

Chemical kinetics of the $\text{CH}_3\text{CH}_2\text{SH} + \text{H}$ abstraction and bond breaking reactions: influence of the methodology on the tunneling effects

Leonardo A. Cunha¹(IC), Daniely V. V. Cardoso¹(PG), Luiz F. A. Ferrão¹(PQ), Rene F. K. Spada¹(PD), Orlando Roberto-Neto²(PQ)*, Francisco B. C. Machado²(PQ)

¹Instituto Tecnológico de Aeronáutica (ITA), São José dos Campos-SP

²Instituto de Estudos Avançados (IEAv), São José dos Campos-SP

*orlando@ieav.cta.br

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INTRODUCTION

An unquestionable fact is that organic sulfur compounds play an important role on human daily life.^{1,2} We studied elementary reactions involving the $\text{CH}_3\text{CH}_2\text{SH}$ molecule and the hydrogen atom (R1-A and R1-B: $\text{CH}_2\text{CH}_2\text{SH} + \text{H}_2$; R2: $\text{CH}_3\text{CHSH} + \text{H}_2$; R3: $\text{CH}_3\text{CH}_2\text{S} + \text{H}_2$ and R4: $\text{CH}_3\text{CH}_2 + \text{H}_2\text{S}$). Two different electronic structure methods are employed and the results are compared.

METHODS

The geometries of the stationary points of the minimum energy paths (MEP) for each reaction path were optimized using the BB1K/maug-cc-pV(D+d)Z and MP2/6-311+G(2d,p) methods. The thermochemical properties were refined using the single-point coupled-cluster (CCSD(T)) calculations, followed by the extrapolation to the complete basis set (CBS), which usually gives reliable results when compared with experimental data.²⁻⁴ The thermal rate constants were calculated using the canonical variational transition state (CVT) method including the zero-curvature tunneling (ZCT) and small-curvature tunneling (SCT) corrections. GAUSSIAN G09 and POLYRATE codes were used to carry out electronic structure and rate constants calculations, respectively.

RESULTS AND DISCUSSION

The lowest adiabatic barriers are $1.51 \text{ kcal}\cdot\text{mol}^{-1}$ and $2.34 \text{ kcal}\cdot\text{mol}^{-1}$, respectively, computed with CCSD(T)/CBS//MP2 and CCSD(T)/CBS//BB1K methods (Table 1) for the hydrogen abstraction involving the -SH group (R3). The imaginary frequencies of the transition states of R3 are $822i$ and $1688i$, respectively, calculated with the BB1K and MP2 methods. Calculated thermal rate constants are given in Figure 1. At 298 K, the CVT/SCT rate constants obtained with MP2 method agree well with experimental data^{3,4} and with previous theoretical results⁵

Table 1. Energetics (kcal/mol) calculated with CCSD(T)/CBS//BB1K and CCSD(T)/CBS//MP2 (in parentheses) methods.

	$\Delta V_a^{G,\#}$	$\Delta H_0^\#$		$\Delta V_a^{G,\#}$	$\Delta H_0^\#$
R1-A	10.63	-3.28	R3	2.34	-17.98
	(10.63)	(-3.15)		(1.51)	(-18.01)
R1-B	11.05	-3.28	R4	3.76	-17.82
	(11.17)	(-3.15)		(3.41)	(-17.41)
R2	6.87	-10.39			
	(6.78)	(-10.06)			

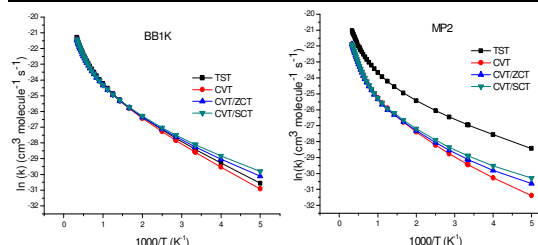


Figure 1. BB1K and MP2 rate constants.

CONCLUSIONS

The MP2 method overestimates the values of the imaginary normal mode frequencies resulting in a sharp potential energy surface and higher values of tunneling coefficients. Despite of the small difference between the adiabatic barriers calculated with the MP2 and BB1K methods, variational effects and SCT corrections play an important role, especially for the rate constants calculated with the MP2 method.

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