

Theoretical Investigation of the Formaldehyde Gas-Phase Reaction with Chlorine Atoms

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INTRODUCTION

In recent years, an increasing interest in chlorine atom reactions with volatile compounds at atmospheric conditions is observed. Formaldehyde is an important atmospheric compound, for which only few works were dedicated to the determination of rate coefficients and the comprehension of the Cl reaction mechanism.^{1,2} Despite the effort in explaining the reaction energetics and activation parameters for the H₂CO + Cl reaction, the role played by pre-barrier intermediates and satisfactory rate coefficients prediction remain unclear.

In this work, several theoretical methods are employed for studying the H₂CO + Cl reaction path and rate coefficients are predicted from a chemical model explicitly taking into account the participation of a pre-barrier complex. Our main goals are the comprehension of the reaction energetics and the discussion about the reaction mechanism.

METHODS

H₂CO + Cl reaction was studied at *ab initio* (MP2, CCSD and QCISD) and DFT (B2PLYP, BHandHLYP) levels, adopting the aug-cc-pVDZ (ACCD) and aug-cc-pVTZ (ACCT) basis sets. Single point calculations at CCSD(T) and QCISD(T) levels were also performed. Canonical variational rate coefficients were finally calculated in the range from 200 – 500 K.

RESULTS AND DISCUSSION

Molecular properties were predicted for reactants and products of the H₂CO + Cl reaction in reasonable agreement with the literature data, as evidenced by rms deviations lower than 0.05 Å, 5° and 300 cm⁻¹.

Stabilization energies regarding the pre-barrier intermediates have been found in the range from 4.8 to 1.8 kcal mol⁻¹ (the highest value has been

obtained at B2PLYP level and the lowest value, at the MP2 level).

Previous MRD-CI calculations suggested the saddle point relative energy as 0.17 kcal mol⁻¹.⁴ Our results were found in the range from -0.42 to 1.5 kcal mol⁻¹. Inclusion of zero point energy corrections cause these values to decrease and our resulting B2PLYP value (-0.47 kcal mol⁻¹) agrees with the MRD-CI prediction (-0.5 kcal mol⁻¹).³

Canonical variational rate coefficients were predicted at 200 – 500 K. Rate coefficients were predicted (in 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ units, at 298 K) in the range from 0.56 – 54, in agreement with the experimental value (7.8), the best values being: $k_{B2PLYP} = 5.3$, $k_{CCSD} = 2.0$, $k_{QCISD} = 4.7$ and $k_{CCSD(T)/B2PLYP} = 10$. Activation energies^{3,4} are found in the range 0.07 – 0.26 kcal mol⁻¹, whereas our best values vary from 0.02 to 0.23 kcal mol⁻¹.

CONCLUSIONS

In this work, the proposal of a reaction mechanism with explicitly participation of the pre-barrier complex is made and variational rate coefficients were predicted, in good agreement with experimental data. Our results suggest that the reaction dynamics can be satisfactorily described from the mechanism in which the pre-barrier intermediate plays a key role.

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