Full Articles

Acyclic and cyclic forms of the radicals $HO_4^\bullet$, $CH_3O_4^\bullet$, and $C_2H_5O_4^\bullet$: *ab initio* quantum chemical calculations

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Acyclic and cyclic structures and total energies of radicals $HO_4^\cdot$, $CH_3O_4^\cdot$, and $C_2H_5O_4^\cdot$ were calculated by *ab initio* quantum chemical methods. Depending on the computational method and basis sets used, the cyclic conformer of the $HO_4^\cdot$ radical is 4.8 to 7.3 kJ mol^{-1} more stable than the acyclic one. For the first two representatives of the homologous series of alkyl tetraoxyl radicals, $CH_3O_4^\cdot$ and $C_2H_5O_4$, MP2/6-311++G** calculations predict insignificant energy differences (1.2 kJ mol^{-1}) between six-membered cyclic and acyclic conformers. Apparently, these radicals can exist in both forms.

Key words: radicals, ozone, quantum chemical calculations, acyclic and cyclic forms.

The interaction of the $HO^\cdot$ radical with ozone is a process leading to ozone layer depletion in the Earth atmosphere.[1] In this connection, considerable attention has been paid to this reaction. The potential energy surface (PES) of atmospheric reaction $HO^\cdot + O_3$, in which the adduct $HO_4^\cdot$ (^2A) was considered as an intermediate, was calculated by the DMBE method.[2] It was assumed[3] that the $HO_4^\cdot$ radical* can be an intermediate in the sequence of efficient conversions of biologically hazardous energy of UV radiation in the upper atmosphere. Possible reactions in the upper troposphere and in the lower and middle stratosphere (altitudes 16—30 km, temperature 217—227 K, pressure 10^4—$1.2 \cdot 10^3$ Pa)[1] where the ozone layer is mainly located are as follows (the corresponding ΔH°_{298} values for the standard states[4] are given in kJ mol^{-1}):

$$H_2O_{vap} + h\nu \longrightarrow H^\cdot + HO^\cdot,^{1} \qquad (1)$$

$$HO^\cdot + O_3 \longrightarrow HO_4^\cdot\ ^{2} \qquad (\Delta H^\circ_{298} = -59.5), \qquad (2)$$

$$HO_4^\cdot \longrightarrow HO_2^\cdot + O_2(X^3\Sigma_g^-)\ ^{2} \quad (\Delta H^\circ_{298} = -110.0) \qquad (3)$$

$$(\text{or } HO_4^\cdot \longrightarrow HO_2^\cdot + O_2(a^1\Delta_g) \quad (\Delta H^\circ_{298} = -15.7)),$$

where H_2O_{vap} denotes water vapor.

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* In the gas phase one has $\Delta H^\circ_{f,298}$ ($HO_4^\cdot$) = 122.6±13.7 kJ mol^{-1} (calculated from the data of Ref. 4 without inclusion of the energy of a feasible intramolecular hydrogen bond).

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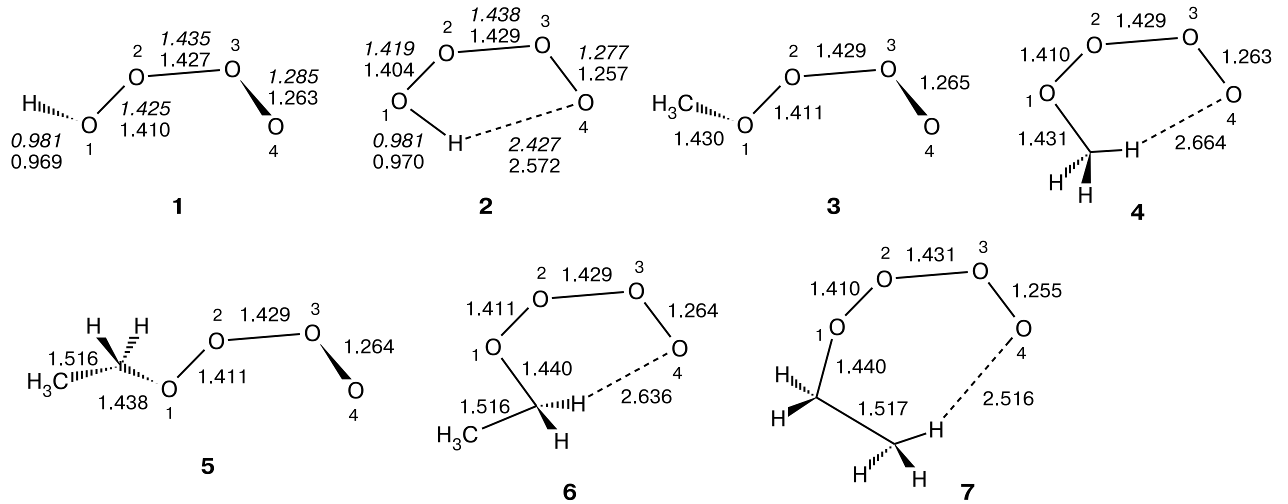

Fig. 1. Bond lengths (in Å) in conformers of the $HO_4^{\bullet}$ (**1**, **2**), $CH_3O_4^{\bullet}$ (**3**, **4**), and $C_2H_5O_4^{\bullet}$ (**5**—**7**) radicals optimized by the MP2/6-311++G** method and the MP2(full)/6-31G(d) method (figures in italics).

The decay of the $HO_4^{\bullet}$ radical may occur not only through dissociation, but also in the disproportionation reaction with a molecule, a free radical, or an atom. Note that emission of $O_2(a^1\Delta_g)$ is observed at altitudes 30—80 km,[5] while emission of $O_2(b^1\Sigma_g^+)$ is observed at altitudes 40—130 km.

A species with the chemical composition HO_4 was first postulated[6] as an intermediate of the addition of $HO^{\bullet}$ to ozone in aqueous solution. In a pulsed radiolysis study[7] of ozone decomposition in water containing ozone (~10^{-4} mol dm^{-3}) and oxygen at 294 K, the UV spectrum with an optical absorption maximum near 260 nm ($\varepsilon(HO_4)_{280\ nm} = 320\pm15$ m^2 mol^{-1}) was attributed to that intermediate. The absorption spectra of HO_4 and ozone are similar, but the molar extinction coefficient of the former, $\varepsilon(HO_4)_{\lambda_{max}}$, is about twice larger than that of the latter.[7]

The HO_4 intermediate was also considered[3] as a low-reactivity hydrotetraoxyl radical $HO_4^{\bullet}$, which is not involved in the chain propagation reaction and therefore shortens the kinetic chains, thus inhibiting unbranched chain oxidation of hydrogen, which occurs at moderate temperatures and pressures without transition to non-steady-state critical regimes. The average lifetime of the $HO_4^{\bullet}$ radical in water at 294 K estimated[3] from the inverse rate constant[7] for reaction (3) is $(3.6\pm0.4)\cdot10^{-5}$ s. This is 3.9 times longer than the analogously determined[3] average lifetime of linear radical $HO_3^{\bullet}$ (see Refs 9 and 10) under identical conditions.[8] Taking account of this fact, it was assumed[3,11] that, structurally, radical $HO_4^{\bullet}$ represents a closed five-membered ring $[\overline{\text{OO—H}\cdots\text{OO}}]^{\bullet}$ owing to formation of an intramolecular hydrogen bond stabilizing the species.

In the present work, the structure of the $HO_4^{\bullet}$ radical was studied by *ab initio* quantum chemical methods in order to elucidate the possibility for this species to mainly exist in cyclic form (*i.e.*, the possibility for this form to be more stable than acyclic helical conformation optimized earlier).[9,12] Acyclic and cyclic structures of radical homologs $CH_3O_4^{\bullet}$ and $C_2H_5O_4^{\bullet}$ (organic analogs of the radical $HO_4^{\bullet}$) were calculated analogously. Like other low-reactivity radicals $RO_4^{\bullet}$, these two species can be inhibitors of initiated oxidation of hydrocarbons by the nonbranched chain mechanism proposed in Ref. 11.

Calculation Procedure

All calculations were carried out with the GAUSSIAN-98 program.[13] Geometric parameters of free radicals were optimized in the framework of the second-order Møller—Plesset perturbation theory by the MP2(full)/6-31G(d) method and then used for the calculation of the properties of the systems under study by the MP2/6-311G(d,p), MP2/6-311+G(3df,2p), and QCISD(T)/6-311G(3df,2p) methods, as in Ref. 9.

Results and Discussion

The PES of the $HO_4^{\bullet}$ system was calculated by the MP2(full)/6-31G(d) method. Two minima were located, which correspond to acyclic conformer **1** calculated earlier[9,12] and to a quasi-cyclic conformer **2** with a weak H-bond between the O(4) atom and the H atom bonded to the O(1) atom (Fig. 1). According to calculations, ring formation is accompanied by slight elongation of the O(2)—O(3) bond and by some shortening of the O(1)—O(2) and O(3)—O(4) bonds. The total energies of acyclic and cyclic conformers of the $HO_4^{\bullet}$ radical were calculated (Table 1). For the acyclic form, the results obtained are the same as those reported earlier.[9]

From the data in Table 1 it follows that the total energy difference between cyclic and acyclic conformers depends only slightly on the computational method and lies in the range –(5.8—7.3) kJ mol^{-1}, which suggests a

Table 1. Total energies of acyclic (**1**) and cyclic (**2**) conformers of the $HO_4^{\bullet}$ radical (E_1 and E_2, respectively) and the relative stabilities of conformers $\Delta E = E_2 - E_1$

Computational method	$-E_1$	$-E_2$	$-\Delta E$
	au		/kJ mol^{-1}
MP2(full)/6-31G(d)	300.408842	300.411221	6.2
MP2/6-311G(d,p)//MP2(full)/6-31G(d)	300.556391	300.558611	5.8
MP2/6-311+G(3df,2p)//MP2(full)/6-31G(d)	300.744322	300.746706	6.3
QCISD(T)/6-311G(3df,2p)//MP2(full)/6-31G(d)	300.611754	300.614550	7.3
MP2/6-311+G(3df,2p)	300.745581	300.747979	6.3
MP2/6-311++G**	300.573702	300.575515	4.8

Table 2. Bond angles (ω/deg) and dihedral angles (θ/deg) in acyclic (**1**, **3**, **5**) and cyclic (**2**, **4**, **6**, **7**) conformers of the $HO_4^{\bullet}$, $CH_3O_4^{\bullet}$, and $C_2H_5O_4^{\bullet}$ radicals (see Fig. 1) optimized by the MP2/6-311++G** method

Conformer	ω			θ	
	R—O(1)—O(2)*	O(1)—O(2)—O(3)	O(2)—O(3)—O(4)	R—O(1)—O(2)—O(3)*	O(1)—O(2)—O(3)—O(4)
1	101.6	106.5	110.9	90.0	−82.5
2	101.7	106.7	111.0	89.3	−67.2
3	107.6	106.7	110.8	87.3	−82.7
4	108.5	106.2	110.5	88.2	−106.2
5	108.1	106.6	110.8	87.7	−82.8
6	108.6	105.5	110.0	104.1	−127.8
7	109.0	106.2	110.6	89.8	−104.8

* Here R = H, Me, or Et.

higher stability of the cyclic form. MP2(full)/6-31G(d) calculations give a value of −6.2 kJ mol^{-1}. Taking account of the difference in the zero-point vibrational energy corrections (ZPE) for two conformers reduces this value by an additional 1.1 kJ mol^{-1}. The entropy of conversion of the acyclic form of $HO_4^{\bullet}$ to the cyclic form calculated in the same approximation is $\Delta S^{\circ}_{298} = -1.6$ J mol^{-1} K^{-1}. Therefore, although the $HO_4^{\bullet}$ radical can exist in both forms under standard conditions with ZPE included, the cyclic form ($K_e = 6.5$) obviously dominates (87%).

Calculations of two forms of the $HO_4^{\bullet}$ radical using other basis sets and procedures for inclusion of electron correlation energy gave similar results in each case (see Table 1). According to MP2/6-311++G** calculations, the cyclic conformer of the $HO_4^{\bullet}$ radical is 4.8 kJ mol^{-1} more stable than the acyclic helical form and 10.3 kJ mol^{-1} more stable than the system $HO^{\bullet}—O_3$, being at the same time 125.2 kJ mol^{-1} less stable than the system $HO_2^{\bullet}—O_2$. The bond angles and dihedral angles for the two forms of the $HO_4^{\bullet}$ radical are listed in Table 2. The results obtained for acyclic conformer **1** are similar to those reported earlier.[9]

The structures of the $CH_3O_4^{\bullet}$ and $C_2H_5O_4^{\bullet}$ radicals (see Tables 2 and 3) were also studied by the MP2/6-311++G** method with full geometry optimization. Of two energy minima located for the $CH_3O_4^{\bullet}$ radical, one corresponds to acyclic helical conformer **3** while the other corresponds to cyclic conformer **4** (see Fig. 1). Structure **3** is only 1.2 kJ mol^{-1} more stable than form **4**. Three minima on the PES were located for the $C_2H_5O_4^{\bullet}$ radical. They correspond to structures **5**—**7** (see Fig. 1). Acyclic conformer **5** is also only 1.2 kJ mol^{-1} more stable than its six-membered cyclic analog **6**. The least stable is the seven-membered quasi-cyclic conformer **7** with shortened contact between the O(4) atom and an H atom of the Me-group; the energy of this species is 6.7 kJ mol^{-1} higher than that of the acyclic conformer **5**.

Thus, we have calculated the acyclic and cyclic structures and the total energies of free radicals $HO_4^{\bullet}$, $CH_3O_4^{\bullet}$, and $C_2H_5O_4^{\bullet}$ in the gas phase using *ab initio* quantum chemical methods. According to our calculations, the

Table 3. Total (E) and relative (ΔE) energies of acyclic (**3**, **5**) and cyclic (**4**, **6**, **7**) conformers of the $CH_3O_4^{\bullet}$ and $C_2H_5O_4^{\bullet}$ radicals obtained from MP2/6-311++G** calculations

Conformer	$-E$ /au	ΔE /kJ mol^{-1}
3	339.757281	0
4	339.756839	1.2
5	378.958543	0
6	378.958066	1.2
7	378.956000	6.7

cyclic conformer of the $HO_4^{\bullet}$ radical should be 4.8 to 7.3 kJ mol^{-1} more stable than the acyclic one (depending on the computational method and basis sets used). For the first two representatives of the homologous series of alkyltetraoxyl radicals, $CH_3O_4^{\bullet}$ and $C_2H_5O_4$, MP2/6-311++G** calculations predict insignificant energy differences (1.2 kJ mol^{-1}) between six-membered cyclic and acyclic conformers. Apparently, these radicals can exist in both forms.

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