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Transition State Geometry and Polar Effect in the Addition of Peroxyl Radicals to Olefins

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Abstract—Transition-state interatomic distances in the addition of peroxyl radicals to the double bond of olefins are estimated from experimental data (activation energies and rate constants) using a new algorithm combining quantum chemical and parabolic model calculations. An aromatic ring in the α-position with respect to the double bond elongates the C···O distance by 0.02×10^{-10} m. Polar groups adjacent to the double bond affect this distance considerably. The geometric parameters of the transition states in the abstraction and addition of peroxyl radicals are compared.

Peroxyl addition to the double bond plays the key role in the liquid-phase oxidation of olefins and other unsaturated compounds and in the spontaneous polymerization of monomers [1–4]. Factors in the reactivity of olefins in these reactions were analyzed in an earlier work [5]. The parabolic model was successfully used to analyze kinetic data on abstraction reactions involving peroxyl radicals [6–9]. We have recently shown that this model in combination with quantum chemical calculations can also be used to describe the geometry of radical abstraction reactions involving peroxyl radicals [10]. Here, we report the solution of a similar problem for the addition of $RO_2^{\cdot}$ to unsaturated compounds. The parameters obtained by the combined method enabled us to analyze the factors in the transition state geometry of the reactions considered and to compare the transition state geometries of the abstraction and addition reactions involving peroxyl radicals.

COMPUTATIONAL PROCEDURES

Quantum Chemical Calculations

The B3LYP hybrid density functional method was used in the theoretical study of the addition of peroxyl radicals to molecules with double bonds. The calculations were carried out using the GAUSSIAN 98 program [11]. The geometry of stationary points was determined by an optimization procedure using the 6-31G* basis set. This geometry was used to calculate the energy of the system in the 6-311++G** basis set taking into account zero-point energies in the B3LYP/6-31G* approximation. These calculations were performed for $HO_2^{\cdot}$ addition to the double bond of ethylene.

$$HO_2^{\cdot} + CH_2{=}CH_2 \longrightarrow HOOCH_2C^{\cdot}H_2.$$

The results of these calculations are presented in Table 1 and Fig. 1.

The data listed in Fig. 1 show that the reaction center of the transition state has an angled configuration (φ(O···C···C) = 105.6°), the C=C bond is somewhat elongated (by 0.08 Å), and the C···O distance is almost 0.5 Å longer than the C–O bond distance in the forming radical.

Intersecting Parabolas Model

In the parabolic model, the transition state of this reaction is considered to result from the intersection of

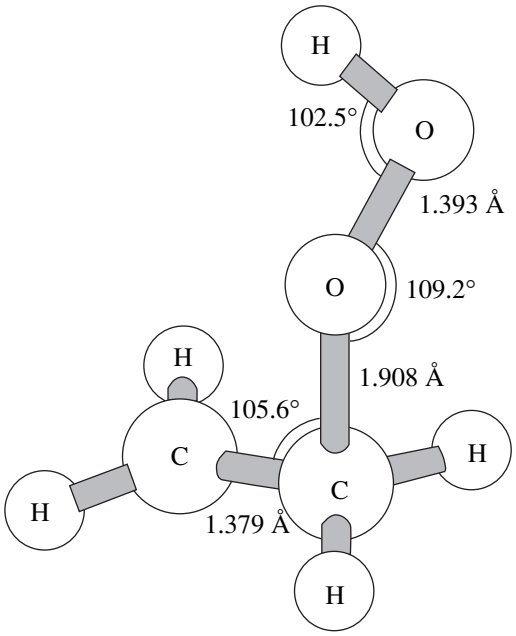

Fig. 1. Transition state in the addition of the hydroperoxyl radical to ethylene.

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Table 1. Energy and geometric parameters of the reactants and the transition state for the reaction $HO_2^{\bullet} + CH_2{=}CH_2$

System	Geometric parameters (bond length, Å; angle, deg)	B3LYP/6–31G*, Hartree	B3LYP/6–311++G**, Hartree	ZPE*, Hartree
$CH_2{=}CH_2$	C–C = 1.330	–78.58746	–78.61547	0.05123
$HO_2^{\bullet}$	O–O = 1.332	–150.89916	–150.95797	0.01404
$HOOCH_2CH_2^{\bullet}$	O–O = 1.456 C–O = 1.433 φ(O–C–C) =107.1 C–C = 1.484 θ(H–C–C–O) = 45.00	–229.49181	–229.57476	0.06819
$HO_2^{\bullet} + CH_2{=}CH_2$**	O–O = 1.393	–229.47196	–229.55689	0.06768
TS***	C–O = 1.908 φ(O–C–C) = 105.6 C–C = 1.379			

* ZPE = zero-point energy.
** ΔE = 47.7 kJ/mol.
*** TS = transition state.

two potential curves [12]. One of them describes the vibration of the C=C bond (vibration frequency ν_i), and the other describes the vibration of the forming C–O bond (vibration frequency ν_f). These vibrations are considered to be harmonic, so their potential energies are $U_i = b_i^2 \nu_i^2$ and $U_f = b_f^2 \nu_f^2$, where b_i and b_f are coefficients (see below). In the framework of the parabolic model, the addition reaction is characterized by the following physical parameters:

(1) enthalpy ΔH_e, which includes the difference between the zero-point energies and is related to the reaction enthalpy ΔH by the equation [12]

$$\Delta H_e = \Delta H + 0.5hN_A(\nu_i - \nu_f), \quad (1)$$

where h and N_A are Planck's constant and Avogadro's number, respectively;

(2) activation energy E_e, which is related to the Arrhenius activation energy E by the equation [12]

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

where R is the universal gas constant, and T is absolute temperature;

(3) coefficients b_i and b_f ($b_i = b = \pi\nu_i(2\mu_i)^{1/2}$ and $b_f = \pi\nu_f(2\mu_f)^{1/2}$, where μ_i and μ_f are the reduced masses of the C=C and C–O bonds; and

(4) distance r_e, which is the displacement of the C and O atoms upon the elementary reaction.

In the parabolic model, these quantities are related by the equation [12]

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}, \quad (3)$$

where $b = b_i$ and $\alpha = b_i/b_f$. The parameter br_e characterizes the activation energy of the thermally neutral reaction $E_{e,0}$ for a group of reactions with br_e = const:

$$E_{e,0} = (br_e)^2(1 + \alpha)^{-2}. \quad (4)$$

The activation energy E, which is related to the rate constant k by the Arrhenius equation, was calculated as

$$E = RT\ln(nA/k), \quad (5)$$

where T is the absolute temperature at which the rate constant is measured, n is the number of C atoms subjected to the attack (for example, $n = 2$ in ethylene and $n = 1$ in propylene), and A is the preexponential factor typical of a given series of reactions [5]. For $RO_2^{\bullet}$ addition to the C=C bond, the above-listed parameters take the following values [5]:

$0.5hN_A\nu_i$, kJ/mol	$0.5hN_A(\nu_i - \nu_f)$, kJ/mol	$b \times 10^{-10}$, $(kJ/mol)^{1/2}$ m^{-1}	α	A, l mol^{-1} s^{-1}
9.9	4.6	53.89	1.737	10^9

The parameter br_e enables one to calculate the activation energy of the reaction, E_e, from the reaction enthalpy ΔH_e using the equation [5]

$$\sqrt{E_e} = \frac{br_e}{\alpha^2 - 1}\left[\alpha\left(\sqrt{1 - \frac{\alpha^2 - 1}{(br_e)^2}\Delta H_e} - 1\right)\right]. \quad (6)$$

The enthalpy of $HO_2^{\bullet}$ addition to ethylene is

$$\Delta H_e = \Delta H(HOOCH_2C^{\bullet}H_2) - \Delta H(HO_2^{\bullet}) - \Delta H(CH_2{=}CH_2) + 4.6\ (kJ/mol). \quad (7)$$

In turn, the enthalpy of formation of the 2-hydroperoxyethyl radical is calculated by the equation

$$\Delta H(HOOCH_2C^{\bullet}H_2) = \Delta H(HOOCH_2CH_3) + D(RCH_2{-}H) - \Delta H(H^{\bullet}). \quad (8)$$

The enthalpy of formation of ethyl hydroperoxide is $\Delta H(HOOCH_2CH_3) = -169.4$ kJ/mol [13], the dissociation energy of the C–H bond in the methyl group is $D(RCH_2{-}H) = 422$ kJ/mol [14], $\Delta H(H^{\bullet}) = 218$ kJ/mol [15], and, hence, $\Delta H(HOOCH_2C^{\bullet}H_2) = 34.6$ kJ/mol. Accordingly, the enthalpy of the reaction is $\Delta H_e = 34.6 - 14.6\ (\Delta H(HO_2^{\bullet})) - 52.5\ (\Delta H(CH_2{=}CH_2)) + 4.6\ (0.5hN_A(\nu_i - \nu_f)) = -27.9$ kJ/mol. The activation energy calculated by formula (6) (with $br_e = 24.85\ (kJ/mol)^{1/2}$) is $E_e = 65.3$ kJ/mol.

Algorithm for the Calculation of Transition-State Interatomic Distances

Let us compare bond elongation data provided by quantum chemical calculations and by the intersecting parabolas method for the transition state of $HO_2^{\bullet}$ addition to ethylene. The C–O bond length in alkyl hydroperoxides is 1.439×10^{-10} m [13], and the C=C bond length in ethylene is 1.299×10^{-10} m [15]. According to the quantum chemical calculations, the elongation of the C–O bond in the transition state is $\Delta r(C\cdots O) = (1.908 - 1.439) \times 10^{-10} = 0.469 \times 10^{-10}$ m. The elongation of the C=C bond is only $\Delta r(C\cdots C) = (1.379 - 1.299) \times 10^{-10} = 0.080 \times 10^{-10}$ m. The total elongation of two bonds is 0.549×10^{-10} m. The parabolic model gives a similar value of $r_e = br_e/b = (24.85/53.89) \times 10^{-10} = 0.461 \times 10^{-10}$ m. The ratio of Δr(quantum) to r_e(parabolic) is 1.19. Using this coefficient, we can calculate, from r_e, the total elongation of the C–O and C=C bonds in the transition state of the addition of peroxyl radicals to unsaturated compounds, as was done for radical abstraction reactions [10]. According to the quantum chemical calculation, the elongation of the double bond in the transition state is only 14.6%. It seems appropriate to use this coefficient to reconcile the interatomic distances calculated using the parabolic model and the quantum chemical method. Thus, the parabolic model algorithm fitted to quantum chemical data will appear as

$$r(C\cdots O) \times 10^{10}\ (m) = 1.439 + 3.276 \times 10^{-2}\sqrt{E - \Delta H + 13.3}, \quad (9)$$

$$r(C\cdots C) \times 10^{10}\ (m) = 1.299 + 3.224 \times 10^{-3}\sqrt{E + 8.7}. \quad (10)$$

Calculation of the Enthalpies of Addition Reactions

The enthalpy of the addition of a peroxyl radical to an olefin, ΔH (kJ/mol), was calculated by the formula

$$\Delta H = \Delta H(CH_3CH_2Y) - \Delta H(CH_2{=}CHY) + D_1 + D_2 - D_3 - D_{H-H}, \quad (11)$$

where $\Delta H(CH_3CH_2Y)$ and $\Delta H(CH_2{=}CHY)$ are the enthalpies of formation of the respective compounds in the gas phase under standard conditions (298 K, 1 atm), D_1 and D_2 are the dissociation energies of the $YCH_2CH_2{-}H$ and $CH_3CYH{-}H$ bonds, D_3 is the dissociation energy of the C–O bond in the peroxide $ROO{-}CH_2CH_2Y$, and $D_{H-H} = 436$ kJ/mol is the dissociation energy of the hydrogen molecule. The dissociation energy of the C–O bond in the ethyl peroxide molecule was derived from the following thermochemical data [13]:

ΔH(EtOOEt)	ΔH(EtOOH)	D(EtOOCH$_2$CH$_2$–H)	D(EtOO–H)
–192.8 kJ/mol	–169.4 kJ/mol	422.0 kJ/mol	365.5 kJ/mol

From these data, the enthalpy of formation of the ethylperoxyl radical was calculated to be $\Delta H(EtOO^{\bullet}) = -21.9$ kJ/mol and the dissociation energy of the C–O bond in ethyl peroxide was calculated to be 290.2 kJ/mol. For other primary and secondary alkyl peroxides, D_3 was assumed to be the same as observed (empirically) for the R–O bond in ethers [16]. The dissociation energy of the tertiary C–O bond was calculated in the same way from the following thermochemical data [13]:

$\Delta H(Me_3COOCMe_3)$, kJ/mol	$\Delta H(Me_3COOH)$, kJ/mol	$D(Me_3COO{-}H)$, kJ/mol	$\Delta H(Me_3C^{\bullet})$, kJ/mol
–340.7	–245.8	358.6	48

Table 2. Enthalpy (ΔH), activation energies (E), br_e (formula (3)), and interatomic distances in the transition state (formulas (9) and (10)) for $RO_2^{\bullet}$ addition to olefins

Olefin	$RO_2^{\bullet}$ (n*)	$-\Delta H$, kJ/mol	E, kJ/mol	br_e, (kJ/mol)$^{1/2}$	$r(C\cdots O)\times 10^{10}$, m	$r(C\cdots C)\times 10^{10}$, m	Reference
CH_2=CH_2	n-$RO_2^{\bullet}$ (1)	19.1	63.4	25.49	1.920	1.381	[1]
CH_2=CHMe	n-$RO_2^{\bullet}$ (1)	16.9	60.8	24.91	1.909	1.379	[1]
CH_2=CHEt	*sec*-$RO_2^{\bullet}$ (1)	18.2	53.8	23.95	1.891	1.376	[1]
E-MeCH=CHMe	n-$RO_2^{\bullet}$ (1)	16.5	59.2	24.63	1.903	1.378	[1]
CH_2=CMe_2	n-$RO_2^{\bullet}$ (1)	21.8	56.9	24.76	1.906	1.379	[1]
MeCH=CMe_2	n-$RO_2^{\bullet}$ (1)	25.5	55.8	24.93	1.909	1.379	[1]
Me_2C=CMe_2	n-$RO_2^{\bullet}$ (1)	33.0	53.7	25.27	1.916	1.380	[1]
CH_2=$CH(CH_2)_3Me$	*sec*-$RO_2^{\bullet}$ (1)	17.3	58.4	24.58	1.902	1.378	[1]
CH_2=$CHCMe_3$	*sec*-$RO_2^{\bullet}$ (1)	29.3	55.9	25.28	1.916	1.380	[1]
	*sec*-$RO_2^{\bullet}$ (1)	27.4	56.6	25.21	1.915	1.380	[1]
	*sec*-$RO_2^{\bullet}$ (1)	19.5	55.8	24.38	1.899	1.378	[1]
CH_2=CHPh	$HO_2^{\bullet}$ (1)	58.5	43.9	25.94	1.928	1.383	[17]
CH_2=CHPh	*sec*-$RO_2^{\bullet}$ (17)	58.5	43.2	25.83	1.926	1.382	[17–19]
CH_2=CHPh	*tert*-$RO_2^{\bullet}$ (8)	51.8	48.6	26.09	1.931	1.383	[17, 20–22]
CH_2=CMePh	*sec*-$RO_2^{\bullet}$ (5)	58.5	43.1	25.80	1.926	1.382	[17, 23]
CH_2=CMePh	*tert*-$RO_2^{\bullet}$ (8)	51.8	47.0	25.85	1.927	1.382	[17, 22, 24]
MeCH=CHPh	*tert*-$RO_2^{\bullet}$ (1)	57.6	48.6	26.49	1.938	1.384	[25]
CH_2=CPh_2	*tert*-$RO_2^{\bullet}$ (1)	67.1	46.8	27.04	1.949	1.386	[21]

* n is the number of experiments.

Based on these values, we calculated $\Delta H(Me_3COO^{\bullet})$ = –105/2 kJ/mol and the dissociation energy of the C–O bond in *tert*-butyl peroxide. The latter turned out to be 283.5 kJ/mol, lower than the same value for ethyl peroxide. The same trend is observed for C–O bonds in ethers [16].

RESULTS AND DISCUSSION

Addition of Peroxyl Radicals to Olefins

The results of the calculation of ΔH by formula (11), br_e by formula (3), and interatomic distances in the transition state by formulas (9) and (10) for $RO_2^{\bullet}$ addition to olefins are presented in Table 2.

Nearly equal br_e parameters are obtained for the reactions of $RO_2^{\bullet}$ with aliphatic and alicyclic olefins: $br_e = 24.85 \pm 0.43$ (kJ/mol)$^{1/2}$, while the enthalpy of these reactions varies between –17 and –33 kJ/mol. Furthermore, the transition-state interatomic distances in these reactions are almost equal. Thus, all of these reactions belong to the same class, which is characterized by the following parameters:

br_e, (kJ/mol)$^{1/2}$	$E_{e,0}$, kJ/mol	Δr(C···O) × 10^{10}, m	Δr(C···C) × 10^{10}, m
24.85 ± 0.43	82.4 ± 1.4	1.908 ± 0.030	1.379 ± 0.001

Triplet Repulsion

A special group of olefins is made up by styrenes, in which a phenyl group is in the α-position with respect to the double bond. The additions of $RO_2^{\cdot}$ to these olefins are characterized by higher values of br_e (26.00 ± 0.23 (kJ/mol)$^{1/2}$) and, correspondingly, higher activation energies of the thermally neutral reaction.

Olefin	br_e, (kJ/mol)$^{1/2}$	$E_{e,0}$, kJ/mol	r(C…O) × 10^{10}, m	r(C…C) × 10^{10}, m
CH_2=CRPh	26.00 ± 0.23	90.2 ± 0.8	1.929 ± 0.004	1.383 ± 0.001
CH_2=CPh_2	27.04	97.6	1.949	1.386

The phenyl group elongates the C–O distance in the transition state. The br_e and $E_{e,0}$ values for $RO_2^{\cdot}$ addition to 1,1-diphenylethylene are still larger. Comparison of ΔH, E, and br_e for CH_2=CHR, CH_2=CHPh, and CH_2=CPh_2 shows that the introduction of one or two phenyl groups into olefin in positions adjacent to the double bond has a dual effect on the activation energy.

Olefin	CH_2=CHMe	CH_2=CHPh	CH_2=CPh_2
$-\Delta H$, kJ/mol	16.9	58.5	67.1
E, kJ/mol	60.8	43.5	46.8
$E_{e,0}$, kJ/mol	82.4	90.2	97.6
ΔE_π, kJ/mol	0	7.8	15.2
Δr(C···O) × 10^{-10}, m	1.908	1.929	1.949

On the one hand, the replacement of R by phenyl in an olefin decreases the activation energy of the reaction due to the decrease in the enthalpy of reaction. On the other hand, the replacement of R by Ph increases $E_{e,0}$. As a result, the difference between the E values for alkyl- and phenyl-substituted ethylenes is not so large as would be expected from the change in ΔH. The difference between $E_{e,0}$ for CH_2=CHR and CH_2=CHPh (ΔE_π) can be attributed to the interaction between the π electrons of the phenyl ring and the O···C···C reaction center in the transition state. By increasing the electron density on the reaction center, the π electrons enhance the triplet repulsion and heighten the activation barrier of the reaction. The interatomic distance Δr(C···O) elongates in parallel.

Polar Interaction

Similar calculations were carried out for the addition of $RO_2^{\cdot}$ to CH_2=CXY unsaturated compounds with a polar substituent Y (Y = COOMe, AcO, CN). The results of these calculations are presented in Table 3.

As can be seen from the br_e data, each reaction is characterized by its particular value of this parameter. This is due to the polar interaction in the transition state. The contribution from the interaction between the Y group and the O···C···C reaction center in the transition state to the activation energy (ΔE_μ) can be estimated in terms of br_e using the formula [7]

$$\Delta E_\mu = [(br_e)_Y^2 - (br_e)_R^2](1 + \alpha)^{-2}. \quad (12)$$

The ΔE_μ data listed in Table 3 suggest that the addition of peroxyl radicals to the double bond of methyl acrylate and methyl methacrylate decreases the activation energy by 1.7–9.9 kJ/mol. The Δr(C···O) distance in the transition state shortens in parallel. By contrast, the acetoxy group in vinyl acetate increases the activation energy of addition by 1.1–9.9 kJ/mol. Likewise, the cyano group of acetonitrile raises the activation energy by 4.8–9.7 kJ/mol. Evidently, the influence of the cyano group is due to the increase in the electron density on the reaction center, as in the case of the phenyl group, and to the polar interaction in the transition state. There

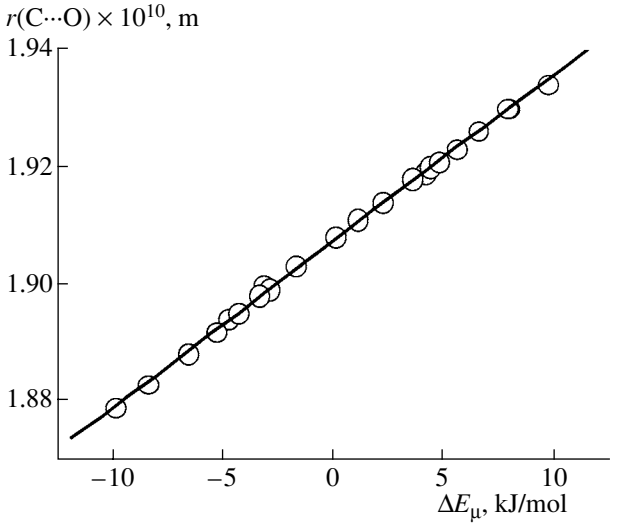

Fig. 2. Δr(C···O) distance in the transition state versus the contribution from the polar interaction to the activation energy (ΔE_μ) for peroxyl radical addition to polar monomers.

Table 3. Estimation of the polar effect (ΔE_μ, formula (12)) on the addition of peroxyl radicals to unsaturated compounds containing polar groups (n is the number of measurements)

Unsaturated compound	$RO_2^\bullet$ (n)	$-\Delta H$, kJ/mol	E, kJ/mol	br_e, (kJ/mol)$^{1/2}$	r(C···O) × 10^{10}, m	r(C···C) × 10^{10}, m	ΔE_μ, kJ/mol	References
CH_2=CHCOOMe	*sec*-$RO_2^\bullet$ (3)	22.5	52.3	24.11	1.894	1.377	–4.8	[17]
CH_2=CHCOOMe	*tert*-$RO_2^\bullet$ (6)	15.8	57.9	24.36	1.900	1.377	–3.2	[17, 26]
CH_2=CHCOOMe	~$CH_2CH(COOMe)O_2^\bullet$ (1)	22.5	54.2	24.41	1.899	1.378	–2.9	[3]
CH_2=CHCOOMe	~$CH_2CH(OAc)O_2^\bullet$ (1)	22.5	54.2	24.41	1.899	1.378	–2.9	[3]
CH_2=CMeCOOMe	$HO_2^\bullet$ (1)	24.7	46.0	23.32	1.879	1.374	–9.9	[13]
CH_2=CMeCOOMe	*sec*-$RO_2^\bullet$ (5)	24.7	50.5	24.03	1.892	1.376	–5.3	[13, 18]
CH_2=CMeCOOMe	*tert*-$RO_2^\bullet$ (9)	18.0	55.5	24.19	1.895	1.379	–4.3	[13, 18, 22]
CH_2=CMeCOOMe	~$CH_2CMe(COOMe)O_2^\bullet$ (1)	24.7	54.1	24.59	1.903	1.378	–1.7	[3]
CH_2=CMeCOOMe	~$CH_2CH(COOMe)O_2^\bullet$ (1)	24.7	52.4	24.33	1.898	1.377	–3.4	[3]
CH_2=CMeCOOMe	~$CH_2CH(OAc)O_2^\bullet$ (1)	24.7	49.2	23.83	1.888	1.376	–6.6	[3]
CH_2=CMeCOOMe	~$CH_2CH(CN)O_2^\bullet$ (1)	24.7	47.4	23.54	1.883	1.375	–8.4	[3]
CH_2=CHOAc	$HO_2^\bullet$ (1)	33.5	50.7	24.86	1.908	1.379	0.1	[13]
CH_2=CHOAc	*sec*-$RO_2^\bullet$ (4)	33.5	54.8	25.48	1.919	1.381	4.2	[13]
CH_2=CHOAc	*tert*-$RO_2^\bullet$ (2)	26.8	61.1	25.82	1.926	1.385	6.6	[13]
CH_2=CHOAc	~$CH_2CH(OAc)O_2^\bullet$ (1)	33.5	52.9	25.19	1.914	1.380	2.3	[3]
CH_2=CHOAc	~$CH_2CH(COOMe)O_2^\bullet$ (1)	33.5	54.2	25.39	1.918	1.381	3.6	[3]
CH_2=CHOAc	~$CH_2CH(CN)O_2^\bullet$ (1)	33.5	51.7	25.01	1.911	1.380	1.1	[3]
CH_2=CHOAc	~$CH_2CMe(COOMe)O_2^\bullet$ (1)	33.5	55.0	25.51	1.920	1.381	4.4	[3]
CH_2=CHCN	$HO_2^\bullet$ (1)	49.6	46.3	25.57	1.921	1.381	4.8	[13]
CH_2=CHCN	*sec*-$RO_2^\bullet$ (3)	49.6	49.3	26.01	1.930	1.383	7.9	[13]
CH_2=CHCN	*tert*-$RO_2^\bullet$ (4)	42.9	54.8	26.27	1.934	1.384	9.7	[13]
CH_2=CHCN	~$CH_2CH(CN)O_2^\bullet$ (1)	49.6	49.3	26.01	1.930	1.383	7.9	[3]
CH_2=CHCN	~$CH_2CH(COOMe)O_2^\bullet$ (1)	49.6	47.1	25.69	1.923	1.382	5.6	[3]
CH_2=CHCN	~$CH_2CH(OAc)O_2^\bullet$ (1)	49.6	49.4	26.03	1.930	1.383	8.0	[3]
CH_2=CHCN	~$CH_2CMe(COOMe)O_2^\bullet$ (1)	49.6	49.3	26.01	1.930	1.383	7.9	[3]

is a linear correlation between the interatomic distance Δr(C···O) (in m) in the transition state and the contribution from the polar interaction to the activation energy in kJ/mol (Fig. 2):

$$r(\mathrm{C}\cdots\mathrm{O}) \times 10^{10} = 1.9074 \pm 1.0 \times 10^{-4} + (2.84 \pm 0.02) \times 10^{-3} \Delta E_{\mu}. \quad (13)$$

A similar regularity is observed for hydrogen abstraction by peroxyl radicals from polar molecules [7–9].

Thus, the combined approach to the analysis of the transition state of $RO_2^{\cdot}$ addition to unsaturated compounds leads to the following conclusions. The free-valence-bearing oxygen atom of the peroxyl radical attacks the double bond at an angle of 106° (Fig. 1). The double bond in the transition state elongates insignificantly (by ~0.08×10^{-10} m). By contrast, the C···O distance is much longer than the C–O bond in the forming radical (it is equal to 1.908×10^{-10} m, while the C–O bond length in the peroxide molecule is 1.44×10^{-10} m). The Δr(C···O) distance elongates on going from olefins to styrenes due to the enhancement of the triplet repulsion in the addition reaction. The polar interaction affects the activation energy and Δr(C···O) distance. A linear dependence is observed between the Δr(C···O) and the contribution from the polar interaction to the activation energy (Fig. 2).

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