

# Semiempirical Analysis of the Homolytic Decomposition of Peresters with the Concerted Cleavage of Two Bonds

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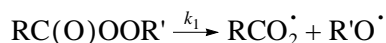
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**Abstract**—The parabolic model of a bimolecular reaction is modified to study the monomolecular decomposition of molecules into radicals by the cleavage of several bonds. Together with the oscillation model of molecule decomposition with the concerted cleavage of several bonds, this model is used to analyze the kinetic data on the decomposition of 16 peresters with the simultaneous cleavage of C–C and O–O bonds. Parameters characterizing this decomposition are obtained and multiple variants in representing such decomposition in terms of the parabolic model are discussed.

## INTRODUCTION

Peresters  $\text{RC(O)OOR'}$  with weak O–O bonds are widely used as initiators of radical processes in chemical technology and laboratory practice [1, 2]. Perester decomposition with O–O bond cleavage via the reaction



is characterized by the following kinetic parameters [3, 4]:

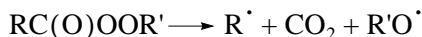
1. The activation energy of such decomposition ( $125 \pm 8$  kJ/mol) is close to the O–O bond strength and slightly depends on the structure of the R and R' substituents [3].

2. The activation entropy is positive and equals  $36\text{--}54$  J mol<sup>−1</sup> K<sup>−1</sup> [3, 4].

3. The rate constant for the decomposition depends on the solvent viscosity. The  $k_1$  value decreases with an increase in the solvent viscosity because of the cage effect [3].

4. The  $k_1$  value decreases with a pressure increase because the volume of the transition state ( $V^*$ ) is larger than the volume of the initial molecule ( $V$ ). A change in the activation volume is  $\Delta V^* = V^* - V = 10 \pm 2$  cm<sup>3</sup>/mol [4].

Along with O–O bond homolysis, several peresters decompose to radicals via the reaction



with simultaneous (concerted) cleavage of two bonds. The homolytic character of such decomposition was verified by the initiating effect of these peresters on radical polymerization [3]. The concerted decomposition of peresters is characterized by the following parameters:

1. The activation energy of the concerted decomposition of a perester is much lower than the O–O bond

strength ( $D_{\text{O-O}} = 125$  kJ/mol) and strongly depends on the structure of the R substituent [3, 4].

2. The activation entropy of the concerted decomposition is much lower than  $\Delta S^* = 36\text{--}54$  J mol<sup>−1</sup> K<sup>−1</sup> typical of the non-concerted decomposition [3]. For example, the decomposition of  $\text{PhCH}_2\text{C(O)OOCMe}_3$  perester with the cleavage of C–C and O–O bonds is characterized by  $\Delta S^* = 8.4$  J mol<sup>−1</sup> K<sup>−1</sup> [5].

3. The  $\text{R}\cdot$  and  $\text{R'O}\cdot$  radicals formed in the cage recombine to form the (ROR') product different from the initial peroxide. Therefore, the solvent viscosity has no effect on the rate constant of the concerted decomposition of perester.

4. During concerted decomposition, the cleavage of the C–C and O–O bonds is accompanied by the simultaneous formation of a C=O  $\pi$ -bond in  $\text{CO}_2$ . The transition state has a tight structure and, hence,  $\Delta V^* \approx 0$  ( $\Delta V^* = 0.0 \pm 1.6$  cm<sup>3</sup>/mol).

For certain (rare) structures, concerted decomposition is accompanied by the cleavage of several bonds, for example [6],

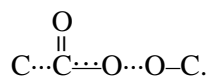


In this work, we used the parabolic model to study the decomposition of peresters with the concerted cleavage of two bonds. Earlier, we successfully used this model to analyze the bimolecular reactions of radical abstraction, addition, and substitution [7–10].

## MODEL AND CALCULATION PROCEDURE

In perester decomposition with the concerted cleavage of two bonds, the O–O and C–C bonds break and the single ester C–O bond is transformed into the double C=O bond in the carbon dioxide molecule simulta-

neously. The reaction center of a decomposing perester has the following configuration:



In the framework of the parabolic model, the transition state of this reaction is considered to be a result of the intersection of the potential curves, which describe the stretching vibrations of two breaking bonds and one forming bond in the coordinates of the vibration amplitude vs. the activation energy. Then the activation energy of concerted decomposition may be represented as the point of the intersection of the potential curves of the stretching vibrations of either (a) the C–C and C=O or (b) the O–O and C=O bonds.

When analyzing the concerted decomposition of peresters in terms of the parabolic model, we used the following parameters [7] to characterize the reaction.

1. The reaction enthalpy  $\Delta H_e$ , which includes the difference in the zero-point energies of the breaking (i) and forming (f) bonds:

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

where  $\Delta H$  is the experimental reaction enthalpy;  $\nu_i$  and  $\nu_f$  are the frequencies of the stretching vibrations of the breaking and forming bonds, and  $h$  and  $N_A$  are the Planck and Avogadro constants, respectively.

2. The activation energy  $E_e$ , which includes the energy of the zero-point vibration of a breaking bond, is related to the experimental activation energy  $E$  as follows ( $\nu = \nu_i$ ):

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

where  $R$  is the gas constant, and  $T$  is the temperature, K.

3. The sum of the amplitudes of the vibration of the breaking and forming bonds in the transition state  $r_e$ .

4. The  $b_i$  and  $b_f$  parameters ( $2b_i^2$  is the force constant of the  $i$ th bond) that are the dynamic characteristics of the breaking ( $b_i = \pi\nu_i(2\mu_i)^{1/2}$ ) and forming ( $b_f = \pi\nu_f(2\mu_f)^{1/2}$ ) bonds. Here  $\mu_i$  and  $\mu_f$  are the reduced weights of atoms involved in the formation of these bonds. The above five parameters are related to each other as follows ( $\alpha = b_i/b_f$ ,  $b = b_i$ ):

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

Using the  $br_e$  parameter, one can calculate the activation energy of a thermally neutral reaction  $E_{e,0}$  ( $br_e = \text{const}$ ,  $\Delta H_e = 0$ )

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

Let us show how the main parameter of the parabolic model  $br_e$  can be calculated for the concerted decomposition of perester  $(\text{CH}_3)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3 \rightarrow (\text{CH}_3)_3\text{C}^\bullet + \text{CO}_2 + (\text{CH}_3)_3\text{CO}^\bullet$ .

In the calculation, two cases ((a) and (b)) of the transition state are considered separately.

1. The parameters  $b_i$ ,  $\alpha$ ,  $0.5hN_A\nu_i$ ,  $0.5hN_A(\nu_i - \nu_f)$ , and  $E_e - E$  are considered below for each particular case.

Reaction center	$b_i \times 10^{11},$ (kJ/mol) <sup>1/2</sup> m <sup>-1</sup>	$\alpha$	$0.5hN_A\nu_i$	$E_e - E$ , kJ/mol	$0.5hN_A(\nu_i - \nu_f)$
C...C...O	4.483	0.547	8.2	6.8	-5.8
O...O...C	3.238	0.396	5.1	3.7	-8.9

The enthalpy of decomposition  $\Delta H$  was calculated by the equation:

$$\Delta H = \Sigma \Delta H_f^0 (\text{decomposition products}) - \Delta H_f^0 (\text{perester}). \quad (5)$$

For  $(\text{CH}_3)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3$  decomposition, we have

$$\Delta H = \Delta H_f^0((\text{CH}_3)_3\text{C}^\bullet) + \Delta H_f^0(\text{CO}_2) + \Delta H_f^0((\text{CH}_3)_3\text{CO}^\bullet) - \Delta H_f^0((\text{CH}_3)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3).$$

The enthalpies of formation taken from handbooks [11, 12] are  $\Delta H_f^0(\text{CH}_3)_3\text{C}^\bullet = 48.0$  kJ/mol,  $\Delta H_f^0(\text{CO}_2) = -395.5$  kJ/mol, and  $\Delta H_f^0((\text{CH}_3)_3\text{CO}^\bullet) = -90.4$  kJ/mol.

Because the enthalpies of perester formation  $\Delta H_f^0(\text{CH}_3)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3$  are lacking, we calculated the  $\Delta H_f^0$  value for a perester using the  $\Delta H_f^0$  values for its structural groups, as suggested in [13].

We obtained  $\Delta H_f^0((\text{CH}_3)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3) = 3\Delta H_f^0(\text{C}-(\text{H})_3(\text{C})) + \Delta H_f^0(\text{C}-(\text{C})_3(\text{CO})) + \Delta H_f^0(\text{CO}-(\text{C})(\text{O})) + \Delta H_f^0(\text{O}-(\text{CO})(\text{C})) + \Delta H_f^0(\text{O}-(\text{O})(\text{C})) + \Delta H_f^0(\text{C}-(\text{O})(\text{C})_3) + 3\Delta H_f^0(\text{C}-(\text{H})_3(\text{C})) = -126.6 + 2.5 - 139.7 - 79.4 - 18.8 - 27.6 - 126.6 = -516.2$  kJ/mol.

The reaction enthalpy  $\Delta H$  was determined by Eq. (5):  $\Delta H = 48.0 - 395.5 - 90.4 + 516.2 = 78.3$  kJ/mol.

Similarly, we calculated the enthalpies of formation  $\Delta H_f^0$  of other studied peresters and the enthalpies of their decomposition  $\Delta H$  (Table 1). Note that we failed to find any data on the  $\Delta H_f^0(R^\cdot)$  values for many  $R^\cdot$  radicals when calculating the  $\Delta H$  values for the decom-

position of certain peresters. Therefore, we calculated them by the equation

$$\Delta H_f^0(R^\cdot) = \Delta H_f^0(RH) + D_{C-H}(R-H) - \Delta H_f^0(H), \quad (6)$$

where  $D_{C-H}(R-H)$  is the C–H bond dissociation energy in the corresponding compound. The  $D_{C-H}$  and

**Table 1.** Kinetic ( $k$ ,  $E$ ,  $E_e$ ,  $E_{e,0}$ ,  $br_e$ , and  $r_e$ ) and thermodynamic ( $\Delta H_f^0$ ,  $\Delta H$ , and  $\Delta H_e$ ) parameters for the concerted decomposition of peresters calculated by methods (a) and (b)

Perester		$-\Delta H_f^0$	$\Delta H$	$\Delta H_e$	$T, K$	$k, s^{-1}$	$E$	$E_e$	$E_{e,0}$	$br_e',$ (kJ/mol) <sup>1/2</sup>	$r_e \times 10^{11}, m$
		kJ/mol					kJ/mol				
CH <sub>3</sub> OCH <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	562.4	86.3	80.5	333	$2.35 \times 10^{-3}$ [17]	106.7	113.5	79.6	13.80	3.078
	b	"	"	77.4	"	"	"	110.4	83.8	12.78	3.947
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	598.0	89.7	83.9	313	$2.89 \times 10^{-4}$ [17]	105.7	112.6	76.6	13.54	3.020
	b	"	"	80.8	"	"	"	109.5	81.3	12.59	3.888
(CH <sub>3</sub> ) <sub>2</sub> CHOCH <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	633.9	90.0	84.2	313	$4.28 \times 10^{-4}$ [17]	104.7	111.6	75.3	13.42	2.994
	b	"	"	81.1	"	"	"	108.5	80.0	12.49	3.857
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	455.8	88.5	82.7	313	$1.34 \times 10^{-4}$ [17]	107.7	114.6	79.5	13.79	3.076
	b	"	"	79.6	"	"	"	111.5	84.1	12.80	3.953
CH <sub>3</sub> OCH(CH <sub>3</sub> )C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	605.0	84.3	78.5	313	$4.30 \times 10^{-3}$ [17]	98.8	105.7	72.0	13.13	2.929
	b	"	"	75.4	"	"	"	102.6	76.2	12.19	3.765
(CH <sub>3</sub> ) <sub>3</sub> CC(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	516.2	78.3	72.5	338	$5.81 \times 10^{-5}$ [16]	118.5	125.3	96.2	15.17	3.384
	b	"	"	69.4	"	"	"	122.2	99.6	13.93	4.302
CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	553.1	74.9	69.1	338	$7.76 \times 10^{-5}$ [18]	117.7	124.5	96.9	15.23	3.397
	b	"	"	66.0	"	"	"	121.4	100.1	13.97	4.314
CH <sub>3</sub> CH=CHCH <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	382.0	24.1	18.3	333	$2.92 \times 10^{-5}$ [19]	118.8	125.6	118.9	16.87	3.763
	b	"	"	15.2	"	"	"	122.5	118.1	15.17	4.685
C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	253.0	11.8	6.0	333	$1.16 \times 10^{-4}$ [19]	115.0	121.8	119.5	16.91	3.772
	b	"	"	2.9	"	"	"	118.7	117.9	15.16	4.682
CH <sub>3</sub> C≡CCH <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	222.7	20.2	14.4	333	$3.72 \times 10^{-6}$ [19]	124.0	130.8	125.6	17.34	3.868
	b	"	"	11.3	"	"	"	127.7	124.4	15.57	4.808
C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	81.8	11.3	5.5	333	$7.72 \times 10^{-6}$ [19]	122.4	129.2	127.2	17.45	3.892
	b	"	"	2.4	"	"	"	126.1	125.4	15.63	4.827
CH <sub>3</sub> C≡CCH(CH <sub>3</sub> )C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	252.3	7.2	1.4	333	$6.55 \times 10^{-5}$ [19]	116.5	123.3	122.8	17.14	3.823
	b	"	"	−1.7	"	"	"	120.2	120.7	15.34	4.737
C <sub>6</sub> H <sub>5</sub> C≡CCH(CH <sub>3</sub> )C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	111.3	−1.7	−7.5	333	$1.09 \times 10^{-4}$ [19]	115.2	122.0	124.6	17.27	3.852
	b	"	"	−10.6	"	"	"	118.9	121.9	15.41	4.759
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	320.4	41.5	35.7	364	$3.53 \times 10^{-4}$ [20]	123.1	129.8	116.5	16.70	3.725
	b	"	"	32.6	"	"	"	126.7	117.0	15.10	4.663
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHC(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	—	23.5	17.7	333	$3.10 \times 10^{-4}$ [21]	102.3	109.1	102.6	15.67	3.495
	b	—	"	14.6	"	"	"	106.0	101.7	14.08	4.348
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CC(O)OOC(CH <sub>3</sub> ) <sub>3</sub>	a	—	12.5	6.7	318	$2.31 \times 10^{-3}$ [22]	102.1	109.0	106.6	15.97	3.562
	b	—	"	3.6	"	"	"	105.9	104.9	14.30	4.416

$\Delta H_f^0(\text{RH})$  values were taken from [11, 12, 14]. Table 2 presents the calculated  $\Delta H_f^0(\text{R}^\cdot)$  values and the  $D_{\text{C-H}}(\text{R-H})$  and  $\Delta H_f^0(\text{RH})$  parameters.

We failed to obtain the enthalpies of formation  $\Delta H_f^0$  of two peresters  $(\text{C}_6\text{H}_5)_2\text{CHC}(\text{O})\text{OOC}(\text{CH}_3)_3$  and  $(\text{C}_6\text{H}_5)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3$  as the sum of the enthalpies of formation of their structural groups and calculated them by an alternative method. Two bonds (C–C and O–O) break during the concerted decomposition of peresters. The O–O bond dissociation energy slightly depends on the peroxide structure and is virtually the same for all peresters listed in Table 1 (~150 kJ/mol) [3]. The C–C bond dissociation energy depends on the perester structure and is different for various peresters. It is the change in the C–C bond strength that influences the enthalpy of perester decomposition. Therefore, one can estimate the enthalpy of the concerted decomposition of one perester from that of another by comparing the dissociation energies of their C–C bonds:

$$\Delta H_{\text{II}} = \Delta H_{\text{I}} + \Delta D, \quad (7)$$

Compound	$D_{\text{C-C}}(\text{R-Et}), \text{ kJ/mol}$	$\Delta D, \text{ kJ/mol}$	$\Delta H_{\text{II}}, \text{ kJ/mol}$
$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$	318	–	41.5 ( $\Delta H_{\text{I}}$ )
$(\text{C}_6\text{H}_5)_2\text{CHC}(\text{O})\text{OOC}(\text{CH}_3)_3$	300	–18	23.5
$(\text{C}_6\text{H}_5)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3$	289	–29	12.5

Table 1 presents the  $\Delta H$  values for the relevant reactions.

3. For the decomposition of peresters involving the cleavage of only one O–O bond, the activation energy  $E$  was calculated from the rate constant  $k$  according to the Arrhenius equation

$$E = RT \ln \frac{A_0}{k}, \quad (9)$$

where  $A_0$  is the preexponential factor for decomposition equal to  $A_0 = 1 \times 10^{15} \text{ s}^{-1}$  (the average value for 10 peresters [2]), and  $k$  is the experimental rate constant for decomposition.

In the case of the concerted decomposition of a molecule, the preexponential factor  $A$  in the Arrhenius expression for the rate constant of decomposition depends on both the activation energy of decomposition and the number of concertedly broken bonds. Within the framework of the oscillation model of the concerted decomposition with the cleavage of two bonds, this dependence is described by the formula [15]:

$$A = A_0 \left( \frac{2RT}{\pi E} \right)^{1/2}. \quad (10)$$

where  $\Delta H_{\text{II}}$  is the unknown enthalpy of decomposition of perester II,  $\Delta H_{\text{I}}$  is the available enthalpy of decomposition of perester I, and  $\Delta D$  is the difference in the C–C bond dissociation energies in these esters. Because data on the C–C bond dissociation energies in  $\text{R-C}(\text{O})\text{OOC}(\text{CH}_3)_3$  peresters are lacking, we calculated the  $\Delta D$  values from the C–C bond dissociation energies in the relevant R–Et compounds assuming that the  $\Delta D$  increments are close in both cases and depend exclusively on the R substituent. The C–C bond dissociation energy in R–Et compounds were calculated by the formula:

$$D_{\text{C-C}}(\text{R-Et}) = \Delta H_f^0(\text{R}^\cdot) + \Delta H_f^0(\text{Et}^\cdot) - \Delta H_f^0(\text{R-Et}). \quad (8)$$

The  $\Delta H_f^0(\text{Et}^\cdot)$ ,  $\Delta H_f^0(\text{R-Et})$ , and  $\Delta H_f^0(\text{Et}^\cdot)$  values were taken from [11, 12], whereas some of the  $\Delta H_f^0(\text{R}^\cdot)$  enthalpies were calculated earlier (see Table 2).

Therefore, we have for the chosen parameters

Then, the equation for the reaction rate constant is

$$k = A_0 \left( \frac{2RT}{\pi E} \right)^{1/2} e^{-E/RT} \quad (11)$$

or, in the logarithmic form,

$$\ln k = \ln A_0 + 1/2 \ln(2/\pi) - \left( 1/2 \ln \frac{E}{RT} + \frac{E}{RT} \right). \quad (12)$$

Substituting the available experimental  $k$  and  $A_0$  values into Eq. (12), we obtain the activation energy  $E$ . For the concerted decomposition of  $(\text{CH}_3)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3$  perester, the activation energy  $E = 118.5 \text{ kJ/mol}$  ( $k = 2.10 \times 10^{-4} \text{ s}^{-1}$ ,  $T = 348.6 \text{ K}$  [16], and  $A_0 = 1 \times 10^{15} \text{ s}^{-1}$  (see above)).

Then, the  $E_e$  and  $br_e$  values can be calculated by Eqs. (2) and (4), respectively, and the  $E_{e,0}$  and  $r_e$  parameters for two cases of the transition state can be determined by Eqs. (3) and (4), respectively.

For the concerted decomposition of the  $(\text{CH}_3)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3$  perester, we obtain the following parameters:

Reaction center	$br_e$ , (kJ/mol) <sup>0.5</sup>	$\alpha$	$E_{e,0}$ , kJ/mol	$r_e \times 10^{11}$ , m
C...C—O	15.20	0.547	96.1	3.384
O...O—C	13.95	0.396	96.6	4.302

Table 1 summarizes the calculated  $E_{e,0}$ ,  $br_e$ , and  $r_e$  parameters for the studied peresters.

## RESULTS AND DISCUSSION

Comparison of the  $br_e$  parameters and the activation energies of a thermally neutral reaction  $E_{e,0}$  (see Table 1) suggests that the reactions of the concerted decomposi-

tion of peresters characterized by the  $b$  and  $\alpha$  coefficients can be subdivided into five groups including the reactions of structurally related peresters. These groups are characterized by the same  $br_e$  and  $E_{e,0}$  parameters (see Table 3).

The activation energies for thermally neutral concerted decomposition  $E_{e,0}$  are close for both considered types of the reaction center C...C—O and O...O—C (see Table 3); their difference is within the experimental error in the  $E_{e,0}$  value. This confirms the fact that the parabolic model can successfully be applied to reactions with the concerted cleavage of two bonds. Comparison of the  $br_e$  and  $E_{e,0}$  values for peresters with R substituents of different structures indicates that the  $\pi$ -bonds in the  $\alpha$ -position with respect to the breaking C—C bond favor an increase in the  $E_{e,0}$  value. The same effect is also observed for radical abstraction, addition,

**Table 2.** Enthalpies of formation of RH compounds ( $\Delta H_f^0(\text{RH})$ ) [11, 12], C—H bond dissociation energies ( $D_{\text{C-H}}(\text{R-H})$ ) [14], and calculated enthalpies of radical formation ( $\Delta H_f^0(\text{R}^\cdot)$ )

$\text{R}^\cdot$	$\Delta H_f^0(\text{RH})$	$D_{\text{C-H}}(\text{R-H})$	$\Delta H_f^0(\text{R}^\cdot)$
	kJ/mol		
$\text{CH}_3\text{OC}^\cdot\text{H}_2$	−184.1	411.9	9.8
$\text{CH}_3\text{CH}_2\text{OC}^\cdot\text{H}_2$	−216.3	411.9	−22.4
$(\text{CH}_3)_2\text{CHOC}^\cdot\text{H}_2$	−251.9	411.9	−58.0
$\text{C}_6\text{H}_5\text{CH}_2\text{OC}^\cdot\text{H}_2$	−75.3	411.9	118.6
$\text{CH}_3\text{OC}^\cdot\text{H}(\text{CH}_3)$	−216.3	399.5	−34.8
$(\text{CH}_3)_3\text{C}^\cdot$	−134.0	400.0	48
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}^\cdot(\text{CH}_3)_2$	−174.3	400.0	7.7
$\text{CH}_3\text{CH}=\text{CHC}^\cdot\text{H}_2$	−11.17	356.8	127.6
$\text{C}_6\text{H}_5\text{CH}=\text{CHC}^\cdot\text{H}_2$	113.0	349.7	244.7
$\text{CH}_3\text{C}\equiv\text{CC}^\cdot\text{H}_2$	145.2	354.7	281.9
$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}^\cdot\text{H}_2$	267.8	347.6	397.4
$\text{CH}_3\text{C}\equiv\text{CC}^\cdot\text{H}(\text{CH}_3)$	128.0	348.2	258.2
$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}^\cdot(\text{CH}_3)_2$	276.1	337.0	395.1
$\text{C}_6\text{H}_5\text{CH}_2^\cdot$	50.0	375.0	207.0
$(\text{C}_6\text{H}_5)_2\text{C}^\cdot\text{H}$	138.1	356.8	271.1
$(\text{C}_6\text{H}_5)_3\text{C}^\cdot$	272.0	346.0	400.0
$\text{C}_6\text{H}_5\text{C}^\cdot\text{H}(\text{CH}_3)$	29.3	364.1	175.4
<i>cyclo</i> -[ $\text{C}^\cdot(\text{CH}_3)(\text{CH}_2)_5$ ]	−154.8	395.5	22.7

and substitution [8, 9, 10]. This effect is due to the triplet repulsion in the transition state: the interaction of the  $\pi$ -electrons with the electron pair of a C–C breaking bond causes an increase in the energy of the transition state and, hence, the energy of the nonbonding orbital of the breaking bond, which, in turn, leads to an increase in the activation energy of decomposition. Comparison of the  $E_{e,0}$  values for  $R = R'OCH_2$  and  $R = R(CH_3)_3C$  suggests that methyl groups adjacent to the breaking C–C bond have a negative effect on decomposition because of steric (spatial) hindrances. The effect of the structure of the R substituent on the  $E_{e,0}$  value mentioned above can be expressed in terms of the relevant  $\Delta E$  increments

$$\Delta E = E_{e,0}(RCR'_2C(O)OOC(CH_3)_3) - E_{e,0}(CH_3CH_2OCH_2C(O)OOC(CH_3)_3). \quad (13)$$

Table 4 presents the obtained  $\Delta E$  values, where  $\Delta E_{\pi(=)}$  =  $\Delta E$  if R is alkenyl ( $R' = H$ ),  $\Delta E_{\pi(\equiv)}$  if R is alkynyl ( $R' = H$ ),  $\Delta E_{\pi(Ph)}$  if R is phenyl ( $R' = H$ ), and  $\Delta E_S$  if R is propyl ( $R' = CH_3$ ). In all the cases, the  $\Delta E$  values are rather high (20–48.5 kJ/mol).

The structure of the reaction center of concerted decomposition is similar to that typical of the addition

of carbon-centered radicals to the carbonyl group and oxygen-centered radicals to alkenes.

It sounds reasonable to compare the parameters of these three classes of homolytic reactions (see Table 4).

For these reaction classes, the activation energies  $E_{e,0}$  are close, whereas the  $r_e$  parameters (the sum of the amplitudes of the reacting bond vibrations) substantially differ and the  $r_e$  parameter for the concerted decomposition of peresters is lower than for other reactions. This fact agrees well with Koenig's findings [3]; he hypothesized the more compact structure of the reaction center in the case of concerted decomposition. A noticeable effect of R substituents on the activation energy  $E_{e,0}$  in the concerted decomposition of peresters can also be explained by this compact structure of the reaction center.

The  $br_e$  parameter calculated from the experimental data can be used to determine the activation energy of any individual reaction of a particular group by the following equation [7]:

$$E_e^{1/2} = br_e(1 - \alpha^2)^{-1} \times \{1 - \alpha[1 - (1 - \alpha^2)(br_e)^{-2}\Delta H_e]^{1/2}\}. \quad (14)$$

**Table 3.** The  $br_e$ ,  $E_{e,0}$ , and  $r_e$  parameters for the concerted decomposition of  $RC(O)OOC(CH_3)_3$  peresters with different R structures

R	C...C...O (a)			O...O...C (b)		
	$br_e$ , (kJ/mol) <sup>1/2</sup>	$E_{e,0}$ , kJ/mol	$r_e \times 10^{11}$ , m	$br_e$ , (kJ/mol) <sup>1/2</sup>	$E_{e,0}$ , kJ/mol	$r_e \times 10^{11}$ , m
R' OCH <sub>2</sub>	13.54 ± 0.25	76.6	3.020	12.57 ± 0.22	81.1	3.882
R' (CH <sub>3</sub> ) <sub>2</sub> C	15.20 ± 0.03	96.5	3.390	13.95 ± 0.02	99.9	4.308
Ph <sub>n</sub> CH <sub>3-n</sub>	16.11 ± 0.53	108.4	3.593	14.49 ± 0.44	107.7	4.475
R' CH=CHCH <sub>2</sub>	16.89 ± 0.02	119.2	3.768	15.17 ± 0.01	118.1	4.685
R'C≡CCH <sub>2</sub>	17.30 ± 0.11	125.1	3.859	15.46 ± 0.12	122.6	4.775

**Table 4.** Comparison of the influence of the substituents in the  $\alpha$ -position with respect to the reaction center on the activation energy  $E_{e,0}$  in concerted decomposition and addition

Reaction	Reaction center	$E_{e,0}$ , kJ/mol	$r_e \times 10^{11}$ , m	$\Delta E_{\pi(=)}$	$\Delta E_{\pi(\equiv)}$	$\Delta E_{\pi(Ph)}$	$\Delta E_S$
				kJ/mol			
$RCH_2C(O)OOC(CH_3)_3 \longrightarrow RC^{\cdot}H_2 + CO_2 + (CH_3)_3CO^{\cdot}$	C...C...O	76.6	3.02	42.6	48.5	31.8	19.9
$R^{\cdot} + R'R''C=O \longrightarrow RR'R''CO^{\cdot}$	C...C...O	68.1	3.54	—*	—	—	—
$RO^{\cdot} + CH_2=CHR' \longrightarrow ROCH_2C^{\cdot}HR'$	C...C...O	65.2	3.62	—	—	14.6	—

\* In all the cases, empty entries mean that there are no data.

**Table 5.** Estimated activation energy  $E$  of the concerted decomposition of  $\text{RC}(\text{O})\text{OOC}(\text{CH}_3)_3$  peresters

R	$D_{\text{C-C}}(\text{R-Et})^{\text{a}}$	$\Delta D^{\text{b}}$	$\Delta H^{\text{c}}$	$\Delta H_{\text{e}}$	$br_{\text{e}},$ (kJ/mol) <sup>1/2</sup>	$E_{\text{e}}$	$E_{\text{calcd}}$	$E_{\text{exp}}$	$\Delta E$
	kJ/mol					kJ/mol			
<i>cyclo</i> -[C(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>5</sub> ]	360.0 <sup>d</sup>	−9.6 <sup>e</sup>	68.7	62.9	15.20	121.4	114.6	—	—
C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )	311.6	−40.4	37.9	32.1	16.11	120.4	113.6	—	—
C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub>	298.0	−54.0	24.3	18.5	16.11	115.2	108.4	—	—
CH <sub>2</sub> =CHCH <sub>2</sub>	311.0	−41.0	37.3	31.5	16.89	130.8	124.0	—	—
(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub>	292.6	−59.4	18.9	13.1	16.89	126.1	119.3	—	—
CH≡CCH <sub>2</sub>	303.5	−48.5	29.8	24.0	17.30	133.8	127.0	—	—
CH≡CCH(CH <sub>3</sub> )	300.1	−51.9	26.4	20.6	17.30	132.5	125.7	—	—
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub>	—	—	89.7 <sup>f</sup>	83.9	14.12	112.2	105.4	105.7	−0.3
C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub>	—	—	11.8 <sup>f</sup>	6.0	16.89	121.3	114.5	115.0	−0.5
CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	—	—	74.9 <sup>f</sup>	69.1	15.20	124.1	117.3	117.7	−0.4

<sup>a</sup> Calculated by Eq. (8).<sup>b</sup>  $D_{\text{C-C}}(\text{R-Et})$  is compared with  $D_{\text{C-C}}((\text{CH}_3)_3\text{C-Et}) = 352$  kJ/mol.<sup>c</sup> The  $D_{\text{C-C}}(\text{R-Me})$  value from [11] is used.<sup>d</sup> Compared with  $D_{\text{C-C}}((\text{CH}_3)_3\text{C-Me}) = 350.4$  kJ/mol [11].<sup>e</sup> Calculated by Eq. (7)  $\Delta H = 78.3$  kJ/mol for  $(\text{CH}_3)_3\text{CC}(\text{O})\text{OOC}(\text{CH}_3)_3$  (see Table 1).<sup>f</sup> From Table 1.

Relevant calculation results are presented in Table 5. A good agreement is observed between the calculated and experimental  $E$  values for three esters with the experimentally measured  $E$  values (see the tenth column in Table 5 with  $\Delta E = E_{\text{calcd}} - E_{\text{exp}}$ ).

## CONCLUSION

The parabolic model was used for the first time to analyze concerted decomposition with the cleavage of two bonds. The parameters of this reaction are compared with those of the bimolecular reactions of free radicals with similar reaction centers. Using these parameters, one can calculate the activation energy of the concerted decomposition of peresters of different structures.

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