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Thermochemical properties of hetero-atom substituted cycloalkanes

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1. Introduction

The energy sector experiences rapid fundamental changes due to the problem of global warming and related regulatory policies to control CO_2 emissions. While the long-term solution might be to completely shift from hydrocarbon fuels to alternative energy carriers such as hydrogen or ammonia, the transition to a "carbon-free" economy – if possible – will require some time. For the foreseeable future, hydrocarbon based fuels will still dominate the transportation sector and short-term efforts to reduce the emission of greenhouse gases have to focus on improvements in energy efficiencies and the use of carbon-neutral energy carriers such as lignocellulosic biomass, biodiesel, algae-derived fuels and so on. Such fuels differ from conventional fuels in the chemical composition, e.g. biomass derived fuels generally contain significant amounts of oxygen. Other hetero-atoms such as nitrogen (e.g. from protein-containing bio liquids) and sulphur (e.g. from biogas or gasification gases) can also be present in notable amounts. Consequently, pyrolysis and combustion processes of hetero-atom containing fuels require attention and have increasingly been the subject of recent kinetic studies.

Detailed kinetic models present an important tool for process optimization. Adaptation of those models towards the combustion of hetero-atom containing molecules requires the knowledge of thermodynamic properties of large numbers of species and kinetic parameters for their reactions. The present study addresses one aspect: the impact of four hetero-atoms (O, N, S, P) on the stability of 3, 5 and 6 membered rings and their reaction barriers for abstraction reactions.

2. Theoretical methods

The thermodynamic properties of molecules, radicals and transition states of H abstraction reactions have been calculated with the CBS-QB3 [1] ab initio method as incorporated in the Gaussian 16 suite of programs [2]. This method provides structural information at the B3LYP/6-311G(2d,d,p) level, which is also used to calculate the frequencies of internal modes using the harmonic oscillator approximation. Internal modes representing rotations around single bonds are separately treated as hindered rotors. The CBS-QB3 energies are converted to heats of formation with the atomization method. More details on the calculation method used can be found in previous publications [3]. Some additional calculations at the W1 level of theory [4] are performed to validate the accuracy of the CBS-QB3 method for the hetero-atoms studied.

3. Results and Discussion

Bond dissociation energies (DBE) of CH_2 moieties adjacent to the hetero atom (colored columns) are compared in Figure 1 to those in pure hydrocarbons (grey columns) for non-cyclic molecules and those containing a 3, 5, or 6 membered ring. All four hetero-atoms reduce the bond dissociation energy, hence radicals are easier formed and the substituted molecules should be more reactive. Particularly the BDE of ´N´ and ´S´ containing molecules are clearly lower than the pure hydrocarbon homologues. Another result is that the CH_2 bonds in 5-membered rings are lower than those in the corresponding non-cyclic molecules, while those in 3-membered rings are significantly higher. This points to the fact that the ring strain in 3-membered rings increases when they contain a radical site. The BDE in 6-membered rings are, as expected, similar to those of open-chain molecules.
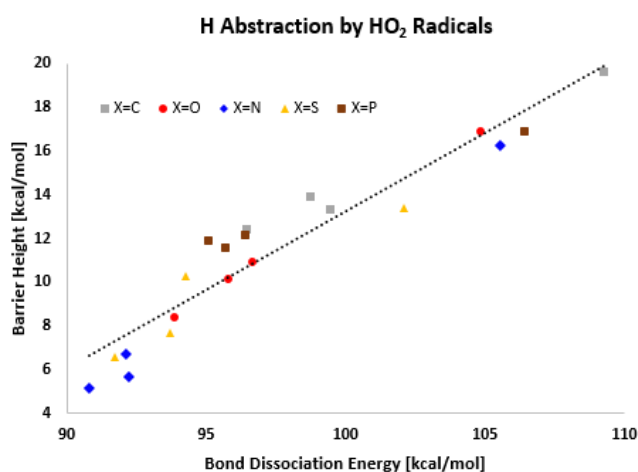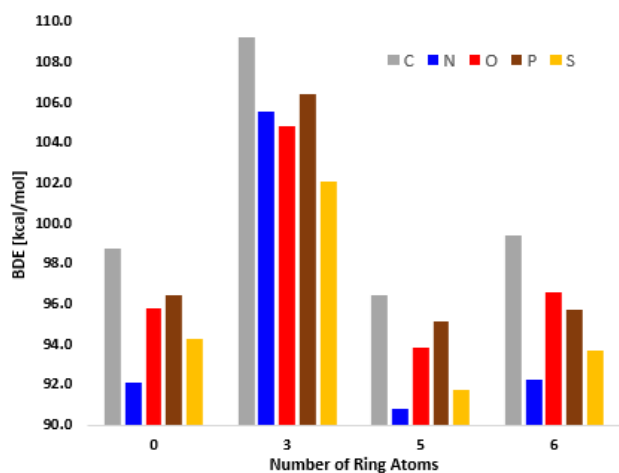
Figure 1: The impact of hetero-atoms on bond dissociation energies

Figure 2: Evans-Polanyi plot for H abstraction by HO$_2$ radical from the CH$_2$ group adjacent to the hetero-atom

W1 calculations are currently performed to validate the accuracy of CBS-QB3 calculations. The few already available preliminary results are premising in the sense that good agreement between all methods of theory is observed. Since for hydrocarbons CBS-QB3 calculations present a good compromise between accuracy and CPU demand, it would be of great value if the same methodology could be used reliably for all the hetero-atoms studied in this work. A more complete set of evaluations will be presented in the meeting.

The second part of the study focuses on H abstraction reactions by H atoms and CH$_3$ and HO$_2$ radicals. The most interesting results are obtained for the abstraction reactions by HO$_2$, which play an important role in the low-temperature oxidation chemistry. Very low barriers are found for H abstraction from cycloalkanes containing a ´N´ hetero-atom. The barriers are even below the values suggested by an Evans-Polanyi relation. Since those rings contain the NH moiety which can form a H bond with the abstracting HO$_2$ radical, these results are reasonable. Incorporation of a sulfur atom also leads to low barriers. This indicates that fuels containing N and S substituted cycloalkanes are very reactive. Of course, a full kinetic analysis is required to confirm this interpretation.

4. Conclusions

Based on the CBS-QB3 method of theory, it is shown that the incorporation of hetero-atoms into cyclic hydrocarbons clearly alters the ring strain and thermochemical properties. Kinetic models need to account for these changes in order to allow accurate predictions of the combustion process. The use of analogous information from pure hydrocarbons can lead to substantial errors. Therefore, more studies on the reactivity of hetero-atom containing hydrocarbons are needed. W1 calculations are on the way to thoroughly test the accuracy of the CBS-QB3 method for the four hetero-atoms investigated in this study.

References

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