Quantum-Chemical Calculations of the Structure of Trioxyl Radicals

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INTRODUCTION

Polyoxides and polyoxide radicals are metastable compounds whose properties have remained almost unstudied. They are, however, formed in quite a number of redox processes in the gas and liquid phases and influence the kinetics of these processes and the composition of the products formed. For instance, ROOO radicals are intermediates in the decomposition of ozone under the action of free radicals [1]. The hydrotrioxyl radical plays an important role in processes with the participation of ozone, for instance, in the chemistry of atmosphere [2] or industrial water treatment [3]. The conclusion was drawn [4, 5] that trioxyl radicals were formed as intermediate active particles in the quadratic decay of peroxy radicals, which is a key stage of the oxidation of organic compounds with air oxygen.

No wonder that considerable effort was made to characterize the properties of such particles. Experimental studies of ROOO are extremely difficult to perform because of their lability. The corresponding works are therefore few. In [2, 6, 7], the enthalpy of formation of HOOO was determined mass spectrometrically, and, in [8], the direct identification of HOOO by infrared spectroscopy in argon matrices was reported. The rotational spectrum of HOOO was studied in [9], where the structure of the species was determined, which was the most convincing proof of the existence of this intermediate.

Theoretical studies of ROOO are mainly directed to establishing the possibility in principle of the existence of such particles (that is, their thermodynamic stability with respect to decomposition products) and their structure and conformational mobility. The results of modeling strongly depend on the theoretical level of studies. For instance, the relative stability of HOOO with respect to its decomposition products, HO and O₂, was estimated at 8.9 kcal/mol in [10]. This result closely agrees with the experimental data [6] (10 ± 5 kcal/mol). The scrupulous selection of an adequate quantum-chemical approach and an analysis of the above experimental data allowed the authors of [11] to estimate the enthalpy of formation of HOOO at 7.1 ± 2 kcal/mol, which was at variance with the value obtained in [6], −1 ± 5 kcal/mol. The enthalpies of formation of ROOO, where R = H, CH₃, and C₂H₅, were calculated using the G2M(RCC) and CBS-QCI/APNO methods in [12]. The special features of the behavior of HOOO in water were studied in [13, 14] using the continual, discrete, and combined models. It was, in particular, found [14] that the lifetime of the solvated hydrotrioxyl radical can be 20–500 times longer than in the gas phase because of the cooperative stabilization effect.

Studies of labile intermediates of redox processes “overloaded” with oxygen atoms is an exceedingly complex problem even at the present level of experimental and theoretical chemistry, in spite of the apparent simplicity of these systems. The literature data on the properties of thioxyl radicals are incomplete and contradictory. The purpose of this work was to analyze the structure and conformational mobility of the simplest ROOO radicals (R = H and CH₃) and construct models of the main channels of the consumption of ROOO.
Quantum-chemical calculations were performed using the Gaussian 03 [15], PC GAMESS 7.0, and US GAMESS 2006 R2 [16] packages. We used density functional theory at the PBE0 [17] and B3LYP [18] levels and the second- and fourth-order perturbation theory MP2 and MP4(SDQ) methods in the frozen core approximation, CCD and CCSD coupled cluster methods, and QCISD configuration interaction method with correlation consistent Dunning basis sets (cc-pVDZ and cc-pVTZ). The total energy of the compounds was calculated using the multireference second-order perturbation theory method MRMP2 with the aug-cc-pVTZ basis set.

RESULTS AND DISCUSSION

The structure and conformational mobility of the two ROOO radicals under consideration (R = H and CH$_3$) were studied by modeling the trioxyl radical rotational potential about the RO–OO bond (relaxed scan in steps of 15°). For HOOO, the results obtained by the MP2 and MP4(SDQ) perturbation theory methods and the CCD coupled-cluster method agree with each other. These methods predict that the HOOO molecule exists predominantly as the cis isomer, whereas the trans conformation corresponds to the top of the potential barrier to rotations about the central O–O bond. The barrier height is 9.7, 7.0, and 5.8 kJ/mol according to MP2, MP4(SDQ), and CCD calculations, respectively.

At the same time, conformational potential calculations by the PBE0 and B3LYP density functional theories and the coupled cluster CCSD and configuration interaction QCISD methods, which are characterized by no less complete inclusion of electron correlation, give a qualitatively different result (some of the potential curves are shown in Fig. 1a). According to these approximations, both the cis and trans structures are stable (the cis isomer is more favorable energetically), and the gauche conformer corresponds to the potential barrier top. In the PBE0/cc-pVTZ approximation, the skewed form is localized as a saddle point and characterized by the presence of one imaginary frequency (ν = 171 cm$^{-1}$), the height of the potential barrier with respect to the cis structure is 3.4 kJ/mol. The feature common to all the methods used is a flattened potential energy surface corresponding to rotations about the central O–O bond. A similar situation with an unsatisfactory description of the conformational potential of the MeOOMe peroxide compound was considered in [19]. The relative energies characterizing the stability of HOOO and CH$_3$OOO conformers are listed in Table 1.

The most important geometric characteristics of HOOO conformers are presented in Table 2. The length of the central O–O bond approximately equals the length of the corresponding bond in HOOH (1.452 ± 0.005 Å [20]), whereas the bond with the terminal oxygen atom is much shorter (1.229–1.274 Å depending on the method of calculations). The values obtained do not agree with the experimental data [9], according to which the stabellest conformation in the gas phase is the trans conformation with $r$(HO–OO) = 1.688 Å and $r$(HOO–O) = 1.225 Å. The quantum-chemical calculations performed by the same authors in the MRCI + Q(19 × 13)/aug-cc-pVTZ approximation closely agree with the experimental data ($r$(HO–OO) = 1.677 Å and $r$(HOO–O) = 1.225 Å). This shows that a correct reproduction of the structure of the hydrotrioxyl radical stringently requires the simultaneous inclusion of both static and dynamic electron correlation. The nonfulfillment of this requirement is the major drawback of our calculations. The multireference nature of HOOO also follows from the CCSD $T_1$ test value of 0.47 [11]. It exceeds the threshold value by 0.02, which is evidence of a substantial contribution of additional electronic configurations.

Calculations of the conformational potential of CH$_3$OOO in turn gave three fundamentally different