Theoretical study of the H_2 + PtO^+ reaction by relativistic methods

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INTRODUCTION

Quantum chemistry has been widely used in kinetics studies of chemical. However, the investigation of the variations caused by relativistic effects over these quantities is still at an early stage.[1]

Recently, Tong and co-workers have made a theoretical study about the activation of H_2 by PtO_2^+ and PtO^+ using the Relativistic Effective Core Potential (RECP) method.[2] Thus, our goal was to analyze the reaction of H_2 with PtO^+ by other relativistic methods: Second-Order Douglas-Kroll-Hess (DKH2) and Zeroth Order Regular Approximation (ZORA).

METHODS

We studied the following reaction:[2]

$$PtO^+ + H_2 \rightarrow Pt^+ + H_2O$$
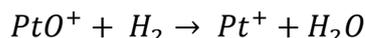
All calculations (geometry optimization, vibrational frequency and Intrinsic Reaction Coordinate-IRC) were performed with the ORCA package[3] by means of the relativistic approximations DKH2 and ZORA, using Density Functional Theory (DFT) with the B3LYP functional and def-SVP basis sets.

RESULTS AND DISCUSSION

First, through optimization and frequency calculations, it was possible to determine the transition states (TSs) and molecular intermediates (MIs) of the studied reaction. In order to characterize these transition states (Figure 1) we performed IRC calculations.

As one can see, both the relativistic methods chosen here have demonstrated similar reaction coordinate profiles (Figure 2). The activation enthalpy (ΔHa) associated with the first transition state (TS1) is 16.4 kcal mol^{-1} according with ZORA and DKH2 approaches. Moreover, the ΔHa values obtained from TS2 are around 25 kcal mol^{-1}.
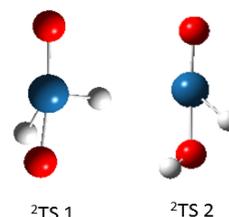

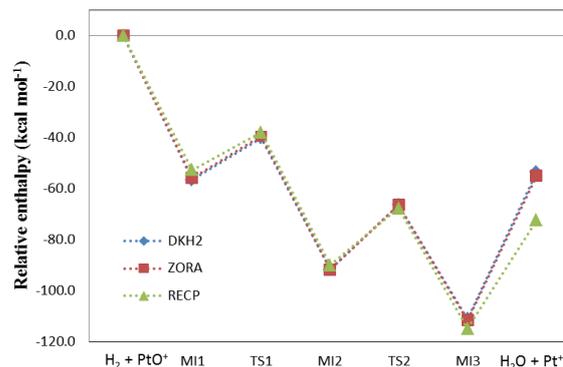Figure 1: Transition state structures optimized by DKH2 – B3LYP/def-SVP calculations

Figure 2: Energetic profile for the reaction H_2 + $PtO^+ \rightarrow Pt^+ + H_2O$

CONCLUSION

The methods used here were able to describe adequately the studied reaction. The activation barriers of the rate determining step obtained by both alternative treatments were very similar.

ACKNOWLEDGMENTS

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