Transition State Geometry and a Polar Effect in the Reactions of Peroxy Radicals with Oxygen-Containing Compounds

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Abstract—The reactions of structurally different peroxy radicals with the C–H bonds of oxygen-containing compounds (ketones, aldehydes, ethers, and esters) were analyzed in terms of a parabolic model. The enthalpies of these reactions and the activation energies of equienthalpic reactions of peroxy radicals with hydrocarbons were calculated, and the contribution of the polar interaction ΔE_μ to the activation energy was evaluated. The geometry parameters of the transition state were calculated with the use of an algorithm developed based on quantum-chemical calculations in combination with the intersecting parabolas method. It was found that the polar interaction resulted in a change in the configuration of the C···H···O reaction center in the transition state from linear to angular. A different angle $\varphi(C \cdots H \cdots O)$ from 180° appeared in this case. The following linear correlation between ΔE_μ (kJ/mol) and $\cos(180° - \varphi)$ was obeyed: $\cos(180° - \varphi) = 1 + 6.76 \times 10^{-3} \Delta E_\mu$.

INTRODUCTION

The polar interaction of reactants in the transition state (TS) clearly manifests itself in the reactions of peroxy radicals with oxygen-containing compounds [1, 2]. First, it reflects on the activation energy of the reaction. Previously, we evaluated the contribution of the polar interaction of reactants ΔE_μ to the activation energies of the reactions of peroxy radicals with compounds containing various functional groups in terms of the intersecting parabolas model [3–5]. However, this calculation for the reactions of peroxy radicals containing functional groups was performed on the assumption that the dissociation energy of the O–H bond in hydroperoxides generated from peroxy radicals is equal to that in alkyl ROOH. In this work, the strengths of these bonds for hydroperoxides containing functional groups were calculated using experimental data, and a new calculation of ΔE_μ was performed.

Second, the polar interaction affects the configuration of the reaction center of the TS of reaction [6]. In the reaction of a peroxy radical with the C–H bond of a hydrocarbon, the C, H, and O atoms in the TS are arranged along a straight line, whereas the C, H, and O atoms form an angle $\varphi(C \cdots H \cdots O) = 160°$ in the reaction of a peroxy radical with the C–H bond of polar ethanol. Previously [6], the parameters of the intersecting parabolas model for the reactions of $\mathrm{RO_2^{\cdot}}$ with ethane and ethanol were compared with the results of quantum-chemical calculations. An algorithm was constructed for calculating interatomic distances and angles in the TS reaction center from experimental data (reaction enthalpy, rate constant, and activation energy). These

interatomic distances and angles were consistent with those obtained by quantum-chemical calculations with the use of Gaussian 98 and the density functional theory. We used this algorithm in this work to construct the TS geometry in the reactions of various peroxy radicals with oxygen-containing compounds, such as aldehydes, ketones, ethers, and esters, in which a polar effect is observed.

CALCULATION PROCEDURE

In terms of the intersecting parabolas model, the reaction

$$\mathrm{RO_2^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}}$$
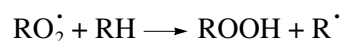
is characterized by the following parameters [7–10]:

(1) an enthalpy ΔH_e, which includes the difference between the zero vibration energies of the cleaved C–H and the formed O–H bonds,

$$\begin{aligned} \Delta H_e(\mathrm{kJ/mol}) &= D(R_i - H) \\ &- D(\mathrm{ROO-H}) - 3.8\,(\mathrm{kJ/mol}); \end{aligned} \tag{1}$$

(2) an activation energy E_e, which also includes the zero vibration energy of the cleaved C–H bond,

$$E_e(\mathrm{kJ/mol}) = E + 17.4\,(\mathrm{kJ/mol}) - 0.5RT; \tag{2}$$

(3) a parameter $\alpha = 0.814$, where α^2 is equal to the ratio between the force constants of the cleaved and formed bonds;

(4) a parameter r_e, which is the sum of the vibrational amplitudes of reacting bonds in the TS; and

(5) a parameter b, where $2b^2$ is the force constant of the attacked C–H bond.

The activation energy E of the reaction of a peroxy radical with a polar compound was calculated from the experimental reaction rate constant k by the Arrhenius equation with the use of the standard preexponential factor A_0 per attacked C–H bond (n_{C-H} is the number of these bonds in the attacked molecule).

$$E = RT \ln(n_{C-H} A_0 / k). \qquad (3)$$

The activation energy E_{RH} of the equienthalpic reaction of $RO_2^{\cdot}$ with hydrocarbon RH ($D(R–H) = D(R_\mu H)$, where $R_\mu H$ is an oxygen-containing compound) was calculated from the following intersecting parabolas model equation [7–10]:

$$E_{RH} = 8.784(br_e)^2 \left\{ 1 - 0.814 \sqrt{1 - \frac{0.337 \Delta H_e}{(br_e)^2}} \right\}^2 \qquad (4)$$
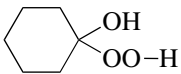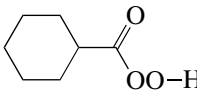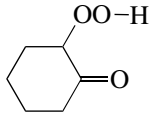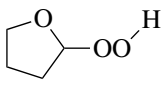$$+ 17.4 - 0.5RT.$$

The parameter br_e is related to the activation energy $E_{e,0}$ of a thermally neutral reaction ($E_{e,0} = E_e$ at $\Delta H_e = 0$) by the following simple relationship:

$$E_{e,0} = [br_e/(1 + \alpha)]^2. \qquad (5)$$

The following intersecting parabolas model parameters were used for calculations [9]:

Parameter	Hydrocarbon		
	paraffin	olefin	alkylaromatic
br_e, (kJ/mol)$^{1/2}$	13.62	15.21	14.32
A_0, l mol^{-1} s^{-1}	1.0×10^8	1.0×10^7	1.0×10^7
$E_{e,0}$, kJ/mol	56.4	70.3	62.3

The reaction enthalpy was calculated from Eq. (1). The dissociation energies of the O–H bond in hydroperoxides containing functional groups were calculated from experimental data on the coupled oxidation of hydrocarbons and the corresponding oxygen-containing compounds [11] by the intersecting parabolas model method [12]. The strengths of the O–H bonds of hydroperoxides, which were obtained by calculations or taken from publications [13, 14], are given below.

Hydroperoxide	D(O–H), kJ/mol
$R_3COO–H$	358.6
⬡(OH)(OO–H)	362.1
PhRC(OH)OO–H	360.0
⬡C(O)OO–H	377.0
$R_3C(O)OO–H$	377.0
$RCH_2OCH(OO–H)R$	367.3
$RC(O)OCH(OO–H)Ph$	374.8
$R_2CHOO–H$	365.5
HOO–H	369.0
$RC(O)OO–H$	387.0
⬡(OO–H)(=O)	369.8
PhC(O)OO–H	403.9
$R_2CHOC(OO–H)R_2$	358.4
⬠(O)(OO–H)	367.6

The values of D(C–H) for oxygen-containing compounds were taken from [15, 16]. The contribution of the polar interaction to the activation energy ΔE_μ was estimated using the equation [3]

$$E_\mu - E_{RH} = \Delta E_\mu = [(br_e)_\mu^2 - (br_e)^2](1 + \alpha)^{-2}, \qquad (6)$$

where E_μ characterizes the reaction of a peroxy radical with a polar compound, and E_{RH} characterizes the equienthalpic reaction of the same peroxy radical with a hydrocarbon (calculated from Eq. (4)). The parameter br_e was calculated by the equation [7–10]

$$br_e = 0.814 \sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \qquad (7)$$

Interatomic distances in the TS were calculated using the following equations, in which E_e refers to the equienthalpic reaction of a peroxy radical with a hydrocarbon [6]:

$$r(C–O) \times 10^{10}/m$$
$$= 2.06 + 3.85 \times 10^{-2}(\sqrt{E_e} + \alpha \sqrt{E_e - \Delta H_e}), \qquad (8)$$

$$r(C–H) \times 10^{10}/m = 1.09 + 3.85 \times 10^{-2} \sqrt{E_e}, \qquad (9)$$

$$r(O–H) \times 10^{10}/m$$
$$= 0.97 + 3.13 \times 10^{-2} \sqrt{E_e - \Delta H_e}. \qquad (10)$$

The angle $\varphi(C\ldots H\ldots O)$ was determined by the equation

$$\cos(\pi - \varphi) = \frac{r_\mu(C\text{–}O)^2 - r(C\text{–}H)^2 - r(O\text{–}H)^2}{2r(C\text{–}H)r(O\text{–}H)}. \quad (11)$$

The parameter $r_\mu(C\text{–}O)$, which characterizes the interatomic distance in the TS of the reaction with a polar compound, was calculated by Eq. (8) through the activation energy $E_{0,\mu}$. The sequence of calculations is given below. The enthalpy ΔH_e of the test reaction $RO_2^\cdot + R_\mu H$ was calculated using Eq. (1). Next, from the experimental rate constant of this reaction and the standard preexponential factor A_0 for this class of reactions, the activation energy was calculated: $E_\mu = RT\ln(n_{C\text{–}H}A_0/k)$. To evaluate ΔE_μ from Eq. (6), the parameter br_e was calculated (Eq. (7)). The TS parameters for each of the test reactions were calculated using Eqs. (8)–(11). For the reactions of peroxy radicals with hydrocarbons, the error in $E_{e,0}$ was ~1 kJ/mol [3]. Correspondingly, the evaluation error in ΔE_μ (see E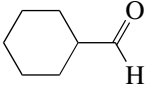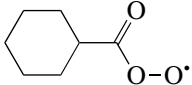q. (6)) was ±2 kJ/mol, and the evaluation error in the parameter r_e was $\Delta r_e = 0.0025 \times 10^{-10}$ m. The lengths of O–H and C–H bonds are known to within $\pm0.01 \times 10^{-10}$ m. Consequently, the values of $r(O\text{–}H)$ and $r(C\text{–}H)$ in the TS are estimated to within $\pm0.012 \times 10^{-10}$ m, and the total distance $r(C\text{–}O)$ is evaluated with an error of $\pm0.025 \times 10^{-10}$ m.

RESULTS AND DISCUSSION
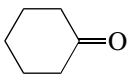
Reactions of Peroxy Radicals with Aldehydes

Table 1 summarizes the calculation data on ΔE_μ and the TS parameters for the reactions of peroxy radicals with aldehydes. As can be seen in Table 1, the reactions of acylperoxy radicals with aldehydes are always exothermic. This is due to, on the one hand, a comparatively weak C–H bond in an aldehyde and, on the other hand, the high strength of the O–H bond formed in a peracid. The polar interaction contributes considerably to the activation energy. The values of ΔE_μ are negative in all the test reactions; that is, the polar interaction accelerates the reaction. The value of ΔE_μ varies within the range from –1.5 to –11 kJ/mol; it is independent of

Table 1. Contributions of the polar interaction to the activation energy (ΔE_μ) and the TS geometry parameters for the reactions of peroxy radicals with aldehydes

Aldehyde	Peroxy radical	ΔH_e, kJ/mol	ΔE_μ, kJ/mol	$r(C\text{–}H) \times 10^{10}$, m	$r(O\text{–}H) \times 10^{10}$, m	$\varphi(CHO)$, deg
$CH_3C(O)H$	$Me_3CO_2^\cdot$	11.4	–7.5	1.373	1.211	161
$CH_3C(O)H$	$MeC(O)O_2^\cdot$	–17.1	–3.7	1.349	1.235	167
$EtC(O)H$	$Me_3CO_2^\cdot$	2.6	–5.8	1.375	1.209	163
$PrC(O)H$	$Me_3CO_2^\cdot$	8.8	–5.7	1.375	1.209	163
$Me(CH_2)_5C(O)H$	$HO_2^\cdot$	–1.6	–6.5	1.360	1.224	162
$Me(CH_2)_5C(O)H$	$Me(CH_2)_5C(O)O_2^\cdot$	–19.7	–2.9	1.348	1.236	168
$Me_3CC(O)H$	$Me_3CC(O)O_2^\cdot$	–5.7	–8.3	1.350	1.234	160
(cyclohexanecarbaldehyde)	(cyclohexanecarbonylperoxy radical)	–8.8	–5.1	1.341	1.243	164
$PhC(O)H$	$Me_3CO_2^\cdot$	–14.4	–4.4	1.378	1.233	166
$PhC(O)H$	$Me_2PhCO_2^\cdot$	–14.4	–5.7	1.378	1.233	165
$PhC(O)H$	$PhC(O)O_2^\cdot$	–59.7	–1.6	1.330	1.281	172
$MeCH=CHC(O)H$	$Me_3CO_2^\cdot$	–23.0	–10.7	1.389	1.257	160
$CH_2=CHC(O)H$	$Me_3CO_2^\cdot$	–23.0	–8.9	1.389	1.257	161

Note: Rate constants required for the calculations were taken from [11, 17].

Table 2. Contributions of the polar interaction to the activation energy ΔE_μ and the TS geometry parameters for the reactions of peroxy radicals generated from ketones with ketones

Ketone	ΔH_e, kJ/mol	E_e, kJ/mol	ΔE_μ, kJ/mol	$r(\text{C–H}) \times 10^{10}$, m	$r(\text{O–H}) \times 10^{10}$, m	$\varphi(\text{CHO})$, deg
$CH_3C(O)CH_3$	31.4	72.0	−13.5	1.446	1.199	156
$MeC(O)CH_2Me$	19.7	65.8	−13.8	1.426	1.219	155
$MeC(O)CH_2Et$	19.7	68.4	−11.1	1.431	1.214	158
$MeC(O)CHMe_2$	17.9	61.1	−17.5	1.417	1.228	152
(cyclohexanone)=O	20.3	61.0	−18.9	1.427	1.218	151
$PhC(O)CH_2Ph$	−9.1	53.8	−12.5	1.386	1.259	157
$PhCH_2C(O)CH_2Ph$	−9.1	60.2	−14.3	1.386	1.259	155
$PhCH_2C(O)CH_2Ph$	−9.1	57.1	−9.2	1.386	1.259	160

Note: Rate constants required for the calculations were taken from [17].

the length of an alkyl substituent for linear aliphatic aldehydes. It is of interest that −1.5…−11 in the reaction of an aldehyde with an acylperoxy radical $|\Delta E_\mu|$ is lower than that in the reaction with an alkylperoxy radical. The reaction center of the TS has a nonlinear structure because of the polar interaction. The greater $|\Delta E_\mu|$, the greater the difference between the angle φ and 180°.

Reactions of Peroxy Radicals with Ketones

Table 2 summarizes the results of calculations of enthalpy, activation energy $E_{e,0}$, and TS geometry parameters (Eqs. (8)–(11)) for the reactions of peroxy radicals with ketones. The TS in the reaction of a peroxy radical with a ketone α-C–H bond ROO…H…C–C(O) is similar to that in the reaction of $RO_2^\cdot$ with an olefin α-C–H bond: ROO…H…C–C=C–, where the π electrons of the C=C bond interact with the electrons of the reaction center. This interaction results in an increase in the activation energy because of an additional triplet repulsion (9). Therefore, ΔE_μ was evaluated with the use of the parameter $br_e = 15.21$ (kJ/mol)$^{1/2}$, which is characteristic of the reactions of peroxy radicals with olefins. As can be seen in Table 2, ΔE_μ varies within the range from −9 to −19 kJ/mol. The angle φ varies from 160° to 151°.

Reactions of Peroxy Radicals with Ethers

Among these reactions, there are reactions in which the polar interaction decreases the energy of interaction (to −10 kJ/mol) or, on the contrary, increases it (to 4 kJ/mol). In the majority of reactions with the participation of ethers, the polar effect is insignificant, and the

value of ΔE_μ varies from −2 to −4 kJ/mol. The angle φ (C…H…O) varies from 180° to 157° (Table 3).

As a rule, a decrease in the activation energy due to the polar interaction increases on going from an alkylperoxy radical to an ether peroxy radical. The difference in the values of ΔE_μ is several kJ/mol (Table 3). For all the above reactions, the following linear correlation between ΔE_μ (negative values) and $\cos \varphi$ (C…H…O) is obeyed:

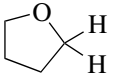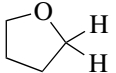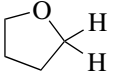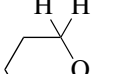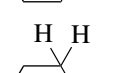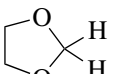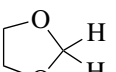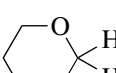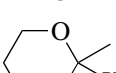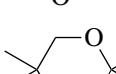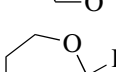$$\cos(180° - \varphi) = 1 + (6.76 \pm 0.21) \times 10^{-3}\Delta E_\mu \quad \text{(kJ/mol)}. \tag{12}$$

Reactions of Peroxy Radicals with Esters

The reactions of peroxy radicals with esters are characterized by high activation energies of thermally neutral reactions (65–83 kJ/mol). A comparison of this activation energy with the $E_{e,0}$ of the corresponding hydrocarbons (paraffins or olefins in the case of the esters of aliphatic or benzyl alcohols, respectively) suggests that the polar effect increases the activation energy of reaction with a peroxy radical by 4–15 kJ/mol (Table 4). These esters are different from other oxygen-containing compounds. It is likely that the configuration of atoms in the TS is close to linear.

Thus, the polar interaction in the TSs of reactions of peroxy radicals with various oxygen-containing compounds significantly affects the activation energy of this reaction. In particular cases, the value of $|\Delta E_\mu|$ is as high as 20 kJ/mol. Simultaneously, it also changes the TS configuration from linear to angular. As in the case of the reactions of peroxy radicals with alcohols [6], a linear correlation between $1 - \cos(\text{C…H…O})$ and ΔE_μ

Table 3. Contributions of the polar interaction to the activation energy ΔE_μ and the TS geometry parameters for the reactions of $RO_2^\bullet$ with ethers

Ether	$RO_2^\bullet$	ΔH_e, kJ/mol	E_e, kJ/mol	ΔE_μ, kJ/mol	$r(\text{C–H}) \times 10^{10}$, m	$r(\text{O–H}) \times 10^{10}$, m	$\varphi(\text{CHO})$, deg
$(PrCH_2)_2O$	$Me_3COO^\bullet$	37.1	72.8	–1.8	1.414	1.170	171
$(PrCH_2)_2O$	$PrCH(OO^\bullet)OCHPr$	28.4	65.5	–4.6	1.400	1.183	165
$(Me_2CH)_2O$	$Me_3COO^\bullet$	28.4	74.0	4.0	1.412	1.172	180
$(Me_2CH)_2O$	$Me_2C(OO^\bullet)OCHMe_2$	28.6	66.3	–3.9	1.412	1.172	166
$(PhCH_2)_2O$	$Me_3COO^\bullet$	–3.4	59.4	–1.4	1.390	1.221	172
$(PhCH_2)_2O$	$EtOCH(OO^\bullet)Me$	–12.1	51.1	0.0	1.377	1.234	180
(tetrahydrofuran, CH₂)	$Me_3COO^\bullet$	29.2	68.6	–1.8	1.412	1.172	171
(tetrahydrofuran, CH₂)	(tetrahydrofuranyl-OO•)	20.5	62.2	–3.9	1.402	1.182	166
(tetrahydrofuran, CH₂)	$EtOCH(OO^\bullet)Me$	20.5	62.1	–4.2	1.403	1.180	166
(tetrahydropyran, CH₂)	$Me_3COO^\bullet$	39.3	75.3	–0.5	1.425	1.159	175
(tetrahydropyran, CH₂)	(tetrahydropyranyl-OO•)	34.4	62.7	–10.8	1.419	1.165	157
$(BuO)_2CH_2$	$Me_2PhCOO^\bullet$	27.7	69.3	–0.4	1.424	1.182	176
$(EtO)_2CHMe$	$Me_2PhCOO^\bullet$	24.8	65.8	–2.4	1.408	1.176	169
$(BuO)_2CHMe$	$Me_2PhCOO^\bullet$	24.8	64.8	–3.4	1.408	1.178	167
(1,3-dioxolane, CH₂)	$Me_2PhCOO^\bullet$	28.8	66.8	–3.5	1.424	1.182	167
(1,3-dioxolane, CH₂)	(dioxolanyl-OO•)	20.1	61.4	–4.5	1.414	1.176	165
(1,3-dioxane, CH₂)	$Me_2PhCOO^\bullet$	28.8	66.8	–3.0	1.412	1.170	168
(1,3-dioxane, CH)	$Me_2PhCOO^\bullet$	25.1	68.1	–0.2	1.391	1.193	177
(5,5-dimethyl-1,3-dioxane, CH₂)	$Me_2PhCOO^\bullet$	28.8	66.5	–3.3	1.411	1.170	167
(1,3-dioxepane, CH₂)	$Me_2PhCOO^\bullet$	31.1	68.0	–3.4	1.415	1.169	167

Note: Rate constants required for the calculations were taken from [11, 18, 19].

Table 4. Enthalpy, activation energy, ΔE_μ, and TS geometry parameters for the reactions of peroxy radicals with esters

Ester	ROO$^\bullet$	ΔH_e, kJ/mol	E_e, kJ/mol	ΔE_μ, kJ/mol	$r(\text{C–H}) \times 10^{10}$, m	$r(\text{O–H}) \times 10^{10}$, m
BuCOOCH$_2$Me	Me$_2$PhCO$_2^\bullet$	37.1	78.7	4.2	1.431	1.172
Me$_2$CHCOOCMe$_3$	Me$_2$PhCO$_2^\bullet$	25.9	77.0	8.5	1.428	1.195
AcOCH$_2$Ph	Me$_3$CO$_2^\bullet$	–3.4	70.5	9.7	1.413	1.239
AcOCH$_2$Ph	Me$_2$PhCO$_2^\bullet$	–3.4	74.2	13.4	1.422	1.246
AcOCH$_2$Ph	AcOCH(OO$^\bullet$)Ph	–25.2	62.0	10.5	1.393	1.262
PhCOOCH$_2$Me	Me$_2$PhCO$_2^\bullet$	37.1	79.9	5.4	1.434	1.162
PhCOOCH$_2$Ph	PhCOOCH(OO$^\bullet$)Ph	–25.2	64.1	12.6	1.398	1.283
PhCOOCH$_2$Ph	Me$_3$CO$_2^\bullet$	–3.4	72.9	12.1	1.419	1.243

Note: Rate constants required for the calculations were taken from [11, 19].

is observed. The error in the estimation of the angle φ can be evaluated from Eq. (12); it is ±1.5°.

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