Physical Chemistry

Conformational analysis of hydrogen polyoxides

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The semiempirical AM1 method was used for the calculation of conformational potential energy surfaces of hydrogen trioxide and tetraoxide. The most stable conformation of trioxide is its *anti*-form, which is characterized by the torsion angle φ = 82.3°, and that of tetraoxide is the *anti,anti*-form with φ = 80.7° (H—O—O—O) and 74.1° (O—O—O—O). The structures of the stable conformers are determined by the interaction between lone electron pairs of oxygen atoms. The dipole-dipole interaction of OH groups is weaker than that in hydrogen peroxide. The results were used for the estimation of the polyoxide increment of the Benson's additivity scheme, $\Delta_f H°[O-(O)_2] = 48\pm6$ kJ mol^{-1}.

Key words: conformational analysis, polyoxides, quantum-chemical calculations, thermochemistry.

Presently, extensive experimental material on synthesis and chemical transformations of organic polyoxides X—O_n—Y is available. The chemistry of peroxides (n = 2) is studied in detail.[1] Several compounds with the trioxide fragment were obtained: hydrotrioxides ROOOH,[2–6] dialkyl and diaryl trioxides ROOOR,[7–9] and primary ozonides (1,2,3-trioxolanes).[10,11] Tetraoxides (n = 4) are intermediate compounds in the recombination of peroxyl radicals.[12–14]

As a rule, compounds with three and four consecutively linked oxygen atoms are thermally stable only in the region of low temperatures (T < −80 °C). Therefore, the experimental determination of their thermochemical parameters is difficult. The enthalpies of the formation of polyoxides are usually calculated in terms of the additive-group method of Benson.[15] The key parameter for the calculations of these values is the polyoxide increment $\Delta_f H°[O-(O)_2]$, for the calculation of which the following equation was used[16]:

$$\Delta_f H°[O-(O)_2] = (\Delta_f H°[RO_nR] - \Delta_f H°[ROOR])/(n-2). \quad (1)$$

An equation similar to Eq. (1) has been used previously[17] for the analysis of thermodynamic properties in the series H_2O_2 — H_2O_3 — H_2O_4. However, in our opinion, Eq. (1) is inappropriate for thermochemical calculations. The form of the equation assumes that the change in different types of interactions (dipole, hyperconjugation, *etc.*) in polyoxides is proportional to the number n. Perhaps, this rough assumption became one

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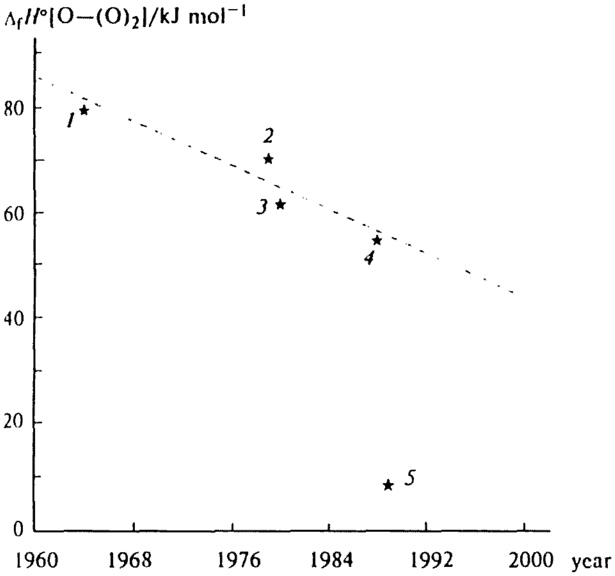


Fig. 1. Values of the increment $\Delta_f H°[O-(O)_2]$ by the data of different authors: *1*, Ref. 18; *2*, Ref. 19; *3*, Ref. 20; *4*, Ref. 16; *5*, Ref. 21.

of the reasons for the periodical revision of the value of the $\Delta_f H°[O-(O)_2]$ increment[16,18-21] (Fig. 1). In this work, the comparative conformational analysis of HOOH, HOOOH, and HOOOOH molecules was performed by the AM1 method[22] to elucidate the nature of intramolecular interactions in polyoxides.

Calculation procedures

Equilibrium structures of polyoxides were calculated with the complete optimization of the geometry by the semiempirical MNDO, AM1, and PM3 methods.[22-24] The main peculiarities of the spatial structure of polyoxides are the zigzag-like oxygen skeleton of a molecule and the torsion angle φ. The latter served as the main criterion for the choice of the calculation method to perform the detailed conformational analysis. The torsion angle φ in hydroperoxide HOOH, according to the data of several authors,[25-27] is in the range of 111 to 120°, which corresponds satisfactorily to φ = 127.9° determined by the AM1 method. The value φ = 171.5° and an almost null conformational *trans*-barrier were obtained by the MNDO method.[28] The use of the PM3 approximation results in the planar conformation of the HOOH molecule with the transoid arrangement of the H atoms.

Since there are no experimental data on the structure of molecules of higher polyoxides, the calculation method was chosen by the comparison of geometric parameters (first of all, angle φ) with the values with various basis sets obtained *ab initio*. The geometric parameters of the equilibrium structures of tri- and tetraoxides are presented in Table 1. In the case of the AM1 method, the values φ(H—O—O—O) = 82.3° (HOOOH) and 80.8° (MeOOOH) agree well with the results of the *ab initio* calculations in more complex bases, φ = 78.1—83.0° (HOOOH)[31,32] and 82.4—82.6° (MeOOOH).[33] The torsion angle φ(O—O—O—C) calculated by both the nonempirical and semiempirical methods is 3 to 5 degrees higher than φ(H—O—O—O). A similar tendency is observed for the φ angle of peroxides HOOH, MeOOH, and $MeOOCH_3$,[33,34] which is explained by the repulsion between electrons of the methyl group and lone electron pairs (LEP) of the oxygen atom.

The values of the torsion angles in higher polyoxides calculated by the MNDO method, φ(H—O—O—O) = 91—95°, agree with the results of the nonempirical calculations in the simplest bases.[29-31] As in the case of peroxides, the PM3 method gives the worst results. The comparison of the results of the quantum-chemical calculations of tri- and tetraoxides by different semiempirical methods results in the conclusion that the best description of the structural peculiarities of polyoxides is provided by the AM1 method, which is used for the further conformational analysis of compounds HOOH, HOOOH, and HOOOOH.

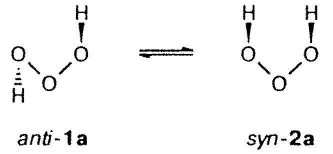
Table 1. Bond lengths (*d*), bond (ω) and torsion (φ) angles of polyoxides $H_1-O_2-O_3-O_4-X$

X	*d*/Å				ω/deg			φ/deg		Method	Reference
	H(1)——O(2)	O(2)——O(3)	O(3)——O(4)	O(4)——X	H(1)——O(2)——O(3)	O(2)——O(3)——O(4)	O(3)——O(4)——X	H(1)—O(2)——O(3)—O(4)	O(2)—O(3)——O(4)—X		
H	0.95	1.44	1.44	0.95	103.6	106.0	103.6	95±5	95±5	4-31G	29
H	*	*	*	*	96.0	*	96.0	94.5	94.5	STO-3G	30
H	1.01	1.40	1.40	1.01	101.3	102.0	101.3	83.0	83.0	STO-4G	31
H	0.97	1.44	1.44	0.97	100.2	106.3	100.2	78.1	78.1	MP2/6-31G*	32
H	0.98	1.29	1.29	0.98	108.9	109.3	108.9	82.3	82.3	AM1	**
OH	*	*	*	*	96.0	*	*	91.0	*	STO-3G	30
OH	*	*	*	*	*	*	*	88.0	*	STO-4G	31
OH	0.99	1.28	1.29	1.29	109.0	110.4	110.4	80.7	74.1	AM1	**
CH_3	1.00	1.39	1.40	1.45	102.4	105.9	106.5	83.5	87.8	STO-3G	33
CH_3	0.96	1.44	1.44	1.44	103.4	106.1	107.7	82.4	85.8	4-31G	33
CH_3	0.96	1.43	1.43	1.44	103.9	106.5	108.1	82.6	86.0	6-31G	33
CH_3	0.98	1.29	1.29	1.44	108.9	109.6	113.4	80.8	85.9	AM1	**
$HOCH_2$	0.98	1.29	1.28	1.45	109.0	109.8	113.5	79.5	84.6	AM1	**

* The parameter was not optimized. ** This work.

Results and Discussion

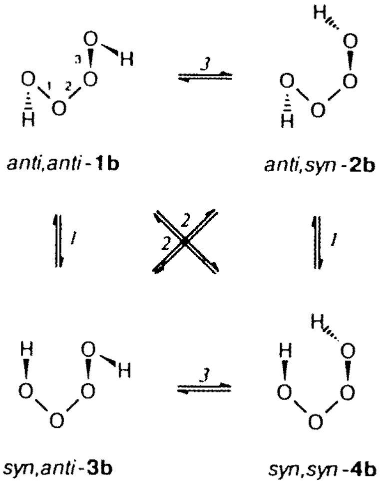
The results of the quantum-chemical semiempirical calculations of stable conformations of polyoxides correspond to those obtained previously[29—33] and are evidence that the *anti*-form of polyoxide is preferable. In the latter, the substituents at the first and third atoms of the oxygen chain are arranged from the different sides of the plane formed by the oxygen atoms. For example, for HOOOH:



ΔH° (kJ mol^{-1}) = 12.6; 12.6 [29]; and 16.8.[35] Previously,[32] using different variants of the *ab initio* method, ΔH° = 14.6—20.1 kJ mol^{-1} was obtained.

Hydrogen tetraoxide has three independent rotation axes (*1—3*), which determine the transitions between the stable conformations according to Scheme 1.

Scheme 1



ΔH° (**1b**→**2b**) = 0.8 kJ mol^{-1}; ΔH° (**1b**→**4b**) = 6.0 kJ mol^{-1}. It is evident that structures **2b** and **3b** are identical.

In order to study the routes of transitions between stable conformations of polyoxides, the conformational potential energy surface (PES) of HOOOH and HOOOOH molecules were studied by the AM1 method at various torsion angles φ_1 and φ_2 determining the position of H atoms relative to the trioxide plane. Despite the fact that the HOOOOH molecule contains one more rotation axis (axis *2*, see Scheme 1), the combination of rotations around axes *1* and *3* gives all stable conformations. The simultaneous change in two torsion angles H—O—O—O in tri- and tetraoxides results in the PES, whose contour profiles are presented in Fig. 2. These surfaces are obtained by the step-by-step calculation of polyoxides with fixed φ_1 and φ_2, and the steps were 20° for HOOOH and 30° for HOOOOH. For plotting PES, its symmetry relative to the planes cross-

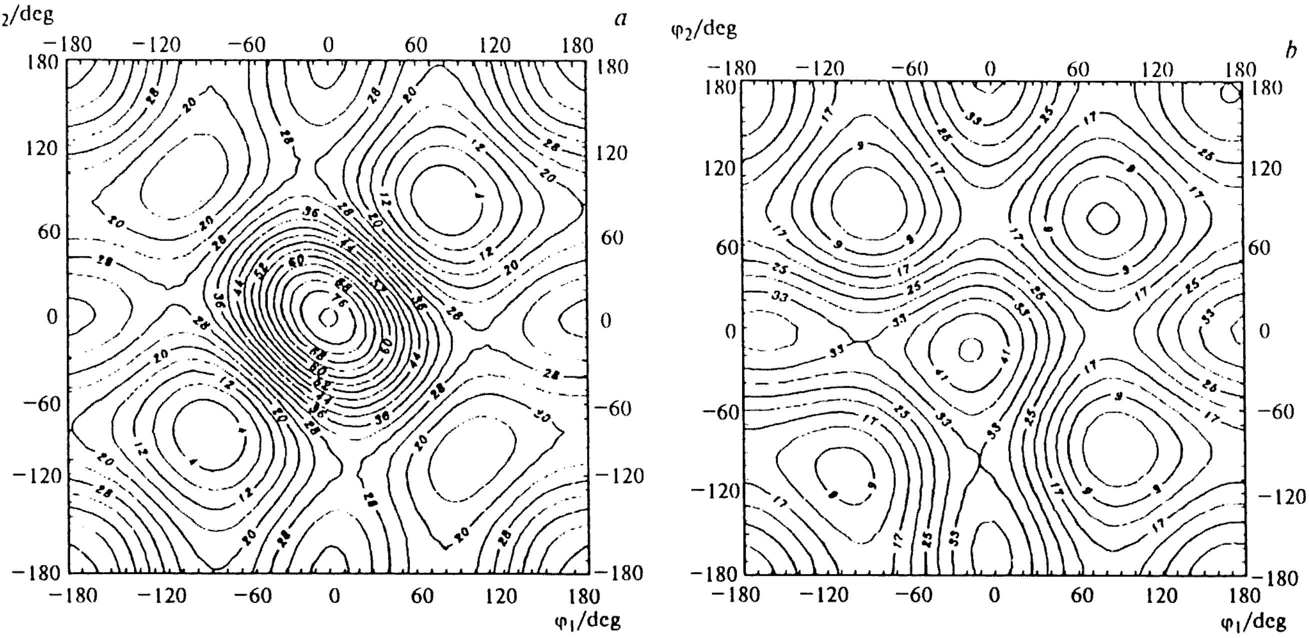


Fig. 2. Contour reliefs of the conformational PES of trioxide (*a*) and tetraoxide (*b*) of hydrogen. Figures in the plot indicate the values of the potential $V(\varphi_1,\varphi_2)$ in kJ mol^{-1}.

Table 2. Coefficients of the Fourier-series expansion (*U*) for conformational PES of hydrogen polyoxides

U /kJ mol^{-1}	HOOOH	HOOOOH
U_{00}	26.86	20.94
U_{10}	4.53	2.33
U_{20}	10.87	8.67
U_{30}	1.47	1.13
U_{11}	12.03	−0.25
U_{21}	2.20	−0.94
U_{31}	0.63	—
U_{22}	2.10	−0.36
U_{32}	0.36	—
U'_{11}	−7.18	2.24
U'_{21}	−3.36	0.81
U'_{31}	−0.60	—
U'_{22}	−1.36	0.30
U'_{32}	−0.31	—
U''_{10}	—	−2.32
U''_{20}	—	−1.76
U''_{30}	—	−0.24
U''_{11}	—	−4.27
U''_{22}	—	0.27

Note. Correlation coefficients $r = 0.9999$ (HOOOH) and 0.9998 (HOOOOH).

ing the lines $\varphi_1 = \varphi_2$ and $\varphi_1 = -\varphi_2$ (HOOOH) and $\varphi_1 = \varphi_2$ (HOOOOH) was taken into account.

The obtained set of the calculated $\Delta_f H^\circ$ values of the molecule at various φ_1 and φ_2 was described by the Fourier series:

$$V(\varphi_1,\varphi_2) = \sum_{i=0}^{3}\sum_{j=0}^{3}\Big\{U_{i,j}\cdot\cos i\varphi_1\cdot\cos j\varphi_2 + U'_{i,j}\cdot\sin i\varphi_1\cdot\sin j\varphi_2 + U''_{i,j}\cdot\left(\cos i\varphi_1\cdot\sin j\varphi_2 + \sin i\varphi_1\cdot\cos j\varphi_2\right)\Big\}, \quad (2)$$

where $V(\varphi_1,\varphi_2) = \Delta_f H^\circ(\varphi_1,\varphi_2) - \Delta_f H^\circ(I)$; $\Delta_f H^\circ(I)$ is the calculated enthalpy of the formation of the most stable conformer; U, U', and U'' are the expansion coefficients.

The evident equalities $U_{i,j} = U_{j,i}$, $U'_{i,j} = U'_{j,i}$, and $U''_{k0} = U''_{0k}$ ($k = i, j = 1, 2, 3$) follow from the PES symmetry $V(\varphi_1,\varphi_2) = V(\varphi_2,\varphi_1)$. The condition $V(\varphi_1,\varphi_2) = V(-\varphi_1,-\varphi_2)$, which is fulfilled for the HOOOH molecule, simplifies the expansion $U''_{i,j} = 0$. Since some coefficients in the expansion are small, they can be neglected without loss of the calculation accuracy: they are U_{33} and U'_{33} for HOOOH* and U_{31}, U'_{31}, U_{32}, U'_{32}, U_{33}, U'_{33}, U''_{12}, U''_{21}, U''_{13}, U''_{31}, U''_{23}, U''_{32}, and U''_{33} for HOOOOH. The values of the expansion coefficients are presented in Table 2.

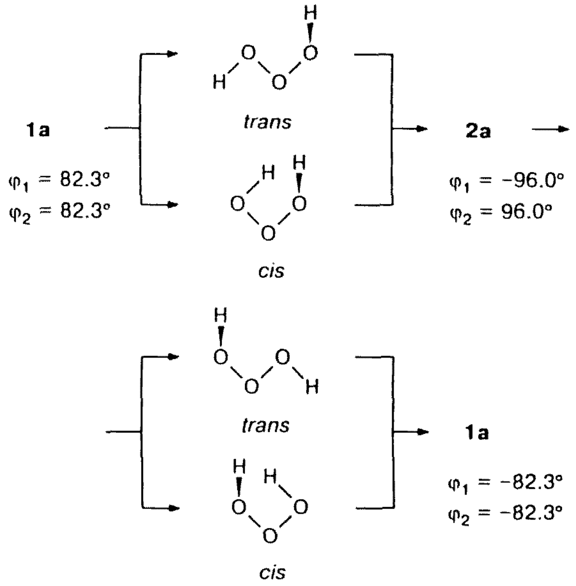
The surfaces $V(\varphi_1,\varphi_2)$ allow one to judge about possible routes of the conformational changes in polyoxide molecules. As follows from Fig. 2, the transition between two most stable conformations of HOOOH ($\varphi_1 = \varphi_2 = 82.3°$ and $\varphi_1 = \varphi_2 = -82.3°$) can occur neither disrotationally nor conrotationally due to the high energy barriers:

$E_{\text{dis}} = 37.4$ (29.3—45.2)* kJ mol^{-1}; $\varphi_1 = 0.0°$; $\varphi_2 = 180.0°$;

$E_{\text{con}} = 46.8$ (35.6—48.1) kJ mol^{-1}; $\varphi_1 = \varphi_2 = 180.0°$.

The two-stage (flip-flop) transition is more probable (Scheme 2).

Scheme 2



The saddle point with the transoid arrangement of atoms is more preferable:

$E_{cis} = 28.3$ (20.5—28.5) kJ mol^{-1}; $\varphi_1 = -13.2°$; $\varphi_2 = 106.1°$;

$E_{trans} = 20.5$ (17.6÷22.6) kJ mol^{-1}; $\varphi_1 = -172.0°$; $\varphi_2 = 78.2°$.

The regularities of the conformational transitions for HOOOOH and HOOOH molecules are similar qualitatively (see Fig. 2, *b*). As in trioxide, the synchronous rotation of OH groups is energetically unfavorable:

$E_{\text{dis}} = 38.7$ kJ mol^{-1}; $\varphi_1 = -2.5°$; $\varphi_2 = -165.9°$;

$E_{\text{con}} = 33.3$ kJ mol^{-1}; $\varphi_1 = \varphi_2 = 170.7°$.

The transition from one stable conformation to another occurs *via* the *trans*-barrier:

for the transition **1b** $\rightleftharpoons$ **2b, 3b**

$E_{cis} = 19.0$ kJ mol^{-1}; $\varphi_1 = -4.3°$; $\varphi_2 = 82.0°$;

$E_{trans} = 18.7$ kJ mol^{-1}; $\varphi_1 = 177.7°$; $\varphi_2 = 82.0°$;

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* Identical transformation of the Fourier-series expansion $V(\varphi_1,\varphi_2)$ for trioxide and further assumptions $U_{31} = U_{32} = U'_{31} = U'_{32} = 0$, $U_{21} = U'_{21}$ result in the formula for PES obtained in the previous work.[32]

* The data[32] obtained by the Hartree—Fock *ab initio* method in the 4-31G and 6-31G* bases or in terms of the Møller—Plesset perturbation theory are presented here and hereinafter in parentheses.

for the transition **2b, 3b** $\rightleftharpoons$ **4b**

E_{cis} = 33.0 kJ mol^{-1}; φ_1 = −10.5°; φ_2 = −95.2°;

E_{trans} = 14.6 kJ mol^{-1}; φ_1 = 178.4°; φ_2 = −91.5°.

The values of the rotation barriers and torsion angles for maxima and saddle points were determined by Eq. (2) and expansion coefficients (see Table 2).

The expansion of the potential V into the components makes it possible to interpret the nature of the rotation barriers.[36] To simplify the analysis, the conformation energies of polyoxides $V(\varphi)$ were calculated in the single rotator approximation by the AM1 method. This approach offers the possibility of using the data on the conformational behavior of HOOH for the comparative analysis. The calculation of $V(\varphi)$ was performed with the increment of 5° by the angle φ(H—O—O—X), X = H for HOOH, and X = O for tri- and tetraoxides. The calculated dependence found was presented as the series:

$$V(\chi) = \sum_{i=1}^{3}\{U_i(1-\cos i\chi)/2 + U'_i \cdot \sin i\chi\}\,, \qquad (3)$$

where $\chi = \varphi - \varphi(I)$, and $\varphi(I)$ is the torsion angle for the most stable conformation of polyoxide.

This form of Eq. (3) is commonly used for the description of single rotators. The asymmetry of the rotation barriers is reflected by the sine functions. U_1 describes the relative effect of the dipole interaction, U_2 — the hyperconjugation effects, and U_3 — the effect of bond vibrations. The expansion coefficients of the unidimensional potential $V(\chi)$ by Eq. (3) are presented in Table 3.

According to these data, the dipole-dipole interaction of OH groups and the interaction of LEP of oxygen atoms exert the maximum effect on the conformational potential of polyoxides, and the first effect predominates in HOOH, while it is lower for hydrogen trioxide and insignificant in the HOOOOH molecule. A decrease in U_1 in this series is associated with an increase in the distance between the OH groups. The energy of the dipole interaction is inversely proportional to the cubic distance between them, which causes a sharp decrease in U_1 on going to HOOOOH. On contrast, the contribution to the conformational energy of the LEP interaction increases compared to that for HOOH and is predominant in higher polyoxides.

Table 3. Coefficients (U) of Eq. (3) for hydrogen polyoxides

U /kJ mol^{-1}	HOOH	HOOOH	HOOOOH
U_1	16.36	12.04	1.14
U_2	3.03	17.61	17.55
U_3	2.11	0.59	0.69
U'_1	−10.51	−3.00	1.03
U'_2	5.98	−0.03	−2.04
U'_3	−0.46	1.17	1.06

Note. Correlation coefficients r = 1.0000, 1.0000, and 0.9999 for HOOH, HOOOH, and HOOOOH, respectively.

The value of U_3 in Eq. (3) exerts an insignificant effect on the V value in all compounds studied. The low value of U_3 justifies the neglecting of the square terms in U_{33} in expansion (2) for hydrogen tri- and tetraoxides. In the latter case, the low values of U_1 and U_3 in the unidimensional expansion are the reason for negligible values of the crossed terms U_{13} and U_{23}.

It is noteworthy that the U_2 values for tri- and tetraoxides almost coincide, which testifies to the resemblance of the conformational behavior of these molecules. The close values of the coefficient U_2 were obtained for hydrotrioxides MeOOOH and HOCH$_2$OOOH. It is seen from Fig. 3 that the φ values corresponding to the absolute minima of the potential curves for higher polyoxides nearly coincide and differ noticeably from the torsion angle in the HOOH molecule.

The conformational analysis of polyoxides shows that the assumption of the linearity of the change in thermochemical properties predicted by Eq. (1) in the series peroxide — trioxide — tetraoxide is groundless. A noticeable conformational rearrangement of the molecule occurs on going from peroxide to trioxide, which is caused by a sharp decrease in the dipole-dipole interactions and characterized by a change in the energy ΔE. This value can be estimated from the conformation curve (see Fig. 3). The coefficient 1/2 is introduced due to the symmetry of the molecule. The conformation of the molecule persists on going from trioxide to tetraoxide, hence, ΔE = 0.

Another method for the estimation of ΔE is the calculation of the structure of trioxide with a fixed φ

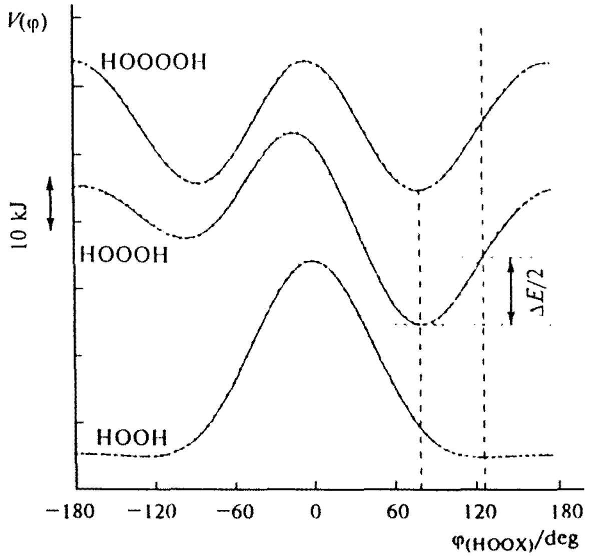

Fig. 3. Unidimensional conformational potential of a polyoxide molecule. Points indicate the calculation by the AM1 method, solid line shows the calculation by Eq. (3).

value equal to the torsion angle in the corresponding peroxide. Both methods for the estimation of ΔE for HOOOH lead to close results: according to Fig. 3, ΔE = 20.0 kJ mol^{-1}, for the calculation of the conformation of hydrogen trioxide with $\varphi_1 = \varphi_2 = 127.9°$, $-\Delta E$ = 22.6 kJ mol^{-1}. For alkyl hydrotrioxides and dialkyl trioxides, the value of ΔE can be higher, because the interaction of the substituent with the LEP of the oxygen atom is more pronounced in peroxides than in trioxide. This is reflected in the higher value of the torsion angle in peroxides: for MeOOMe, φ = 180°; for MeOOH, φ = 126°.[34] Depending on the basis set, the φ value in methyl hydroperoxide changes from 108.9° (STO-3G) to 179.6° (6-31G and 6-31G**).[35]

The use of Eq. (1) for the calculation of $\Delta_f H°[O-(O)_2]$ and then $\Delta_f H°$ of trioxides results in a calculation accuracy of not less than $\Delta E/2$. To avoid this, Eq. (1) should be divided into two equations:

$$\Delta_f H°[O-(O)_2] = \Delta_f H°(ROOOR) - \Delta_f H°(ROOR) - \Delta E, \quad (4)$$

$$\Delta_f H°[O-(O)_2] = \Delta_f H°(ROOOOR) - \Delta_f H°(ROOOR). \quad (5)$$

Thus, the values of $\Delta_f H°[O-(O)_2]$ calculated previously[16,20] are overestimated by at least 10 kJ mol^{-1}, and the real value of this increment is equal to 48±6 kJ mol^{-1}.

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