Free radical abstraction of H atom from peroxides with concerted dissociation of O—O bond*

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Quantum chemical calculations of the dissociation energy of the C—H bond in the α-hydroperoxide fragment of Me_2CHOOH were carried out. It was shown that abstraction of H atom is accompanied by dissociation of the O—O bond. Density functional calculations of transition states of the reactions of $^{\cdot}CH_3$, $CH_3OO^{\cdot}$, and $HO_2^{\cdot}$ radicals with the C—H bond in the α-hydroperoxide fragment of Me_2CHOOH were carried out. It was established that H atom abstraction is accompanied by concerted dissociation of the O—O bond. For 45 peroxides R^1R^2CHOOH, $R^1R^2CHOOR^3$, and $R^1R^2CHOOC(O)R^3$ (R^1, R^2 = H, Me, Et, Ph, $H_2C=CH$), the enthalpies of H atom abstraction from the C—H bond in the α-hydroperoxide fragment with fragmentation of the peroxides at the O—O bond were calculated. The kinetic parameters for 12 classes of radical abstraction reactions with fragmentation of molecules were calculated from experimental data within the framework of the model of intersecting parabolas. The activation energies and reaction rate constants of H atom abstraction from C—H bonds of α-peroxide fragments involving peroxyl and alkyl radicals were determined for 45 peroxides of different structure.

Key words: alkoxyl radical, quantum chemical calculations, density functional theory, rate constant, methyl radical, model of intersecting parabolas, dissociative abstraction, transition state, peroxide, C—H bond in α-peroxide fragments, peroxyl radical, activation energy, bond dissociation energy.

Radical abstraction reactions of the type

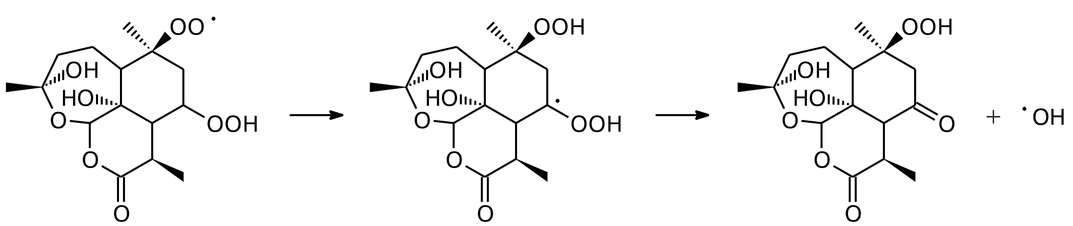
$$X^{\cdot} + RH \longrightarrow XH + R^{\cdot},$$

where $X^{\cdot}$ is an atom or radical, are widespread.[1—3] However, the variety of oxidation reactions also includes processes involving more complex structural rearrangements of the molecule being attacked, which occur in the transition state (TS). A recent kinetic analysis of the radical reactions of artemisinine and its analogs showed how important are hydroxyl radicals for its anti-malarial action.[4,5] The main source of hydroxyl radicals is intramolecular attack of peroxyl radical on the C—H bond in the α-hydroperoxide fragment (see, *e.g.*, Scheme 1).

An alternative reaction route involves one-step formation of hydroxyl radical from peroxyl radical (Scheme 2).

An analogous situation occurs in the interpretation of the mechanism of cyclohexane oxidation. A study of liquid-phase oxidation of cyclohexane using an inhibitor of the chain process revealed[6] that transformation of cyclohexyl hydroperoxide to cyclohexanone follows a chain mechanism involving an attack of a peroxyl radical on the hydroperoxide.[6] The tentative reaction mechanism[7] is shown in Scheme 3.

Scheme 1



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[*] Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on the occasion of his 80th birthday.

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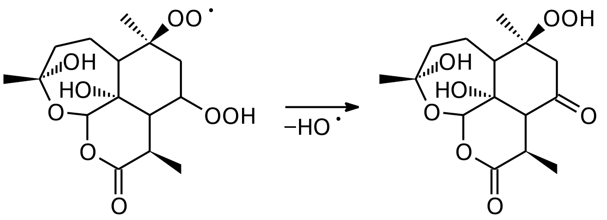
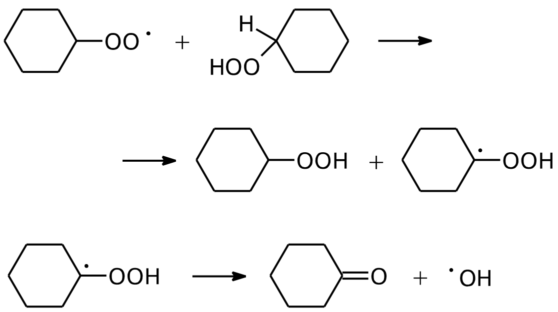
Scheme 2



Scheme 3



Since the strength of the C—H bond in the α-hydroperoxide fragment seems to be close to that in the cyclohexanol molecule (D(>C—HOOH) ≈ (D(>C—HOH), one could expect that the rate constants for H atom abstraction from the corresponding groups in cyclohexyl hydroperoxide and cyclohexanol are close. However, an experiment[8] (348 K) revealed a great difference between them, namely, the rate constant $k(RO_2^{\cdot} + ROOH)$ is ten times higher than $k(RO_2^{\cdot} + ROH)$. Therefore, a hypothesis was put forward[9] that the reaction of $RO_2^{\cdot}$ with the α-C—H bond in hydroperoxide proceeds in one step as concerted abstraction of H atom and dissociation of the O—O bond (Scheme 4) rather than in two steps.

Scheme 4

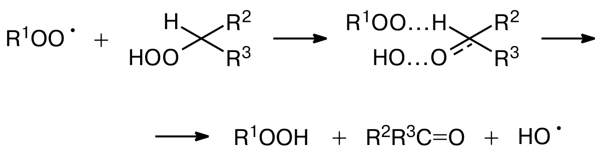
$$R^1O_2^{\cdot} + HC(OOH)R^2R^3 \longrightarrow$$

$$\longrightarrow R^1OOH + R^2R^3C{=}O + HO^{\cdot}$$

Such reactions are called dissociative abstraction reactions. More exactly, they can be defined as radical abstraction reactions with fragmentation of a molecule. The TS of the reaction in question is characterized by concerted dissociation of C—H and O—O bonds and the formation of σ-O—H and π-C=O bonds (Scheme 5).

Concerted structural rearrangement in the TS is due to the high exothermicity of the abstraction reaction with fragmentation. In this study, we performed a quantum chemical analysis of this type of reactions and showed that they do proceed as abstraction reactions with concerted fragmentation of the molecule. This result was used to develop an algorithm for calculating the activation energies and rate constants for such reactions within the framework of the model of intersecting parabolas (MIP).[10]

Scheme 5



Calculation Procedure

Quantum chemical calculations. Theoretical analysis of reactions of radical abstraction of H atom from the α-C—H bond of 2-hydroperoxopropane was carried out by the density functional theory with the PBE nonempirical functional[11] and an extended basis set (H [311/1], C [311/311/11], O [311/311/11]) for the SBK pseudopotential.[12] The types of the stationary points on the potential energy surface were determined by analyzing the Gaussians with analytically calculated second derivatives. The reaction coordinates were constructed by the intrinsic reaction coordinate method. Calculations were carried out with the PRIRODA program[13] on the computational facilities at the Joint Supercomputer Center of the Russian Academy of Sciences.

The bond dissociation energies obtained from the density functional calculations are compared with the available experimental data in Table 1.

There is a reasonable correlation between the calculated and experimentally found bond dissociation energy values, namely, $D_{calc} = D_{exp} - (26.8 \pm 7.3)$ kJ mol^{-1}. Experimental data for the bond of interest, H—C(OOH)Me$_2$, are unavailable. Calculations unambiguously showed that dissociation of the C—H bond is accompanied by that of the O—O bond. A hydroxyl radical thus produced forms a loosely bound adduct with acetone molecule. The O—O bond length in the adduct is 2.36 Å (Fig. 1).

Thermochemical calculations of the enthalpy of H atom abstraction from the α-C—H bond in peroxides with their fragmentation. The reaction of H atom abstraction from the C—H bond

Table 1. Bond dissociation energies obtained from quantum chemical calculations (D_0 and D_{298}) and found experimentally (D)

Bond	D_0	D_{298}	D	Reference
	kJ mol^{-1}			
H—C(O—OH)Me$_2$	204.6	214.7	239.3	—
H—C(OH)Me$_2$	354.8	361.2	390.5	14
MeO—H	400.4	406.0	431.7	14
H$_3$C—H	413.8	420.6	439.3	15
HO—H	473.2	478.0	499.0	15
HOO—H	326.4	334.4	369.0	15
MeOO—H	318.8	324.3	365.5	14
$^{\cdot}$OO—H	185.4	190.4	220.0	16

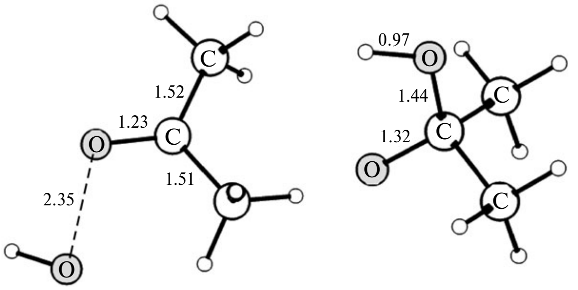


Fig. 1. Geometries of the adduct of acetone molecule with HO$^{\cdot}$ radical (*a*) and CO$^{\cdot}$(OH)Me$_2$ radical (*b*). Here and in Figs 2—5 bond lengths are given in Å.

in the α-hydroperoxide fragment involves simultaneous dissociation of two bonds, C—H and O—O. The corresponding dissociation energy $D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHOOH})$ can be calculated in two ways, first, as the enthalpy of the dissociation reaction

$$\text{R}^1\text{R}^2\text{CHOOH} \longrightarrow \text{R}^1\text{R}^2\text{C=O} + \text{HO}^{\cdot} + \text{H}^{\cdot}$$

from the equation

$$D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHOOH})(1) = \Delta H(\text{R}^1\text{R}^2\text{C=O}) - \Delta H(\text{R}^1\text{R}^2\text{CHOOH}) + 255.2, \qquad (1)$$

where 255.2 kJ mol^{-1} = $\Delta H(\text{H}^{\cdot}) + \Delta H(\text{HO}^{\cdot})$[17].

Second, the enthalpy of H atom abstraction with concerted dissociation of the O—O bond can be expressed through the sum of the dissociation energies of the peroxide O—O bond and the C—H bond in the alkoxyl radical, presenting the process as two consecutive steps:

$$\text{R}^1\text{R}^2\text{CHOOH} \longrightarrow \text{R}^1\text{R}^2\text{CHO}^{\cdot} + \text{HO}^{\cdot},$$

$$\text{R}^1\text{R}^2\text{CHO}^{\cdot} \longrightarrow \text{R}^1\text{R}^2\text{C=O} + \text{H}^{\cdot}.$$

In this case, one has

$$D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHOOH})(2) = D_{\text{O—O}} + D_{\text{C—H}}(\text{R}^1\text{R}^2\text{C(O}^{\cdot}\text{)—H}). \qquad (2)$$

In turn, $D_{\text{C—H}}$ for the alkoxyl radical is calculated as follows:

$$D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHO}^{\cdot}) = \Delta H(\text{R}^1\text{R}^2\text{C=O}) - \Delta H(\text{R}^1\text{R}^2\text{CHO}^{\cdot}) + \Delta H(\text{H}^{\cdot}). \qquad (3)$$

Having expressed the enthalpy of formation of the alkoxyl radical $\text{R}^1\text{R}^2\text{CHO}^{\cdot}$ through the enthalpy of formation of alcohol and the energy of O—H bond dissociation in the alcohol molecule ($\Delta H(\text{R}^1\text{R}^2\text{CHO}^{\cdot}) = \Delta H(\text{R}^1\text{R}^2\text{CHOH}) + D_{\text{O—H}} - \Delta H(\text{H}^{\cdot})$), we have:

$$D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHOOH})(2) = \Delta H(\text{R}^1\text{R}^2\text{C=O}) - \Delta H(\text{R}^1\text{R}^2\text{CHOH}) + D_{\text{O—O}} - D_{\text{O—H}} + 2\Delta H(\text{H}^{\cdot}). \qquad (4)$$

For hydroperoxides, $D_{\text{O—O}}$ = 180 kJ mol^{-1}; this value is independent of the structure of the alkyl radical $\text{R}^1\text{R}^2\text{C}$,[18] the O—H bond dissociation energy $D_{\text{O—H}}$ for the primary and secondary alcohols is 432±2 kJ mol^{-1};[14] also, $\Delta H(\text{H}^{\cdot})$ = 218 kJ mol^{-1}.[17] Therefore, the last three terms in Eq. (4) are $D_{\text{O—O}} - D_{\text{O—H}} + 2\Delta H(\text{H}^{\cdot}) = 184.0$ kJ mol^{-1}. The results of $D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHOOH})$ calculations using these two methods are listed in Table 2.

The root-mean-square deviation between the results obtained by these two methods is small, *viz.*, merely 2.4 kJ mol^{-1}. Since the data array for the enthalpies of formation of alcohols is much larger than that for hydroperoxides,[18] the $D_{\text{C—H}}$ values were calculated from Eq. (4).

An analogous concerted abstraction of H atom from the C—H bond with fragmentation of the molecule should also be expected for the reactions of radicals with other peroxides, such as dialkyl peroxides and peresters. The O—O bond in the dialkyl peroxide molecule is weaker than in hydroperoxide ($D_{\text{O—O}}$ = 162.0±1.5 kJ mol^{-1}), being independent of the structure of the alkyl substituent R.[18] Therefore, the $D_{\text{C—H}}$ value for H atom abstraction from ROOR with dissociation of the O—O bond can be calculated from the equation

$$D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHOOCHR}^1\text{R}^2) = \Delta H(\text{R}^1\text{R}^2\text{C=O}) - \Delta H(\text{R}^1\text{R}^2\text{CHOH}) + 166.0, \qquad (5)$$

where $D_{\text{O—O}} + D_{\text{O—H}} - 2\Delta H(\text{H}^{\cdot})$ = 166.0 kJ mol^{-1}.[14,16,18]

The O—O bond in alkyl peresters is even weaker ($D_{\text{O—O}}$ = 149.5 kJ mol^{-1})[18] and one obtains the following expression for calculations of $D_{\text{C—H}}$ in these compounds:

$$D_{\text{C—H}}(\text{R}^2\text{R}^3\text{CHOOC(O)R}^1) = \Delta H(\text{R}^2\text{R}^3\text{C=O}) - \Delta H(\text{R}^2\text{R}^3\text{CHOH}) + 153.5\ \text{кДж}\cdot\text{моль}^{-1}. \qquad (6)$$

Table 2. Dissociation energies $D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHOOH})$* calculated by two methods

Hydroperoxide	$-\Delta H(\text{R}^1\text{R}^2\text{CHOOH})$	$-\Delta H(\text{R}^1\text{R}^2\text{C=O})$	$-\Delta H(\text{R}^1\text{R}^2\text{CHOH})$	$D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHOOH})(1)$	$D_{\text{C—H}}(\text{R}^1\text{R}^2\text{CHOOH})(2)$
	kJ mol^{-1}				
MeOOH	132.2	108.8	201.5	278.6	276.7
EtOOH	169.4	165.7	235.2	258.9	253.5
Me$_2$CHOOH	198.3	217.1	272.8	236.4	239.7
Bu^{n}OOH	205.0	207.5	275.0	252.7	251.5
cyclo-C$_6$H$_{11}$OOH	214.9	225.9	286.2	244.2	244.3

* The enthalpies of formation of hydroperoxides,[18] the $D_{\text{O—H}}$ values for alcohols,[14] and the enthalpies of formation of carbonyl compounds[17] were taken from the corresponding references.

Kinetic parameters of the abstraction reactions with fragmentation within the framework of the MIP. Within the framework of the MIP method, a radical abstraction reaction

$$\mathrm{Y^{\bullet} + HR \longrightarrow YH + R^{\bullet}}$$

is characterized by the following parameters.[10]

1. The classical enthalpy (ΔH_e) related to the enthalpy of reaction ($\Delta H = D_{R-H} - D_{Y-H}$):

$$\Delta H_e = \Delta H + 0.5hN_A(\nu_{C-H} - \nu_{Y-H}),$$

where ν_{Y-H} and ν_{C-H} are the stretching vibration frequencies of the reactng bonds, h is the Planck constant, and N_A is the Avogadro constant.

2. The classical potential barrier to reaction E_e, which includes the activation energy, the zero-point vibrational energy of the bond being cleaved, and the average kinetic energy of H atom. The E_e parameter is related to the activation energy E as follows:

$$E_e = E + 0.5hN_A\nu_{C-H} - 0.5RT. \qquad (7)$$

3. The distance r_e characterizing elongation of the reacting bonds (in this case, R—H and H—Y) in TS.

4. The b parameter ($2b^2$ is the force constant of the H—Y bond being cleaved), the b_f parameter ($2b_f^2$ is the force constant of the Y—H bond being formed), and the coefficient $\alpha = b/b_f$.

5. The pre-exponent A.

The values of the parameters and coefficients outlined above for the reaction classes under study are collected in Table 3.

The MIP relates[10] the classical potential barrier E_e to the classical enthalpy of reaction ΔH_e

$$br_e = \alpha(E_e - \Delta H_e)^{0.5} + E_e^{0.5}, \qquad (8)$$

which makes it possible, on the one hand, to determine the br_e parameter from experimental data (ΔH and E) and, on the other hand, to calculate the activation energy for any reaction from a given class (provided that the br_e parameter is known) taking into account its enthalpy using the equation

$$E = B^2\left(1 - \alpha\sqrt{1 - \frac{\Delta H_e}{Bbr_e}}\right)^2 - 0.5(hN_A\nu_{C-H} - RT), \qquad (9)$$

where $B = br_e/(1 - \alpha^2)$. For reactions with transfer of H atom from a C atom to a C atom upon attack of alkyl radical on the C—H bond, $\alpha = 1$ and the expression for the activation energy is simplified:

$$E = \left(\frac{br_e}{2} + \frac{\Delta H}{2br_e}\right)^2 - 0.5(hN_A\nu_{C-H} - RT). \qquad (10)$$

The br_e parameter also allows the classical potential barrier to a thermally neutral ($\Delta H_e = 0$) reaction[10] to be calculated:

$$E_{e0} = [br_e/(1 + \alpha)]^2. \qquad (11)$$

In the case of concerted decomposition of a molecule involving more than one bond, the probability of localization of the activation energy on these bonds depends on the number of bonds. In the framework of the oscillator model for a reacting molecule, which treats the molecule as a group of coupled oscillators, the pre-exponent A depends on the number of bonds n, which are rearranged in the TS of the reaction.[19] For the reactions analyzed in this work, $n = 2$ and the pre-exponent A has the form[19]:

$$A = A_0\sqrt{\frac{2RT}{\pi E}}. \qquad (12)$$

Having expressed the rate constant (k) for this reaction in the Arrhenius form and, since A depends on T (see relation (12)), we get

$$E = RT^2(d\ln k/dT) = E_{exp} - 0.5RT,$$

and the equation for k can be written in the form

$$k = A\exp[-E/(RT)] = n_{C-H}A_0\sqrt{\frac{2RT}{\pi E}}\exp[-E/(RT)], \qquad (13)$$

where n_{C-H} is the number of attacked equireactive C—H bonds.

Abstraction of H atom with fragmentation of molecule was experimentally studied taking the reaction of cyclohexylperoxyl radical with cyclohexyl hydroperoxide[8] as an example. The rate constant for this reaction in chlorobenzene at

Table 3. Kinetic parameters of reactions of H atom abstraction from peroxide C—H bonds with fragmentation

Reaction class	α	E_{e0}	$-\Delta\Delta H_e$	br_e /kJ$^{0.5}$ mol$^{-0.5}$	A_0 /L mol^{-1} s^{-1}
		kJ mol^{-1}			
$\mathrm{(R^1)^{\bullet} + R^3R^4CHOOHR^2}$	1.000	121.2	0.0	22.00	$1.0 \cdot 10^9$
$\mathrm{(R^1)^{\bullet} + CH_2{=}CHCH_2OOR^2}$	1.000	132.9	0.0	23.05	$1.0 \cdot 10^8$
$\mathrm{(R^1)^{\bullet} + PhCH_2OOR^2}$	1.000	125.6	0.0	22.41	$1.0 \cdot 10^8$
$\mathrm{R^1O^{\bullet} + R^3R^4CHOOR^2}$	0.796	96.6	4.3	17.65	$1.0 \cdot 10^9$
$\mathrm{R^1O^{\bullet} + CH_2{=}CHCH_2OOR^2}$	0.796	106.8	4.3	18.56	$1.0 \cdot 10^8$
$\mathrm{R^1O^{\bullet} + PhCH_2OOR^2}$	0.796	103.1	4.3	18.24	$1.0 \cdot 10^8$
$\mathrm{R^1O_2^{\bullet} + R^3R^4CHOOR^2}$	0.814	102.7	3.8	18.38	$1.0 \cdot 10^8$
$\mathrm{R^1O_2^{\bullet} + CH_2{=}CHCH_2OOR^2}$	0.814	116.6	3.8	19.60	$1.0 \cdot 10^7$
$\mathrm{RO_2^{\bullet} + PhCH_2OOR}$	0.814	108.7	3.8	18.91	$1.0 \cdot 10^7$
$\mathrm{PhO^{\bullet} + R^2R^3CHOOHR^1}$	0.802	119.8	4.1	19.72	$1.0 \cdot 10^9$
$\mathrm{AmO^{\bullet} + R^2R^3CHOOHR^1}$	0.802	109.4	4.1	18.84	$1.0 \cdot 10^9$
$\mathrm{Am^{\bullet} + R^2R^3CHOOHR^1}$	0.866	120.0	2.6	20.47	$1.0 \cdot 10^9$

$T = 348$ K is 17 L mol^{-1} s^{-1}. The reaction involves a concerted dissociation of the C—H and O—O bonds. According to the oscillator theory of reactions involving several bonds, the rate constant for this two-center reaction is given by Eq. (13). The A_0 factor for the $RO_2^{\cdot}$ + RH reactions is 10^8 L mol^{-1} s^{-1} for aliphatic compounds RH and 10^7 L mol^{-1} s^{-1} for alkylaromatic and unsaturated hydrocarbons.[10]

Solving the transcendent equation (k = 17 L mol^{-1} s^{-1} at $T = 348$ K)

$$\ln k = \ln\{10^8(2RT)^{1/2}\} - \ln(0.5\pi E) - E/(RT), \qquad (14)$$

we get $E = 40.6$ kJ mol^{-1}.

This reaction is highly exothermic and characterized by $\Delta H = -117.4$ kJ mol^{-1}; $\Delta H_e = -117.4 - 3.8 = -121.2$ kJ mol^{-1}. According to Eq. (7), the classical potential barrier is $E_e = 40.6 + 17.4 - 0.5RT = 56.6$ kJ mol^{-1}. From these data using Eq. (8) at $\alpha = 0.814$ (see Table 1), we get $br_e = 18.38$ kJ$^{0.5}$ mol$^{-0.5}$ and the classical potential barrier to thermally neutral reaction is $E_{e0}(RO_2^{\cdot} + ROOH) = 102.7$ kJ mol^{-1}. The E_{e0} value for the $RO_2^{\cdot}$ + RH abstraction reactions with only one C—H bond being cleaved is much lower, namely, $E_{e0}(RO_2^{\cdot} + RH) = 56.3$ kJ mol^{-1}.[10] The higher barrier $E_{e0}(RO_2^{\cdot} + ROOH)$ is apparently due to the need for cleaving two bonds, C—H and O—O, rather than one bond. The principle of additivity of the partial activation energies[20] holds for the decomposition of molecules with concerted dissociation of two bonds. Therefore, E_{e0} for the reaction in question can be represented by the sum of two addends, *viz.*, $E_{e0}(RO_2^{\cdot} + ROOH) = \Delta E_{e0}(C—H) + \Delta E_{e0}(O—O)$. Assuming that $\Delta E_{e0}(C—H) = E_{e0}(RO_2^{\cdot} + RH)$, we estimate $\Delta E_{e0}(O—O)$: $\Delta E_{e0}(O—O) = E_{e0}(RO_2^{\cdot} + ROOH) - E_{e0}(RO_2^{\cdot} + RH) = 102.7 - 56.3 = 46.4$ kJ mol^{-1}. This allows one to evaluate, within the framework of the MIP, the kinetic parameters of reactions of other radicals with the peroxide α-C—H bonds using the equation

$$E_{e0}(X^{\cdot} + ROOH) = E_{e0}(X^{\cdot} + RH) + \Delta E_{e0}(O—O) =$$
$$= E_{e0}(X^{\cdot} + RH) + 46.4 \text{ kJ mol}^{-1}. \qquad (15)$$

The values of the br_e parameter were determined from the relation

$$br_e = (1 + \alpha)E_{e0}^{0.5}. \qquad (16)$$

The E_{e0} and br_e values thus obtained ($br_e(X^{\cdot} + RH)$ and α values taken from Ref. 10) are listed in Table 3.

Results and Discussion

Quantum chemical calculations. Quantum chemical calculations of TS were carried out for three reactions of $HO_2^{\cdot}$, $MeO_2^{\cdot}$ and $^{\cdot}CH_3$ radicals and oxygen molecule O_2 with 2-propylhydroperoxide and, for comparison, for the reactions of $HO_2^{\cdot}$ and $MeO_2^{\cdot}$ with propan-2-ol. The results obtained are presented in Table 4 and in Figs 2—5.

In all cases, the calculated structure of the O—H—C reaction center is close to nearly linear TS except some variations of the C—H and O—H bond lengths, although the sum of these distances has a constant value within 2.58—2.60 Å. The highly exothermic reaction of 2-propylhydroperoxide with methyl radical is characterized by the early TS with the sum of the bond lengths equal to 2.76 Å. The O—O bond length remains almost unchanged (with one exception) and all reactions of $H—C(OOH)Me_2$ with radicals involve cleavage of the O—O bond. Thus, quantum chemical calculations confirmed the occurrence of abstraction reactions with fragmentation of molecules.

An interesting feature of the reaction of oxygen molecule with peroxide is that the formally low-endothermic reaction of peroxide with O_2 is characterized by a marked elongation of the peroxide O—O bond to 1.75 Å in the TS despite structural similarity between the reaction centers. Thus, in this case the C—H and O—O bonds are also cleaved simultaneously. A possible reason is that once the $HO^{\cdot}$ radical is formed it immediately attacks the $HO_2^{\cdot}$ radical being formed. As a result, a highly exothermic decomposition of 2-peroxopropane to acetone and water proceeds instead of an almost thermally neutral formation of a radical pair $HO_2^{\cdot} + HO^{\cdot} + O{=}CMe_2$; the oxygen molecule acts as a catalyst of this process.

Considering the reaction with the $HO_2^{\cdot}$ radical, the orientation of the $^{\cdot}OH$ radical in the post-reaction complex is unfavorable for the reaction with H_2O_2 (see Fig. 2, *c*).

Table 4. Enthalpies (ΔH_e), activation energies (E), and energies of formation of the pre-reaction ($\Delta H_{298}{}^{c}$) and post-reaction ($\Delta H_{298}{}^{p}$) complexes in radical reactions with 2-propylhydroxyl and propan-2-ol (DFT calculations, the results obtained by the MIP method are given in parentheses)

Reaction	$-\Delta H_e$	E	$\Delta H_{298}{}^{c}$	$\Delta H_{298}{}^{p}$
	kJ mol^{-1}			
$HOO^{\cdot} + H—C(OOH)Me_2 \rightarrow HOOH + HO^{\cdot} + O{=}CMe_2$	119.7 (133.5)	60.8 (36.1)	52.5	48.1
$MeOO^{\cdot} + H—C(OOH)Me_2 \rightarrow MeOOH + HO^{\cdot} + O{=}CMe_2$	109.7 (130.0)	35.8 (37.9)	26.6	11.9
$Me^{\cdot} + H—C(OOH)Me_2 \rightarrow MeH + HO^{\cdot} + O{=}CMe_2$	205.9 (200.7)	8.7 (25.5)	—	—
$HOO^{\cdot} + H—C(OH)Me_2 \rightarrow HOOH + C^{\cdot}(OH)Me_2$	–26.8 (–25.3)	45.9 (43.5)	46.0	31.0
$MeOO^{\cdot} + H—C(OH)Me_2 \rightarrow MeOOH + C^{\cdot}(OH)Me_2$	–36.9 (–21.8)	27.7 (41.9)	18.1	32.0
$^{\cdot}OO^{\cdot} + H—C(OOH)Me_2 \rightarrow {}^{\cdot}OO^{\cdot} + HOH + O{=}CMe_2$	237.2	117.3	0.6	25.1*, 1.4**

* Relative to $O_2 + HOH + O{=}CMe_2$.

** Relative to O_2 and a complex of HOH with $O{=}CMe_2$.

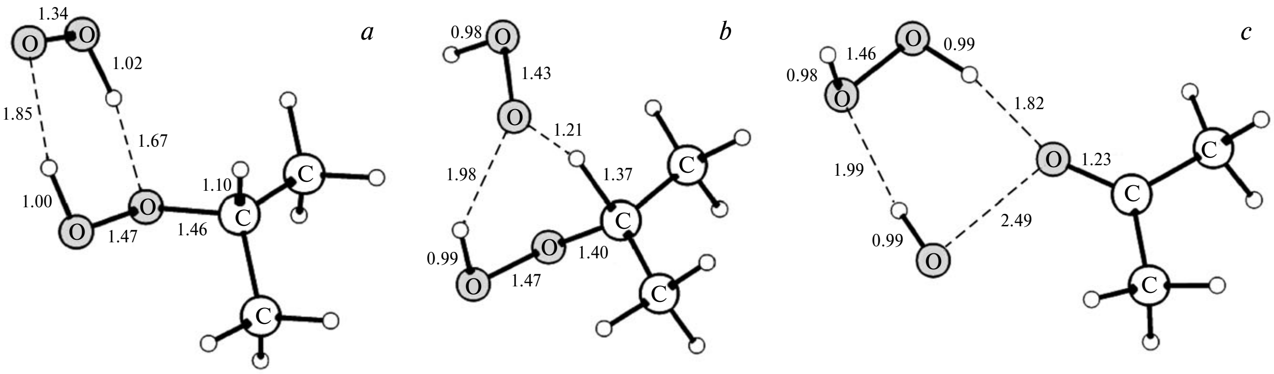


Fig. 2. Structures of the pre-reaction complex (*a*), transition state (*b*), and post-reaction complex (*c*) for the reaction of HOO$^{\bullet}$ radical with HC(OOH)Me$_2$ molecule.

Clearly, reorientation of $^{\bullet}$OH accompanied by cleavage of certain hydrogen bonds and formation of other hydrogen bonds (see Fig. 3, *a*—*c*) does not require a high activation barrier. Therefore, due to the cage effect, there exists a rather high probability for exothermic reaction of water formation to occur as a result of the reaction of hydroxyl with hydrogen peroxide. In this case, the HO$_2^{\bullet}$ radical acts as a catalyst of 2-propylydroxide decomposition, as in the reaction with oxygen. The same considerations also hold for the MeO$_2^{\bullet}$ radical.

From Table 4 it follows that the energies of formation of hydrogen-bonded pre-reaction complexes (ΔH_c) are comparable with the activation energies. That formally makes low the activation barrier for noninteracting reactants. However, one should take into account that in a polar medium, both peroxo radicals and peroxides exist as constituents of hydrogen-bonded complexes. The formation of a complex with one water molecule causes the enthalpy to decrease by 44.3, 30.3, 14.9, and 31.6 kJ mol^{-1} for HOO$^{\bullet}$, HOOH, MeOO$^{\bullet}$, and MeOOH, respectively. The energy barriers obtained considering these species as reactants and products differ by 20—50 kJ mol^{-1} from the values calculated relative to the pre-reaction complexes. The enthalpies of reactions calculated theoretically are close to the thermochemical values given in parentheses. Most theoretically obtained activation energies are close to those determined using the MIP method.

The enthalpies of H atom abstraction with fragmentation of peroxides. The enthalpies of H atom abstraction from the α-C—H bond of some hydroperoxides, dialkyl

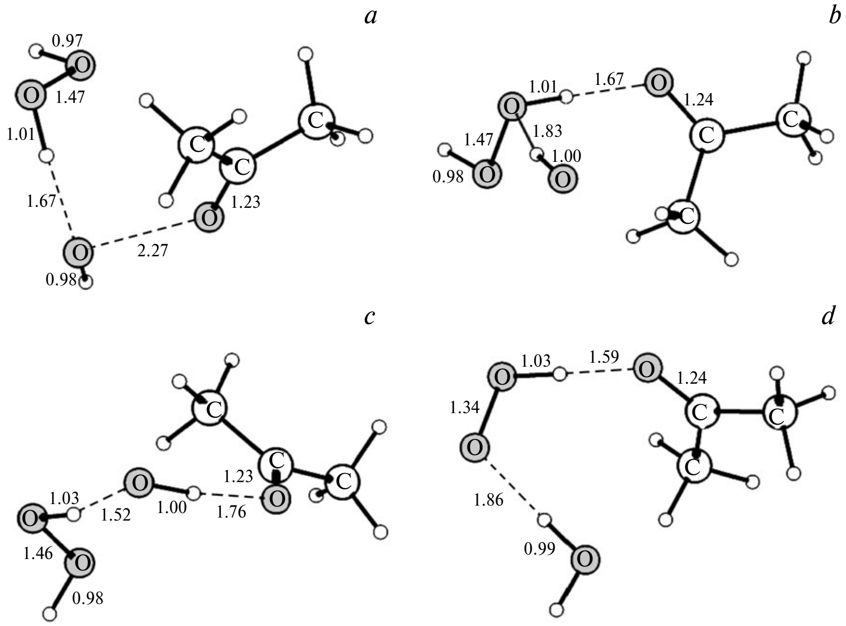


Fig. 3. Structures of intermediates of the reaction of HOO$^{\bullet}$ radical with HC(OOH)Me$_2$ molecule with different orientations of HO$^{\bullet}$ radical (*a*—*c*) and the end product, a complex of the HOO$^{\bullet}$ radical with water and acetone molecules (*d*).

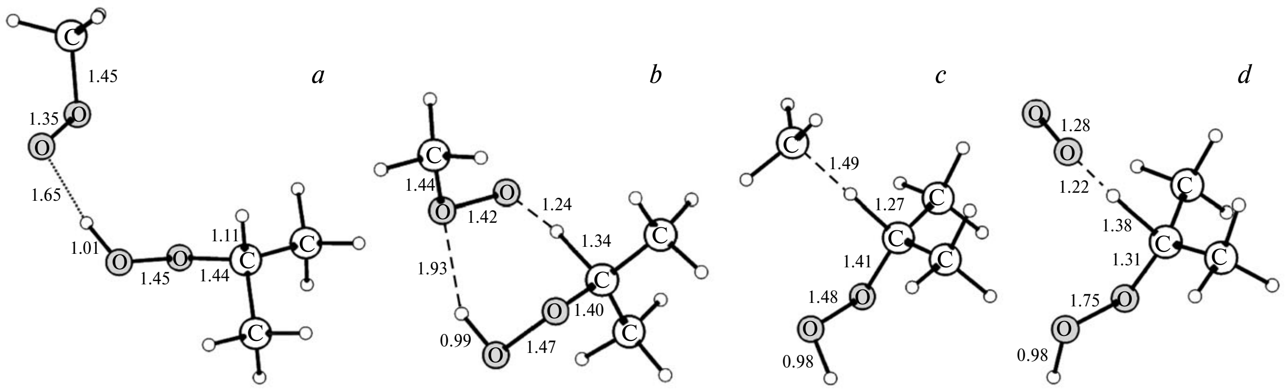


Fig. 4. Structure of pre-reaction complex in the reaction of MeOO$^{\bullet}$ radical with HC(OOH)Me$_2$ molecule (*a*); transition-state geometries for the reactions of MeOO$^{\bullet}$ radical (*b*), Me$^{\bullet}$ radical (*c*) and triplet O$_2$ molecule (*d*) with HC(OOH)Me$_2$ molecule.

peroxides, and peresters calculated using Eqs (4)—(6) with allowance for the enthalpies of formation of corresponding alcohols and carbonyl compounds are listed in Table 5.

These enthalpies are much lower than the dissociation energies of α-C—H bonds in aliphatic alcohols ($D_{C—H}$ = = 400 kJ mol^{-1}).[14] It can be therefore inferred that radical reactions of H atom abstraction from the α-C—H bond of peroxides with their fragmentation are highly exothermic. For instance, the enthalpy of abstraction of an H atom of the *sec*-RO$_2^{\bullet}$ group from the α-C—H bond in alcohol molecule is 400 – 365.5 = 34.5 kJ mol^{-1} and the enthalpy of H atom abstraction from the α-C—H bond in 2-propylhydroperoxide with fragmentation is ΔH = 239.3 – 365.5 = = –126.2 kJ mol^{-1}. On going from hydroperoxide to a structurally similar peroxide and perester the energy $D_{C—H}$ of abstraction with fragmentation decreases following a decrease in the O—O bond dissociation energy.

Reactions of peroxyl radicals with hydroperoxides. Since hydroperoxides are intermediates of the oxidation of hydrocarbons, their further transformations are of importance. Probing the oxidation of cyclohexane by introducing an inhibitor in the course of the reaction showed that hydroperoxide is transformed to ketone following a chain mechanism of the reaction[6,9]

$$R^1O_2^{\bullet} + H—C(OOH)R^2R^3 \longrightarrow R^1OOH + R^2R^3C=O + HO^{\bullet}.$$

Using the energies $D_{C—H}$ of H atom abstraction from the C—H(OOH) bond with dissociation of the O—O bond

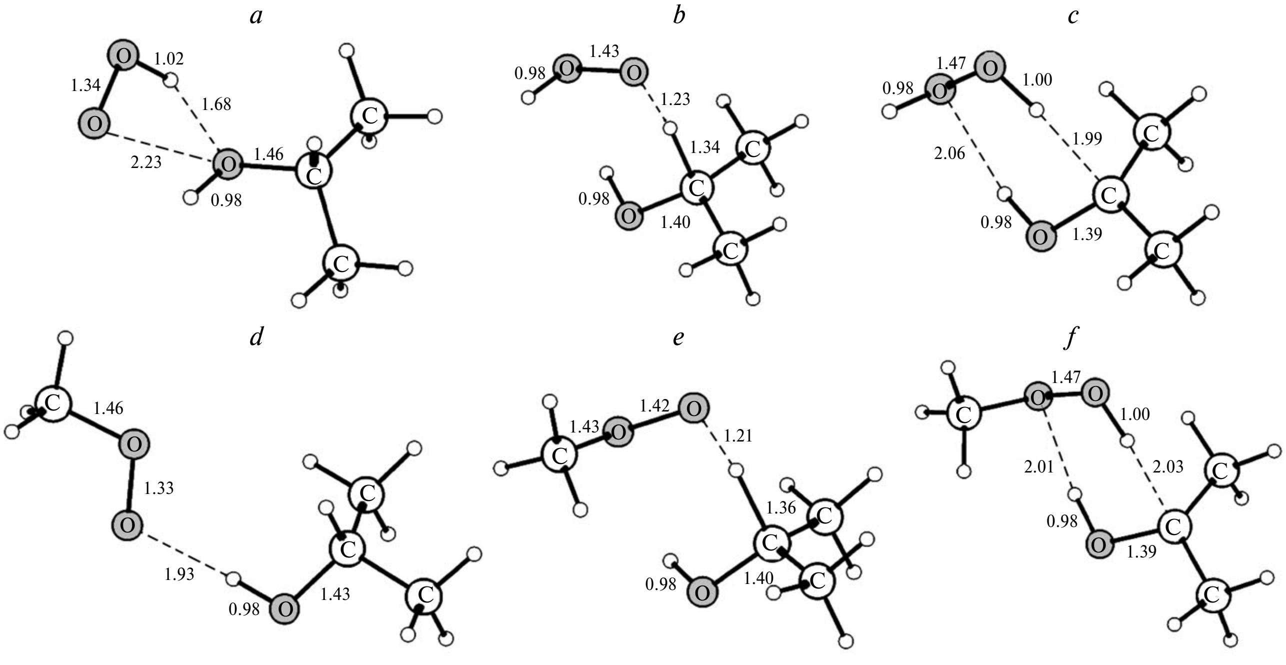


Fig. 5. Results of quantum chemical calculations of the reactions of HC(OH)Me$_2$ molecule with HOO$^{\bullet}$ (*a*—*c*) and MeOO$^{\bullet}$ (*d*—*f*) radicals: the structures of the pre-reaction complexes (*a*, *d*), transition states (*b*, *e*), and post-reaction complexes (*c*, *f*).

Table 5. Energies of concerted abstraction of H atom and dissociation energies of O—O bond in hydroperoxides, dialkyl peroxides, and peresters calculated from Eqs (4)—(6), and the enthalpies of formation alcohols and carbonyl compounds[17]

R^1R^2CHOOX	$-\Delta H(R^1R^2CO)$	$-\Delta H(R^1R^2CHOH)$	D_{C-H}/kJ mol^{-1}		
	kJ mol^{-1}		X = H	X = R	X = C(O)R
H_2C—HOOX	108.8	201.7	276.9	258.9	246.4
MeCH—HOOX	165.7	234.7	253.0	235.0	222.5
EtCH—HOOX	187.4	254.8	251.4	233.4	220.9
PrCH—HOOX	207.5	274.9	251.4	233.4	220.9
Me_2C—HOOX	217.1	272.4	239.3	221.3	208.8
MeEtC—HOOX	240.6	295.8	239.2	221.2	208.7
cyclo-[$(CH_2)_4$C—HOOX]	192.5	242.7	234.2	216.2	203.7
cyclo-[$(CH_2)_5$C—HOOX]	225.9	290.0	248.1	230.1	217.6
cyclo-[$(CH_2)_6$C—HOOX]	247.3	307.3	244.0	226.0	213.5
PhCH—HOOX	37.7	100.4	246.7	228.7	216.2
PhMeC—HOOX	86.6	138.1	235.5	217.5	205.0
Ph_2C—HOOX	−50.2	−4.4	229.8	211.8	192.3
H_2C=CHCH—HOOX	75.3	125.5	244.2	226.2	213.7
H_2C=CHCMe—HOOX	138.1	159.8	205.7	187.7	175.2
MeCH=CHCMe—HOOX	175.7	189.1	197.4	179.4	166.9

(see Table 5), one can calculate the enthalpy and activation energy of the reaction of $RO_2^{\cdot}$ with the C—H bond of hydroperoxide. This was done by the MIP method using the D_{C-H} values from Table 5, Eqs (4) and (9), and the MIP parameters for this class of liquid-phase reactions (see Table 3). The results of calculations are presented in Table 6.

As can be seen, all the reactions of interest are highly exothermic (ΔH varies from −168 to −89 kJ mol^{-1}). However, in spite of their high exothermicities, the activation energies are rather high and vary in the range from 38 to 50 kJ mol^{-1}. It is appropriate to compare the rate constants for the reactions of peroxyl radicals with hydroperoxides and with the initial hydrocarbons. This is done in Table 7; the E and k values for the reactions $RO_2^{\cdot}$ + RH were determined using the MIP method (for the D_{C-H} values for hydrocarbons, see Ref. 14; for the MIP parameters, see Ref. 10).

From the data of Table 7 it follows that reactions of *sec*-$RO_2^{\cdot}$ with paraffin hydrocarbons are endothermic with the activation energies 21—28 kJ mol^{-1} higher than those of the reactions of H atom abstraction from ROOH (see Table 6). In addition, the reactivities of C—H bonds in the α-hydroperoxide fragments are two—three orders of magnitude higher than those of the C—H bonds in the corresponding hydrocarbons. Therefore, the rates of the reactions $RO_2^{\cdot}$ + RH and $R^1O_2^{\cdot}$ + R^2R^3CHOOH become comparable at a hydroperoxide concentration of 0.02—0.4 mol L^{-1}. Since the oxidation of paraffins and polymers proceeds as a combination of bimolecular abstraction of H atom by the $RO_2^{\cdot}$ radical and its isomerization of the type

$$RCH(OO^{\cdot})CH_2CH_2R \longrightarrow RCH(OOH)CH_2C^{\cdot}HR,$$

dissociative abstraction should also occur in the intramolecular oxidation reactions as a sequence of reactions

$$RCH(OOH)CH_2C^{\cdot}HR + O_2 \longrightarrow$$
$$\longrightarrow RCH(OOH)CH_2CH(OO^{\cdot})R,$$

$$RCH(OOH)CH_2CH(OO^{\cdot})R \longrightarrow$$
$$\longrightarrow RC(O)CH_2CH(OOH)R + HO^{\cdot}.$$

This pattern of the chain oxidation reaction leads to concurrent formation of hydroperoxyl and carbonyl groups

Table 6. Enthalpies, activation energies, and rate constants for *sec*-$R^1O_2^{\cdot}$ + R^2R^3CHOOH → *sec*-R^1OOH + R^2R^3C(O) + $HO^{\cdot}$ reactions calculated by the MIP method (see Eqs (4), (7), (9) and (13))

R^2R^3CHOOH	$-\Delta H$	E	$A \cdot 10^{-7}$	k (350 K)
	kJ mol^{-1}		L mol^{-1} s^{-1}	
H_2CHOOH	88.6	50.1	5.76	1.92
$MeCH_2OOH$	112.5	42.2	4.20	21.4
$EtCH_2OOH$	114.1	41.6	4.22	25.6
$PrCH_2OOH$	114.1	41.6	4.22	25.6
Me_2CHOOH	126.2	37.9	2.21	49.2
MeEtCHOOH	126.3	37.8	2.21	49.7
cyclo-[$(CH_2)_4$CHOOH]	131.3	36.3	2.26	85.4
cyclo-[$(CH_2)_5$CHOOH]	117.4	40.6	2.14	18.6
cyclo-[$(CH_2)_6$CHOOH]	121.5	39.3	2.17	29.3
$PhCH_2OOH$	118.8	45.8	2.02	5.96
PhMeCHOOH	130.0	42.2	2.10	10.4
Ph_2CHOOH	135.7	40.5	2.14	19.4
H_2C=$CHCH_2OOH$	121.3	52.2	3.37	0.60
H_2C=CHCHMeOOH	159.8	40.3	2.14	20.4
MeCH=CHCHMeOOH	168.1	38.0	2.21	47.8

Table 7. Enthalpies, activation energies, and rate constants for $RO_2^{\cdot}$ + RH reactions calculated by the MIP method (see Eqs (4), (7), (9) and (13))

RH	ΔH	E	k(R—H) (350 K)	k(ROOH) (350 K)
	kJ mol^{-1}		L mol^{-1} s^{-1}	
CH_4	74.5	78.0	$9.14 \cdot 10^{-4}$	1.92
RCH_3	52.7	67.2	$2.81 \cdot 10^{-2}$	21.4
R_2CH_2	46.5	61.6	0.13	49.2

from peroxyl radicals. Intramolecular isomerization of $RO_2^{\cdot}$ involving C—H bonds in α-hydroperoxide fragments plays an important role in the antimalarial action of artemisinine and its derivatives.[4,5]

The inhibition of the oxidation of hydroperoxide-containing RH with phenolic antioxidants can be accompanied by an abstraction reaction with fragmentation involving the phenoxyl radical entering the reaction:

$$ArO^{\cdot} + R^1R^2CHOOH \longrightarrow ArOH + R^1R^2C{=}O + HO^{\cdot}.$$

For instance, the MIP method (see Table 3, Eqs (4) and (9)) gives the following kinetic parameters for the reaction of $PhO^{\cdot}$ with Me_2CHOOH: $\Delta H = 239.3 - 369.0 = -129.7$ kJ mol^{-1}, $E = 52.9$ kJ mol^{-1}, and $k = 12.7$ L mol^{-1} s^{-1} (350 K).

Reactions of peroxyl radicals with dialkyl peroxides. Peroxides are used as initiators of chain polymerization and oxidation reactions; they decompose into radicals following the reaction

$$R^1R^2CHOOCHR^1R^2 \xrightarrow{k_i} 2R^1R^2CHO^{\cdot}.$$

If these compounds initiate a chain oxidation of a hydrocarbon RH, they can undergo a chain decomposition under the action of peroxyl radicals:

$$R^1O_2^{\cdot} + R^2R^3CHOOCHR^2R^3 \xrightarrow{k}$$

$$\longrightarrow R^1OOH + R^2R^3C(O) + R^2R^3CHO^{\cdot}.$$

Table 8 lists the enthalpies of such reactions (calculated for sec-$RO_2^{\cdot}$ with D_{O-H} = 365.5 kJ mol^{-1} using Eq. (5)), the activation energies (calculated from Eq. (9)), and the rate constants for the reactions (calculated from Eq. (13)).

The data of Table 8 show that these reactions are highly exothermic (ΔH = –(106—186) kJ mol^{-1}) and require activation energies E in the range 31—46 kJ mol^{-1} to proceed. The corresponding rate constants vary from 0.9 to 1400 L mol^{-1} s^{-1} at 350 K.

As described above, the reaction of dissociative abstraction of H atom from ROOR creates prerequisites for chain decomposition of peroxide to proceed; here, the role of the medium is played by the hydrocarbon being oxidized. The chain character of this reaction depends on the competition between the dissociative abstraction of H atom and the initiation reaction. We will consider it taking the decomposition of diisopropyl peroxide as an example. Assuming a chain decomposition of this compound, the chain length is

Table 8. Enthalpies, activation energies and rate constants for sec-$R^1O_2^{\cdot} + R^2R^3CHOOCHR^2R^3 \rightarrow sec$-$R^1OOH + R^2R^3C(O) + R^2R^3CHO^{\cdot}$ reactions calculated by the MIP method (see Eqs (5), (7), (9) and (13))

$(R^2R^3CHO)_2$	$-\Delta H$	E	$A \cdot 10^{-8}$	k (350 K)
	kJ mol^{-1}		L mol^{-1} s^{-1}	
$(H_2CHO)_2$	106.6	44.1	1.26	$3.34 \cdot 10$
$(MeCH_2O)_2$	130.5	36.6	1.01	$3.41 \cdot 10^2$
$(EtCH_2O)_2$	132.1	36.1	1.03	$4.22 \cdot 10^2$
$(PrCH_2O)_2$	132.1	36.1	1.03	$4.22 \cdot 10^2$
$(Me_2CHO)_2$	144.2	32.5	0.57	$8.05 \cdot 10^2$
$(MeEtCHO)_2$	144.2	32.5	0.57	$8.05 \cdot 10^2$
$cyclo$-$[(CH_2)_4CHO]_2$	149.3	31.1	0.60	$1.37 \cdot 10^3$
$cyclo$-$[(CH_2)_5CHO]_2$	135.4	35.1	0.53	$3.06 \cdot 10^2$
$cyclo$-$[(CH_2)_6CHO]_2$	139.5	33.9	0.54	$4.71 \cdot 10^2$
$(PhCH_2O)_2$	136.8	40.1	$9.24 \cdot 10^{-2}$	9.57
$(PhMeCHO)_2$	148.0	36.8	$5.04 \cdot 10^{-2}$	$1.62 \cdot 10$
$(Ph_2CHO)_2$	153.7	35.2	$5.26 \cdot 10^{-2}$	$2.94 \cdot 10$
$(H_2C{=}CHCH_2O)_2$	139.3	46.5	$7.96 \cdot 10^{-2}$	$9.15 \cdot 10^{-1}$
$(H_2C{=}CHCHMeO)_2$	177.8	35.2	$5.26 \cdot 10^{-2}$	$2.94 \cdot 10$
$(MeCH{=}CHCHMeO)_2$	186.1	33.0	$5.62 \cdot 10^{-2}$	$6.68 \cdot 10^5$

$$\nu = \frac{k[R^2R^3CHOOCHR^2R^3][R^1O_2^{\cdot}]}{k_i[R^2R^3CHOOCHR^2R^3]} =$$

$$= \frac{k[R^2R^3CHOOCHR^2R^3]^{0.5}}{\sqrt{2k_tk_i}}, \qquad (17)$$

where k is the rate constant for H atom abstraction by peroxyl radical from the peroxide with its fragmentation, k_i is the rate constant for initiation by peroxide, and $2k_t$ is the rate constant for disproportionation of peroxyl radicals of the hydrocarbon being oxidized. Now we will give an estimate for the case of chain consumption of isopropyl peroxide in cyclohexane being oxidized at T = 400 K. For this system, one has $k_i = 2.5 \cdot 10^{16}\exp[-162/(RT)] = 1.75 \cdot 10^{-5}$ s^{-1},[18] $2k_t = 2 \cdot 10^7\exp[-5.4/(RT)] = 3.94 \cdot 10^6$ L mol^{-1} s^{-1},[16] and $k = 4.9 \cdot 10^7\exp[-32.5/(RT)] = 2.79 \cdot 10^3$ L mol^{-1} s^{-1} (see Table 8). Substituting these values into Eq. (17), for the chain length of induced decomposition of peroxide at 400 K and at a peroxide concentration of 0.01 mol L^{-1}, one gets ν = 34. As temperature increases, the chain length decreases. Transformation of Eq. (17) taking into account the temperature dependence of the rate constants k, k_i, and k_t gives the following equation for ν (at $[Me_2CHOOCHMe_2]$ = 0.01 mol L^{-1}):

$$\ln\nu = -11.88 + 51200/(RT). \qquad (18)$$

It follows that chain decomposition of peroxide ceases at $T > 518$ K.

Induced decomposition of peroxides in radical polymerization. Peroxides are widely used as initiators of radical polymerization.[21] In the peroxide—monomer systems, induced decomposition of peroxides can proceed as reaction of dissociative abstraction of H atom by macroradicals. The following reactions occur[2] in the M—peroxide system:

$$\mathrm{R^1R^2CHOOCHR^1R^2} \xrightarrow{k_i} \mathrm{2\,R^1R^2CHO^{\bullet}},$$

$$\mathrm{{\sim}M^{\bullet} + M} \xrightarrow{k_p} \mathrm{{\sim}M^{\bullet}},$$

$$\mathrm{{\sim}M^{\bullet} + R^1R^2CHOOCHR^1R^2} \xrightarrow{k}$$

$$\longrightarrow \mathrm{{\sim}MH + R^1R^2C(O) + R^1R^2CHO^{\bullet}},$$

$$\mathrm{{\sim}M^{\bullet} + {\sim}M^{\bullet}} \xrightarrow{k_p} \mathrm{Pol},$$

where Pol is a polymer.

The rate of induced decomposition of peroxide in the quasi-stationary polymerization regime is

$$v = k[\mathrm{R^1R^2CHOOCHR^1R^2}][{\sim}\mathrm{M}^{\bullet}] =$$

$$= kk_i^{-0.5}(2k_t)^{-0.5}[\mathrm{R^1R^2CHOOCHR^1R^2}]^{3/2}. \qquad (19)$$

Induced decomposition, first, reduces the efficiency of initiation because a fraction of the initiator is consumed in the reaction with macroradicals, and, second, the length of macromolecules decreases as a result of chain transfer in the reaction of macroradical with the peroxide.

Table 9 lists the enthalpies, activation energies, and rate constants for the reactions of the macroradical of methacrylate being polymerized ($\mathrm{{\sim}CH_2C^{\bullet}COOMe}$) with a number of peresters and peroxides. Calculations were carried out by the MIP method using Eqs (5), (7), (10), and (13), the kinetic parameters listed in Table 3, and $D_{\mathrm{C-H}}(\mathrm{{\sim}CH_2C{-}HC(O)OMe}) = 399$ kJ mol^{-1} (see Ref. 14). As can be seen, for the reactions of macroradicals with dialkyl peroxides we have $\Delta H = -(220-140)$ kJ mol^{-1}, $E = 30-45$ kJ mol^{-1}, and $k = 19-7.6 \cdot 10^3$ L mol^{-1} s^{-1}.

Table 9. Enthalpies, activation energies, and rate constants for $\mathrm{{\sim}CH_2C^{\bullet}COOMe + R^1R^2CHOOCHR^1R^2 \rightarrow {\sim}CH_2CHCOOMe + R^1R^2C(O) + R^1R^2CHO^{\bullet}}$ reactions calculated by the MIP method (see Eqs (5), (7), (10) and (13))

$\mathrm{(R^1R^2CHO)_2}$	$-\Delta H$	E	$A \cdot 10^{-8}$	k (350 K)
	kJ mol^{-1}		L mol^{-1} s^{-1}	
$\mathrm{(H_2CHO)_2}$	140.1	45.1	12.1	$2.11 \cdot 10^2$
$\mathrm{(MeCH_2HO)_2}$	164.0	36.9	8.96	$2.79 \cdot 10^3$
$\mathrm{(EtCH_2O)_2}$	165.6	36.4	9.02	$3.37 \cdot 10^3$
$\mathrm{(PrCH_2O)_2}$	165.6	36.4	9.02	$3.37 \cdot 10^3$
$\mathrm{(Me_2CHO)_2}$	178.7	32.1	4.80	$7.65 \cdot 10^3$
$\mathrm{(MeEtCHO)_2}$	177.8	32.4	4.80	$6.91 \cdot 10^3$
cyclo-$\mathrm{[(CH_2)_4CHO]_2}$	182.8	30.9	4.90	$1.21 \cdot 10^4$
cyclo-$\mathrm{[(CH_2)_5CHO]_2}$	168.9	35.3	4.58	$2.48 \cdot 10^3$
cyclo-$\mathrm{[(CH_2)_6CHO]_2}$	173.0	34.0	4.67	$3.99 \cdot 10^3$
$\mathrm{(PhCH_2O)_2}$	170.3	38.8	$8.73 \cdot 10^{-1}$	$1.39 \cdot 10^2$
$\mathrm{(PhMeCHO)_2}$	181.5	35.2	$4.58 \cdot 10^{-1}$	$2.56 \cdot 10^2$
$\mathrm{(Ph_2CHO)_2}$	187.2	33.4	$4.71 \cdot 10^{-1}$	$4.88 \cdot 10^2$
$\mathrm{(H_2C{=}CHCH_2O)_2}$	172.8	44.5	$8.16 \cdot 10^{-1}$	$1.88 \cdot 10$
$\mathrm{(H_2C{=}CHCHMeO)_2}$	211.3	32.2	$4.79 \cdot 10^{-1}$	$7.54 \cdot 10^2$
$\mathrm{(MeCH{=}CHCHMeO)_2}$	219.6	29.7	$4.99 \cdot 10^{-1}$	$1.83 \cdot 10^3$

Consider the competition between decomposition and dissociative decomposition of peroxide taking methacrylate polymerization initiated by diisopropyl peroxide as an example. In this system at $T = 350$ K, the rate constants for the reactions mentioned above are as follows: $k_i = 2.5 \cdot 10^{16}\exp[-162/(RT)] = 1.66 \cdot 10^{-8}$ s^{-1},[18] $k_p = 1.1 \cdot 10^6\exp[-17.6/(RT)] = 2.60 \cdot 10^3$ L mol^{-1} s^{-1},[21] $k = 4.80 \cdot 10^8\exp[-32.1/(RT)] = 7.65 \cdot 10^3$ L mol^{-1} s^{-1}, $2k_t = 9.5 \cdot 10^6$ L mol^{-1} s^{-1},[21] $[\mathrm{M}] = 11.0$ mol L^{-1}. The chain length for induced decomposition peroxide is great

$$\nu = \frac{k[\mathrm{R^2R^1CHOOCHR^2R^1}][\mathrm{M}^{\bullet}]}{k_i[\mathrm{R^2R^1CHOOCHR^2R^1}]} =$$

$$= \frac{k[\mathrm{R^2R^1CHOOCHR^1R^2}]^{0.5}}{\sqrt{2k_t k_i}} =$$

$$= 1.93 \cdot 10^4[\mathrm{R^2R^1CHOOCHR^1R^2}]^{0.5}. \qquad (20)$$

However, the degree of polymerization of the monomer P_n remains rather high, *viz.*, $P_n = k_p[\mathrm{M}]/k[\mathrm{R^1R^2CHOOCHR^1R^2}] = 476$ at a peroxide concentration of 0.01 mol L^{-1}. In the solution of a hydrocarbon, *e.g.*, heptane, the chain length of induced decomposition is much smaller due to high radical recombination rate ($2k_t \approx 4.9 \cdot 10^9$ L mol^{-1} s^{-1}),[18] namely, $\nu = 940[\mathrm{R^1R^2CHOOCHR^1R^2}]^{0.5} = 94$ at a peroxide concentration of 0.01 mol L^{-1}. As temperature increases, the ν parameter decreases, as in the case of oxidation (see above).

Analogous calculations were carried out for peresters as initiators of methacrylate polymerization (Table 10). They react with polymer macroradicals even faster, namely, $E = 26-41$ kJ mol^{-1}, $k = 82-4.8 \cdot 10^4$ L mol^{-1} s^{-1}.

Summing up, our density functional calculations provided evidence for the occurrence of hydrogen abstraction reactions with fragmentation taking reactions of various radicals with the α-C—H bond in peroxides $\mathrm{R^2R^3CHOOX}$ ($\mathrm{X = H, R^1, R^1C(O)}$) as examples. Abstraction of H atom, accompanied by concerted dissociation of the weak O—O bond and formation of the π-bond carbonyl group, determines the exothermicity of the reaction. The energies of dissociation of α-C—H bonds accompanied by dissociation of the O—O bond were calculated for some hydroperoxides, dialkyl peroxides, and peresters. Based on experimental data, we calculated the kinetic parameters of the reaction of cyclohexylperoxyl radical with cyclohexyl hydroperoxide. These parameters serve to calculate the activation energies and rate constants for reactions of $\mathrm{R}^{\bullet}$,

Table 10. Enthalpies, activation energies and rate constants for $\sim CH_2C^{\bullet}COOMe + R^1R^2CHOOC(O)Me \rightarrow$ $\rightarrow \sim CH_2CHCOOMe + R^1R^2C(O) + MeCO_2^{\bullet}$ reactions calculated by the MIP method (see Eqs (6), (7), (10) and (13))

$R^1R^2CHOOC(O)Me$	$-\Delta H$	E	$A \cdot 10^{-8}$	k (350 K)
	kJ mol^{-1}		L mol^{-1} s^{-1}	
$H_2CHOOC(O)Me$	152.6	40.9	$1.28 \cdot 10$	$1.01 \cdot 10^3$
$MeCH_2HOOC(O)Me$	176.5	32.8	9.49	$1.19 \cdot 10^4$
$EtCH_2OOC(O)Me$	178.1	32.3	9.57	$1.43 \cdot 10^4$
$PrCH_2OOC(O)Me$	178.1	32.3	9.57	$1.43 \cdot 10^4$
$Me_2CHOOC(O)Me$	190.2	28.6	5.09	$2.76 \cdot 10^4$
$MeEtCHOOC(O)Me$	190.3	28.5	5.09	$2.79 \cdot 10^4$
cyclo-$[(CH_2)_4CHOOC(O)Me]$	195.3	27.0	5.23	$4.80 \cdot 10^4$
cyclo-$[(CH_2)_5CHOOC(O)Me]$	181.4	31.3	4.86	$1.04 \cdot 10^4$
cyclo-$[(CH_2)_6CHOOC(O)Me]$	185.5	30.0	4.96	$1.64 \cdot 10^4$
$PhCH_2OOC(O)Me$	182.8	34.8	$9.22 \cdot 10^{-1}$	$5.93 \cdot 10^2$
$PhMeCHOOC(O)Me$	194.0	31.3	$4.86 \cdot 10^{-1}$	$1.04 \cdot 10^3$
$Ph_2CHOOC(O)Me$	199.7	29.5	$5.00 \cdot 10^{-1}$	$1.94 \cdot 10^3$
$H_2C=CHCH_2OOC(O)Me$	185.3	40.3	$8.57 \cdot 10^{-1}$	$8.19 \cdot 10$
$H_2C=CHCHMeOOC(O)Me$	223.8	28.5	$5.10 \cdot 10^{-1}$	$2.85 \cdot 10^3$
$MeCH=CHCHMeOOC(O)Me$	232.1	26.1	$5.32 \cdot 10^{-1}$	$6.72 \cdot 10^3$

$RO^{\bullet}$, and $RO_2^{\bullet}$ with the α-C—H bond of peroxides of different structure within the framework of the MIP model. The possibility of chain consumption of peroxides to occur in the course of liquid-phase oxidation of hydrocarbons and radical polymerization of monomers was analyzed and it was shown that secondary peroxides are rapidly consumed in chain manner.

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