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Reactions of Peroxy Radicals with Hydrocarbons and Alcohols: Transition State Geometry and the Polar Effect

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Abstract—The reaction $EtOO^{\bullet} + EtH \longrightarrow EtOOH + Et^{\bullet}$ was studied by the intersecting parabolas method and calculated using density functional theory. The interatomic C–H, O–H, and C–O distances of the transition state for this reaction were calculated using these methods. The formulas for calculating these distances from experimental data were obtained. Similar calculations and comparisons were carried out for the reaction $EtOO^{\bullet} + MeCH_2OH \longrightarrow EtOOH + Me\dot{C}HOH$. The polar effect of the hydroxy groups on the transition state manifested itself in a decrease in the activation energy and in the formation of a nonlinear structure of the transition state. An empirical formula for estimating the C–H–O angle in the transition state from the enthalpy and activation energy was derived.

INTRODUCTION

The reaction of peroxy radicals with the C–H bonds of organic compounds is central to the chain liquid-phase oxidation of these compounds. We have previously examined the reactivity of reactants in this reaction in the framework of the parabolic model and revealed several factors influencing the activation energy of the reaction [1]

$$RO_2^{\bullet} + R_iH \longrightarrow ROOH + R_i^{\bullet}.$$

The peroxy radical is a polar reactant with a high dipole moment. According to quantum chemical data, the dipole moment of the peroxy radical is $\mu = 1.95$ for $HO_2^{\bullet}$, 2.33 for $Me_3COO^{\bullet}$, 2.45 for $PhCH(OH)OO^{\bullet}$, and 3.87 D for $PhC(O)OO^{\bullet}$ [2]. The dipole–dipole interaction is observed in reactions of radical abstraction of the hydrogen atom from the $R_{\mu}H$ polar molecule by the polar radical ($HO^{\bullet}$, $RO^{\bullet}$, or $RO_2^{\bullet}$) [3]. The contribution of the dipole–dipole interaction to the activation energy for the reactions of $RO_2^{\bullet}$ with various oxygen-containing compounds was estimated in [4–9].

The model of radical abstraction as a result of intersecting two parabolas (intersecting-parabolas method (IPM)) [8–12] makes it possible to calculate such geometric characteristics of the transition state as interatomic distances in the reaction site using the experimental data [13]. The same parameters can be calculated by the quantum chemical methods (QCM). Two problems are analyzed in this work. First, the C–H and O–H distances in the transition state of the reaction $RO_2^{\bullet}$ + RH, where RH is a hydrocarbon, were calculated and compared by the IPM and QCM methods. Second, the influence of the polar interaction on the geometry of the transition state was revealed for the reaction $RO_2^{\bullet}$ + ethanol. The results obtained were used for estimating the C–H and O–H distances and φ(C–H–O) angle in the reactions of peroxy radicals with the C–H bonds of alcohols. IPM and density functional theory were used in the calculations.

CALCULATION PROCEDURES

Intersecting-Parabolas Method

In the reactions of hydrogen abstraction by peroxy radicals ($RO_2^{\bullet}$) from hydrocarbons and alcohols (ROH), the weakest C–H bond is cleaved and the O–H bond is formed. The IPM transition state of this reaction is considered as the result of two intersecting parabolic potential curves [8–12]. One of them represents the potential energy of stretching vibration of the attacked C–H bond as a function of the amplitude of its stretching vibration, and the other curve represents the potential energy of stretching vibration of the O–H bond formed. Each reaction is characterized by the following values [8–12]: the enthalpy ΔH_e, the activation energy E_e, the sum of amplitudes of vibration of the reacting bonds in the transition state r_e, the coefficients b (which refers to the attacked bond; $2b^2$ is the force constant of this bond) and b_f (which refers to the formed bond), and the coefficient $\alpha = b/b_f$. The position of the transition state $r_0^{\neq}$ in the segment r_e in the thermoneutral reaction is calculated as $r_0^{\neq} = r_e(1+\alpha)^{-1}$. The enthalpy ΔH_e of the abstraction reaction is equal to the difference between the dissociation energies of the cleaved (D_i) and formed (D_f) bonds taking into account the zero-point energy of these bonds

$$\Delta H_e = D_{i(C-H)} - D_{f(ROO-H)} + 0.5hN_A(\nu_i - \nu_f), \quad (1)$$

where ν_i and ν_f are the frequencies of the zero-point vibration of the reacting and formed bonds, respectively; h is the Planck constant; and N_A is Avogadro's number. The activation energy E_e calculated using this model includes the zero-point energy of the attacked bond and is related to the experimental activation energy E:

$$E_e = E + 0.5(hN_A\nu_i - RT). \quad (2)$$

The reaction rate constant k was calculated by the Arrhenius equation

$$k = A\exp(-E/RT), \quad (3)$$

where A is the empirical preexponential factor, which is constant for reactions of the same class per one attacked C–H bond. The br_e parameter for these reactions was determined from the experimental E values using the equation

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \quad (4)$$

The radical abstraction reaction with the C··H··O reaction site is characterized by the following parameters: $b = b_i = 3.743 \times 10^{11}$ (kJ/mol)$^{1/2}$ m^{-1}, $b_f = 4.600 \times 10^{11}$ (kJ/mol)$^{1/2}$ m^{-1}, $\alpha = 0.814$, $0.5h\nu N_A = 17.4$ kJ/mol, and $0.5hN_A(\nu_{C-H} - \nu_{O-H}) = -3.8$ kJ/mol [9]. The br_e and A_{C-H} parameters for the reactions of peroxy radicals with hydrocarbons are (R^1H is aliphatic hydrocarbon, R^2H is olefin, and R^3H is alkylaromatic hydrocarbon) [9–12]:

RH	R^1H	R^2H	R^3H
br_e, (kJ/mol)$^{1/2}$	13.62	15.21	14.32
A_{C-H}, l mol^{-1} s^{-1}	1.0×10^8	1.0×10^7	1.0×10^7

The dissociation energies of the C–H bonds in hydrocarbons are taken from [14, 15], D_{C-H} in alcohols are available in [16], and $D_{O-H} = 365.5$ kJ/mol in *sec*-ROOH and 369.0 kJ/mol in hydrogen peroxide formed from the $HO_2^{\bullet}$ radical [1]. For the reactions of *sec*-$RO_2^{\bullet}$ with R_iH at $\alpha \neq 1$ and $\Delta H_e < \Delta H_{e,\max}$, the activation energies were calculated using the IPM formula [8]

$$\sqrt{E_e} = \frac{br_e}{1-\alpha^2}\left[1 - \alpha\sqrt{1 - \frac{1-\alpha^2}{(br_e)^2}\Delta H_e}\right]. \quad (5)$$

The C–H, O–H, and C–O bond lengths in the transition state were estimated using formulas (6)–(8) [8]:

$$r_{C-H} = r_{CH} + \frac{\sqrt{E_e}}{b}, \quad (6)$$

where r_{CH} is the equilibrium distance between the C and H atoms in the RH molecule;

$$r_{O-H} = r_{OH} + \alpha\frac{\sqrt{E_e - \Delta H_e}}{b}, \quad (7)$$

where r_{OH} is the equilibrium distance between the O and H atoms and $2(b/\alpha)^2$ is the force constant of the O–H bond in the ROOH molecule. The C–O distance in the transition state is

$$r_{C-O} = r_{CH} + r_{OH} + b^{-1}(\sqrt{E_e} + \alpha\sqrt{E_e - \Delta H_e}). \quad (8)$$

The results of calculation of the thermodynamic characteristics of the reaction of peroxy radicals with hydrocarbons calculated from the experimental data by the intersecting-parabolas method using formulas (1) and (5) and the geometric parameters of the transition state of these reactions calculated using formulas (6)–(8) are presented below. The contribution of the polar interaction to the activation energy was estimated using the formula [3]

$$\Delta E_{\mu} = \{(br_e)_{\mu}^2 - (br_e)_{RH}^2\}(1+\alpha)^{-2}, \quad (9)$$

where the $(br_e)_{\mu}$ and $(br_e)_{RH}$ parameters are attributed to the reactions involving the polar compound and reference compound RH, respectively.

Quantum Chemical Calculation

The B3LYP hybrid density functional method approximation, which provides acceptable accuracy for simple reactions, was used for the theoretical study of intermolecular reactions of hydrogen abstraction by the $C_2H_5OO^{\bullet}$ peroxy radical [17]. The calculations were carried out using GAUSSIAN 98 program [18]. The geometry of stationary points and zero-point energies were found by optimization in the 6-31G basis set and then the energy of the system was calculated in the 6-311++G(d,p) basis set. The results of quantum chemical calculation are presented in Table 1 and Fig. 1.

RESULTS AND DISCUSSION

Reactions of $RO_2^{\bullet}$ with Hydrocarbons

The calculation of the transition state (TS) geometry of the reaction $C_2H_5OO^{\bullet} + HC_2H_5$ (TS1) by the density functional theory shows that for this reaction the angle is φ(O–H–C) = 176.2°, i.e., close to 180° (see Fig. 1). The kinetic parameters of this reaction calculated using IPM are as follows. The enthalpy is $\Delta H_e = D_i(C-H) - D_f(ROO-H) - 3.8 = 422.0 - 365.5 - 3.8 = 52.7$ kJ/mol

[1]. For the reaction of $RO_2^\bullet$ with the aliphatic C–H bond, the parameters are $br_e = 13.62$ (kJ/mol)$^{1/2}$ and $\alpha = 0.814$, and the activation energy is calculated by formula (5) as $E_e = 83.4$ kJ/mol. The geometric parameters of the transition state were determined and the lengthening of the C–H and O–H bonds in this transition state was calculated using formulas (6)–(8). In the starting molecules, $r_{CH} = 1.092 \times 10^{-10}$ m and $r_{OH} = 0.970 \times 10^{-10}$ m [19]. The interatomic distances (expressed in 10^{-10} m) obtained by IPM calculation are presented below.

Bond	In reactants	In the transition state	Lengthening	%
C–H	1.092	1.336	0.244	22
O–H	0.970	1.090	0.120	12
C···H···O	2.062	2.426	0.364	18

The results obtained by density functional theory (see below and in Fig. 1) are rather close to the IPM data (interatomic distances are expressed in 10^{-10} m).

Bond	In reactants	In the transition state	Lengthening	%
C–H	1.097	1.470	0.373	34
O–H	0.984	1.115	0.131	13
C···H···O	2.081	2.585	0.504	24

The C··H··O distance characterizes a group of reactions $RO_2^\bullet + R^1H$, where R^1H is an aliphatic hydrocarbon. Comparing the $r_{C\cdot\cdot H\cdot\cdot O}$ value obtained by QCM with that given by IPM, one can correct the lengthening of the bonds obtained by the semiempirical IPM method brought in correspondence with the density functional theory. Comparison of the $r_{C\cdot\cdot H\cdot\cdot O}$ values shows that the lengthening of the bonds $r_{C\cdot\cdot H\cdot\cdot O} - r_{C\text{–}H} - r_{O\text{–}H} = (2.585\text{–}2.062) \times 10^{-10}$ m $= 5.23 \times 10^{-11}$ m (QCM) is 1.44 times greater than $r_e = 3.64 \times 10^{-11}$ m calculated by IPM. This makes it possible to calculate the inter-

Table 1. Energy (E), zero-point energy (ZPE), and dipole moments (μ) of the reactants and transition states of the reactions of the ethylperoxyl radical with ethane and ethanol calculated at the B3LYP/6-31G and B3LYP/6-311++G** level

System	E, hartree		ZPE, hartree	μ, D	
	B3LYP/6–31G	B3LYP/6–311++G**		B3LYP/6–31G	B3LYP/6–311++G**
$C_2H_5OO^\bullet + HC_2H_5$ (TS1)					
C_2H_6	–79.81274	–79.85650	0.07563	0.00	0.00
$CH_3CH_2OO^\bullet$	–299.47161	–299.60567	0.07166	3.28	3.30
TS1	–309.24774	–309.42657	0.14190	2.39	2.35
$C_2H_5OO^\bullet + HCHOHCH_3$ (TS2)					
C_2H_5OH	–154.99018	–155.09434	0.08016	1.88	1.78
$CH_3CH_2OO^\bullet$	–299.47161	–299.60567	0.07166	3.28	3.30
TS2	–384.44325	–384.67610	0.14799	2.71	2.78
$C_2H_5^\bullet$	–79.14114	–79.18997	0.05999	0.26	0.32
$CH_3C^\bullet HOH$	–154.33198	–154.43517	0.06598	1.58	1.39
CH_3CH_2OOH	–230.10412	–230.24538	0.08291	0.96	0.97

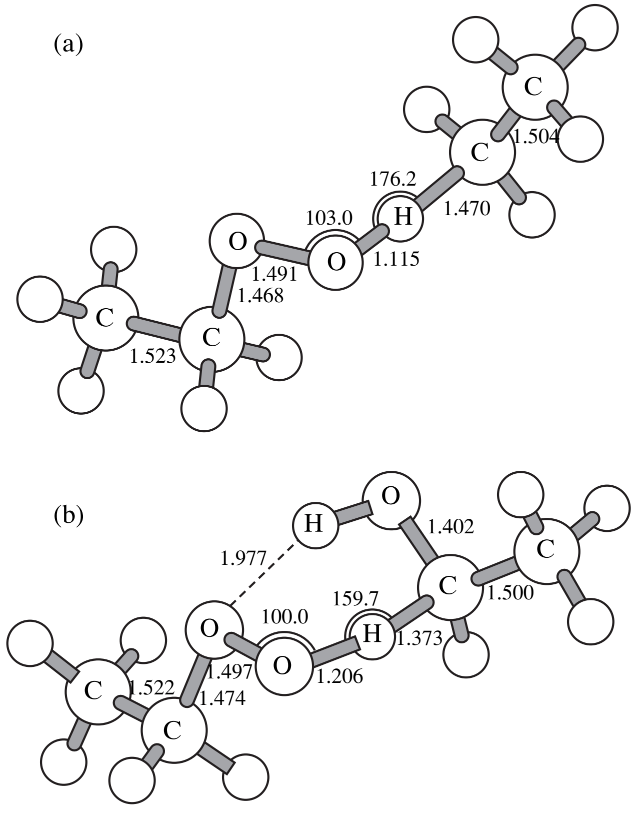


Fig. 1. Structures of the transition states (a) TS1 and (b) TS2 according to the data of the B3LYP/6-31G calculations for the reactions $C_2H_5OO^{\bullet}$ + HC_2H_5 and $C_2H_5OO^{\bullet}$ + $HCHOHCH_3$, respectively.

atomic distances in the transition state for the $\mathrm{RO}_2^{\bullet}$ + RH reaction using the experimental data (E_e and ΔH_e values) by formulas (6)–(8). These formulas corrected by the quantum chemical calculation results for the $\mathrm{RO}_2^{\bullet} + \mathrm{R}^1\mathrm{H}$ reactions take the following form:

$$r_{\text{C–H}} \times 10^{10}\ (\mathrm{m}) = 1.09 + 3.85 \times 10^{-2}\sqrt{E_e}, \tag{10}$$

$$\begin{aligned} &r_{\text{O–H}} \times 10^{10}\ (\mathrm{m}) \\ &= 0.97 + 3.13 \times 10^{-2}\sqrt{E_e - \Delta H_e}, \end{aligned} \tag{11}$$

$$\begin{aligned} &r_{\text{C–O}} \times 10^{10}\ (\mathrm{m}) \\ &= 2.06 + 3.85 \times 10^{-2}(\sqrt{E_e} + 0.814\sqrt{E_e - \Delta H_e}), \end{aligned} \tag{12}$$

where E_e and ΔH_e are in kJ/mol. The interatomic distances calculated using formulas (10)–(12) are presented in Table 2.

Reactions of $\mathrm{RO}_2^{\bullet}$ with Alcohols

Comparison of the geometry of transition states for $C_2H_5OO^{\bullet}$ + HC_2H_5 (TS1) and $C_2H_5OO^{\bullet}$ + $HCHOHCH_3$ (TS2) calculated by the density functional theory shows that for the reaction with ethane the φ(O–H–C) angle is close to 180°, whereas for the reaction with ethanol the angle is 159.7° (see Fig. 1). The sum of the O–H and C–H distances in both transition states remains virtually unchanged and equal to 2.58 Å. At the same time, in the case of ethane, the O–H bonds elongate and the C–H bonds are shortened compared to those for the transition state in the reaction with ethanol. A polar effect is observed in the reaction of the peroxy radical with ethanol and other alcohols [3]. The hydroxy group of the alcohol interacts with the reaction site of the transition state to decrease the activation energy in most cases (negative ΔE_μ values, Table 3).

For ethanol, $D_{\text{C–H}}$ = 399.8 kJ/mol [16] and the enthalpy of the reaction $\mathrm{RO}_2^{\bullet}$ + ethanol is ΔH = 34.3 kJ/mol and ΔH_e = 30.5 kJ/mol. The rate constant of the reaction $\mathrm{RO}_2^{\bullet}$ + ethanol at 333 K is 1.9 $\mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ and, correspondingly, the activation energy is $E = RT\ln(2 \times 10^8/1.9)$ = 51.1 kJ/mol and, according to formula (2), E_e = 67.1 kJ/mol. The br_e parameter is 13.11 $(\mathrm{kJ/mol})^{1/2}$ and $r_e = 3.50 \times 10^{-11}$ m. If ethanol reacted with $\mathrm{RO}_2^{\bullet}$ as a paraffinic hydrocarbon with $D_{\text{C–H}}$ = 399.8 kJ/mol, the activation energy would be $E_{e,\,\mathrm{RH}}$ = 71.1 kJ/mol (formula (5)). The difference between $E_{e,\,\mathrm{RH}}$ and E_e equal to 4 kJ/mol is the result of the polar interaction in the transition state. What does the polar interaction consists of? The answer is the configuration of the transition state for this reaction calculated using density functional theory. The configuration is nonlinear (Fig. 1). The angle is φ(C–H–O) = 159.7°. At the same time, the sum of the distances $r_{\text{C–H}} + r_{\text{O–H}} = 2.580 \times 10^{-10}$ m, which is the same as in the reaction of the peroxy radical with the C–H bond of ethane. Therefore, the polar effect in the $\mathrm{RO}_2^{\bullet}$ + ethanol reaction appears as a nonlinear (angular) configuration of the reaction site of the transition state. A decrease in the r_e parameter (IPM) on going from the $\mathrm{RO}_2^{\bullet}$ + ethane reaction to $\mathrm{RO}_2^{\bullet}$ + ethanol can be solely attributed to the appearance of the angular configuration of atoms at the reaction site in the latter reaction. Therefore, the r_e parameter calculated for the $\mathrm{RO}_2^{\bullet}$ + alcohol reaction can be treated as a distance between the C and O atoms in the transition state. Then,

Table 2. Thermodynamic and geometric parameters of the transition state for the reaction $sec\text{-}RO_2^{\bullet} + RH \longrightarrow sec\text{-}ROOH + R^{\bullet}$ calculated using formulas (1), (5), and (10)–(12)

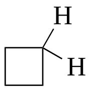
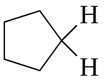
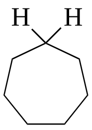
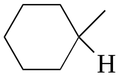
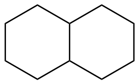
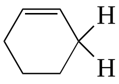
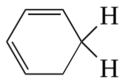
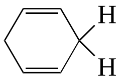
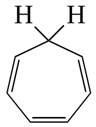
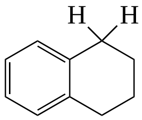
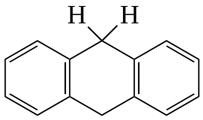
RH	ΔH_e, kJ/mol	E_e, kJ/mol	$r_{C–H} \times 10^{10}$, m	$r(O–H) \times 10^{10}$, m	$r_{C–O} \times 10^{10}$, m
$MeCH_2$–H	52.7	83.4	1.442	1.143	2.585
EtMeCH–H	43.7	78.1	1.432	1.154	2.586
Me_3C–H	30.7	71.1	1.416	1.169	2.585
	49.2	81.2	1.439	1.147	2.586
	39.1	75.6	1.426	1.159	2.585
	34.6	73.2	1.421	1.165	2.586
	26.2	68.8	1.411	1.174	2.585
	18.3	64.9	1.402	1.184	2.586
CH_2=$CHCH_2$–H	–1.3	69.6	1.413	1.234	2.647
CH_2=CHCH–HMe	–19.5	61.8	1.394	1.252	2.646
CH_2=CHC–HMe_2	–29.7	57.7	1.384	1.263	2.647
Z-MeCH=CHCH–HMe	–25.3	59.4	1.388	1.258	2.646
Me_2C=CHCH–HMe	–37.3	54.7	1.377	1.270	2.647
Me_2C=CMeC–HMe_2	–46.5	51.2	1.367	1.279	2.646
CH_2=CHCMe–HCH=CH_2	–62.1	45.6	1.352	1.294	2.647
	–27.8	58.4	1.386	1.261	2.647
	–38.4	54.2	1.375	1.271	2.646
	–56.7	47.5	1.357	1.290	2.647
	–68.3	43.5	1.346	1.301	2.647
MeC≡CC–HMe_2	–39.9	53.7	1.374	1.273	2.647
PhMeCH–H	–5.2	60.0	1.390	1.223	2.613
$PhMe_2C$–H	–14.6	56.0	1.380	1.233	2.613
	–23.7	52.2	1.370	1.243	2.613
	–47.3	43.2	1.345	1.268	2.613

Table 3. Kinetic parameters of the radical abstraction reactions *sec*-$RO_2^{\bullet}$ + alcohol calculated from the experimental data by the intersecting parabolas method using formulas (3), (4) and (9)

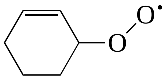
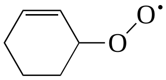
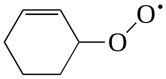
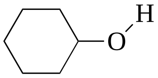
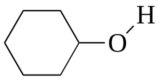
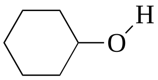
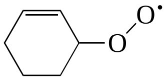
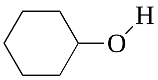
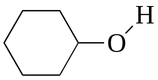
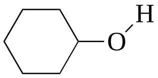
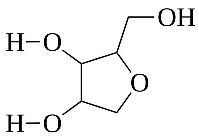
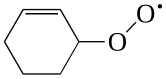
Reaction	T, K	k(333 K), l mol^{-1} s^{-1}	E, kJ/mol	br_e, $(kJ/mol)^{1/2}$	ΔE_{μ}, kJ/mol	Refs.
$A_{C–H} = 10^8$ l mol^{-1} s^{-1}						
MeOH + $HO_2^{\bullet}$	333	3.75	50.35	12.47	–9.15	[20, 21]
MeOH + 	333	1.05	53.87	12.68	–7.50	[22]
EtOH + $HO_2^{\bullet}$	333	19.3	44.69	12.52	–8.76	[3, 21]
EtOH + 	333	1.93	51.07	13.11	–4.11	[22]
Me_2CHOH + $HO_2^{\bullet}$	333	13.36	43.80	13.02	–4.89	[23, 24]
Me_2CHOH + 	333	1.99	49.06	13.46	–1.32	[22]
 + $HO_2^{\bullet}$	333	0.97	51.05	14.03	3.44	[25]
 + $HO_2^{\bullet}$	333	1.07	50.78	14.00	3.16	[24]
 + 	333	2.47	48.47	13.51	–0.88	[22]
 + $CCl_3CCl_2OO^{\bullet}$	348	2500	30.64	13.60	–0.19	[26]
 + $CHCl_2CCl_2OO^{\bullet}$	348	1000	33.29	13.85	1.91	[26]
 + $MePhOO^{\bullet}$	333	0.29	54.39	13.82	1.62	[26]
CH_2OHCH_2OH + $MeCH(OO^{\bullet})(CH_2)_{13}Me$	403	28.1	55.15	13.48	–1.14	[27]
$CH_2OH(CH_2)_2CH_2OH$ + $MeCH(OO^{\bullet})(CH_2)_{13}Me$	403	30.4	54.89	13.27	–2.88	[27]
$CH_2OHCH_2CHOHMe$ + $MeCH(OO^{\bullet})(CH_2)_{13}Me$	403	36.0	49.68	13.67	0.40	[27]
$Me_2C(CH_2OH)_2$ + $MeCH(OO^{\bullet})(CH_2)_{13}Me$	403	964	43.31	11.68	–14.89	[27]
$EtC(CH_2OH)_3$ + $MeCH(OO^{\bullet})(CH_2)_{13}Me$	403	296	48.63	12.44	–9.35	[27]
$Me(CHOH)_2OPr$ + $MeCH(OO^{\bullet})(CH_2)_{13}Me$	403	56	50.52	14.03	3.48	[27]
 + $MeCH(OO^{\bullet})(CH_2)_{13}Me$	403	680	42.16	13.01	–4.91	[27]
$A_{C–H} = 10^7$ l mol^{-1} s^{-1}						
$PhCH_2OH$ + $HO_2^{\bullet}$	333	3.16	43.33	14.28	–0.35	[28]
$PhCH_2OH$ + 	333	5.55	41.77	13.92	–3.46	[22]

Table 3. (Contd.)

Reaction	T, K	k(333 K), l mol^{-1} s^{-1}	E, kJ/mol	br_e, (kJ/mol)$^{1/2}$	ΔE_μ, kJ/mol	Refs.
$PhCH_2OH + Me_2PhCOO^\bullet$	333	0.66	47.66	14.24	–0.68	[29]
$PhMeCHOH + HO_2^\bullet$	333	3.21	41.37	14.59	2.34	[28]
$PhMeCHOH + HO_2^\bullet$	333	3.45	41.17	14.40	0.66	[30]
$PhCH_2OH + MePhCHOO^\bullet$	333	2.17	44.37	14.22	–0.86	[29]
$PhCH_2OH + Ph_2CHOO^\bullet$	333	1.17	46.08	14.42	0.85	[29]

we obtain the following empirical formula for the calculation of the φ angle using the experimental data:

$$\cos(180° - \varphi) = \frac{r^2_{\mu(C\text{–}O)} - r^2_{C\text{–}H} - r^2_{O\text{–}H}}{2r_{C\text{–}H}r_{O\text{–}H}}, \qquad (13)$$

where $r_{\mu(C\text{–}O)} = r_{CH} + r_{OH} + r_{e,\mu}$, $r_{e,\mu} = r_e$ for the reaction of $RO_2^\bullet$ with polar compound $R_\mu H$ (in our case, ethanol), and $r_{C\text{–}H} = r_{CH} + r^{\neq}$ and $r_{O\text{–}H} = r_{OH} + r_e - r^{\neq}$, where r_e and $r^{\neq}$ refer to the reaction of $RO_2^\bullet$ with hydrocarbon with the same bond strength as the polar compound. The calculation by formula (13) for ethanol using experimental data (see above) gives the angle φ = 165.0°, which agrees well with the quantum chemical calculation data. The results of calculation of the geometric parameters for a series of reactions between $RO_2^\bullet$ and polar molecules obtained using formulas (10)–(13) are presented in Table 4. We see that the total distance $r_{C\text{–}O} = r_{C\text{–}H} + r_{O\text{–}H}$ is practically the same in all reactions of peroxy radicals with alcohols and the φ angle changes from 150° to 180° depending on the structure of alcohol, which is attacked by the peroxy radical. For the reaction of the peroxy radical with ethanol, the results of calculation of the φ angle are close: 165.0° (IPM) and 159.7° (QCM, Fig. 1). We expect that the greater $|\Delta E_\mu|$, the stronger the difference between the arrangement of the C, H, and O atoms in the transition state and the linear structure (see Table 3). Indeed, as can be seen in Fig. 2, a good linear correlation is observed between cos(180° – φ) and $-\Delta E_\mu$:

$$\cos(180° - \varphi) = 1 - (8.14 \pm 0.56)\Delta E_\mu \times 10^{-3}. \quad (14)$$

It is of interest to compare the dipole moments of transition states for the reactions $C_2H_5OO^\bullet + HC_2H_5$ (TS1) and $C_2H_5OO^\bullet + HCHOHCH_3$ (TS2) with the dipole moments of the reactants (Table 1). The ethane molecule has no dipole moment, and that of the ethyl radical is low too. Therefore, a decrease in the dipole moment of TS1 compared with that of the $C_2H_5OO^\bullet$ radical by 0.95 D can only be related to the appearance of a new group of atoms, namely, the OH group bearing a dipole moment oriented at an angle to the dipole moment of the peroxy radical. The dipole moment of the TS2 transition state is only slightly higher (by 0.43 D) than that of TS1, despite the presence of the alcohol group bearing a dipole moment of 1.78 D. Taking into account that TS2 has a less late character than TS1, their values indicate such a relative orientation of the polar groups at which their dipole moments are efficiently quenched. It is clear that the energy gain of the dipole–dipole interaction is realized, which is apparently a reason of the nonlinear character of TS2. Perhaps, the weak hydrogen bond shown by the dotted line in Fig. 1 also plays some role in these processes. Thus, IPM can be used to estimate the geometric parameters of the transition state

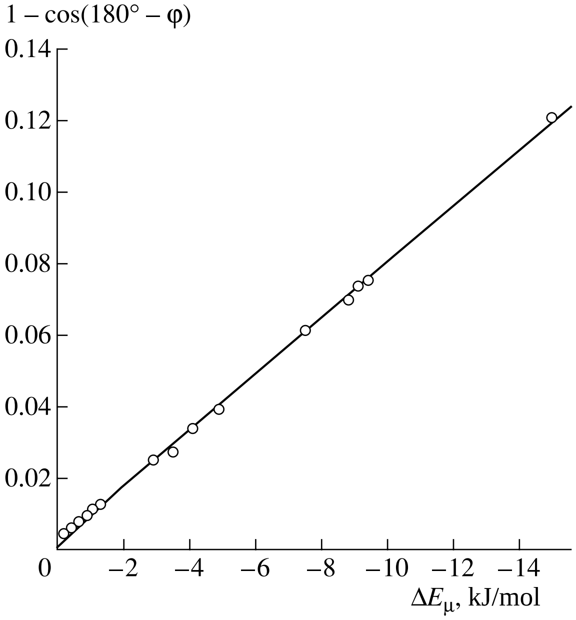


Fig. 2. Plot of cos(180° – φ) vs. $-\Delta E_\mu$ for the reaction $sec\text{-}RO^\bullet + ROH \longrightarrow sec\text{-}ROOH + R'^\bullet OH$.

Table 4. Thermodynamic and geometric parameters of the transition state for the reaction *sec*-$RO_2^\bullet$ + ROH ⟶ *sec*-ROOH + $R'^\bullet$OH calculated using formulas (1), (5), and (10)–(13)

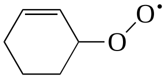
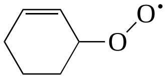
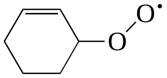
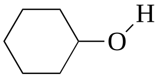
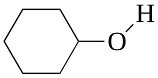
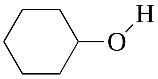
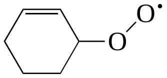
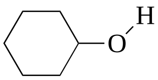
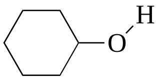
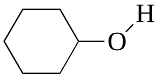
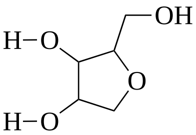
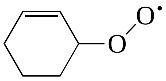
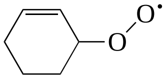
Reaction	ΔH_e, kJ/mol	E_e, kJ/mol	$r_{C-H} \times 10^{10}$, m	$r_{O-H} \times 10^{10}$, m	$r_{C-O} \times 10^{10}$, m	φ, deg
$A_{C-H} = 10^8$ l mol^{-1} s^{-1}						
MeOH + $HO_2^\bullet$	38.2	66.4	1.404	1.136	2.540	157.8
MeOH + 	41.7	69.9	1.412	1.136	2.548	159.9
EtOH + $HO_2^\bullet$	27.0	60.7	1.390	1.152	2.542	158.4
EtOH + 	30.5	67.1	1.405	1.159	2.565	165.0
Me_2CHOH + $HO_2^\bullet$	17.7	59.8	1.388	1.173	2.561	163.7
Me_2CHOH + 	21.2	65.1	1.401	1.177	2.578	170.8
 + $HO_2^\bullet$	15.6	67.1	1.405	1.195	2.600	180.0
 + $HO_2^\bullet$	15.6	66.8	1.405	1.194	2.599	180.0
 + 	19.1	64.5	1.399	1.181	2.580	171.9
 + $CCl_3CCl_2OO^\bullet$	–22.6	46.6	1.353	1.230	2.583	174.3
 + $CHCl_2CCl_2OO^\bullet$	–21.2	49.2	1.360	1.233	2.593	180.0
 + $MePhOO^\bullet$	26.0	70.4	1.413	1.179	2.592	180.0
CH_2OHCH_2OH + $MeCH(OO^\bullet)(CH_2)_{13}Me$	32.2	70.9	1.414	1.165	2.579	171.5
$CH_2OH(CH_2)_2CH_2OH$ + $MeCH(OO^\bullet)(CH_2)_{13}Me$	34.9	70.6	1.413	1.157	2.570	167.2
$CH_2OHCH_2CHOHMe$ + $MeCH(OO^\bullet)(CH_2)_{13}Me$	18.4	65.4	1.401	1.185	2.586	180.0
$Me_2C(CH_2OH)_2$ + $MeCH(OO^\bullet)(CH_2)_{13}Me$	34.9	59.0	1.386	1.124	2.509	151.5
$EtC(CH_2OH)_3$ + $MeCH(OO^\bullet)(CH_2)_{13}Me$	34.9	64.3	1.399	1.140	2.538	157.5
$Me(CHOH)_2OPr$ + $MeCH(OO^\bullet)(CH_2)_{13}Me$	13.8	66.2	1.403	1.197	2.600	180.0
 + $MeCH(OO^\bullet)(CH_2)_{13}Me$	13.8	57.9	1.383	1.178	2.561	163.9
$A_{C-H} = 10^7$ l mol^{-1} s^{-1}						
$PhCH_2OH$ + $HO_2^\bullet$	–5.9	59.3	1.386	1.223	2.609	173.7
$PhCH_2OH$ + 	–2.4	57.7	1.382	1.213	2.595	166.6

Table 4. (Contd.)

Reaction	ΔH_e, kJ/mol	E_e, kJ/mol	$r_{C–H} \times 10^{10}$, m	$r_{O–H} \times 10^{10}$, m	$r_{C–O} \times 10^{10}$, m	φ, deg
$PhCH_2OH + Me_2PhCOO^{\bullet}$	4.5	63.7	1.397	1.211	2.608	172.7
$PhMeCHOH + HO_2^{\bullet}$	–16.8	57.4	1.382	1.239	2.621	180.0
PhMeCHOH + 	–13.3	57.2	1.381	1.233	2.614	180.0
$PhCH_2OH + MePhCHOO^{\bullet}$	–2.4	60.4	1.389	1.218	2.607	172.3
$PhCH_2OH + Ph_2CHOO^{\bullet}$	–2.4	62.1	1.393	1.221	2.615	180.0

using experimental data (the enthalpy and activation energy of the reaction). This estimation performed for the reaction of the peroxy radical with ethanol is consistent with the quantum chemical calculation using density functional theory.

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