Thermochemical and Kinetics studies of the H (^{2}S) + CH_3SH reaction

Daniely V. V. Cardoso[1] (PG) *, Leonardo A. Cunha[1] (IC), Rene F. K. Spada[1] (PQ), Luiz F. A. Ferrão[1] (PQ), Corey A. Petty[1] (PQ), Orlando Roberto-Neto[2] (PQ), Francisco B. C. Machado[1] (PQ)

[1] *Departamento de Química, Instituto Tecnológico de Aeronáutica, São José dos Campos-SP, Brazil*
[2] *Departamento de Química, Instituto de Estudos Avançados (IEAv), São José dos Campos-SP, Brazil*
**daniely@ita.br*

Keywords: methanethiol, CCSD(T), DFT, elementary reactions, rate constants.

INTRODUCTION

Sulfur-containing molecules have a significant impact on the atmosphere and biosphere [1]. In this work, we study the reaction system formed by the methanethiol molecule (CH_3SH) and a hydrogen atom. Specifically, the elementary reaction of hydrogen abstractions (R1 = $CH_3SH + H \rightarrow CH_3S + H_2$; R2= $CH_3SH + H \rightarrow CH_2SH + H_2$) and cleavage (R3= $CH_3SH + H \rightarrow CH_3 + H_2S$). These elementary reactions are studied by utilizing electronic structure and chemical kinetics methodologies.

METHODS

The geometrical structures of the reactants, products, and transition states for the three reaction paths were optimized using BB1K with the aug-cc-pV(T+d)Z basis set. The thermochemical properties were refined using single-point coupled-cluster (CCSD(T)) calculations on the BB1K geometries, followed by extrapolation to the complete basis set (CBS) limit. For each reaction path, the thermal rate constants were calculated using the Improved Canonical Variational Transition State (ICVT) including the zero-curvature tunneling (ICVT/ZCT) and the small-curvature tunneling (ICVT/SCT). All electronic structure calculations were carried out with the Gaussian G09 code and the thermal rate constants were computed with the Polyrate program.

RESULTS AND DISCUSSION

Figure 1 presents the adiabatic energy profile of studied reaction paths obtained with BB1K and single-point CCSD(T). The lowest adiabatic barriers calculated with these methods are 2.17 and 2.33 kcal.mol^{-1}, respectively, which correspond to the hydrogen abstraction from the thiol group (R1).

Figure 2 shows the Arrhenius plot of the overall rate constants for this reaction system (CH_3SH+H). The kinetic parameters obtained are of the same order of magnitude of previous experimental and theoretical data [2–4].

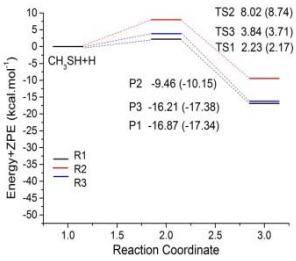

Figure 1: Adiabatic energy profile for the three reaction paths.

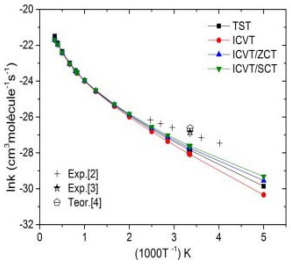

Figure 2: Overall rate constants for the CH_3SH + H reaction.

CONCLUSIONS

The reaction path R1, corresponding to the hydrogen abstraction from the thiol group (–SH) is the most important in all temperatures. The ICVT/SCT results for the overall rate constants at 298 K ($k_{ICVT/SCT}$= 1.0 x 10^{-12} cm^{3}molecule^{-1}s^{-1}) are in good agreement with the available experimental data (k_{exp}= 2.0–2.2 x 10^{-12} cm^{3}molecule^{-1}s^{-1}).

ACKNOWLEDGMENTS

The authors are grateful for the support given from the FAPESP, CNPQ and CAPES.

[1] T. E. Graedel, Chemical Compounds in the Atmosphere, Academic, New York, 1978.
[2] P. H. Wine, et al. J. Phys. Chem., v. 85, n. 18, p. 2660–2665, (1981).
[3] D. Martin, et al. Int. J. Chem. Kinet., v. 20, n. 11, p. 897–907, (1988).
[4] Y. X. Wang et al. Acta Physico-Chimica Sinica, v. 26, n. 1, p. 183-187, (2010).