

## Sudden Changes in Atomistic Mechanisms for the Cl<sup>-</sup>+ CH<sub>3</sub>I S<sub>N</sub>2 Reaction with Increasing Collision Energy

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Abstract: Studies have shown that the gas-phase  $X^- + CH_3Y \rightarrow XCH_3 + Y^- S_N2$ nucleophilic substitution may occur via direct mechanisms as well as many indirect mechanisms, including pre- and/or post-reaction complex formation, central barrier recrossing and roundabout mechanisms [1-4]. For the  $Cl^- + CH_3I \rightarrow ClCH_3 + I^$ reaction, there is a sudden change from predominantly indirect to direct mechanisms as the collision energy is increased [3]. However, there is some uncertainty regarding when the change occurs. Experiments show that for a collision energy of 0.39 eV the  $Cl^-$  + CH<sub>3</sub>I S<sub>N</sub>2 reaction occurs by an indirect mechanism, but at 0.70 eV it occurs by a direct one [1]. On the other hand, direct dynamics simulations employing the MP2 and DFT/BhandH theories and the ECP/d basis set indicate that the reaction mechanisms are predominantly direct at 0.39 eV collision energy, but indirect at 0.20 eV [3]. In this work, the transition from indirect to direct mechanism was studied for collision energies of 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40 eV through BHandH/ECP/d direct dynamics simulations. Impact parameters of 0 and 1 Å were investigated and the trajectories were integrated for 15 ps. For these collision energies, the only direct mechanism found was the direct rebound (DR). Direct stripping only occurs for higher collision energies. Regarding the indirect mechanisms, the same mechanisms found on previous simulations were observed for these collision energies, namely, pre- and/or postreaction complex formation, central barrier recrossing and roundabout. Furthermore, indirect reactions also occurred by combinations of the three aforementioned mechanisms.

**Key-words**: direct dynamics, nucleophilic substitution, reaction mechanisms, density functional theory

**Support:** Capes, Robert A. Welch Foundation Grant No. D-0005. **References:** 

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