Electronic Supporting Information for:

**Gas-phase electrophilic aromatic substitution mechanism with strong electrophiles explained by *ab initio* non-adiabatic dynamics.†**

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1 Computational Details

The complete active space of the CASSCF calculations included six electrons in seven orbitals, comprising all π and π* orbitals of the benzene plus the initially empty p orbital on the methyl cation carbon, see Figure S1. The basis set employed is the Dunning type double-zeta basis set, cc-pVDZ.1

![Figure S1. Active space employed in the CASSCF calculations – here displayed for a Benzene – CH₃ distance of r = 5.0 Å.](image)

This level of theory was employed to obtain on-the-fly potential energies, gradients, and non-adiabatic coupling elements required for the *ab initio* non-adiabatic molecular dynamics simulations. The Newton-X/COLUMBUS interface2–7 was used for this purpose. Integration of the equations of motion was done with the Velocity-Verlet algorithm.8 The time-dependent electronic Schrödinger equation (TDSE) was solved with the fifth-order Butcher algorithm.9,10 Surface hopping probabilities for nonadiabatic transitions were evaluated at each time step with the fewest switches algorithm11,12 in the version developed by Hammes-Schiffer and Tully13 based on the local diabatization method14 as implemented in the Newton-X program. The time step chosen was 0.5 fs.

A total of 246 trajectories were simulated describing a direct facial attack of the methyl towards the center of mass of benzene. Each trajectory began with a non-rotating CH₃⁺ 7Å away from the center of mass of the benzene ring, CMB. Other initial conditions, where the methyl cation was located away from the perpendicular r-vector, collapsed all to CMB. r represents the distance between the methyl cation carbon atom and CMB.

The initial conditions for both, the methyl cation and benzene, were represented by a Wigner distribution around their respective vibrational normal modes in the electronic ground state. Hence, each trajectory
began with the vibrational energy equivalent to the quantum-mechanical zero-point energy of about 2eV. The relative kinetic energy imparted to the $\text{CH}_3^+$ towards to $\text{CM}^-$ was set to 0.01 eV.

The potential energy curves along the coordinate $r$ shown in Figure 3 of the manuscript were calculated at the multi-state complete active space second order perturbation theory (MS-CASPT2) level of theory using four averaged roots. A total of 51 ab initio points were calculated between $r = 0.0$ and $r = 10.0$ Å, with a spacing of 0.2 Å. An additional single point calculation has been performed for a Benzene - CH$_3$ distance of $r = 50$ Å to ensure a correct asymptotical behavior of the potential curves at large distances. These calculations were performed with the MOLCAS package. Figure S2 shows a comparison of the potential energy profiles obtained with CASSCF and MS-CASPT2. As it can be seen, at the CASSCF level of theory the [ArH $E^+$] state is relatively shifted up in energy, i.e. CASSCF overestimates the closed-shell configuration. As a consequence, the conical intersection is shifted to $r = 3.0$ Å. The local minimum, however, stays at $r = 2.5$ Å and the overall qualitative picture (order of the states) is the same as in MS-CASPT2. Therefore, a qualitative correct dynamics is expected when using CASSCF, although the quantitative time in which electron transfer happens should change slightly from one to the other picture. On a MS-CASPT2 level of theory we would expect ET to happen even earlier/farther away from benzene. But the overall reaction should be represented qualitatively correct on CASSCF level and the conclusions of the paper will be the same. Please also be aware that in Figure S2 only one coordinate is represented, which is mainly responsible for the ET process. Towards the $\sigma$-complex of course different coordinates are important, however at that stage the system is already in the electronic ground state.

To calculate the hole density, the following procedure was followed. The integration of the semi-classical version of the TDSE during the on-the-fly simulations gives the adiabatic populations of the electronic states. Thus, the total electronic wavefunction, $\Psi(t)$, of each individual trajectory at each time step is the linear combination of the electronic wavefunctions of each state $i$, $\psi_i(t)$:

$$|\Psi(t)\rangle = \sum_i c_i(t) |\psi_i(t)\rangle,$$

where $c_i(t)$ are the time-dependent adiabatic coefficients. For each trajectory, the time-dependent electron

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**Figure S2.** Potential energy surfaces at (a) SA4-CASSCF(6,7) and (b) MS-CASPT2(6,7) /cc-pVDZ level of theory. Circles on the ground state potential represent the calculated points.
density, $\rho(t)$ is then calculated as:

$$\rho_{\text{adiab}}(t) = |\Psi(t)|^2 = \sum_i c_i(t)^2 |\psi_i(t)|^2.$$  \hspace{1cm} (2)

Furthermore, the time-dependent electron density of the corresponding ground state of the neutral system, $\rho_{\text{neutral}}(t)$, is calculated by forcing the occupation numbers of the active space orbitals to be “2 2 2 1 0 0 0” for each trajectory and time step:

$$\rho_{\text{neutral}}(t) = |\psi_{2221000}(t)|^2.$$  \hspace{1cm} (3)

The time-dependent “hole” density of each trajectory, $\rho_{\text{hole}}(t)$ is then the difference of the neutral density and the adiabatic density:

$$\rho_{\text{hole}}(t) = \rho_{\text{neutral}}(t) - \rho_{\text{adiab}}(t)$$  \hspace{1cm} (4)

As a consequence, visualization of the hole density shows the localized positive charge of the $[\text{ArH} + \text{E}]^+$ system.
References


