Predictive Theory for the Addition Kinetics of $^{1}CH_{2}$ with Unsaturated Hydrocarbons

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The combination of methylene with unsaturated species is an important class of reactions that can lead to the growth of aromatic compounds, a crucial issue in combustion chemistry. For example, propargyl radical (C_3H_3) is thought to be an important precursor for the formation of aromatic and soot compounds (Leung and Lindstedt 1995)[1] and one of the main routes to propargyl formation is the reaction of the first excited state of methylene, $^{1}CH_2$, 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 to the quantitative prediction of the addition kinetics for these three reactions. We employ direct evaluations of the orientation dependent interaction energies at the CASPT2/cc-pVDZ level, with the CAS space consisting of two orbitals and two electrons. One dimensional corrections to these interaction energies are obtained from geometry relaxation calculations and CCSD(T)/CBS evaluations. For the $^{1}CH_2 + C_2H_2$ reaction the rate coefficient been measured by several authors at room temperature (Canosa-Mas et al.[2], Hack et al.[3], Hayes et al.[4], Adamson et al.[5]), while only Blitz et al.[6] and Gannon et al.[7] have made more comprehensive temperature dependent kinetic analyses (205-773 K). Prior theoretical studies of this particular reaction carried out by Guadagnini et al.[8], and by Yu and Muckerman[9], 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 $^{1}CH_2 + C_2H_2$ combination reaction and reproduces the negative temperature dependence found in the experimental works of Blitz et al.[6] and Gannon et al.[7]. The extension to the reactions with ethylene and benzene yield important new data for combustion modelers.

References

(1) Leung, K.M.; Lindstedt, R.P. *Combust. Flame* **1995**, 102, 129.
(2) Canosa-Mas, C.E., Frey, H.M.; Walsh, R. *J. Chem. Soc. Fraday Trans. 2* **1985**, 81, 283-300.
(3) Hack, W.; Koch, M.; Wagner, H.G.; Wilms, A. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1988**, 92, 674
(4) Hayes, F.; Gutsche, G.J.; Lawrance, W.D.; Staker, W.S.; King, K.D. *Combust. Flame* **1995**, 100, 653.
(5) Adamson, J.D.; Morter, C.L.; DeSain, J.D.; Glass, G.P.; Curl, R.F. *J. Phys. Chem.* **1996**, 100, 2125-2128
(6) Blitz, M.A.; Beasley, M.S.; Pilling, M.J.; Robertson, S.H. *Phys. Chem. Chem. Phys*. **2000**, 2, 805-812.
(7) Gannon, K.L.; Blitz, M.A.; Liang, C.H.; Pilling, M.J.; Seakins, P.W.; Glowacki, D.R. *J. Phys. Chem. A* **2010**, 114, 9413-9424
(8) Guadagnini, R; Schatz, G.C.; Walch, S.P. *J. Phys. Chem. A* **1998**, 102, 5857-5866
(9) Yu, H.-G.; Muckerman, J.T. *J. Phys. Chem. A* **2005**, 109, 1890-1896