Decomposition of 1-propenol: theoretical investigation

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Research into unimolecular decomposition can provide valuable insights about complex chemical dynamics of combustion systems. Moreover, it also suggests paths by which large molecules can be formed for example in astrochemistry.

In present work we studied thermal decomposition of 1-propenol theoretically using quantum chemistry tools which allow one to achieve errors of relative energies less than 1 kcal mol^{-1} according to the assessment by Zhang and Valeev [1]. The C_3H_6O-PES was compiled using geometry optimization of local minima (reactants, intermediates, and products) and transition states at the density functional B3LYP/6-311G(d,p) level of theory [2,3]. Energies of structures were refined by singlepoint calculations that employed the explicitly-correlated coupled clusters CCSD(T)-F12 [4,5] method with Dunning's correlation-consistent cc-pVTZ (E_{TZ}) and cc-pVQZ (E_{QZ}) basis sets [6]. Then final values (E_{CBS}) were calculated for the complete basis set limit $E_{CBS} = E_{QZ} + 0.69377 \cdot (E_{QZ} - E_{TZ})$.

The constructed PES profile suggests that the decomposition of cis- and trans-1-propenol will be carried out mainly by two mechanisms - this is the direct detachment of a hydrogen molecule with the formation of acrolein and, through an intermediate transition to propanal, decomposition into 3 molecules: ethylene, carbon monoxide and hydrogen. For reverse fusion, the $CCH_2 \rightarrow 2-$ propenol $\rightarrow$ acetone $\rightarrow$propanal $\rightarrow$ cis-/transpropenol mechanism seems to be the most promising taking into account only energy requirements. The second variant, although it has a higher barrier, stems from more stable acrolein and hydrogen molecules which recombination immediately leads to propenol. The reactions of ethynol with methane and propyne with water, another possible routes to initial reagent, are characterized by higher (by approximately 20 kcal/mol) barriers. The barrier for the three-molecular mechanism $C_2H_4+CO+H_2 \rightarrow$ cis-/transpropenol is approximately 10 kcal/mol lower than for the previous two pathways, but such collisions are much more rare.

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