

OH radical initiated oxidation of the volatile organic compound 3-methyl-3-buten-1-ol under atmospheric conditions

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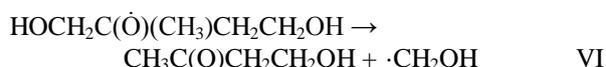
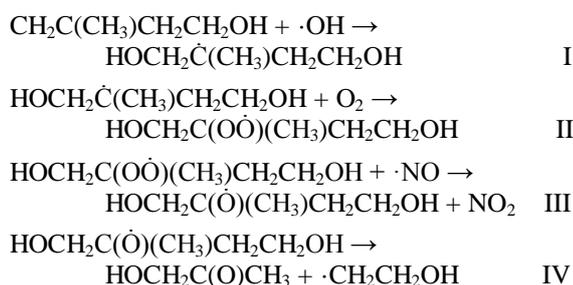
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INTRODUCTION

Unsaturated alcohols are important constituents of the volatile organic compounds (VOC) emissions. Products of its atmospheric decomposition can lead to the formation of secondary organic aerosols, which are involved in the climate regulation of the planet. The reactions of a lot of unsaturated alcohols with the atmospheric oxidants OH, NO₃ and Cl have been studied, but investigations about mechanism or product determination are scarce, because these reactions generate several intermediate radical whose decomposition can occur in several steps. In this way, performing a thermochemical study may be useful to determine the viability of possible steps before a kinetic investigation. In this work, we have investigated the thermochemistry of the atmospheric decomposition of the 3-methyl-3-buten-1-ol by ·OH radical, considering several steps of reaction.

METHODS

All species were optimized and frequencies calculations were done at the MP2/cc-pVTZ level of theory. Single point calculations were done at the MP2/cc-pVDZ, MP2/cc-pVQZ and CCSD/cc-pVTZ levels in order to achieve the limit for an infinite basis set function and a better accuracy to the electron correlation. In this way, our best level of calculation is CCSD/CBS. Based on mechanisms proposed to similar reactions, the following reaction steps were considered:



RESULTS AND DISCUSSION

The enthalpies and Gibbs free energies of reaction for the six steps investigated are presented in Table 1. Steps I to III are exothermic and spontaneous. Considering that they are consecutive, we can say that this sequence of steps will be exothermic and spontaneous too. Steps IV to VI represent different possibilities of decomposing the radical HOCH₂C(·O)(CH₃)CH₂CH₂OH and they are competitive. Although the three steps being spontaneous, only the Step IV is exothermic, indicating that it may be preferential.

Table 1. Reaction enthalpies and Gibbs free energies for the reaction steps investigated.

Step	ΔH _r / kJ mol ⁻¹	ΔG _r / kJ mol ⁻¹
I	-116.4	-75.2
II	-127.5	-74.5
III	-17.1	-20.7
IV	-2.8	-60.8
V	16.5	-37.8
VI	30.7	-33.7

CONCLUSIONS

The thermochemistry of the first steps of the reaction of atmospheric decomposition of the 3-methyl-3-buten-1-ol with ·OH radical was investigated theoretically. Our results show that steps I to III can be occur consecutively. Concerning considering the competitive steps (IV to VI), only step IV is thermodynamically feasible. Kinetic studies are in progress.

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