Study of Aromatic + OH Reactions at the Density Functional Theory Level

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Keywords: 2,5-Dimethylfuran, Benzene, Toluene, Aromatic + OH, Variational Rate Coefficients

INTRODUCTION

Theoretical description of the reactions of OH radicals with unsaturated compounds has received great attention on the last years. OH addition is believed to be main channel, at atmospheric conditions, following a mechanism in which a pre-barrier complex is reversibly formed and further reacts, forming a radical. The successful performance of the BHandHLYP functional in describing OH reactions with alkenes has been demonstrated.[1]

In this work, a more difficult case is evaluated: the OH reactions with aromatic compounds. Three models for aromatic + OH reactions were studied: 2,5-dimethylfuran (DMF), benzene (Bz) and Toluene (Tol). Our main goal is to assess the possibility of describing the reaction kinetics at the DFT level.

METHODS

Theoretical calculations for the DMF + OH, Bz + OH and Tol + OH reactions include geometry optimizations and vibrational frequencies and reaction path calculations at DFT level, adopting the BHandHLYP and M06-2X functionals and the aug-cc-pVDZ (ACCD) basis set. Single point calculations at the CCSD(T) level have also been performed. Variational rate coefficients were finally calculated in the range from 200 – 500 K.

RESULTS AND DISCUSSION

Our BHandHLYP calculations for the DMF + OH reactions suggest that a π-prebarrier complex is formed, stabilized by 2.78 kcal mol^{-1} (including zero point energy corrections). Saddle points for the C2 and C3 additions have been located, with relative energies -1.37 and 2.22 kcal mol^{-1}, respectively. Differently, a σ-prebarrier complex has been located at M06-2X level, with relative energy -5.68 kcal mol^{-1}. The Saddle points, despite the geometrical resemblance with the BHandHLYP saddle points, show relative energies -5.27 and -2.16 kcal mol^{-1}. CCSD(T) single point calculations have been performed, supporting the M06-2X results. Rate coefficients have been calculated on the basis of both CCSD(T)//BHandHLYP and CCSD(T)//M06-2X results, showing good agreement with the experimental value,[2] at 298 K ($k^{predicted}/k^{literature}$ = 2).

For Bz and Tol, the BHandHLYP functional was unable to predict a prebarrier complex, and saddle points have been located above the isolated reactants. At the M06-2X level, the relative energies found for the prebarrier complex and saddle point for the OH addition to Bz were -5.15 and 0.24 kcal mol^{-1}, respectively. Rate coefficients have been predicted at the M06-2X level and compared to literature data.[3] The ratio $k^{predicted}/k^{literature}$ = 30, for T = 298 K, has been achieved. Hydrogen abstraction shows minor contribution to the global rate coefficient at room temperature. Similar results for the Tol + OH reaction have been obtained.

CONCLUSIONS

The OH reactions with aromatic compounds can be satisfactorily described at the M06-2X level but not at the BHandHLYP level, despite the good performance of the latter function in describing OH reactions with simple alkene compounds. Kinetic results, based on a mechanism in which a σ-type prebarrier complex is formed, are generally found in good agreement with the experimental values.

ACKNOWLEDGMENTS

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