

PREDICTIVE THEORY FOR THE ADDITION KINETICS OF $^1\text{CH}_2$ WITH UNSATURATED HYDROCARBONS

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Abstract

The combination of methylene with unsaturated species is an important class of reactions that can lead to the growth of aromatic compounds. For example, propargyl radical (C_3H_3) is thought to be an important precursor for the formation of aromatic and soot compounds[1] and one of the main routes to propargyl formation is the reaction of the first excited state of methylene, $^1\text{CH}_2$, with acetylene. Similarly, the addition of singlet methylene to ethylene yields allyl radical, which has also been postulated to be important in the formation of the first aromatic ring. Meanwhile, its addition to benzene yields toluene and/or benzyl radical, which may be a key step in the expansion from the first to the second aromatic ring. In this work we apply the direct variable reaction coordinate transition state theory (VRC-TST) approach[2-5] to the quantitative prediction of the addition kinetics for these three reactions. In order to identify the better approach to employ for the direct evaluations of the interaction energies, we investigated the effect of the method, the active space and basis set on the accuracy of the potential energy surface for the methylene plus acetylene benchmark reaction. In Fig. 1 results are shown for calculations of the approximate minimum energy path potential at the CASPT2, CAS+1+2+QC, and CCSD(T) levels along the distance between methylene carbon atom and the centre of mass (CoM) of acetylene. The CASPT2 results are in remarkably good agreement with the CCSD(T) results with a deviations of less than 5%. The CAS+1+2+QC results are also in good agreement with the CCSD(T) ones, but with a somewhat larger maximum deviation of about 13%. These results provided the motivation for our decision to employ the CASPT2 method in our direct evaluation of the interaction energies within the VRC-TST simulations. The excellent agreement between the CASPT2(2e,2o) and CCSD(T) calculations suggests that the (2e,2o) active space is adequate. Nevertheless, it is interesting to examine the effect on the CASPT2 predictions of including the π and π^* orbitals of acetylene to obtain a (6e,6o) active space. The dimension of the active space has only a minor affect on the potential energy surface, further confirming the appropriateness of the (2e,2o) space.

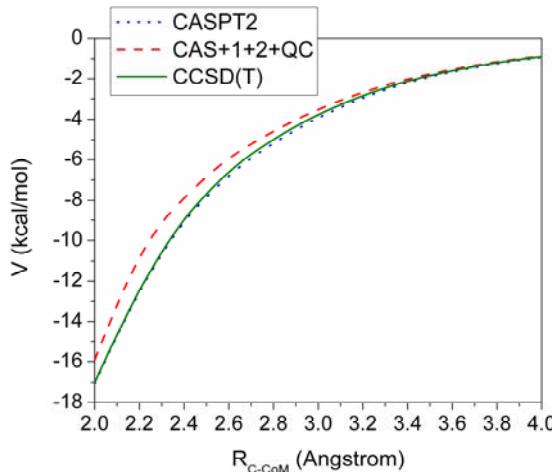


Figure 1. One-dimensional potential energy surface for $^1\text{CH}_2 + \text{C}_2\text{H}_2$ with CASPT2/cc-pVDZ (blue dotted), CAS+1+2+QC/cc-pVDZ (red dashed) and CCSD(T)/cc-pVDZ (green solid) calculations.

Finally, we investigated the dependence on the size of the basis set with CASPT2(2e,2o) calculations using Dunning's correlation consistent polarized valence double, triple and quadruple- ζ basis sets. The results are illustrated in Fig. 2 where it can be seen that increasing the basis set from double- ζ to triple- ζ yields a significantly more attractive potential, with a maximum deviation of 20% at a C-CoM distance of 2 Å. In contrast, the increase from triple- ζ to quadruple- ζ does not substantially modify the PES, with a maximum deviation of only 4%. The relatively modest extent of the increased attractiveness for the basis set limit implies that the present scheme based on explicit cc-pVDZ orientational samplings coupled with one-dimensional corrections for the effect of the basis set on the minimum energy path potential should be satisfactory.

One-dimensional corrections (ΔV_{corr}) to these interaction energies are obtained from geometry relaxation calculations and CCSD(T)/CBS evaluations as described by the following expression:

$$\Delta V_{corr} = \left[E(\text{CCSD}(T)/\text{CBS}) - E(\text{CASPT2}/\text{cc}-\text{pVDZ})_{\text{fixed}} \right] + \left[E(\text{CASPT2}/\text{cc}-\text{pVDZ})_{\text{relaxed}} - E(\text{CASPT2}/\text{cc}-\text{pVDZ})_{\text{fixed}} \right] \quad (1)$$

In this expression, the subscript "fixed" means that the calculations were carried out while keeping the geometries fixed at their asymptotic equilibrium geometries, while the subscript "relaxed" corresponds to energy evaluations allowing for the relaxation of the internal degrees of freedom of the two fragments. The term in the first brackets accounts for limitations in the accuracy of the CASPT2/cc-pVDZ method. This correction is based on CCSD(T)/CBS(cc-pVTZ;cc-pVQZ)[6-7] one-dimensional orientation independent evaluations along the minimum energy path.

The extrapolation to the complete basis set limit was obtained using the scaling coefficient proposed by Martin.[8] The term in the second brackets accounts for the contribution due to the relaxation of the conserved modes. To obtain this correction we optimized the internal fragment geometries (at the CASPT2/cc-pVDZ level) at various points along the reaction coordinate, while also constraining the relative orientation of the two fragments.

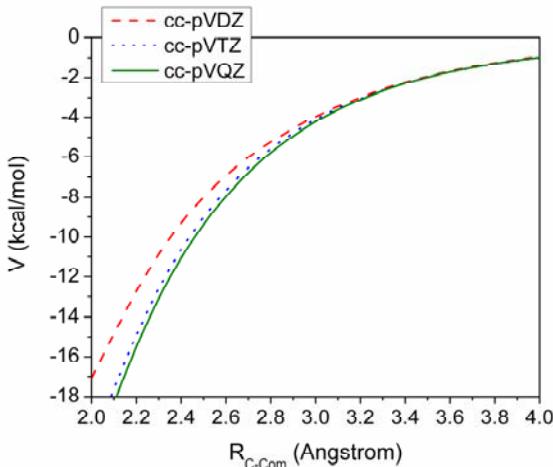


Figure 2. Potential energy surface for $^{1}\text{CH}_2 + \text{C}_2\text{H}_2$ with CASPT2(2e,2o) calculations employing a cc-pVDZ (blue dotted), cc-pVTZ (red dashed) or cc-pVQZ (green solid) basis set.

The present dynamically corrected VRC-TST predictions for the temperature dependent rate coefficient, based on the corrected CASPT2/cc-pVDZ energies, are plotted in Fig. 3 for the addition reaction of $^{1}\text{CH}_2$ with acetylene. These rate predictions are plotted together with a $\pm 10\%$ confidence limit that reflects the uncertainty level adopted for the Monte Carlo simulations. The variations in the various correction terms discussed above suggest that the overall uncertainty in the rate predictions is on the order of 20-30%. The experimental data and theoretical results available in the literature are also compared with these predictions. The calculated VRC-TST rate coefficient is in very good agreement with the numerous experimental rates measured at room temperature (Canosa-Mas et al.[9], Hack et al.[10], Hayes et al.[11], Adamson et al.[12]). Moreover, our predictions quantitatively reproduce the temperature dependence found in the experimental work of Blitz et al.[13] and Gannon et al.[14]. Prior theoretical studies of this particular reaction carried out by Guadagnini et al.[15], and by Yu and Muckerman[16], fail to reproduce the observed temperature dependence. In contrast, the corrected direct CASPT2/cc-pvdz VRC-TST approach provides quantitatively accurate predictions for the rate constant of the $^{1}\text{CH}_2 + \text{C}_2\text{H}_2$ combination reaction and reproduces the negative temperature dependence found in the experimental works of Blitz et al.[13] and Gannon et al.[14]. It is important to point out that all the experimental

data are based on removal measurements of ${}^1\text{CH}_2$ and thereby contain information about both reaction with acetylene and physical deactivation to the triplet ground state. Hack et al.[10] measured the contribution from relaxation to the total removal rate of singlet methylene in the presence of acetylene to be 0.22 ± 0.07 at room temperature. Hence, all experimental results shown in Fig. 3 were plotted after subtracting this contribution, which was maintained constant for all temperatures. This choice is motivated by the lack of experimental data on the temperature dependence of physical deactivation.

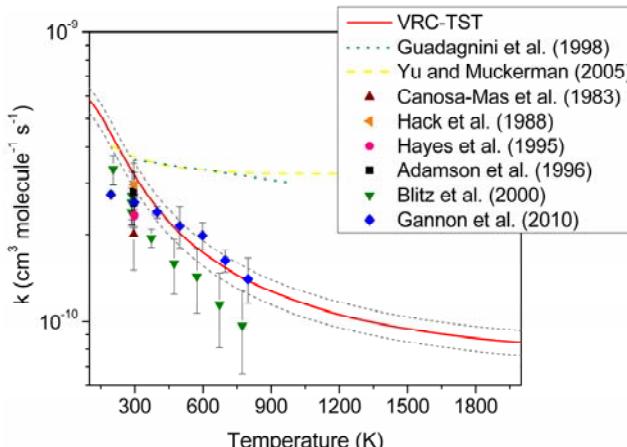


Figure 3. VRC-TST high pressure limit rate coefficient for the ${}^1\text{CH}_2 + \text{C}_2\text{H}_2$ reaction (solid red line) with 10% confidence limit compared with experimental measurements (symbols) and other theoretical predictions.

The present dynamically corrected VRC-TST predictions for the temperature dependent rate coefficient in the reaction of singlet methylene with ethylene is plotted in Fig. 4 together with the available experimental data (Langford et al.[17], Canosa-mas et al.[9], Hack et al.[18], Wagener[19] Staker et al.[20] Hayes et al.[11, 21] and Gannon et al.[14]). These calculations also employed a corrected CASPT2/cc-pVDZ potential. However, in this case it was necessary to introduce a 4 electron 4 orbital CAS active space in order to correctly follow the potential energy surface. The present a priori predictions again show good agreement with both the rate values measured at room temperature, and also the temperature dependence found by Gannon et al.[14]. The plotted experimental values were again reduced by a temperature independent factor of 20%, in order to account for the contribution from deactivation to the measured total removal rates. The predicted addition rate constant of singlet methylene to benzene is plotted in Fig. 5 along with the experimental data from the works of Hack et al.[10], Wagener[19] and Hayes et al.[21]. Again the agreement with their measurements is satisfactory, as we underestimate their values by less than a factor of two, which is essentially within the error bars.

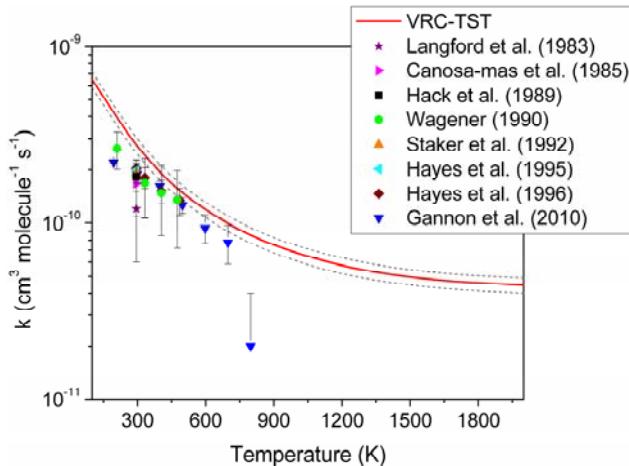


Figure 4. VRC-TST high pressure limit rate coefficient for the $^1\text{CH}_2 + \text{C}_2\text{H}_4$ reaction (solid red line) with 10% confidence limit compared with experimental measurements (symbols) and other theoretical predictions.

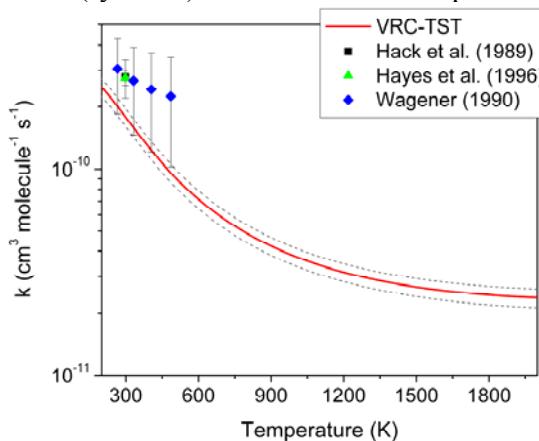


Figure 5. VRC-TST high pressure limit rate coefficient for the $^1\text{CH}_2 + \text{C}_6\text{H}_6$ reaction (solid red line) with 10% confidence limit compared with experimental measurements (symbols) and other theoretical predictions.

The generally good agreement found in the comparisons with experimental data suggests that the dynamically corrected VRC-TST approach adopted in this study provides a reliable treatment of the high pressure rate coefficients for the addition of singlet methylene to unsaturated hydrocarbons. Moreover the extension of the predictions to higher temperatures yield important new data for combustion modelers.

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