

Abstract

Molecular reaction dynamics is the study of chemical reactions at the atomic level. Quantum mechanical investigation of dynamics is computationally challenging even for medium sized molecules. On the other hand, classical trajectory simulations based on either Newton's or Hamilton's equations is an affordable method. Advantages and limitations of using classical trajectory methods are well known. Gas phase experiments such as ion-imaging techniques and crossed-beam experiments provide information about chemical reactions such as translational and internal energy distributions of reaction products, scattering angles, and branching ratios. Such information can also be extracted from accurately performed classical trajectory simulations and by comparison with experimental data, atomic level mechanisms can be postulated. Accuracy of classical trajectory simulations depend primarily on the potentials used when the quantum mechanical effects are unimportant. Conventional classical trajectory simulations involve using classical force fields. Owing to the development in computing power and algorithms, it is now possible to directly compute the potentials from quantum mechanics by solving the electronic Schrödinger equation at each integration step. This method, known as *direct dynamics*, can be used to study atomic level dynamics of chemical reactions. This method, in combination with advanced electronic structure theory and Rice-Ramsperger-Kassel-Marcus (RRKM) rate constant calculations, is used to study interesting gas phase chemical reactions in the present work. Three reactions relevant in atmospheric and synthetic chemistry were studied in detail.

3-oxetanone is a strained cyclic molecule which plays an important role in synthetic chemistry. A few studies exist in the literature about the equilibrium properties of this molecule and the dissociation patterns of substituted 3-oxetanones. Two primary dissociation channels viz., ketene and ethylene oxide formation exist. Electronic structure calculations showed that the ethylene oxide channel has high energy barrier and lower rate constant. In a experimental study, it was found that both channels are equally important. In here, gas phase dissociation chemistry of 3-oxetanone was investigated in detail. The dynamics simulations were performed at three different total energies, viz., 150, 200, and 300 kcal/mol, and multiple reaction pathways and varying branching ratios observed. A new dissociation channel involving a ring-opened isomer of ethylene oxide was identified in the simulations. This pathway had a lower energy barrier and accounted for the similar branching ratios obtained for the ketene and ethylene oxide channels in the experiments.

Halons (halomethanes) such as CF_2Cl_2 , CF_2Br_2 , CHBr_3 and CH_2BrCl play a central role in ozone depletion and much attention has been paid to the decomposition properties of these molecules. The dissociation dynamics of these molecules were studied in detail using classical dynamics simulations and the competition between radical and molecular pathways investigated. The results of the simulations showed that the molecular products were dominant in the decomposition of all the four molecules. A variety of reaction mechanisms occurring via concerted multi-center transition states, isomerization via iso-halons, and radical recombinations via roaming were identified in the simulations.

Curtius rearrangement is the elimination of N_2 from carbonyl azides RC(O)N_3 to form isocyanates RNCO . Two mechanisms viz., step-wise and concerted have been proposed in the literature for this reaction. The step-wise mechanism involves the formation of a nitrene RC(O)N by elimination of N_2 followed by an intramolecular rearrangement of the nitrene to form the isocyanate. Concerted mechanism is a single-step pathway forming the $\text{N}_2 + \text{RNCO}$ products directly. Previous experimental and theoretical studies have indicated that the mechanism

is usually concerted for thermal reactions and both step-wise and concerted are preferred under photochemical conditions. In here, the mechanism of Curtius rearrangement of two carbonyl azides with different substituents ($R = \text{CH}_3$ and F) were investigated. Atomic level reaction mechanisms were studied using chemical dynamics simulations under thermal reaction conditions. Simulation results showed dominant concerted mechanism for $\text{CH}_3\text{C}(\text{O})\text{N}_3$ and the operation of both the mechanisms for $\text{FC}(\text{O})\text{N}_3$ under similar conditions.

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