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Variational Transition State Theory Calculations of the Hydrogen Abstraction Reactions O (^{3}P) + *cis*-CH_3OCHO: Effects of Multidimensional Tunneling on the Rate constants and Branching Ratio

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Abstract: Thermal rate constants and product branching ratio of hydrogen abstraction from *cis*-CH_3OCHO by O (^{3}P) giving as products CH_3OCO + OH (R1) and CH_2OCHO + OH (R2) [1] were computed with variational transition state theory including microcanonically optimized multidimensional tunneling. The dynamics calculations include anharmonicity and hindered rotational corrections for the torsion around the C–O bond in methyl formate. Benchmark calculations of barrier heights and the reaction energetic have been carried out by coupled cluster theory with extrapolation to the complete basis set (CBS) limit method [2] using various basis sets. $CBS/_{D-T}$ results for enthalpy of reaction at 0 K for R1 (–3.1 kcal/mol) and R2 (–2.7 kcal/mol) are in good agreement with the values obtained through the Hess' law a 298 K, i.e. –2.61 and –1.81. At 298 K, the calculated value of the rate constant with the CVT/μOMT method is 8.1 x 10^{-15}cm^{3}molecule^{-1}s^{-1} which agrees well with the single-temperature discharge-flow measurement value of 9.3 x 10^{-15} cm^3 molecule^{-1} s^{-1} [3]. The branching ratio predict by the present work shows that the formation of CH_3OCO + OH (R1) reaction path is the dominant reaction path from 200 to 1300 K.

Key-words: methyl formate; hydrogen abstraction; M06-2X, CCSD(T), rate constants
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