

Materials and Methods

Experimental: The experiments were conducted under single collision conditions utilizing a universal crossed molecular beam machine.^[1] The dicarbon beam, $C_2(X^1\Sigma_g^+, a^3\Pi_u)$, was generated via laser ablation of graphite by seeding the ablation species in helium gas. The molecular beam passed a skimmer and a four-slot chopper wheel, which selected a segment of the pulsed dicarbon beam with a well-defined peak velocity of $2077 \pm 50 \text{ ms}^{-1}$ and speed ratio 2.0 ± 0.4 . The segment of the pulsed dicarbon beam then crossed a pulsed 2-methyl-1,3-butadiene beam perpendicularly in the interaction region. The 2-methyl-1,3-butadiene peak velocity of $720 \pm 10 \text{ ms}^{-1}$ and speed ratio 8.3 ± 0.2 results in a collision energy of $42.7 \pm 1.5 \text{ kJ mol}^{-1}$ and center-of-mass angle $44.1 \pm 1.3^\circ$. The neutral reaction products were analyzed by a triply differentially pumped rotatable mass spectrometer operated in time-of-flight (TOF) mode and ionized by electron impact at 80 eV, which then passed through a quadrupole mass filter and reached a Daly type ion detector. The TOF spectra were recorded at multiple angles and then integrated to obtain the angular distribution of the product(s). A forward-convolution routine^[2] was used to fit the experimental data. The rovibrational distributions of the singlet ($X^1\Sigma_g^+$) and triplet ($a^3\Pi_u$) electronic states of the dicarbon beam were characterized spectroscopically *in situ* via laser induced fluorescence (LIF).^[1]

Theoretical : Stationary points on the singlet and triplet C_7H_8 PES accessed by the reaction of dicarbon, $C_2(X^1\Sigma_g^+/a^3\Pi_u)$, with 2-methyl-1,3-butadiene, including intermediates, transition states, and possible products, were optimized at the hybrid density functional B3LYP level of theory with the 6-311G** basis set. Vibrational frequencies were computed using the same B3LYP/6-311G** method and were used to obtain zero-point vibrational energy (ZPE) corrections. Relative energies of various species were refined employing the coupled cluster CCSD(T) method with Dunning's correlation-consistent cc-pVDZ and cc-pVTZ basis sets. The total energies were extrapolated to the complete basis set (CBS) limit using the equation $E_{\text{total}}(\text{CBS}) = (E_{\text{total}}(\text{VTZ}) - E_{\text{total}}(\text{VDZ}) \times 2.5^3/3.5^3) / (1 - 2.5^3/3.5^3)$.^[3] For selected reaction products, we carried out CCSD(T)/cc-pVQZ calculations and extrapolated CCSD(T)/CBS total energies using the following formula, $E_{\text{tot}}(x) = E_{\text{tot}}(\infty) + Be^{-Cx}$, where x is the cardinal number of the basis set (2, 3, and 4) and $E_{\text{tot}}(\infty)$ is the CCSD(T)/CBS total energy.^[4] Relative energies discussed in the paper are thus computed at the CCSD(T)/CBS//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory with two-point (dt) and three-point (dtq) CBS extrapolations and are expected to be accurate within ± 15 and $\pm 10 \text{ kJ mol}^{-1}$, respectively. The B3LYP and CCSD(T) quantum chemical calculations were performed using the GAUSSIAN 09^[5] and MOLPRO 2010^[6] program packages. Unimolecular rate constants were computed using Rice-Ramsperger-Kassel-Marcus (RRKM) theory,^[7] the rate constants were then utilized to calculate product branching ratios by solving first-order kinetic equations within steady-state approximation.

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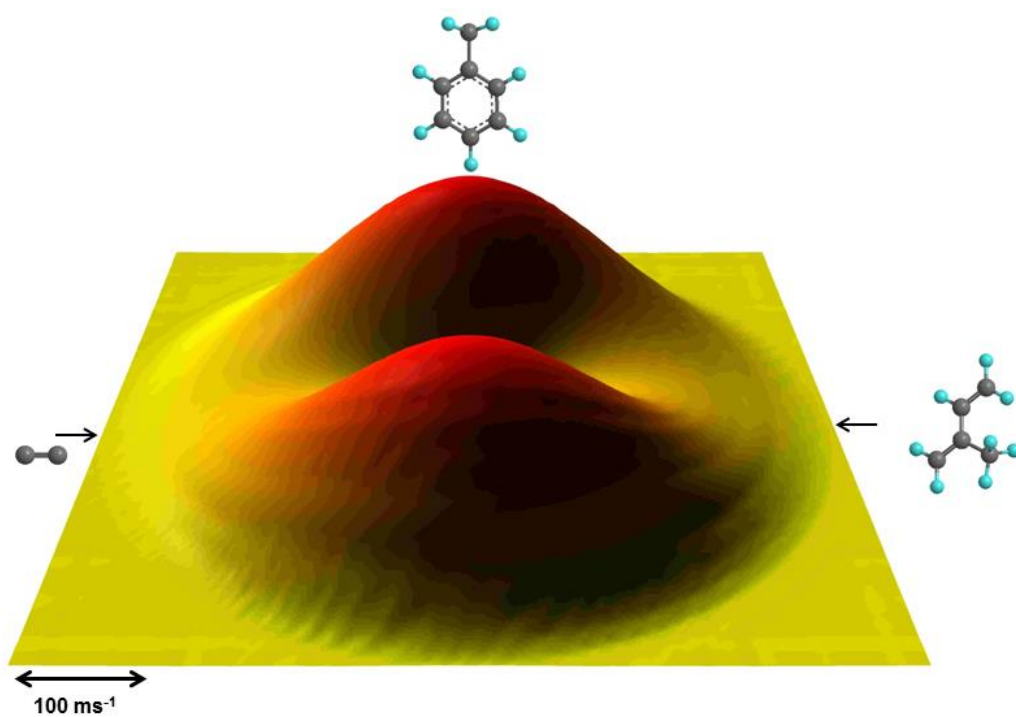


Figure: TOC

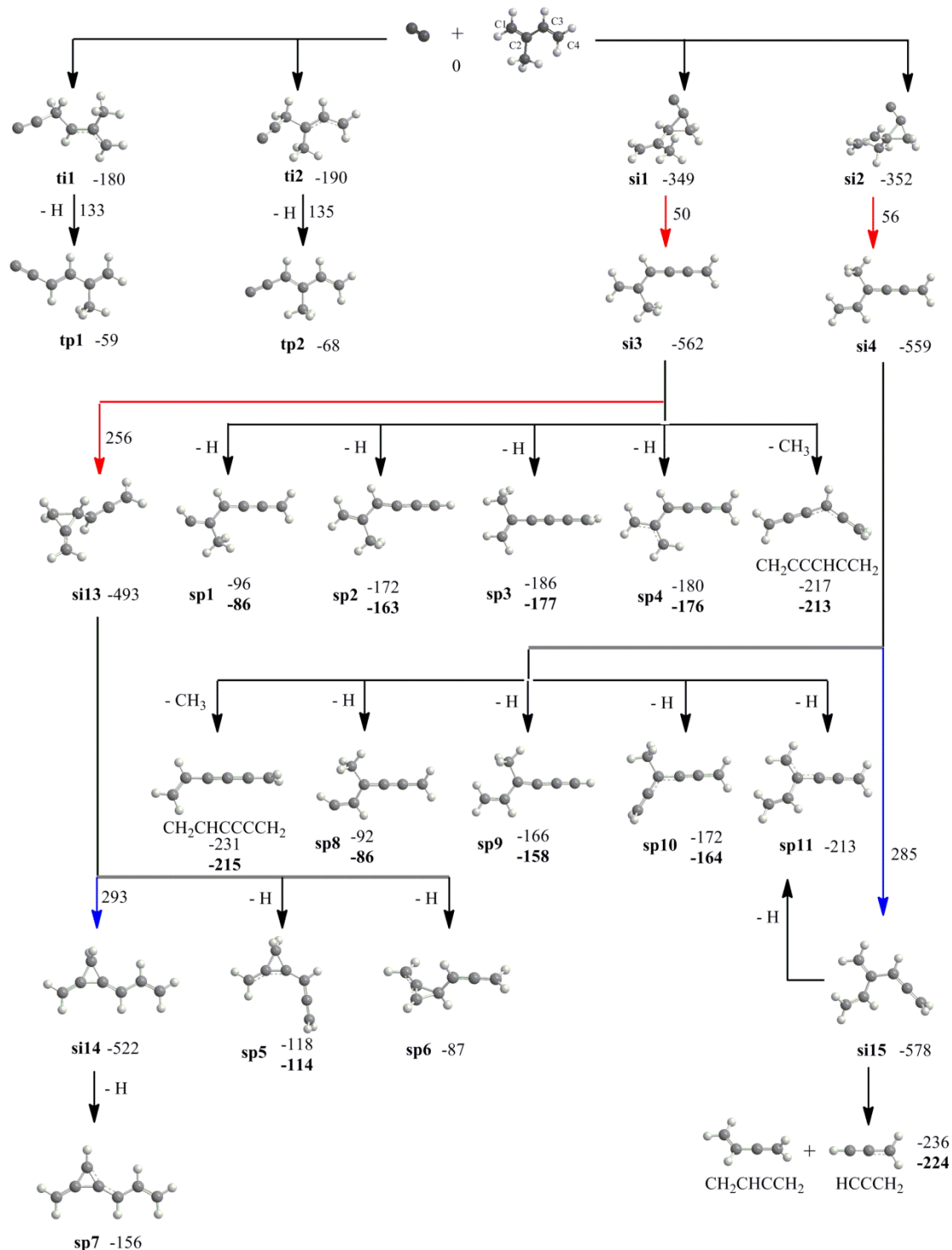


Figure S1: Reaction paths leading to the acyclic or tricyclic products in the dicarbon isoprene reaction. **t**, **s**, **i** and **p** represent the triplet, singlet, intermediate and product, respectively. Corresponding total energies with respect to the reactants and barrier heights (where applicable) are also shown in the units of kJ mol^{-1} as calculated at the CCSD(T)/CBS(dt)//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) (plain numbers) and CCSD(T)/CBS(dtq)//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) (bold numbers) levels of theory. Hydrogen shifts and isomerization via ring closure/opening are presented via blue and red arrows, respectively. For clarification, the carbon atoms in isoprene are labeled as C1 to C4.