

Revealing a new mechanism feature of $F^- + CH_3Cl \rightarrow Cl^- + CH_3F$ reaction by using ab initio molecular dynamics

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Abstract. S_N2 reaction gained much attention because of its vital role in biomolecular and organic chemistry. In the past decades, great progress on mechanism understanding of S_N2 reaction has been made by a lot of papers. However, atomic details of the reaction are complicated and hard to explore without precise potential energy surface. In this report, an ab initio molecular dynamics method shed light on the reaction explorations. Although a potential energy surface is disable, we can still make contributions on the mechanism study. Here, we found a novel mechanism in $F^- + CH_3Cl \rightarrow Cl^- + CH_3F$ that shared common transition state with abstract mechanism but avoid the proton transfer channel. It is a combination of proton roundabout and classical back-side attack mechanism, which is never observed in previous papers. Interestingly, a hydrogen bond transfer process exists in the novel mechanism which simultaneously involved in both C-H-F and Cl-H-F hydrogen bond. It provides another channel of proton transfer in low collision energy, and shows that more explorations have to be carried out even though various mechanism of S_N2 reaction have been reported.

1. Introduction

It takes decades for researchers to explore and understand the S_N2 reaction mechanism. Since these mechanisms play a vital role on revealing dynamics of biomolecular reaction and a large amount of papers on S_N2 reaction pathway have been reported. [1-21] Especially these involved in halogen atoms, which explored frequently because of their strong electronegativity. There is a classical mechanism called "back-side attack" in the textbook that the nucleophile attack the C atom and make the bond between C atom and leaving group weaken. The back-side attack mechanism has a central barrier connected by two minima, which is considered as direct mechanism. However, various indirect mechanisms contained pre-complex and non-covalent interaction has been revealed gradually in last decade. For instance, indirect mechanisms, such as hydrogen-bond in $F^- + CH_3Cl$ reaction mainly results from electrostatic interaction between one H atom in CH_3Cl complex and F atom, which impelled by the significant electronegativity. Besides, the so-called "roundabout" mechanism is predominantly caused by initial angular momentum and Van del Waals. Very recently, a double inversion mechanism observed by Gabor et al has a long-lived hydrogen bond before the Walden inversion, which is a special hydrogen-bond mechanism to some extent. [6,7]

So far there are two mainly mechanisms revealed in S_N2 reaction, direct and indirect pathway. [8] Direct mechanism typically contains both rebound and stripping. In rebound mechanism, a bond between nucleophile and C atom come

into being along with leaving group getting most translational energy. On the contrary, the nucleophile take the CH_3 away and left the leaving group nearby initial position in stripping mechanism. And the indirect one consist of different pathway in which pre-reaction complexes existed. Hase et al summarized principal mechanism of S_N2 reaction in a previous paper. In retrospect, all indirect mechanisms were attributable to the complex formation. Since the descriptions of pre-reaction complex are complicated so as to Hase et al argued that much explorations to describe features of S_N2 pathway need to be done. As is known, F atom has significant orientation in S_N2 reaction, besides, chlorine is supported by much basis sets. Thus, in this paper, we reported a novel reaction pathway of $F^- + CH_3Cl$ as well as $F^- + CH_3I$ with an ab initio molecular dynamics method which is capable of visualizing the initio coordinate conditions.

Traditionally, molecular dynamics simulations required a potential energy surface prepared in advance, which is hard to fit in polyatomic system. Here we apply an 'on the fly' method to carry out the dynamics simulations where an accurate potential surface is disabled. A module performing adiabatic ab initio molecular dynamics is implemented recently in nwchem.[22] The integration of nuclei and electronic potential calculated by using velocity-Verlet algorithm and Gaussian basis set based methods, respectively.[23] We found a novel pathway that the non-covalent interaction not only exists between HF and C atom but also HF and Cl atom. Briefly, the attacking atom F get a H atom and form hydrogen-bond complex with C atom at the beginning, then the bond between H atom and C would be break along with a new hydrogen-bond between Cl and HF formed. At the end of pre-reaction complex, a hydrogen-bond between HF and C reformed, that process is never observed in previous reports. And the rest of

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part is known as back-side attack pathway. Interestingly, the C-Cl bond has nearly rotated a whole circle in the entire pre-reaction, as shown in Figure 1.1. That results from the convenience provided by visible initio conditions. On the basis of trajectories, we have indeed verified a series of pattern that the indirect mechanism occurred on certain range of alpha along with impact parameter changed from 0 to b_{max} in where the reaction possibility reduced to zero.

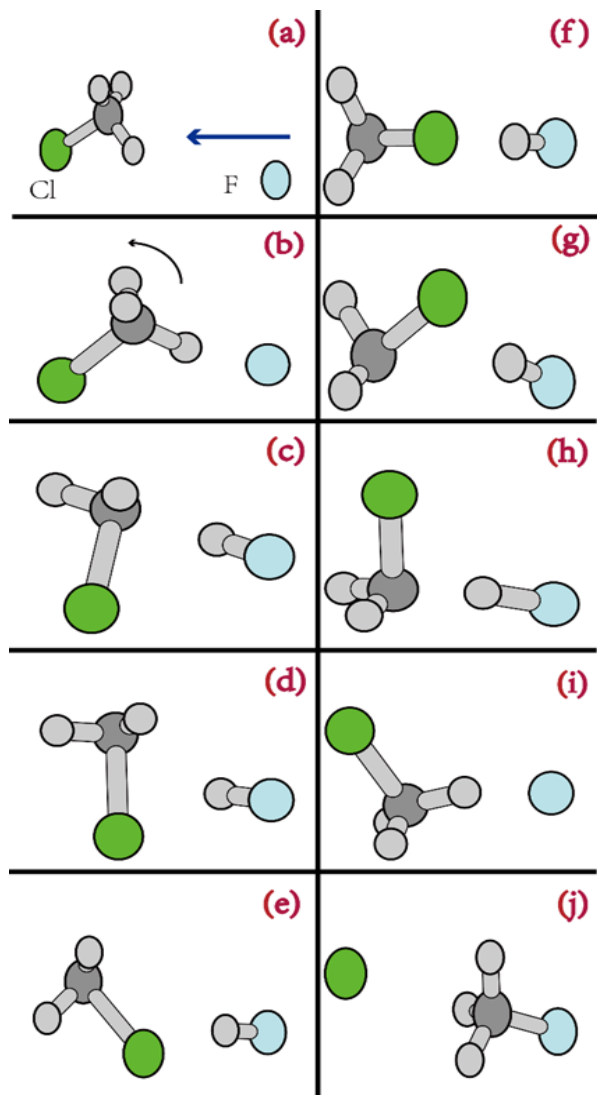


Figure 1.1: The evolution pathway of novel mechanism presented as proton transfer then come back to back-side attack. (PTCB).

In this work, we observed a novel reaction pathway that has never been found in any S_N2 reactions before: a reaction mechanism which is mixture of a proton-abstracted mechanism and a backside attack mechanism, also called proton transfer then come back (PTCB): the nucleophile F^- attacks the side of CH_3Cl and forms a hydrogen bond with one H atom, and the nucleophile then abstracts the proton (proton-abstracted) inducing the rotational of the rest of substrate, CH_2Cl^- (roundabout); after one rotation of the CH_2Cl nucleophile releases the proton and forms the hydrogen-bond complex again; the following part of reaction is the traditional,

back-side attack process. This reaction mechanism (proton-abstracted roundabout and back-side attack) is a new reaction mechanism not seen before. Furthermore, the proton-abstracted roundabout mechanism is different from the roundabout mechanism, where the nucleophile attacks the side of the substrate to cause the rotation of the whole substrate; here the nucleophile attracts proton and the HF induces part of the substrate rotated (CH_2Cl^-). The new findings of this study shows, on one hand, that some mechanisms of the S_N2 at C center should also observed by BOMD method without a precise potential energy surface, for example the new found double-inversion mechanism; on the other hand, the new finding of this study, the proton-abstracted roundabout and backside attack mechanism, shows, so far, the S_N2 mechanisms have not been completely discovered. Additional work needs to be done to probe the reaction mechanism and dynamics of the S_N2 reaction in general.

2. Theoretical methods

2.1 ab initio molecular dynamics (AIMD)

Ab initio calculations combine classical molecular dynamics simulations with electronic structure calculations on the fly. To perform AIMD simulations where the only assumptions are the validity of classical mechanics to describe ionic motion and the Born-Oppenheimer (BO) approximation to separate nuclear and electronic coordinates. Car and Parrinello kick started and dominated the AIMD field and their methods stays at the beginning of all new developments in this field.[24] The vast majority AIMD is to propagate the nuclei classically and solve Schrödinger equation for every step 'on the fly' with using a updated orbital stem from last step. As a state-of-art in BOMD, a module to perform BOMD in any of the Gaussian basis sets based methods in nwchem package is implemented. In view of F^- has significant orientation impact on CH_3Cl , we have to deal with the initio coordinates conditions cautiously. The initio conditions will be discussed in next part, but briefly, we exert two different settings to the beginning position and velocity. First things first, we build a frame of axes with the original point is the mass-center of CH_3Cl optimized in DFT level (m06-2x/mg3s), in that case, there is no necessary to move or change the CH_3Cl complex. Our aim is to find novel pathway of $CH_3Cl + F^-$, therefore no-limitations on impact parameter (called b) as well as beginning position of F^- ion make sense indeed, which means we rotate the F^- randomly along the axes and give it different impact parameter in a variety of collision energy from 0.68eV to 2.49 eV. From these thousands of trajectories, we gain a general view of mechanisms that might happen. Calculating potential energy in every step makes BOMD a costly method. Thus, the value of using mg3s basis set to carry out the trajectories is considering the cost and efficiency simultaneously. Another setting for initio conditions is fix the impact parameter and rotate the CH_3Cl complex along axis crossing the mass-center. That calculation was performed in DFT level (m06-2x/cc-pvtz). Based on the results, we pick up the novel pathway considered and clarify the existence of their