

Full Articles

Acyclic and cyclic forms of the radicals HO_4^\bullet , $\text{CH}_3\text{O}_4^\bullet$, and $\text{C}_2\text{H}_5\text{O}_4^\bullet$: *ab initio* quantum chemical calculations

I. V. Trushkov,^a M. M. Silaev,^{a*} and N. D. Chuvylkin^b

^aDepartment of Chemistry, M. V. Lomonosov Moscow State University,
Bldg. 1/3, Leninskie Gory, 119991 Moscow, Russian Federation.

Fax: +7 (495) 932 8846. E-mail: trush@org.chem.msu.ru

^bN. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.

Fax: +7 (499) 135 5328

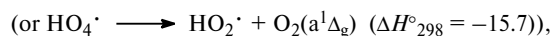
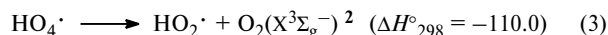
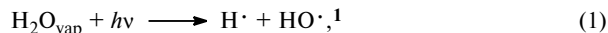
Acyclic and cyclic structures and total energies of radicals HO_4^\bullet , $\text{CH}_3\text{O}_4^\bullet$, and $\text{C}_2\text{H}_5\text{O}_4^\bullet$ were calculated by *ab initio* quantum chemical methods. Depending on the computational method and basis sets used, the cyclic conformer of the HO_4^\bullet 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, $\text{CH}_3\text{O}_4^\bullet$ and $\text{C}_2\text{H}_5\text{O}_4^\bullet$, 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^\bullet 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 $\text{HO}^\bullet + \text{O}_3$, in which the adduct HO_4^\bullet (²A) was considered as an intermediate, was calculated by the DMBE method.² It was assumed³ that the HO_4^\bullet radical* can be an intermediate in the sequence of efficient conversions of biologically hazardous energy

* In the gas phase one has $\Delta H_{f,298}^\circ(\text{HO}_4^\bullet) = 122.6 \pm 13.7 \text{ kJ mol}^{-1}$ (calculated from the data of Ref. 4 without inclusion of the energy of a feasible intramolecular hydrogen bond).

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 – $1.2 \cdot 10^3 \text{ Pa}$)¹ where the ozone layer is mainly located are as follows (the corresponding ΔH_{298}° values for the standard states⁴ are given in kJ mol^{-1}):



where $\text{H}_2\text{O}_{\text{vap}}$ denotes water vapor.

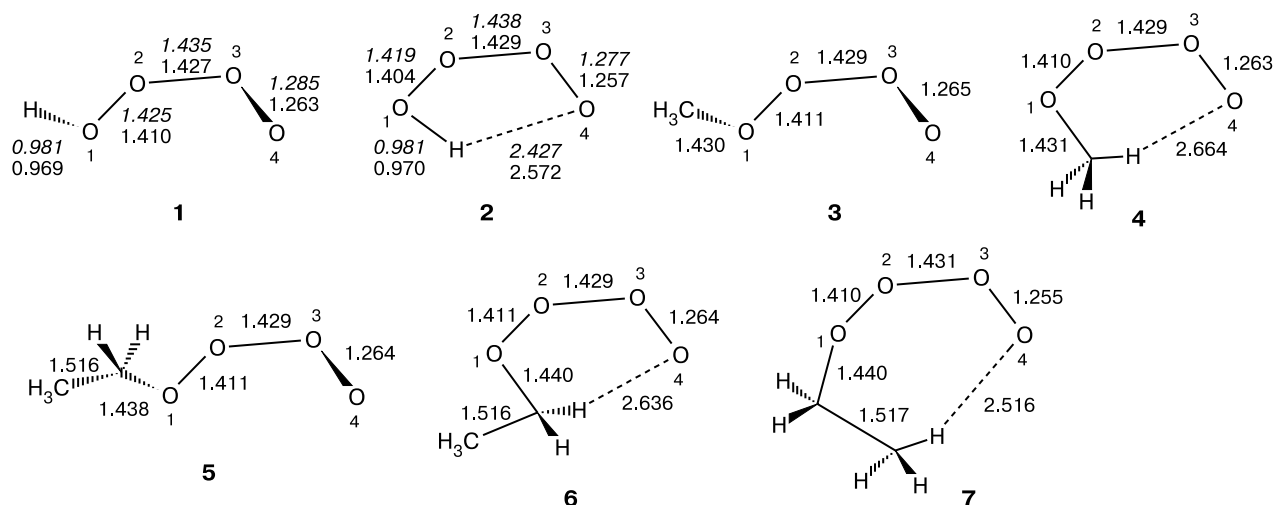


Fig. 1. Bond lengths (in Å) in conformers of the $\text{HO}_4\cdot$ (1, 2), $\text{CH}_3\text{O}_4\cdot$ (3, 4), and $\text{C}_2\text{H}_5\text{O}_4\cdot$ (5–7) radicals optimized by the MP2/6-311++G** method and the MP2(full)/6-31G(d) method (figures in italics).

The decay of the $\text{HO}_4\cdot$ 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 $\text{O}_2(\text{a}^1\Delta_g)$ is observed at altitudes 30–80 km,⁵ while emission of $\text{O}_2(\text{b}^1\Sigma_g^+)$ is observed at altitudes 40–130 km.

A species with the chemical composition HO_4 was first postulated⁶ as an intermediate of the addition of $\text{HO}\cdot$ to ozone in aqueous solution. In a pulsed radiolysis study⁷ of ozone decomposition in water containing ozone ($\sim 10^{-4}$ mol dm^{-3}) and oxygen at 294 K, the UV spectrum with an optical absorption maximum near 260 nm ($\epsilon(\text{HO}_4)_{260\text{ nm}} = 320 \pm 15$ $\text{m}^2 \text{mol}^{-1}$) was attributed to that intermediate. The absorption spectra of HO_4 and ozone are similar, but the molar extinction coefficient of the former, $\epsilon(\text{HO}_4)_{\lambda_{\text{max}}}$, is about twice larger than that of the latter.⁷

The HO_4 intermediate was also considered³ as a low-reactivity hydrotetraoxyl radical $\text{HO}_4\cdot$, 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 $\text{HO}_4\cdot$ radical in water at 294 K estimated³ from the inverse rate constant⁷ for reaction (3) is $(3.6 \pm 0.4) \cdot 10^{-5}$ s. This is 3.9 times longer than the analogously determined³ average lifetime of linear radical $\text{HO}_3\cdot$ (see Refs 9 and 10) under identical conditions.⁸ Taking account of this fact, it was assumed^{3,11} that, structurally, radical $\text{HO}_4\cdot$ represents a closed five-membered ring $[\text{OO}-\text{H}\cdots\text{OO}]^\cdot$ owing to formation of an intramolecular hydrogen bond stabilizing the species.

In the present work, the structure of the $\text{HO}_4\cdot$ 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 $\text{CH}_3\text{O}_4\cdot$ and $\text{C}_2\text{H}_5\text{O}_4\cdot$ (organic analogs of the radical $\text{HO}_4\cdot$) were calculated analogously. Like other low-reactivity radicals $\text{RO}_4\cdot$, 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 $\text{HO}_4\cdot$ 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 $\text{HO}_4\cdot$ 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 HO₄· 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 HO₄·, CH₃O₄·, and C₂H₅O₄· 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 HO₄· to the cyclic form calculated in the same approximation is $\Delta S_{298}^{\circ} = -1.6$ J mol⁻¹ K⁻¹. Therefore, although the HO₄· radical can exist in both forms under standard conditions with ZPE included, the cyclic form ($K_c = 6.5$) obviously dominates (87%).

Calculations of two forms of the HO₄· 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 HO₄· 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·—O₃, being at the same time 125.2 kJ mol⁻¹ less stable than the system HO₂·—O₂. The bond angles and dihedral angles for the two forms of the HO₄· radical are listed in Table 2. The results obtained for acyclic conformer **1** are similar to those reported earlier.⁹

The structures of the CH₃O₄· and C₂H₅O₄· 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 CH₃O₄· 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 C₂H₅O₄· 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 HO₄·, CH₃O₄·, and C₂H₅O₄· 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 CH₃O₄· and C₂H₅O₄· 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 HO₄· 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 alkyl-tetraoxyl radicals, CH₃O₄· and C₂H₅O₄·, 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.

References

1. *Atmosfera. Spravochnik [The Atmosphere. A Handbook]*, Gidrometeoizdat, Leningrad, 1991, 510 pp. (in Russian).
2. A. J. C. Varandas, L. Zhang, *Chem. Phys. Lett.*, 2000, **331**, 474.
3. M. M. Silaev, *Khim. Vys. Energ.*, 2008, **42**, 124 [*High Energy Chem. (Engl. Transl.)*, 2008, **42**, 95].
4. J. S. Francisco, I. H. Williams, *Int. J. Chem. Kinet.*, 1988, **20**, 455.
5. H. Okabe, *Photochemistry of Small Molecules*, A Wiley-Interscience Publication—Wiley and Sons, New York—Chichester—Brisbane—Toronto, 1978.
6. D. Bahnemann, E. J. Hart, *J. Phys. Chem.*, 1982, **86**, 252.
7. J. Staehelin, R. E. Bühler, J. Hoigné, *J. Phys. Chem.*, 1984, **88**, 5999.
8. R. E. Bühler, J. Staehelin, J. Hoigné, *J. Phys. Chem.*, 1984, **88**, 2560.
9. D. J. McKay, J. S. Wright, *J. Am. Chem. Soc.*, 1998, **120**, 1003.
10. F. Cacace, G. de Petris, F. Pepi, A. Troiani, *Science*, 1999, **285**, 81.
11. M. M. Silaev, *Oxid. Commun.*, 1999, **22**, 159.
12. E. H. Timokhina, K. B. Bozhenko, A. E. Gekhman, N. I. Moiseeva, I. I. Moiseev, *Dokl. Akad. Nauk*, 2002, **384**, 645 [*Dokl. Phys. Chem. (Engl. Transl.)*, 2002, **384**, 134].
13. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *GAUSSIAN 98, Revision A.7*, Gaussian, Inc., Pittsburgh (PA), 1998.

Received June 25, 2008;
in revised form September 17, 2008