

Structure and thermochemical properties of C₆ volatile unsaturated alcohols

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INTRODUCTION

A significant class of compounds emitted to the atmosphere is the volatile organic compounds (VOC). The atmospheric oxidation of these compounds leads to the formation of organic aerosols. The presence of these particles in the atmosphere has important environmental consequences, because they are involved in the climate regulation of the planet. Among the oxygenated VOC, the most relevant are the unsaturated alcohols C₄, C₅, C₆ e C₈. Concerning the C₆ alcohols, there are some experimental studies on its atmospheric decomposition.¹ However, structural and thermochemical properties are not known with accuracy. In this work, our aim is to investigate the structural properties of the VOC (Z)-hex-3-en-1-ol (leaf alcohol), (E)-hex-3-en-1-ol, (Z)-hex-4-en-1-ol and (E)-hex-4-en-1-ol and to determine its thermochemical properties.

METHODS

Initially, it was conducted a conformational analysis in order to determine the most stable structure for the species in study. The energy optimization calculations and determination of harmonic frequencies were done at the MP2/cc-pVTZ level. Single point calculations were performed at the MP2/cc-pVDZ, MP2/cc-pVQZ and CCSD(T)/cc-pVTZ levels in order to achieve the limit for an infinite basis set function and a better accuracy to the electron correlation. For the study of the thermochemical properties, isodesmic reactions were used to provide errors minimization. Using values obtained from the literature for the standard enthalpy and Gibbs energies of formation of other species involved in the reactions studied, and the values of standard enthalpy and Gibbs energies of reaction obtained at the CCSD(T)/CBS level of theory, the standard enthalpy and Gibbs energies of formation of alcohols of interest were determined theoretically.

RESULTS AND DISCUSSION

The values calculated for the species of interest are presented in Table 1. Because this is the first determination of these thermochemical properties, there is no data in the literature for comparison. Nevertheless, we can see that the values are intermediate between those already established for hexene and hexanol, which is expected. Furthermore, our results show that (E) isomers are more stable than the (Z) ones, which is also observed for similar compounds.

Table 1. Standard Enthalpy and Gibbs free energies of formation in kJ/mol (298.15 K, 1 atm).

| Species | ΔH_f | ΔG_f |
|-------------------|--------------|--------------|
| (Z)-hex-4-en-1-ol | -117.7 | 38.7 |
| (E)-hex-4-en-1-ol | -136.3 | 22.3 |
| (Z)-hex-3-en-1-ol | -132.4 | 25.5 |
| (E)-hex-3-en-1-ol | -136.4 | 20.6 |

CONCLUSIONS

The most stable conformation of the volatile organic compounds (Z)-hex-3-en-1-ol, (E)-hex-3-en-1-ol, (Z)-hex-4-en-1-ol and (E)-hex-4-en-1-ol were determined theoretically, and the standard enthalpy and Gibbs energies of formation for these species were calculated. According to our knowledge, there are no values in the literature for comparison, but the high level of calculation used enables us to say that our results are reliable. This is the first structural and thermochemical characterization of these compounds and these values are will be useful in a future study of the atmospheric decomposition of these compounds.

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¹ M. E. Davis, J. B. Burkholder, *Atmos. Chem. Phys.*, 11, 3347 (2011).