4.00	10^9	75.3
$R^{\bullet} \longrightarrow R^{1\bullet}$ (seven-membered transition state)					
$RC^{\bullet}H(CH_2)_4(C–H)HY$	15.11	57.1	4.04	10^9	74.8
$RC^{\bullet}H(CH_2)_4(C–H)HPh$	15.61	60.1	4.17	10^8	79.2
$RC^{\bullet}H(CH_2)_4(C–H)HCH{=}CH_2$	16.41	67.3	4.38	10^8	86.5
$RO^{\bullet} \longrightarrow R^{1\bullet}$ (six-membered transition state)					
$Me_2C(O^{\bullet})(CH_2)_2(C–H)HR$	13.13	53.4	3.51	2×10^9	53.2
$Me_2C(O^{\bullet})(CH_2)_2(C–H)HPh$	13.53	56.8	3.61	2×10^8	56.5
$Me_2C(O^{\bullet})(CH_2)_2(C–H)HCH{=}CH_2$	14.17	62.2	3.79	2×10^8	62.0
$RO_2^{\bullet} \longrightarrow R^{1\bullet}$ (six-membered transition state)					
$RCH(OO^{\bullet})R(C–H)HR$	13.23	53.2	3.53	2×10^9	56.3
$RCH(OO^{\bullet})R(C–H)HPh$	14.38	62.8	3.84	2×10^8	62.3
$RCH(OO^{\bullet})R(C–H)HCH{=}CH_2$	14.82	66.7	3.96	2×10^8	70.2
$RO_2^{\bullet} \longrightarrow R^{1\bullet}$ (seven-membered transition state)					
$RCH(OO^{\bullet})RCH_2(C–H)HR$	13.43	54.8	3.59	2×10^9	56.3
$RCH(OO^{\bullet})RCH_2(C–H)HPh$	14.58	64.6	3.90	2×10^8	62.3
$RCH(OO^{\bullet})RCH_2(C–H)HCH{=}CH_2$	15.02	68.6	4.01	2×10^8	70.2
$R^{1\bullet} \longrightarrow RO_2^{\bullet}$ (six-membered transition state)					
$RCH(OO–H)RC^{\bullet}HR$	16.25	53.2	3.53	2×10^8	56.3
$RCH(OO–H)RC^{\bullet}HPh$	17.67	62.9	3.84	2×10^8	62.3
$RCH(OO–H)RC^{\bullet}HCH{=}CH_2$	18.21	66.8	3.96	2×10^8	70.2
$R^{1\bullet} \longrightarrow RO_2^{\bullet}$ (seven-membered transition state)					
$RCH(OO–H)RCH_2C^{\bullet}HR$	16.50	54.8	3.59	2×10^8	56.3
$RCH(OO–H)RCH_2C^{\bullet}HPh$	17.91	64.6	3.89	2×10^8	62.3
$RCH(OO–H)RCH_2C^{\bullet}HCH{=}CH_2$	18.45	68.6	4.01	2×10^8	70.2

Notes: * The br_e parameters and activation energies for a thermally neutral reaction $E_{e,0}$ are calculated by Eqs. (4) and (5) for $T = 350$ K.
** $E_{e,0}$(bimol.) is the activation energy for intermolecular H-atom abstraction.

$A \approx 10^9$–10^{10} s^{-1} for radical isomerization in agreement with the empirical value $A_{C–H} = 10^9$ s^{-1} (see Table 3).

Using the kinetic parameters for alkyl radical isomerization, one can calculate similar parameters for radical isomerization involving the cleavage of the C–H bonds adjacent to either the phenyl ring resulting in benzyl radical formation or the double bond resulting in allyl radical formation:

$$RC^{\bullet}H(CH_2)_3CH_2Ph \longrightarrow RCH_2(CH_2)_3C^{\bullet}HPh,$$

$$RC^{\bullet}H(CH_2)_3CH_2CH{=}CHR$$

$$\longrightarrow RCH_2(CH_2)_3C^{\bullet}HCH{=}CHR.$$

The reaction center of the transition state in these reactions (more precisely, its three electrons involved in rearrangement) interacts with the adjacent π-electrons of either the double bond or the aromatic ring. This results in the formation of a stronger $C\cdot\cdot H\cdot\cdot C$ bond in the transition state and an increase in both triplet repulsion and the br_e parameter [10]. Then, the phenyl ring adjacent to the Attacked C–H bond in H-atom abstraction by the alkyl radical favors an increase in the br_e parameter by $\Delta br_e = 0.5$ (kJ/mol)$^{1/2}$, whereas the vinyl group enhances it by $\Delta br_e = 1.30$ (kJ/mol)$^{1/2}$ [10]. Using these increments, we obtained the parameters listed in Table 3 for the isomerization of these structures. We assume that the preexponential factor ($A_{C–H}$) for these two reactions is an order of magnitude lower (10^8 rather than 10^9 s^{-1}) because of the inability of the vinyl and phenyl groups to rotate in the transition state and because of entropy loss. The activation energy and rate constants for the isomerization of various alkyl radicals were calculated using the α, br_e, and $A_{C–H}$ parameters (Tables 1 and 3). The activation energy E was evaluated using Eq. (2), whereas the E_e energy was calculated by Eq. (7) using the ΔH_e value [10]:

$$\sqrt{E_e} = \frac{br_e}{1-\alpha^2}\left[1-\alpha\sqrt{1-\frac{1-\alpha^2}{(br_e)^2}\Delta H_e}\right]. \qquad (7)$$

Relevant calculation results are presented in Table 4. The activation energy for these reactions changes with the enthalpy from 7.5 to 30.7 kJ/mol, whereas the rate constant k(350 K) ranges from 5.2×10^4 to 7.7×10^7 s^{-1}. The activation energy for bimolecular H-atom abstraction by alkyl radicals is higher than that for isomerization (Table 4): $E(R^{\bullet} + R^1H) - E$ (isomerization) = 28.0 ± 0.6 kJ/mol.

ALKOXY RADICAL ISOMERIZATION

Alkoxy radicals are very active [10] and rapidly enter the reaction:

$$RO^{\bullet} + R^1H \longrightarrow ROH + R^{1\bullet}.$$

Moreover, alkoxy radicals with sufficiently long alkyl substituents isomerize into alkyl radicals, for example [24]:

$$R(CH_2)_3Me_2CO^{\bullet} \longrightarrow RC^{\bullet}H(CH_2)_2Me_2COH.$$

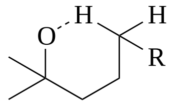
Therefore, the chain chlorination of hydrocarbons with alkyl hypochlorite results in the formation of chlorine-containing alcohols because of a more rapid bimolecular reaction compared to isomerization [24]:

$$RC^{\bullet}H(CH_2)_2Me_2COH + R^1OCl$$

$$\longrightarrow RCHCl(CH_2)_2Me_2COH + R^1O^{\bullet}.$$

The available data on the competition of $RC^{\bullet}H(CH_2)_2Me_2COH$ isomerization (k) [24] and $R^1R^2R^3CO^{\bullet}$ decomposition (k_d) [25] were used to estimate the k values and to calculate the br_e parameter for $RO^{\bullet}$ isomerization. Table 5 presents the initial data and the calculation results. The average br_e value is 13.13 ± 0.18 (kJ/mol)$^{1/2}$, which is close to the br_e parameter for $RO^{\bullet} + R^1H$ bimolecular reactions [10]. Therefore, the $RO^{\bullet} + R^1H$ bimolecular reactions and $RO^{\bullet}$ isomerization accompanied by H-atom abstraction and are characterized by the same kinetic parameters (α, b, and r_e) that describe the activation energy. The activation energy for the thermally neutral isomerization of $RO^{\bullet}$ radicals is $E_{e,0} = 53.4 \pm 1.5$ kJ/mol. In the above cases (Tables 3 and 5), $RO^{\bullet}$ isomerization occurs via the formation of a six-membered activated complex:

$$R(CH_2)_3Me_2CO^{\bullet} \longrightarrow$$



$$\longrightarrow RC^{\bullet}H(CH_2)_2Me_2COH.$$

Using the br_e parameter, one can calculate the activation energy for any $RO^{\bullet}$ isomerization accompanied by H-atom abstraction from the δ-C–H bond according to Eq. (7) [10]. Table 1 lists parameters necessary for such calculation. The ΔH_e values were calculated using Eq. (1), and the E activation energy was calculated using Eq. (2) for $T = 350$ K. The dissociation energies for the C–H bonds were taken from [6], and we assumed that $D_{O–H} = 437.2$ kJ/mol for the forming alcohol group [25]. The rate constant was calculated by Eq. (3) using the same value of $A_{C–H} = 2.0 \times 10^9$ s^{-1}, as for peroxy radical isomerization (see below). Table 6 presents the $RO^{\bullet}$ structures and the calculation results for the E and k parameters. For the reactions under consideration, the activation energy ranges from 4.7 to 29.3 kJ/mol, whereas the rate constant k(350 K) varies from 2.5×10^5 to 4.0×10^8 s^{-1}. The $k/k(RO^{\bullet} + R^1H)$ ratio is

Table 4. Enthalpies ΔH_e, activation energies E, and rate constants k for alkyl radical isomerization calculated by Eqs. (1), (2), and (7)*

Radical $R^{\bullet}$	D_i, kJ/mol	D_f, kJ/mol	ΔH_e, kJ/mol	E, kJ/mol	k (350 K), s^{-1}	$E(R^{\bullet} + R^1H)$, kJ/mol
$C^{\bullet}H_2(CH_2)_3(C–H)HMe$	412.0	422.0	10.0	25.9	2.7×10^5	54.0
$MeC^{\bullet}H(CH_2)_3(C–H)HMe$	412.0	412.0	0	30.7	5.2×10^4	58.9
$MeC^{\bullet}H(CH_2)_3(C–H)Me_2$	400.0	412.0	–12.0	24.9	1.9×10^5	53.0
$MeC^{\bullet}H(CH_2)_2NH(C–H)HMe$	378.6	412.0	–33.4	15.6	9.6×10^6	43.2
$MeC^{\bullet}H(CH_2)_2NMe(C–H)HMe$	367.1	412.0	–44.9	11.0	4.6×10^7	38.2
$Me_2C^{\bullet}(CH_2)_2NH(C–H)Me_2$	357.0	400.0	–43.0	11.7	1.8×10^7	39.0
$Me_2C^{\bullet}(CH_2)_2NMe(C–H)Me_2$	345.5	400.0	–54.5	7.5	7.7×10^7	34.2
$MeC^{\bullet}H(CH_2)_3(C–H)HOH$	397.4	412.0	–14.6	23.7	5.7×10^5	51.8
$MeC^{\bullet}H(CH_2)_3(C–H)MeOH$	391.5	412.0	–20.5	21.1	7.2×10^5	49.0
$MeC^{\bullet}H(CH_2)_2C(O)(C–H)H_2$	410.0	412.0	–2.0	29.8	1.1×10^5	57.9
$MeC^{\bullet}H(CH_2)_2C(O)(C–H)HMe$	397.8	412.0	–14.2	23.9	5.4×10^5	52.0
$MeC^{\bullet}H(CH_2)_2C(O)(C–H)Me_2$	392.7	412.0	–19.3	21.6	6.0×10^5	49.6
$MeC^{\bullet}H(CH_2)_3(C–H)(O)$	385.6	412.0	–26.4	18.5	1.7×10^6	46.3
$MeC^{\bullet}H(CH_2)_3(C–H)HPh$	368.7	412.0	–43.3	14.9	1.2×10^6	43.1
$Me_2C^{\bullet}(CH_2)_3(C–H)MePh$	354.7	400.0	–45.3	14.1	7.8×10^5	42.3
$Me_2C^{\bullet}(CH_2)_3(C–H)HCH{=}CH_2$	349.8	400.0	–50.2	17.8	4.5×10^5	47.3
$Me_2C^{\bullet}(CH_2)_3(C–H)MeCH{=}CH_2$	339.6	400.0	–60.4	13.9	8.4×10^5	43.0

* The α, A, and br_e values are presented in Tables 1 and 3. The A and br_e parameters for $E(R^{\bullet} + R^1H)$ are taken from [10]. The bonds being attacked are denoted as (C–H).

determined by the ratio of the preexponential factors and equals $2.0 \times 10^9/1.0 \times 10^9 = 2$ mol/l, that is, the rates of these reactions are identical at $[R^1H] = 2$ mol/l. The activation energies for the bimolecular reaction of H-atom abstraction by the alkoxy radical and $RO^{\bullet}$ isomerization are virtually the same ($E - E(RO^{\bullet} + R^1H) = 0.2$ kJ/mol, see Table 6).

PEROXY RADICAL ISOMERIZATION

Experimental data on peroxy radical isomerization

$$RCH(OO^{\bullet})(CH_2)_nCH_2R^1$$

$$\longrightarrow RCH(OOH)(CH_2)_nC^{\bullet}HR^1,$$

where $n = 1$ or 2, are summarized in Table 7 [26–39]. The reaction enthalpy ΔH was calculated using the $D_{C–H}$ and $D_{O–H}$ values from [6]. The activation energy for isomerization E was calculated by Eq. (3) using the standard preexponential factor $A_{C–H} = 2.0 \times 10^{9 \pm 0.12}$ s^{-1} obtained by averaging the experimental A values for the reactions studied. The ΔH_e, E_e, and br_e values were evaluated by Eqs. (1), (2), and (4) using parameters from Table 1. Table 7 lists the calculated br_e parameters. Peroxy radical isomerization involving the formation of a six-membered activated complex is energetically more

Table 5. Initial data and calculated kinetic parameters for alkoxy radical isomerization [24, 25]*

Radical $RO^{\bullet}$	k/k_p (273 K)	k_p (273 K) × 10^{-4}, s^{-1}	k (273 K) × 10^{-4}, s^{-1}	E, kJ/mol	E_e, kJ/mol	ΔH_e, kJ/mol	br_e, $(kJ/mol)^{1/2}$
$(C–H)H_2(CH_2)_2Me_2CO^{\bullet}$	0.29	3.57	1.03	30.1	46.4	–19.5	13.27
$(C–H)H_2MeCHCH_2Me_2CO^{\bullet}$	0.67	3.57	2.41	29.8	46.1	–19.5	13.24
$Me(C–H)H(CH_2)_2Me_2CO^{\bullet}$	6.15	2.20	13.5	23.4	39.7	–28.5	12.87

* The activation energies (E) are experimentally determined. The br_e parameter is calculated by Eq. (4) for T = 350 K. The bonds being attacked are denoted as (C–H)

Table 6. Enthalpies ΔH_e, activation energies E, and rate constants k for alkoxy radical isomerization calculated by Eqs. (1), (2), and (7), respectively*

Radical $RO^{\bullet}$	D_i, kJ/mol	ΔH_e, kJ/mol	E, kJ/mol	k (350 K), s^{-1}	$E(RO^{\bullet} + R^1H)$, kJ/mol
$Me_2C(O^{\bullet})(CH_2)_2(C–H)H_2$	422.0	–19.5	29.3	2.5×10^5	29.1
$Me_2C(O^{\bullet})(CH_2)_2(C–H)HMe$	412.0	–29.5	25.4	6.4×10^5	25.2
$Me_2C(O^{\bullet})(CH_2)_2(C–H)Me_2$	400.0	–41.5	21.1	1.4×10^6	20.8
$Me_2C(O^{\bullet})CH_2NH(C–H)HMe$	378.6	–62.9	14.0	3.3×10^7	13.7
$Me_2C(O^{\bullet})CH_2NMe(C–H)HMe$	367.1	–74.4	10.5	1.1×10^8	10.3
$Me_2C(O^{\bullet})CH_2NH(C–H)Me_2$	357.0	–84.5	7.7	1.4×10^8	7.5
$Me_2C(O^{\bullet})CH_2NMe(C–H)Me_2$	345.5	–96.0	4.7	4.0×10^8	4.5
$Me_2C(O^{\bullet})(CH_2)_2(C–H)HOH$	397.4	–44.1	20.1	3.9×10^6	19.9
$Me_2C(O^{\bullet})(CH_2)_2(C–H)MeOH$	391.5	–50.0	18.1	3.9×10^6	17.9
$Me_2C(O^{\bullet})CH_2C(O)(C–H)H_2$	410.0	–31.5	24.7	1.2×10^6	24.5
$Me_2C(O^{\bullet})CH_2C(O)(C–H)HMe$	397.8	–43.7	20.3	3.8×10^6	20.1
$Me_2C(O^{\bullet})CH_2C(O)(C–H)Me_2$	392.7	–48.8	18.5	3.4×10^6	18.3
$Me_2C(O^{\bullet})(CH_2)_2(C–H)(O)$	385.6	–55.9	16.2	7.7×10^6	15.9
$Me_2C(O^{\bullet})(CH_2)_2(C–H)HPh$	368.7	–72.8	14.0	3.3×10^6	13.7
$Me_2C(O^{\bullet})(CH_2)_2(C–H)MePh$	354.7	–86.8	9.9	6.6×10^6	9.7
$Me_2C(O^{\bullet})(CH_2)_2(C–H)HCH{=}CH_2$	349.8	–91.7	13.4	4.0×10^6	13.2
$Me_2C(O^{\bullet})(CH_2)_2(C–H)MeCH{=}CH_2$	339.6	–101.9	10.6	5.2×10^6	10.4

* $D_{O–H}$ = 437.2 kJ/mol. The α, A, and br_e values are presented in Tables 1 and 3. The A and br_e parameters for the $RO^{\bullet} + R^1H$ bimolecular reaction were presented in [10]. The bonds being attacked are denoted as (C–H).

Table 7. Thermodynamic and kinetic parameters for peroxy radical isomerization*

Radical $RO_2^{\bullet}$	E, kJ/mol	D_i, kJ/mol	D_f, kJ/mol	ΔH_e, kJ/mol	br_e, (kJ/mol)$^{1/2}$	Cycle**	Reference
$PhCH(O_2^{\bullet})O(C–H)HPh$	44.2	366.9	365.5	–2.4	14.18	6	[26–28]
$Me_2C(O_2^{\bullet})CH_2(C–H)Me_2$	57.4	400.0	358.6	37.6	13.43	6	[29]
$Me_2C(O_2^{\bullet})O(C–H)Me_2$	55.2	390.8	358.6	28.4	13.75	6	[26, 30]
$MeCH(O_2^{\bullet})CH_2(C–H)HMe$	68.9	413.0	365.5	43.7	14.43	6	[31]
$MeCH(O_2^{\bullet})CH_2(C–H)H(CH_2)_9Me$	58.8	415.7	365.5	46.4	12.97	6	[32]
$Me(C–H)HCH_2CH(O_2^{\bullet})(CH_2)_{11}Me$	62.2	413.0	365.5	43.7	13.62	6	[33]
$MeCH(O_2^{\bullet})CH_2(C–H)(O_2H)(CH_2)_{11}Me$	48.3	391.5	365.5	22.2	13.29	6	[33]
$Me_2CHCH_2C(O_2^{\bullet})(Me)(CH_2)(C–H)Me_2$	54.5	400.0	358.6	37.6	13.05	6	[34]
$Me_2C(O_2^{\bullet})C(O)(C–H)Me_2$	59.0	392.7	358.6	30.3	14.09	6	[35]
$(Me(CH_2)_5C(O)OCH_2)_3CCH_2OC(O)–CH_2CH(O_2^{\bullet})CH_2(C–H)HCH_2Me$	56.8	413.0	365.5	43.7	12.92	6	[36]
$(Me(CH_2)_5C(O)OCH_2)_3CCH_2OC(O)–(CH_2)_3CH(O_2^{\bullet})CH_2(C–H)H_2$	56.9	422.0	365.5	52.7	12.18	6	[36]
$Ph(C–H)(O_2H)OCH(O_2^{\bullet})Ph$	47.7	366.9	365.5	–2.4	14.59	6	[28, 37]
$(Me(CH_2)_5C(O)OCH_2)_3CCH_2OC(O)–(CH_2)_2(C–H)CH_2CH(O_2^{\bullet})Me$	56.8	415.7	365.5	46.4	12.71	6	[36]
$(Me(CH_2)_5C(O)OCH_2)_3CCH_2OC(O)–CH_2CH(O_2^{\bullet})CH_2(C–H)(O_2H)CH_2Me$	41.9	391.5	365.5	22.2	12.46	6	[36]
$MeCH(O_2^{\bullet})(CH_2)_2(C–H)H(CH_2)_{10}Me$	63.1	415.7	365.5	46.4	13.53	7	[33, 38]
$MeCH_2C(O)OCH_2Me_2C–CH(O_2^{\bullet})OC(O)(C–H)HMe$	52.5	398.8	365.5	29.5	13.35	7	[39]
$(MeCH_2C(O)OCH_2)_3C–CH(O_2^{\bullet})OC(O)(C–H)HMe$	53.5	398.8	365.5	29.5	13.47	7	[39]
$MeCH_2CH(O_2^{\bullet})(CH_2)_2(C–H)H(CH_2)_9Me$	62.3	415.7	365.5	46.4	13.44	7	[33]
$Me(C–H)H(CH_2)_2CH(O_2^{\bullet})(CH_2)_{10}Me$	62.3	413.0	365.5	43.7	13.63	7	[33]
$MeCH(O_2^{\bullet})(CH_2)_2(C–H)(O_2H)(CH_2)_{10}Me$	52.7	391.5	365.5	22.2	13.82	7	[33]
$(MeCH_2C(O)OCH_2)_2(MeCH_2)–CCH(O_2^{\bullet})OC(O)(C–H)HMe$	53.4	398.8	365.5	29.5	13.45	7	[39]
$(Me(CH_2)_5C(O)OCH_2)_3CCH_2OC(O)–CH_2CH(O_2^{\bullet})(CH_2)_2(C–H)(O_2H)Me$	46.2	391.5	365.5	22.2	13.02	7	[36]
$(Me(CH_2)_5C(O)OCH_2)_3CCH_2OC(O)–CH_2(C–H)(O_2H)(CH_2)_2(C–H)(O_2^{\bullet})Me$	47.0	391.5	365.5	22.2	13.12	7	[36]

Notes: * The activation energies (E) are experimentally determined. The br_e parameter is calculated by Eq. (4) for T = 350 K. The bonds being attacked are denoted as (C–H).

** A cycle is a number of atoms in the cyclic transition state.

Table 8. Enthalpies ΔH_e, activation energies E, and rate constants k for peroxy radical isomerization calculated by Eqs. (1), (2), and (7), respectively*

Radical $RO_2^{\bullet}$	D_i, kJ/mol	D_f, kJ/mol	ΔH_e, kJ/mol	ΔE_{μ}, kJ/mol	E, kJ/mol	k (350 K), $l\ mol^{-1}\ s^{-1}$	$E(RO_2^{\bullet} + R^1H)$, kJ/mol
$CH_2(OO^{\bullet})CMe_2CH_2–H$	422.0	365.5	52.7	0	64.3	1.5	67.2
$MeCH(OO^{\bullet})CH_2(C–H)HMe$	412.0	365.5	42.7	0	58.7	7.0	61.6
$Me_2C(OO^{\bullet})CH_2(C–H)Me_2$	400.0	358.6	37.6	0	55.9	9.2	58.9
$MeCH(OO^{\bullet})NH(C–H)HMe$	378.6	365.5	9.3	0	41.6	2.5×10^3	44.7
$MeCH(OO^{\bullet})NMe(C–H)HMe$	367.1	365.5	–2.2	0	36.3	1.5×10^4	39.4
$Me_2C(OO^{\bullet})NH(C–H)Me_2$	357.0	358.6	–5.4	0	34.9	1.2×10^4	38.0
$Me_2C(OO^{\bullet})NMe(C–H)Me_2$	345.5	358.6	–16.9	0	30.0	6.6×10^4	33.1
$CH(OH)(OO^{\bullet})CH_2(C–H)HOH$	397.4	371.6	22.0	–2.2	45.5	6.4×10^2	48.6
$MeC(OH)(OO^{\bullet})CH_2–(C–H)MeOH$	391.5	371.6	16.1	–2.2	42.6	8.7×10^2	45.7
$CH_2(OO^{\bullet})C(O)(C–H)H_2$	410.0	365.5	40.7	–15.4	42.2	3.1×10^3	45.1
$MeCH(OO^{\bullet})C(O)(C–H)HMe$	397.8	365.5	28.5	–15.4	35.7	1.9×10^4	38.7
$Me_2C(OO^{\bullet})C(O)(C–H)Me_2$	392.7	358.6	30.3	–15.7	36.3	7.7×10^3	39.3
$C(O)(OO^{\bullet})CH_2(C–H)(O)$	385.6	406.1	–24.3	–8.8	18.3	3.8×10^6	21.3
$PhCH(OO^{\bullet})CH_2(C–H)HPh$	364.1	365.5	–5.2	0	44.6	8.7×10^1	44.1
$PhC(OO^{\bullet})CH_2(C–H)MePh$	354.7	358.6	–7.7	0	43.5	6.3×10^1	43.0
$CH_2{=}CHCH(OO^{\bullet})CH_2–(C–H)HCH{=}CH_2$	349.8	365.5	–19.5	0	42.4	1.9×10^2	45.9
$CH_2{=}CHC(OO^{\bullet})MeCH_2–(C–H)MeCH{=}CH_2$	339.6	358.6	–22.8	0	41.2	1.5×10^2	44.5

* The α, A, and br_e values are presented in Tables 1 and 3. The A and br_e parameters for $E(RO_2^{\bullet} + R^1H)$ were presented in [10]. The bonds being attacked are denoted as (C–H).

favorable: the br_e parameter is 13.23 ± 0.48 $(kJ/mol)^{1/2}$ and the activation energy of a thermally neutral reaction $E_{e,0}$ is 53.2 ± 3.9 kJ/mol. For the seven-membered transition state, the $E_{e,0}$ value (54.8 ± 1.9 kJ/mol) is slightly higher and the br_e parameter is 13.43 ± 0.23 $(kJ/mol)^{1/2}$.

The isomerization of $RCH(OO^{\bullet})CH_2(C–H)HPh$ peroxy radicals is characterized by $br_e = 14.38 \pm 0.20$ $(kJ/mol)^{1/2}$ (Tables 3 and 7). The calculated br_e parameter for the six-membered transition state (13.23 $(kJ/mol)^{1/2}$) is close to the br_e value (13.62 $(kJ/mol)^{1/2}$) for monomolecular H-atom abstraction from the aliphatic C–H bond by the peroxy radical [6]. Therefore, the kinetic parameters for isomerization $RO_2^{\bullet}$ are close to those for bimolecular H-atom abstraction by the peroxy radical.

This allows the estimation of the kinetic parameters for peroxy radical isomerization

$$\mathrm{RCH(OO^{\bullet})(CH_2)_{\mathit{n}}CH{=}CH_2}$$

$$\longrightarrow \mathrm{RCH(OOH)CH_2C^{\bullet}HCH{=}CH_2}.$$

To estimate the br_e parameter for this isomerization reaction, one can use data for the corresponding bimolecular $RO_2^{\bullet} + RCH_2CH{=}CH_2$ reaction [6]. Relevant results of calculation are presented in Table 8. The br_e parameter for the isomerization of $RCH(OO^{\bullet})CH_2CH_2Ph$ and $RCH(OO^{\bullet})CH_2CH_2CH{=}CH_2$ radicals are higher than 13.23 (kJ/mol)$^{1/2}$, whereas the $A_{C–H}$ value is lower for the same reason as for the isomerization of similar alkyl radicals (see above). The E and k values for the isomerization of various $RO_2^{\bullet}$ radicals were calculated from the α, br_e, and A parameters (Tables 1 and 3). The E_e value was evaluated by Eq. (7) [10]. The ΔH_e and E values were calculated by Eqs. (1) and (2), respectively. The C–H and O–H bond dissociation energies were taken from [6]. When calculating the E parameter for the isomerization of radicals with polar oxygen-containing groups (alcohols, ketones, and aldehydes), we took into account the contribution of the polar effect to the activation energy $\Delta E_{e,\mu}$ and added this increment, which had been determined earlier when analyzing the $RO_2^{\bullet}$ + RH reactions involving these compounds [40–42] (see Table 8). Table 8 shows that the activation energy for peroxy radical isomerization ranges from 18.3 to 64.3 kJ/mol, whereas the rate constant k (350 K) varies from 1.5 to 3.8×10^6 s^{-1}.

To determine how the competition between intra- and intermolecular hydrogen transfers changes on switching from the C–H to OO–H bond, we calculated the E and k (350 K) values for $RO_2^{\bullet} + R^1H$ reactions using the corresponding α, br_e, and A parameters ($A_{C–H} = 1.0 \times 10^8$ l mol^{-1} s^{-1}) [10] and the ΔH values for isomerization. Relevant calculated results (E ($RO_2^{\bullet} + R^1H$) are presented in Table 8. The activation energy for bimolecular H-atom abstraction by peroxy radicals $E(RO_2^{\bullet} + R^1H)$ is slightly higher than that for isomerization E (Table 8): $E(RO_2^{\bullet} + R^1H) - E = 2.7 \pm 1.2$ kJ/mol. The $k/k(RO_2^{\bullet} + R^1H)$ ratio ranges from 54 to 58 mol/l for the $RCH(OO^{\bullet})Y(C–H)HR$ radical and takes values of 16.6 and 66–68 for the $RCH(OO^{\bullet})Y(C–H)HPh$ and $RCH(OO^{\bullet})Y(C–H)HCH{=}CH_2$ radicals, respectively. The effect of the cycle size in the transition state on the E and k parameters for $RO_2^{\bullet}$ isomerization was considered earlier $k_5 \ll k_6 \approx k_7 \gg k_8$ [5].

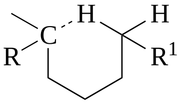
Using the parameters for $RO_2^{\bullet} \longrightarrow R^{1\bullet}$ isomerization (see Table 1), one can calculate the E and k values for reverse isomerization:

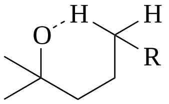
$$\mathrm{RC(OOH)CH_2C^{\bullet}R \longrightarrow RC(OO^{\bullet})CH_2CHR}.$$

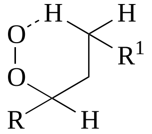
Relevant parameters are presented in Table 3.

CONCLUSION

In this work, the parabolic model of a bimolecular reaction was first used to analyze and to describe monomolecular radical isomerization involving intramolecular hydrogen-atom abstraction. The possibility of such a description was demonstrated. Our parameters can be used to estimate the activation energies and the rate constants for such reactions (see Tables 3, 4, 6, and 8). The six-membered activated complex is the most favorable for the isomerization of alkyl, alkoxy, and peroxy radicals, as follows from the parameters describing the activation energy:







Obviously, this configuration is the best for radical isomerization involving hydrogen-atom abstraction. The effect of the cycle size in the transition state on the activation energy of abstraction can be estimated for intramolecular H-atom abstraction in alkyl and peroxy radicals. For $RO_2^{\bullet}$ reactions, we used the estimates from [5] along with our own results. Below are the activation energy $E_{e,0}$ and the cycle strain energy E(cycle strain) (kJ/mol) [43]:

Cycle size:	5	6	7	8
$\Delta E_{e,0}(R^{\bullet} \longrightarrow R^{1\bullet})$	12.8	0	10.5	–
$\Delta E_{e,0}(RO_2^{\bullet} \longrightarrow R^{1\bullet})$	>13.9	0	1.6	>8.9
E (cycle strain) [43]	26.4	0	26.8	41.4

Comparison of the $\Delta E_{e,0}$ values with the cycle strain energy in cyclohexane C_nH_{2n} suggests their similarity, except for the case of the seven-membered cycle in peroxy radical isomerization. An interesting conclusion follows from comparing the activation energies for intra- and intermolecular H-atom abstraction. It is known that the bimolecular abstraction reaction always implies the linear atom arrangement in the reaction center of the transition state. It is this linear atom configuration that ensures the minimal activation barrier for the hydrogen atom. In the case of intramolecular abstraction, only a nonlinear reaction center is possible. Taking into account that it is less energetically favorable, one can expect that $E_{e,0}$ (isomerization) > $E_{e,0}$ (radical + molecule) for the reactions of all radicals ($R^{\bullet}$, $RO^{\bullet}$, and $RO_2^{\bullet}$). Below are the $E_{e,0}$ values for intra- and intermolecular H-atom transfer in $R^{\bullet}$, $RO^{\bullet}$, and $RO_2^{\bullet}$ reactions (the $E_{e,0}$ values for intermolecular H-atom transfer are taken from [10]). The $E_{e,0}$ values are expressed in kJ/mol.

Reaction center:	C…H…C	O…H…C	O–O…H…C
$E_{e,0}$ (isomerization, six-membered cycle):	46.6	53.4	53.2
$E_{e,0}$ (bimolecular abstraction):	74.8	53.2	56.3

The $E_{e,0}$ values for H-atom abstraction by $RO^{\bullet}$ and $RO_2^{\bullet}$ radicals are close, whereas, in the case of alkyl radicals, $E_{e,0}$ (isomerization) < $E_{e,0}$ ($R^{\bullet}$ + R^1H). It is interesting to elucidate the reasons for this unique specific feature of the six-membered reaction center in H-atom abstraction.

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