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Full Articles

Molecular structure and decomposition mechanism of peracetic acid esters AcOOR (R = Me, Bu^t)

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The molecular structure and conformational mobility of methyl and *tert*-butyl esters of peracetic acid AcOOR (R = Me (**1**), Bu^t (**2**)) were studied by the *ab initio* MP4(SDQ)//MP2(FC)/6-31G(d,p) method and density functional B3LYP/6-31G(d,p) approach. The B3LYP calculated equilibrium conformations of the molecules are characterized by the C—O—O—C torsion angles of 93.6° (**1**) and 117.0° (**2**). Structural features of the molecules under study and a distortion of tetrahedral bond configuration at the C_α atom were explained using the natural bonding orbital approach. The standard enthalpies of formation of AcOOMe (–328.5 kJ mol^{-1}) and AcOOBu^t (–440.4 kJ mol^{-1}) were determined using the G2 and G2(MP2) computational schemes and the isodesmic reaction approach. The transition state of AcOOMe decomposition into AcOOH and formaldehyde was calculated (E_a = 122.8 kJ mol^{-1}). The thermal effects of homolytic decomposition of the peroxy esters following a concerted mechanism ($Me^\bullet + CO_2 + {}^\bullet OR$) and simple homolysis of the peroxide bond ($AcO^\bullet + {}^\bullet OR$) were found to be 97.5±0.3 and 155.1±0.3 kJ mol^{-1}, respectively. At temperatures below 400 K, the most probable decomposition mechanism of peroxy esters **1** and **2** involves simple homolysis of the O—O bond.

Key words: methyl peroxy acetate, *tert*-butyl peroxy acetate, *ab initio* quantum-chemical calculations, quantum-chemical calculations, molecular structure, conformational analysis, thermochemistry.

Peroxy esters RC(O)OOR´ are efficient radical initiators. They are used in bulk, solution, and suspension polymerization of vinyl monomers, in high-temperature solidification of polyester resins, and in curing of elastomers and acrylic resins.[1,2] Depending on the molecular structure of peroxy esters, thermolysis of these compounds can involve (i) homolysis of the peroxide bond or simultaneous cleavage of two bonds, O—O and R—C(O), or

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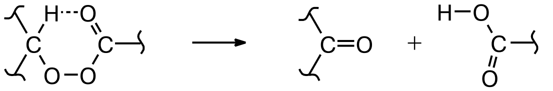
(ii) rearrangement in an organic derivative of carbonic acid, ROC(O)OR´.

The presence of H_α atoms allows a ketone and an acid to be formed as a result of cyclic bond rearrangement (Scheme 1).

Scheme 1



The efficiency of this reaction must depend on the structure and stability of the newly formed carbonyl compound. For instance, a study of thermolysis of *n*-butyl peroxy acetate and *tert*-butyl peroxy acetate vapors revealed[3] that the kinetic parameters of the decomposition of these compounds are independent of additional dissolution with CO_2, C_2F_6, and $MeCF_3$ molecules, being very similar to the kinetic parameters of the decomposition of the same compounds in a chlorobenzene solution. The activation energy for decomposition of *n*-butyl peroxy acetate is only slightly lower than that of *tert*-butyl peroxy acetate, which substantiates the conclusion that thermolysis of these compounds in the vapor phase involves a simple homolysis of the O—O bond.

Peroxy esters RC(O)OOR´ can be divided into two types in relation to thermal decomposition mechanism.[4] Type I compounds are those which decompose producing no stable free radical R. Decomposition of type II compounds can lead to stabilization of the radical R owing to delocalization of the unpaired electron. Type II peroxy esters decompose much faster than type I compounds. Thermolysis of the type II peroxy esters mainly involves simultaneous cleavage of the O—O and R—C(O) bonds. Usually, the stronger the starting carboxylic acid, the lower the decomposition rate of peroxy esters.

A semiempirical parabole model of bimolecular reaction[5,6] modified to calculate the kinetic and thermodynamic parameters of radical decomposition reactions involving simultaneous cleavage of several bonds was employed[7] to determine the parameters of the peroxy ester decomposition reactions that tentatively involve simultaneous cleavage of the R—C(O) and O—O bonds. It was shown[7] that the reaction center of concerted decomposition reaction is structurally similar to the reaction centers of addition reactions of carbon-centered radicals to carbonyl group and of oxygen-centered radicals to alkenes.

Clearly, the thermal stability and decomposition mechanism of a peroxy ester depend on the molecular structure and conformational mobility. Since relevant information is scarce,[8] the aim of this study was to investigate stable molecular conformations and conformations corresponding to free rotation of molecules about the peroxide bond using *ab initio* and density functional approaches taking methyl peroxy acetate (**1**) and *tert*-butyl peroxy acetate (**2**) as examples. To reveal the most probable mechanism of thermolysis of peroxy esters, we calculated the enthalpies of formation of compounds **1** and **2** and studied the possibility of nonradical decomposition of peroxy acetate **1** into AcOOH and formaldehyde.

Calculation Procedure

The *ab initio* restricted Hartree—Fock (RHF) calculations and density functional (DFT) calculations with the B3LYP hybrid functional[9] were carried out using the GAMESS [10] and GAUSSIAN-98 [11] programs. The RHF calculations were carried out with inclusion of electron correlation effects at the second and fourth order levels of Møller—Plesset perturbation theory (MP2 and MP4, respectively). All calculations were performed with the 6-31G(d,p) basis set (the 6-31G split valence basis set augmented with polarization d-functions for the nonhydrogen atoms and p-functions for H atoms).

The ground-state geometries of the molecules of the compounds under study were determined by full geometry optimization by the MP2/6-31G(d,p) and B3LYP/6-31G(d,p) methods. The potential curves of internal rotation about the peroxide bond were obtained by calculations with the constant value of the dihedral, or torsion, angle φ, which characterizes the mutual arrangement of the atoms in the C—O—O—C fragment, and full optimization of the remaining geometric parameters. These calculations were carried out with a φ increment of 15° in the range 0—180° with allowance for symmetry of the potential curve.

The relative energies of conformers were calculated as the total energy differences between the given state and the ground state of the peroxy ester molecule. In performing MP2 optimizations the relative energies of different conformers were also estimated at the MP4 level with inclusion of the single, double, and quadruple excitations (MP4-SDQ) by carrying out single-point calculations with fixed geometric parameters in the same basis set. MPn optimizations were carried in the "frozen core" approximation.

To interpret structural peculiarities of the molecules under study using the orbital populations of chemical bonds and the molecule-stabilizing orbital effects, the natural bonding orbital (NBO) approach[12] was employed in the framework of the B3LYP/6-31G(d,p) approximation.

The enthalpies of formation of peroxy esters were calculated from the thermal effects of isodesmic reactions (IDRs).[13] The enthalpies of the compounds involved in the IDRs were calculated by the MP4//MP2/6-31G(d,p) and B3LYP/6-31G(d,p) methods and using two composite computational schemes, G2 [14] and G2(MP2).[15]

Results and Discussion

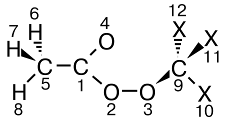
Structure. The calculated values of the main geometric parameters of the equilibrium structures of molecules **1** and **2** are listed in Table 1. The results obtained by both computational methods (MP2 and B3LYP) are in good

Table 1. Geometric parameters of methyl peroxy acetate (**1**) and *tert*-butyl peroxy acetate (**2**) molecules and the *cis*- and *trans*-barrier heights

Parameter	AcOOMe (**1**)		$\mathrm{AcOOBu^t}$ (**2**)	
	MP4//MP2	B3LYP	MP4//MP2	B3LYP
Interatomic distance		r/Å		
O(2)—O(3)	1.460	1.450	1.465	1.454
C(1)—O(2)	1.383	1.376	1.382	1.373
O(3)—C(9)	1.426	1.424	1.450	1.455
C(1)=O(4)	1.209	1.202	1.209	1.202
C(1)—C(5)	1.506	1.512	1.508	1.514
C(9)—X(10)	1.088	1.094	1.523	1.534
C(9)—X(11)	1.089	1.095	1.521	1.532
C(9)—X(12)	1.089	1.094	1.521	1.531
Bond angle		θ/deg		
C(1)—O(2)—O(3)	110.2	111.4	109.8	111.1
O(2)—O(3)—C(9)	106.1	107.4	108.0	109.4
O(4)=C(1)—O(2)	125.1	125.0	125.8	125.7
O(4)=C(1)—C(5)	127.3	126.7	127.0	126.4
O(3)—C(9)—X(10)	103.5	103.7	100.6	100.6
O(3)—C(9)—X(11)	110.9	111.3	109.9	110.1
O(3)—C(9)—X(12)	111.1	111.4	110.7	110.7
Torsion angle		φ/deg		
O(4)=C(1)—O(2)—O(3)	−6.7	−7.3	−5.9	−6.7
O(4)=C(1)—O(2)—C(5)	−179.2	−179.5	−178.6	−178.7
C(5)—C(1)—O(2)—O(3)	172.5	172.1	172.7	172.0
C(1)—O(2)—O(3)—C(9)	91.7	93.6	113.1	117.0
O(2)—O(3)—C(9)—X(10)	176.1	175.3	−180.0	179.5
O(2)—O(3)—C(9)—X(11)	57.9	57.5	62.2	61.8
O(2)—O(3)—C(9)—X(12)	−66.0	−66.8	−62.2	−62.8
Barrier height		ΔE/kJ mol^{-1}		
ΔE_{cis}	45.3	38.0	66.0	52.9
ΔE_{trans}	5.1	2.9	5.6	3.0

agreement; therefore, in the text below we will use the results of B3LYP/6-31G(d,p) calculations.

The O—O bond length in the peroxy esters (1.450—1.454 Å) is similar to the r(O—O) distance in alkyl peroxides (*cf.* 1.463 Å for dimethyl peroxide molecule[16,17]). In contrast to this, the O(3)—C(9) interatomic distance is appreciably different from both the sum of the covalent radii of the atoms involved in this bond and the r(C—O) value for the MeOMe molecule (1.410 Å). The bond length (O(3)—C(9)) in molecule **2** is 1.455 Å due to the effect of the bulky *tert*-butyl substituent. Indeed, in the di-*tert*-butyl peroxide the r(C—O) distance also increases to 1.443 Å.[16,17] Replacement of the *tert*-butyl substituent by a Me group causes a decrease in the O(3)—C(9) interatomic distance in molecule **1** down to a "normal" value of 1.424 Å (see Table 1).



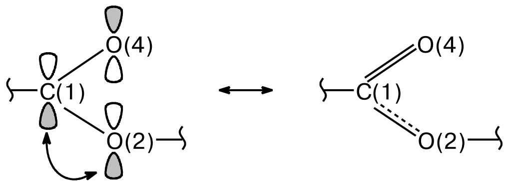
The length of the bond between the carboxylic carbon atom and the peroxy oxygen atom (1.373—1.376 Å) is much shorter than the bond lengths typical of alkyl peroxides. Shortened are also the C(1)—C(5) (1.512—1.514 Å, *cf.* 1.530 Å for ethane) and C(1)=O(4) (1.202 *vs.* 1.226 Å for acetone) bonds. These structural features are due to stabilization of the carboxylic fragment by strong nonvalent orbital interactions. The results of the NBO analysis indicate that the electron density of the nonbonding electron pairs of the O(2) atom is transferred to the antibonding orbitals of the C=O bond.

Orbital interaction	Interaction energy/ kJ mol^{-1}	
	1	**2**
n_σ(O(2)) → σ^*(C(1)—O(4))	23.1	23.6
n_π(O(2)) → π^*(C(1)—O(4))	161.8	157.9
n_π(O(4)) → σ^*(C(1)—O(2))	165.0	165.1
n_π(O(4)) → σ^*(C(1)—C(5))	79.6	80.7

As a result, the interatomic bonding becomes stronger and the bond is shortened. In turn, the π-type lone electron pair (LEP) of the carbonyl oxygen atom is involved in efficient overlap with the antibonding orbitals of the neighboring bonds C(1)—O(2) and C(1)—C(5), thus being responsible for their stabilization and shortening.

The high $n_\pi(O(2)) \rightarrow \pi^*(C(1)-O(4))$ interaction energy allows the C(1)—O(2) bond to be formally treated as a partially multiple bond (Scheme 2).

Scheme 2



Therefore, free rotation about the C(1)—O(2) bond must be hindered. Indeed, all conformations of the peroxy ester molecules **1** and **2** studied in this work are characterized by a planar C(5)—C(1)(O(4))—O(2)—O(3) fragment and a small deviation of the O(3) atom (by only 7°) from the carboxylic group plane (see Table 1). Earlier, high barrier to rotation about the C(O)—O bond was reported for peroxy acetyl nitrate.[18,19]

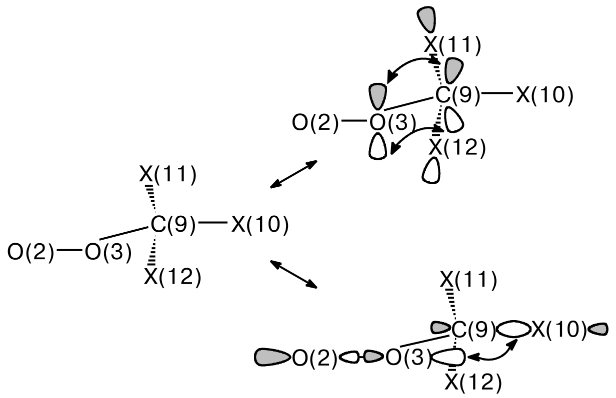
A characteristic feature of the molecular structure of peroxides is distortion of the tetrahedral configuration at the sp^3-hybridized carbon atom bonded to the peroxy group. The O(3)—C(9)—H(10) bond angle in molecule **1** (103.7°) is much less than the bond angles involving the atoms H(11) and H(12) that are *gauche*-oriented relative to the O(2) atom (111.3 and 111.4°, respectively). A qualitatively similar situation with the O(3)—C(9)—X angles was also found for molecule **2** (see Table 1). This structural feature called the "d-effect" (distortion effect) was first reported in Ref. 20 and then analyzed in detail.[17] Therefore, here we will only note that peroxy esters **1** and **2** possess the d-effect due to the influence of the LEP of the $O_\alpha(3)$ atom on the bonds formed by the *gauche*-oriented atoms and to the effect of the $O_\beta(2)$ atom owing to the overlap of the peroxide bond orbitals with orbitals of the C(9)—X(10) (X = H, C) bonds, where X is the atom in the antiperiplanar conformation with respect to the atom O_β (Scheme 3).

NBO analysis allows the energies of the interactions responsible for the d-effect to be evaluated.

Orbital interaction	Interaction energy/ kJ mol^{-1}	
	1 (X = H)	**2** (X = C)
$n_\pi(O(3)) \rightarrow \sigma^*(C(9)-X(11))$	19.1	18.5
$n_\pi(O(3)) \rightarrow \sigma^*(C(9)-X(12))$	26.7	25.1
$\sigma(O(2)-O(3)) \rightarrow \sigma^*(C(9)-X(10))$	6.4	10.8
$\sigma(C(9)-X(10)) \rightarrow \sigma^*(O(2)-O(3))$	23.8	19.1

The most important geometric parameter characterizing the structure of a peroxide molecule is the torsion angle, φ, between substituents at the peroxy group. This angle can vary from 0 in the peroxyacetic acid molecule[21] to 180° in the dicumyl peroxide molecule.[22] Stable conformations of molecules **1** and **2** are characterized by φ values of 93.6 and 117.0°, respectively. Preferableness of *gauche*-conformations of the molecules with polar bonds is basic to the anomeric effect.[23] By studying the conformational mobility of peroxide molecules during rotation about the O—O bond it is possible to determine the factors responsible for the conformational behavior of the molecules and the structure of stable conformations.[16,17,21]

Scheme 3



The energies of molecules **1** and **2** are plotted *vs*. the angle φ(C(1)—O(2)—O(3)—C(9)) in Fig. 1. The potential curve minima corresponding to the mirror conformations are separated by some potential barriers, namely, a *trans*-barrier ($\Delta E_{trans} \approx 3$ kJ mol^{-1}) and a *cis*-barrier ($\Delta E_{cis} \approx 38$ (**1**) and 53 kJ mol^{-1} (**2**)). The steric strain produced by the bulky *tert*-butyl substituent in the *cis*-conformation of molecule **2** is greater than that in molecule **1** and causes an increase in ΔE_{cis} by 15 kJ mol^{-1}. Transoid arrangement of substituents at the peroxy group minimizes both steric repulsion and the repulsion between the LEPs, thus resulting in the same ΔE_{trans} values for both peroxy esters.

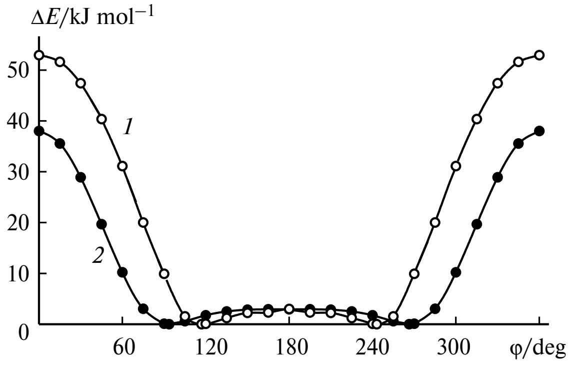


Fig. 1. Potential curves of internal rotation about the O—O bond in peroxy esters AcOOR (R = Bu^t (*1*), Me (*2*)) obtained from B3LYP/6-31G(d,p) calculations.

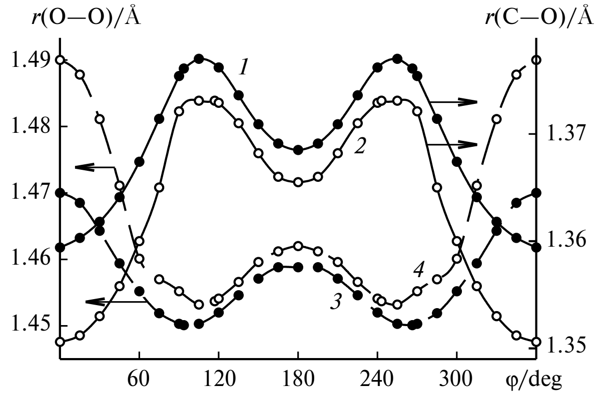
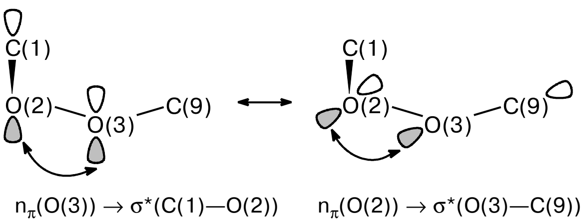


Fig. 2. B3LYP/6-31G(d,p) calculated changes in the C—O (*r*(C—O)) (*1*, *2*) and O—O (*r*(O—O)) (*3*, *4*) bond lengths in the course of internal rotation about the O—O bond in peroxy esters AcOOR (R = Me (*1*, *3*), Bu^t (*2*, *4*)).

Anomeric stabilization of molecules **1** and **2** is due to the n(O) → σ*(C—O) interactions. The most efficient overlap between the nonbonding σ-orbitals and the σ*-orbitals of the C—O bonds is attained at φ = 0. The energy of these interactions monotonically decreases as φ increases to 180°, thus partially compensating the destabilizing effects and lowering the *cis*-barrier. The energy of the n_π(O) → σ*(C—O) interactions is maximum at φ ≈ 75—90°. These orbital effects are responsible for stability of the *gauche*-conformations of the peroxy ester molecules. The equilibrium φ value is somewhat larger because of the effect of the destabilizing factors. In particular, steric repulsion between the acetyl and *tert*-butyl groups in molecule **2** is stronger than that in peroxy ester **1** and causes an increase in the angle φ.

Another manifestation of the n_π(O) → σ*(C—O) interactions is a periodic change in the O—O and C—O bond lengths (Fig. 2). At φ ≈ 75—90°, the bonding between the O atoms becomes stronger, which is reflected in a shortening of the O—O bond (Scheme 4).

Scheme 4



On the contrary, efficient population of the antibonding orbitals of the C—O bonds destabilizes these bonds, making them longer. Thus, NBO analysis of the orbital effects provides a consistent explanation for the structural features of molecules **1** and **2**.

Thermochemistry and decomposition mechanism of peroxy esters. Information on the standard enthalpies of formation ($\Delta_f H°$) of peroxy esters is scarce[24] and mainly limited to the data for the condensed phase. In addition, the $\Delta_f H°$ values for the peroxy esters studied in this work are unavailable. We determined the thermodynamic parameters of compounds **1** and **2** using the composite computational schemes G2 and G2(MP2) and the isodesmic approach, which were successfully employed earlier in thermochemistry studies of alkyl peroxides and alkyl hydroperoxides[17] and of peroxy acetic acid.[21]

The following IDRs were used to determine the $\Delta_f H°(\mathbf{1})$ values:

$$\mathbf{1} + \text{MeOMe} \longrightarrow \text{AcOMe} + \text{MeOOMe}, \tag{1}$$

$$\mathbf{1} + \text{HOOH} \longrightarrow \text{AcOOH} + \text{MeOOH}. \tag{2}$$

We calculated the enthalpies ($H°_{298}$) of all compounds involved in the reactions. This allowed the thermal effects

Table 2. Energy characteristics of compounds used in calculations of the standard enthalpies of formation ($\Delta_f H°$/kJ mol^{-1}) of peroxy esters **1** and **2**

Compound	$-E_{tot}$	ZPE	$-E_{tot}$	ZPE	$-H°_{298}$				$-\Delta_f H°_{exp}$
	MP4//MP2/6-31G(d,p)		B3LYP/6-31G(d,p)		MP4//MP2	B3LYP	G2(MP2)	G2	
MeOMe	154.587160	216.5	155.032965	209.8	154.504815	154.950940	154.737481	154.741331	184.1
AcOMe	267.658147	242.5	268.396756	236.1	267.564804	268.303347	267.951158	267.958140	410.0
HOOH	151.164521	70.0	151.543191	69.3	151.134684	151.513626	151.357145	151.361600	136.1
MeOOH	190.350155	147.5	190.856305	143.8	190.292404	190.798468	190.571794	190.577107	131.0
MeOOMe	229.536418	224.3	230.169083	218.3	229.450955	230.082784	229.786438	229.792526	125.5
Bu^tOOH	307.948581	376.1	308.819981	365.3	307.805953	308.677491	—	—	244.1
Bu^tOOBu^t	464.733247	678.2	466.093920	660.0	464.478663	465.838309	—	—	344.6
AcOOH	303.415411	174.7	304.217686	171.0	303.346775	304.148636	303.783199	303.791627	353.2
1	342.597102	250.8	343.523260	243.7	342.499903	343.426012	342.990978	343.000225	—
2	460.195739	477.7	461.486350	464.2	460.013917	461.304513	—	—	—

Note. E_{tot}/hartree denote the total energies, $H°_{298}$/hartree denote the enthalpies of compounds, and ZPE/kJ mol^{-1} denote the zero-point vibrational energies.

Table 3. Calculated thermal effects of isodesmic reactions ($\Delta H°$/kJ mol^{-1}) and standard enthalpies of formation ($\Delta_f H°$/kJ mol^{-1}) of peroxy esters **1** and **2**

Computational method	$\Delta H°$	$\Delta_f H°$(**1**)	$\Delta H°$	$\Delta_f H°$(**1**)	$\Delta H°$	$\Delta_f H°$(**2**)	$\Delta H°$	$\Delta_f H°$(**2**)
	reaction (1)		reaction (2)		reaction (3)		reaction (4)	
MP4//MP2	−29.0	−322.4	−12.1	−336.0	1.2	−442.8	0.8	−438.5
B3LYP	−24.1	−327.3	−19.6	−328.5	−1.4	−440.2	3.9	−440.0
G2(MP2)	−24.0	−327.4	−18.0	−330.1	—	—	—	—
G2	−23.9	−327.5	−18.1	−330.0	—	—	—	—

of the IDRs (1) and (2) to be computed. By combining the $\Delta H°_{298}$ values, reliable experimental data,[24—26] and the calculated enthalpies of formation of the compounds involved in the IDRs[17,21] we calculated the $\Delta_f H°$(**1**) value. The initial data set is listed in Table 2 and the results are given in Table 3. All computational methods, except for MP4//MP2, give consistent values of the standard enthalpies of formation of peroxy ester **1**; averaging gives $\Delta_f H°(\mathbf{1}) = -328.5$ kJ mol^{-1}.

At present, G2 and G2(MP2) calculations of peroxy ester **2** are impossible because of high computational cost. The enthalpy of formation of this compound was determined relative to $\Delta_f H°$(**1**) by the MP4//MP2 and B3LYP methods. To this end, the following IDRs were constructed using Benson's group additivity scheme:

2 + MeOOH ⟶ **1** + Bu^{t}OOH, (3)

2 **2** + MeOOMe ⟶ 2 **1** + Bu^{t}OOBu^t. (4)

This approach permits a much better compensation of the errors due to neglect of electron correlation effects in calculations of the thermal effect of IDR, which justifies the use of the B3LYP and MP4//MP2 methods. Indeed, the thermal effects of reactions (3) and (4) are close to zero (see Table 3). This indicates the absence of unaccounted nonvalent interactions and compensation of errors associated with incomplete allowance for electron correlations. The $\Delta_f H°$(**2**) values were calculated using the thermal effects of reactions (3) and (4) and the known enthalpies of formation of the peroxide compounds involved in the IDRs.[17] All the four calculated values of the standard enthalpy of formation of compound **2** differ by at most 4 kJ mol^{-1} (see Table 3), the average $\Delta_f H°$(**2**) value being equal to −440.4 kJ mol^{-1}.

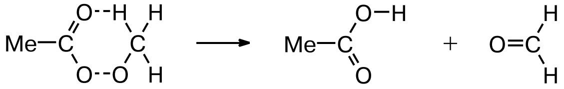
Now we can calculate the energy changes for homolysis of the O—O bond and for concerted decomposition of peroxy esters. The standard enthalpies of formation of decomposition products are $\Delta_f H°$(Me) = 145.7,[26] $\Delta_f H°$(MeO) = 17.0,[24] $\Delta_f H°$(Bu^{t}O) = −95.4,[27] $\Delta_f H°$(AcO) = −190.2,[21] and $\Delta_f H°$(CO_2) = −393.5 kJ mol^{-1}.[24] From here the thermal effects of homolytic decomposition reactions of peroxy esters are as follows.

Reaction	R = Me	R = Bu^t
AcOOR ⟶ AcO$^•$ + $^•$OR	155.3	154.8
AcOOR ⟶ Me$^•$ + CO_2 + $^•$OR	97.7	97.2

The nature of alkyl substituent has no effect on the thermal effects of radical decomposition reactions of peroxy esters. The activation energy for gas-phase thermolysis of AcOOBu^t and AcOOBu^n is[28] ~150 kJ mol^{-1} at lg$A$ ≈ 16 (A is the pre-exponent), which is characteristic of simple one-center homolysis reactions.[29,30] The calculated peroxide bond strength is in good agreement with the experimental activation energy and point to preferableness of decomposition of peroxy esters **1** and **2** into acetoxyl and alkoxyl radicals.

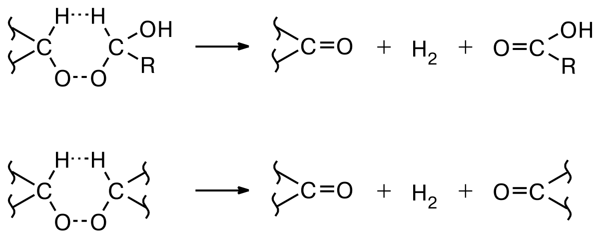
The presence of the C_α—H bond in molecule **1** makes possible the following decomposition route (Scheme 5).

Scheme 5



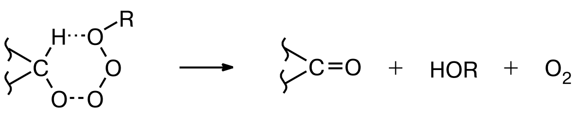
This scheme was realized for different types of peroxides (Scheme 6).

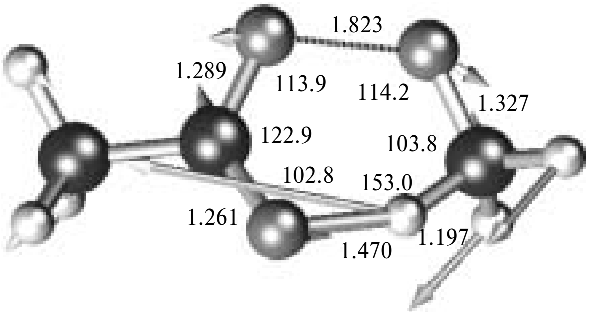
Scheme 6



This scheme is similar to a termination reaction in chain autooxidation[31,32] (Scheme 7).

Scheme 7





Angle	φ/deg	Angle	φ/deg
O—C—O—O	35.4	C—O—H—C	8.1
O—O—C—H	−6.0	O—C—O—H	−32.4
C—O—O—C	−12.1	O—C—H—O	10.7

Fig. 3. Transition state of decomposition of methyl peroxy acetate (**1**) into acetic acid and formaldehyde (E_{tot} = −343.470845 hartree, obtained from B3LYP/6-31G(d,p) calculations). Interatomic distances are given in Å and the angles are given in degrees. The mode corresponding to the imaginary frequency (−1051 cm^{-1}) is arrowed.

The transition state of the decomposition of peroxy ester **1** into AcOOH and formaldehyde (Fig. 3) was located in B3LYP/6-31G(d,p) calculations. The free enthalpy of activation of this rearrangement calculated with inclusion of temperature correction to the total energies of the peroxy ester (see Table 2) and transition state (ZPE = 228.6 kJ mol^{-1}) is 122.8 kJ mol^{-1}. The calculated entropy of activation is $\Delta S^{\neq} = -9.8$ J mol^{-1} deg^{-1}, which gives $\Delta G^{\neq} = 125.7$ J mol^{-1}. Using the thermodynamic form of the main equation of theory of transition state

$$k_{\text{mol}} = (kT/h)\cdot\exp(-\Delta G^{\neq}/RT) = (kT/h)\cdot\exp(\Delta S^{\neq}/RT)\cdot\exp(-\Delta H^{\neq}/RT),$$

where k_{mol} is the rate constant for molecular decomposition of peroxy ester **1**, k is the Boltzmann constant, h is the Planck constant, and R is the universal gas constant, and assuming that the enthalpy of activation ($\Delta H^{\neq}$) and the entropy of activation ($\Delta S^{\neq}$) are temperature-independent in the 298—400 K interval, we get with ease $\lg A_{\text{mol}} = 11.2$ s^{-1} at $T = 400$ K. Indeed, the concerted six-center monomolecular decomposition reactions are characterized by $\lg A \approx 11$—12.[29]

According to calculations, the ratio of the radical and molecular decomposition channels for peroxy ester **1** is given by

$$k_{\text{rad}}/k_{\text{mol}} = 10^{4.8}\exp(-32.5/RT),$$

where k_{rad} is the rate constant for radical decomposition.

Therefore, the probability of nonradical decomposition of compound **1** at temperatures typical of the decomposition of peroxy esters (~400 K) is at most 10—20%.

Thus, our theoretical estimates of the energy characteristics of possible decomposition channels of peroxy esters **1** and **2** show that thermal decomposition of these compounds proceeds *via* simple homolysis of the peroxy bond.

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