

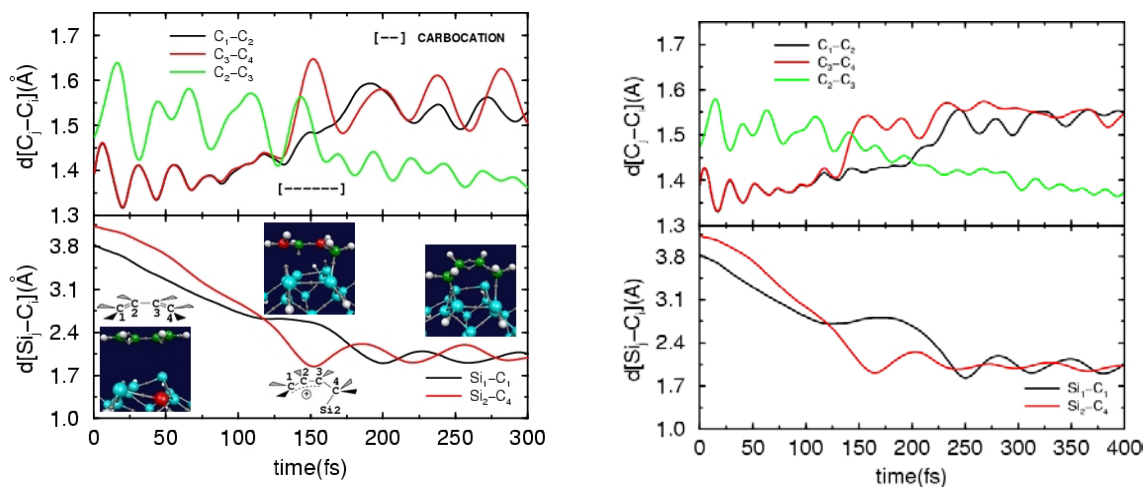
Supporting Information

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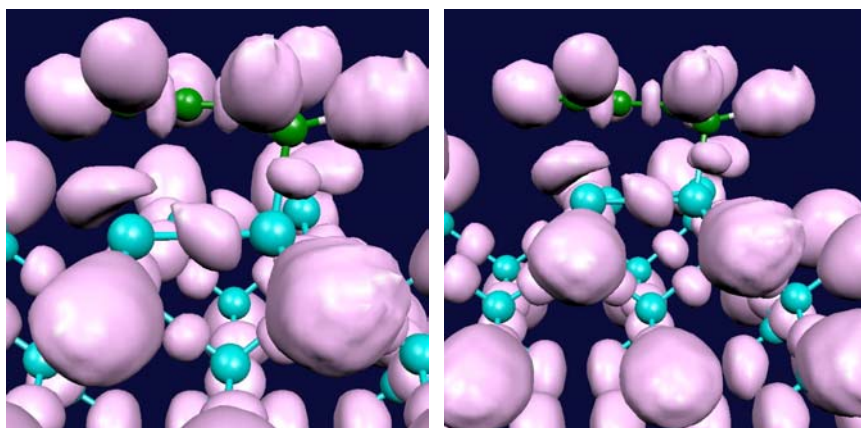
Spin Unrestricted *ab initio* calculations:

In the paper, evidence for a non-concerted zwitterionic mechanism is provided by free energy profile of Fig. 1 together with the time evolution of the Si-C and C-C bond lengths in the butadiene for a representative trajectory, shown in Fig. 2. There is a brief time window in Fig. 2, in which the two Si-C distances become distinctly different, as only one Si-C bond is formed. Moreover, Fig. 2 clearly shows the interchange of CC single and double bonds as the Diels-Alder (DA) adduct is formed. Furthermore, at its maximum value, $d[C_3-C_4] = d(s)$ ($d(s)$ is the single bond length) and $d[C_1-C_2] = d[C_2-C_3] = d(s-d)$ ($d(s) < d(s-d) < d(d)$) suggesting a possible resonant structure (see Scheme 1 in paper) that could help stabilize the carbocation. It has been suggested that a diradical mechanism is also possible. In order to this possibility, spin-unrestricted *ab initio* molecular dynamics calculations (using the same GGA-DFT scheme of the paper) were carried in order to generate a small ensemble of reactive trajectories. Here we provide the comparison of the Si-C and C-C bond lengths along a representative trajectory (shown in Fig. 2 in paper), which was carried out by both spin-restricted (left figure) and spin-unrestricted (right figure) calculations. The bond length changes in the two figures indicate that there is no significant difference between them leading to the same qualitative conclusion. Interestingly, the lifetime of the carbocation species is even more extended in the spin-unrestricted trajectory.



The figure below shows the 0.95 ELF isosurfaces for the spin-up and spin-down densities. Both the spin-up (left picture) and spin-down (right picture) ELF isosurfaces show very similar

characteristics supporting the fact that spin-restricted calculations adequately describe the reaction. The ELF study is performed using configurations captured at $t=163$ fs in the figure above, corresponding to the carbocation formation.



Finally spin polarization is quantitatively measured along the spin-unrestricted Car-Parrinello molecular dynamics trajectory by monitoring the electronic gradients for the spin-up and spin-down orbitals. The nearly identical forces obtained in the 0-300 fs timeframe exclude the presence of any radical mechanism along the [4+2] DA adduct formation.

