Influence of various functional groups on the relative stability of alkylperoxy triplet cations: A theoretical study

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ABSTRACT

CBS-QB3 energy calculations show that the formation of a stable triplet cation for alkylperoxy radicals is dependent on factors other than the stability of the daughter cations exclusively. We have found that in cases where the daughter ions are not capable of stabilizing the cation through hyperconjugation, it is possible for the triplet cation to be bound. In many circumstances, CBS-QB3 calculations have found bound triplet cation states with 'negative dissociation energies.' These results are attributed to the effects that electron donating/withdrawing substituents have on the spin and charge densities of the resulting cations.

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1. Introduction

The structure and stability of alkyl-peroxy (ROO) radicals is of great interest due to their role as intermediates in oxidation of organic compounds in the atmosphere and in combustion. In particular, ROO radicals participate in the tropospheric 'self-cleansing' mechanism, which helps to remove volatile organic compounds from the atmosphere [1,2]. They also play an important role in auto-ignition chemistry where initially slow thermal reactions have a large enough chain-branching component to sustain and accelerate oxidation [3].

A majority of hydrocarbons in the atmosphere are unsaturated alkenes, such as isoprene, which are stable intermediates in the combustion of saturated species. As such, both saturated and unsaturated hydrocarbons play a pivotal role in the modeling of combustion processes in which they take part forming peroxy species. The study of these radicals has previously been conducted through theoretical methods as well as the photoionization or supersonic jet expansion of small alkyl and alkenyl peroxy species [4–6].

Experimental observations of peroxy radicals and their ionic counterparts have been difficult due to their instability and reactivity. However, there has been much effort over the years directed at obtaining an understanding of their electronic structure through the use of computational chemistry, with the first *ab initio* calculation of the equilibrium ground state structures of HO_2, CH_3OO,

and the corresponding hydroperoxides conducted by Bair and Goddard [7] in 1981. More recently, studies have compared the results of energetic and structural calculations of alkyl peroxy radicals to determine the effect that R groups have on the peroxy electronic structure [8–10]. In one such study it was shown that the singly occupied molecular orbital (SOMO) and highest occupied molecular orbital (HOMO) of peroxy radicals are similar in both energy and character, regardless of the size, conformation, or conjugation in the R group. The HOMO and SOMO were also found to consist primarily of the $\pi^*(C_\alpha{-}O)$ and $\sigma^*(C_\alpha{-}O)$ molecular orbitals (MO), respectively [9].

Experiments conducted to isolate or directly detect various peroxy cations have had some success; more so, they have demonstrated that only the smallest alkylperoxy cation CH_3OO^+ is thermodynamically stable [11] while all 1-alkenylperoxy radical cations are stable. To the best of our knowledge in all reported cases ionization of the neutral alkyl-type radical removes an electron from the $\sigma(C_\alpha{-}O)$ bond, creating the triplet ground electronic state of the cation. This leaves one electron in this orbital resulting in significant lengthening of the C—O bond [11]. This is attributed, in part, to the stabilities of the dissociative daughter ions in alkylic fragments, namely, H hyperconjugation from the $\sigma(C_\beta{-}H)$ orbital with the half-filled $p(C_\alpha)$ with stabilization increasing on more highly substituted carbocations [12,13]. Since 1-alkenylperoxy radicals cannot participate in hyperconjugation due to the sp^2 hybridization of the β carbon, there is no added stability in the daughter ions, and therefore, their cations have been observed [5]. Therefore, these two factors govern, in large part, the stability of peroxy cations and without the hydrogen's shared electron density it may be possible to find a stable alkylperoxy cation. Of particular interest is the

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investigation of Blanksby et al. [14] in which the thermochemistry and vibrational features of neutral methyl and ethyl peroxy species have been probed using negative ion photodetachment spectroscopy.

As part of a continuing effort to characterize peroxy species and their cations, this work presents theoretical investigations into the stability of several alkylperoxy cations. The goal of this present study is to utilize *ab initio* calculations in order to explore the effects various electron donating (ED) and electron withdrawing (EW) moieties and their position with respect to the peroxy group have on the relative stability and bond dissociation energies of alkylperoxy cations. Specifically, we will present cases where hyperconjugation interactions from a C_β—H bond cannot stabilize the daughter fragment ion, due to the β carbons sp^2 hybrid character. Another result that will be presented in this Letter is the finding that in some cases DFT and the more stringent CBS-QB3 composite method found some of the cationic species to posses what appears to be a negative C—O bond dissociation energy, i.e., $D_0[R$—$OO^+] < 0$, or, in other words, the energy of the dissociative ionization fragments is lower than the energy of the parent ion. This has been reported in some previous studies however, these investigations involve H-atom hole migration [15,16] or dianion complexes [17]. The phenomenon is most commonly associated with short range electrostatic potentials overcoming long range repulsion interactions.

2. Methods

Molecular structural parameters, such as bond lengths, harmonic vibrational frequencies, force constants, energetics, and electronic structures for 35 alkylperoxy radicals are optimized at the CBS-QB3 level using Gaussian09 [18] for the actual computations and Gaussview 5.0 for visualization purposes [19]. This composite method was developed in order to improve calculations of larger systems while incurring lower computational cost. With a mean absolute deviation of 1.08 kcal mol^{-1} when compared with the results of the G2/97 test set, [20] CBS-QB3 is a method widely used to obtain accurate energies of molecules with varying electronic structures. CBS-QB3 combines different levels of theory in order to maximize efficiency. First, geometries and frequencies are optimized using the unrestricted or restricted Becke, three-parameter, Lee–Yang–Parr exchange correlational (UB3-LYP/RB3-LYP) density functional method with the 6-311G(2d,d,p) basis set. The corresponding zero-point vibrational energy (ZPVE) is then scaled by 0.99. Next, the optimized geometries are used to calculate the energies at the MP2/6-311G(3df, 2df, 2p) level with a complete basis set (CBS) extrapolation. This is followed by MP4/(SDQ)/6-31G(d(f),p) and CCSD(T) computations that are employed to evaluate the ultimate electron correlation and include a spin–orbit correction for atoms, which helps correcting for spin contamination in an unrestricted calculation. The final step is particularly important for calculations involving species that have unpaired electron(s).

Electronic structure calculations are carried out using an unrestricted-spin method, where opposite-spin electrons are located in separate orbitals. Spin unrestricted calculations are advantageous because they are less computationally demanding [21] and provide greater flexibility in describing the electronic structure than that of a single reference restricted calculation. Furthermore, it is ideal for determining bond dissociation energies in open-shell species [22]. However, since the wave function is no longer an eigenfunction of the total expected spin operator $\langle S^2 \rangle$, some error may be introduced into the calculation (spin contamination). This is evident when the $\langle S^2 \rangle$ values deviate from their expected eigenvalue [22]. Spin expectation values for each species have been evaluated and in this study indicated negligible contamination.

Singlet–triplet splittings are calculated for each species, in order to confirm that the ground electronic state of the cation is indeed the triplet. Similarly, bond dissociation energies (BDE) of the C_α—O bond in the cation are calculated by performing open-shell energy calculations on the daughter ions using the CBS-QB3 method, as well as via a potential energy scan utilizing B3LYP/6-31+G(d,p).

In order to obtain preliminary minima and transition state geometries for the C—OO bond cleavage, relaxed 1D potential energy scans (PES) are evaluated at the B3LYP/6-31+G(d,p) level across the C—O bond of the alkylperoxy cations. Using these optimized geometries, minima, transition states, and the daughter ion and neutral fragments are calculated again using the CBS-QB3 method. All frequencies for stable species are found to be real, indicating that the geometry represents a minimum on the potential energy surface. Transition state geometries are confirmed to have a single imaginary frequency, indicating a first-order saddle point along the PES.

3. Results and discussion

In order to ensure the accuracy of the chosen computational methodology, calculations on isopropylperoxy, i-C_3H_7OO, are performed and compared with experimentally determined values in the literature [23,24]. The results obtained for the BDE of C—O (reaction (1)) at the B3LYP/6-31+G(d,p) level ($\Delta_r H_0° = 34.5$ kcal mol^{-1}), as well as using the CBS-QB3 method ($\Delta_r H_0° = 36.2$ kcal mol^{-1}), are found to be in good agreement with the literature value of 37.7 ± 1.8 kcal mol^{-1} [23,24].

$$C_3H_7 + O_2 \rightarrow i\text{-}C_3H_7OO \tag{1}$$

Furthermore, this computational methodology is also tested against experimentally determined [25] barrier heights of H migration from terminal —CH_3 to =CD_2 in 1,3-pentadiene. The literature value of 36.3 ± 0.5 kcal mol^{-1} is in good agreement with our CBS-QB3 calculated barrier of 36.7 kcal mol^{-1}.

Thirty-five alkylperoxy radicals are investigated in the present study. Twenty-five species of the 35 possess no bound triplet cationic potential energy surface dissociating completely upon ionization, while ten are calculated to have stable triplet cations. Table 1 lists the names of all the species included in this study, their molecular formula, the adiabatic ionization energy (AIE), as well as some important geometrical parameters, such as the O—O, C—O, C_α—C_β, and X—C bond distances, where X can be NH_2, CH_3, OH, or F. Table 2 lists those compounds, which do in fact have a stable triplet state, along with changes in bond lengths between the neutral and cation species, dissociation energy of the cations C—O bond, and dissociation barrier (E_a), where E_a is defined as the difference in energy for the cationic peroxy ground electronic states and transition states. Unfortunately, we were unsuccessful in finding a transition state for the (3,5)-dimethyl-benzylperoxyl cation (35dMBp) along the C—O bond.

Similar to the results found by Pratt and Porter [26] adjacent ED/EW groups were found to have a great influence over the BDE's of the C_α—O bond in the radical cations. We found that when the β carbon to the peroxy moiety is bonded to any EW group (—F, —Cl, —NO_2) ionization of the neutral radical results in a barrierless dissociation of the O_2 group. Conversely, ED groups, such as —NH_2, —OH, and to a lesser extent —CH_3 will increase the C—O bond strength proportionally with respect to each moiety ability to donate electrons, number of substituents, and position relative to the peroxy. MO and NBO calculations offer unique insights to the electronic structure of molecules illuminating the complex relationship between the adjacent heteroatom and peroxy group. Most