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Correlation between bond dissociation energies and spin distribution for the radicals of ethers: A DFT study

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ABSTRACT

The bond dissociation energy (BDE) of the C–H bond at the α-position of 43 ethers was examined in terms of the ability of the ether to form peroxide. Density functional theory (DFT) calculations, based on the B3LYP level, were performed to determine essential factors governing the thermochemical stabilisation of the radicals. Analysis of the structural properties of the radical species suggested that hyperconjugation, resonance stabilisation and ring strain are the main features responsible for thermochemical stability. These effects are well reflected in the spin distribution in the radical species, which assists in the understanding of the trend of BDEs for the ethers. A good correlation was obtained between BDE and spin distribution for the whole set of ethers. Improved correlations were obtained by splitting the data set into subcategories based on structural properties, i.e. saturated acyclic ethers, polyethers and 5-membered cyclic ethers.

1. Introduction

Peroxides and peroxide-forming substances are amongst the most common hazardous chemicals handled routinely in the laboratory. Peroxides are hazardous due to their extreme sensitivity to shock, heat, friction, and their action as strong oxidising and reducing agents. In addition, many peroxides are more sensitive to shock than even TNT (trinitrotoluene) and they are highly flammable.

The peroxide-forming properties of chemicals are a result of definable structural characteristics. In general, compounds that contain an α-hydrogen atom on an adjacent carbon atom, or a carbon atom attached to a functional group or a double or triple bond are susceptible to autoxidation and peroxide formation. Examples of such chemicals include the ethers, hydrocarbons, vinyl and allylic compounds and organic chemicals with a carbonyl functional group (e.g. aldehydes, ketones).

Ethers are widely used as solvents and because of the ease with which they form peroxides, they are extremely hazardous. Relatively few experiments to determine the peroxide production of ethers following exposure to air have been reported [1,2]. Therefore due to the paucity of data, it would be very useful to understand and be able to predict the autoxidative ability of ethers.

Autoxidation is a free radical chain process; the greater the stability of radical, the greater the potential for autoxidation. The BDE of the C–H bond reflects the instability of the parent molecule and the stability of the radical formed upon the breaking of the bond. Understanding of the trends of BDE, and study of the factors which may contribute to the thermodynamic stabilisation of radicals, will allow for the prediction of values of BDE for ethers. It would also be useful to design functional ethers that are less likely to produce peroxide. Agapito et al. studied three ethers (dimethyl ether, tetrahydrofuran and 1,4-dioxane) and postulated that hyperconjugation and ring strain are the main factors that should be considered to understand their thermodynamic stabilisation [3]. Hoshino et al. studied cyclopentyl methyl ether and suggested that the instability of the radical, relative to the parent molecule, is caused by the bond angle strain of the cyclopentyl ring. This was reflected in a larger energy difference between the heats of formation between the ether radical and parent ether [1].

Experimental BDEs of the C–H bond are available for a large number of organic compounds [4–7]. For ethers, values for only 14 compounds have been reported in the literature [7]. Examination of the trends in BDE of ethers requires access to a larger, more diverse database. Due to the lack of experimental values, theoretical methods have been adopted to evaluate BDEs. Different quantum mechanical techniques have been assessed to find the optimal compromise between computational speed and accuracy [8–10]. It was also found that accurate predictions are possible when isodesmic and isogyric reactions were investigated [3,11].

Another method to obtain BDEs is their estimation from the rate constants of the radical abstraction reactions based on an empirical parabolic model of the transition state [12,13]. Denisov compiled values of C–H BDEs for 43 ether molecules which were estimated by this method based on rate constants [14]. This is one of the largest sets of BDE data for ethers available in the literature.

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In this paper, we have used the BDEs estimated from the kinetic data for 43 diverse ether molecules [14] and performed DFT calculations to determine the factors governing the stability of the radicals formed. The intention was to comprehend and explain the trend of BDE for the ethers to allow for the prediction of BDE for new ethers and thus help design ethers that are more resistant to autoxidation.

2. The source of data and calculations

BDE values for 43 ethers were retrieved from the literature [14]. They were determined from the rate constants of the radical abstraction reaction based on the empirical parabolic model of the transition state. This method of calculation of the BDE is based on the experimental fact that for reactions of structurally similar compounds (in the same reaction series) the kinetic parameter br_e is constant. br_e is constant when the enthalpy of the reactions ΔH_{ei} lie within the minimum (ΔH_e^{min}) and maximum (ΔH_e^{max}) enthalpies for the reaction class; $\Delta H_e^{min} < \Delta H_{ei} < \Delta H_e^{max}$ [13].

$$br_e = \alpha(E_{ei} - \Delta H_e)^{0.5} + E_{ei}^{0.5} \quad (1)$$

$$\Delta H_e = D_i - D_f + 0.5hL(v_i - v_f) \quad (2)$$

$$E_{ei} = E_i + 0.5(hLv_i - RT) \quad (3)$$

where br_e is a kinetic parameter defined by Eq. (1); ΔH_e is the enthalpy of the reaction (Eq. (2)); v_i and v_f are the frequencies of the stretching vibrations of the cleaved and formed bonds, respectively; h is the Planck constant; L is Avogadro's number; D_i and D_f are the dissociation energies of the cleaved and formed bonds, respectively; the activation energy E_{ei} is measured from the minimum in the potential energy parabola of the cleaved bond energy to the minimum of the transition state (Eq. (3)); R is the universal gas constant, T is the absolute temperature (K); E_i is the experimental activation energy of the radical reaction; r_e is the distance between the two minimum points of intersecting potential energy parabolas and is equal to the sum of amplitudes of valent vibration in the transition state; coefficients b and b_f describe the dependence of the potential energy on the amplitude of vibrations of atoms along the cleaved (i) and formed (f) valence bond and $\alpha = b/b_f$.

When calculations are performed in the reaction series, the "reference" reaction $R^{\cdot} + R'H \rightarrow RH + R'^{\cdot}$, for which all the kinetic and thermodynamic parameters are known, and the reactions $R^{\cdot} + R^iH \rightarrow RH + R^{i\cdot}$, for which the cleaved bond dissociation energy D_i is the subject of estimation, are distinguished. After the determination of the kinetic and thermodynamic parameters for the class of reaction, the critical enthalpies are calculated and then the enthalpies of the reference reaction are estimated. When the enthalpy of the reaction lies within the range $\Delta H_e^{min} < \Delta H_{ei} < \Delta H_e^{max}$, the dissociation energy of the cleaved bond D_i is calculated according to Eq. (4):

$$D_i = \Delta D_i + D_1 \quad (4)$$

where ΔD_i is the difference between the dissociation energy of the cleaved and formed bonds for the i-th reaction and D_1 is dissociation energy obtained from the reference reaction $R^{\cdot} + R'H \rightarrow RH + R'^{\cdot}$.

All calculations were performed using the Gaussian 03 program [15]. All structures were drawn using the GausView application within Gaussian03. Geometries of all molecules and related radical species were optimised at the B3LYP/6-311G** level of theory [16,17]. There is a general consensus that B3LYP methods provide excellent low-cost performance for structure optimisations [18]. The B3LYP/6-311G** level of theory is one of the most reliable computational method for optimisation geometries of small polar compounds [19] as well as being widely used for the calculation of radical species [20,21]. The calculations at the B3LYP/6-311G** level were shown to be sufficient for the estimation of the structure and energies and as our goal was the determination of factors governing the stability of radicals, we were mostly interested in relative values rather than absolute values. For comparison, the fully optimised structures for a few molecules were also obtained employing the MP2 level and the same trend in the calculated values was observed.

Statistical analysis was performed using the MINITAB for Windows (Version 15.1) statistical software (MINITAB, State College, PA, USA).

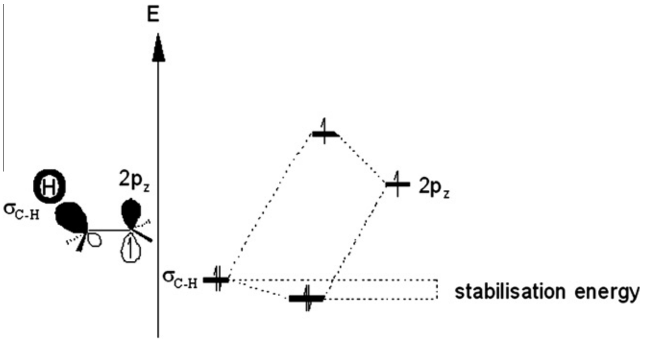

Fig. 1. Stabilisation of the radical by hyperconjugation.

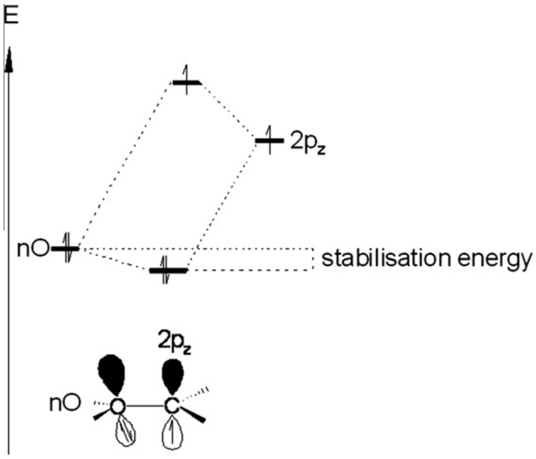

Fig. 2. Stabilisation of the radical by the interaction of the unpaired electron with the p-electrons of the oxygen atom.

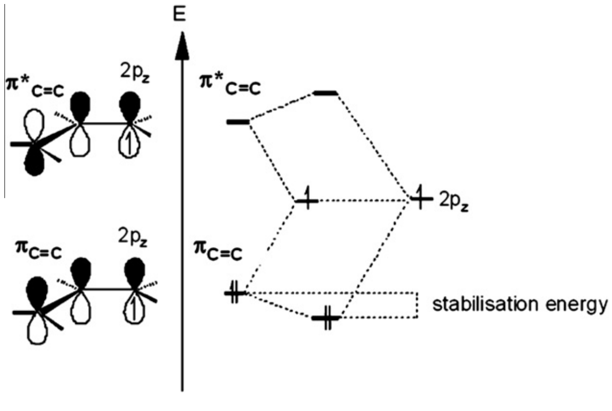

Fig. 3. Stabilisation of the radical by conjugation.