



## Hydrogen Abstraction from the Hydrazine Dimer by an Oxygen Atom

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### INTRODUCTION

The hydrazine molecule ( $N_2H_4$ ) is used as propellant for the attitude-control jets in spacecraft vehicles, as well as satellites. Some of these spacecrafts are in a low earth orbit, above 180 km with a temperature around 880 K, in an ambient atmosphere where ground-state oxygen is abundant. Although the majority of the propellant is consumed in the chamber, some is ejected unburned into the atmosphere, especially during the engine shutdown.

In an earlier work<sup>1</sup> we investigated the dehydrogenation of the hydrazine monomer. In this work, we considered the hydrazine dimer dehydrogenation through four reaction paths, all of them leading to different isomers of  $N_2H_4 \cdot N_2H_3 + OH$ .

### METHODOLOGY

The thermochemical properties were acquired using the CCSD(T) methodology and the M06-2X DFT functional with the aug-cc-pVXZ ( $X = T, Q$ ) and the maug-cc-pVTZ basis sets, respectively. The chemical kinetic properties were calculated with the ICVT approach using the dual-level methodology to build the reaction path. The non-classical effects were considered by means of the SCT approximation. Wells in both sides of the reaction (reactants and products) were found and considered in the chemical kinetics calculations.

### RESULTS AND DISCUSSION

Considering the energy of the reaction, the M06-2X functional predicts values between -17.8 and -20.0 kcal/mol and the CCSD(T) ones are in the interval from -16.2 to -17.8 kcal/mol. For the reactant well and product well, the M06-2X method predicts higher stabilization energies than the CCSD(T), with the larger difference being

4.2 kcal/mol. As these reaction paths present low barriers, using a high correlated methodology is extremely important. We observed that the DFT functional predicts adiabatic barriers below zero, while the CCSD(T) method returns a negative value only for one reaction path (-0.8 kcal/mol). For the other reaction paths, the adiabatic barriers are equal to 2.2, 3.3 and 1.5 kcal/mol.

The calculated rate constants are in good agreement with the literature.<sup>2</sup> The measured value is equal to  $6.2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$  and the calculated result for the most important reaction path is  $4.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ . This reaction path presents a negative temperature dependence in the range of 250 – 400 K. This behavior is also observed experimentally.<sup>2</sup>

### CONCLUSIONS

A reaction path with a negative adiabatic barrier was found and the rate constant exhibits a negative dependence with the temperature below 400 K, agreeing with the experimental measurements.<sup>2</sup> The rate constant results considering the hydrazine dimer are in better concordance with the experimental results by Vaghjiani<sup>2</sup> than our results in a previous work<sup>1</sup> considering the hydrazine monomer. Since Vaghjiani measured the oxygen depletion in a hydrazine atmosphere, it suggests that the hydrazine dimer can play an important role in the mechanism of the global  $N_2H_4 + O$  global reaction.

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<sup>1</sup> Spada, R. F. K., *et al.*, J. Phys. Chem. A, 119 (9), 1628, (2015).

<sup>2</sup> Vaghjiani, G. L., J. Chem. Phys., 104, 5479, (1996).