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GAS-PHASE REACTION OF THE ISOBUTENYL ANION WITH N_2O FROM *AB INITIO* CALCULATIONS

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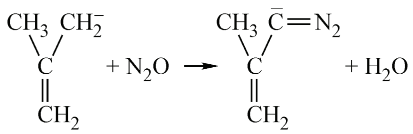
Calculations using conventional *ab initio* theory are performed to investigate the reaction mechanism associated with the gas-phase ion/molecule reaction of isobutenyl anion with N_2O. As a result, our theoretical findings strongly suggest that the main pathway is the reaction pattern of end-N attack and that the corresponding reaction mechanism basically relates to hydrogen migration, which may yield products *cis*-$CH_2(CH_3)CCN_2^-$, *trans*-$CH_2(CH_3)CCN_2^-$, and H_2O. Those are in good agreement with the experimental observations. Moreover, based on the NBO, Activation Strain model and methyl group effect analysis, we also explored the characters of rate-determining step of the main pathway.

K e y w o r d s: isobutenyl anion, reaction mechanism, second-order Møller—Plesset perturbation theory (MP2).

INTRODUCTION

Carbanion, acting as a sort of valuable electron-rich reagent, plays a central role in organic chemistry because of its widespread synthetic utility [1]. In many cases, it is a reactive nucleophilic intermediate [2—7] and is often encountered in organic chemistry, organometallic chemistry, alkyl lithium chemistry and so on [8—14]. Many experiments have demonstrated that the stable carbanions, owing to charge delocalization, do exist [2—15]. However, they have not been successfully isolated, possibly due to their high reactivities [9—11, 14]. Previously, substantial efforts were made to gain and characterize carbanions experimentally [12—14], including bond strengths, [16] energies, [17] and resonance effects. [18] Also, the corresponding gas-phase reactions have been studied extensively. [11—13, 19, 20] Here, the work of Depuy *et al.* in 1977 [19] in which, using a flowing afterglow (FA)-selected ion flow tube (SIFT), they investigated in detail the reaction mechanism of different carbanions with some small molecules, is most representative. Unfortunately, to the best of our knowledge, no theoretical study has hitherto well explored the reaction mechanism of an isobutenyl anion with N_2O, which was only inferred by Depuy from the experiment [20], as shown in Scheme 1.



Scheme 1