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ORIGINAL PAPER

Theoretical investigation on the reaction of HS^+ with CH_3NH_2

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The singlet and triplet potential energy surfaces for the reaction of HS^+ with the simplest primary amine, CH_3NH_2, were determined at the CCSD(T)/6-311+G(d,p) level using the B3LYP/6-311G(d,p) and QCISD/6-311G(d,p) geometries. All possible reaction channels were explored. The results show that three paths on the singlet potential energy surface and one path on the triplet potential energy surface are competitive. These four feasible paths provide products which are presented in the paper and they are consistent with previous experimental results. On the other hand, the stationary points involved in the most favourable path all lie below those of the reactant and thus the title reaction is expected to be rapid, which is also consistent with the experiment.

Keywords: HS^+ with CH_3NH_2, theoretical calculations, reaction mechanism, potential energy surface (PES)

Introduction

Methylamine (CH_3NH_2), the simplest primary amine, has received considerable attention and has played an important role in biology (Hamdani et al., 2009; Xiao & Yu, 2009; Conklin et al., 2004; Choi et al., 2011), chemistry (Lu et al., 2010; Li & Oshima, 2005; Atroshchenko et al., 2005; Cho & Choi, 2011), and astrochemistry (Singh et al., 2010). Consequently, it has been the subject of many experimental and theoretical studies (Jackson et al., 2005; Ilyushin et al., 2005; Lin et al., 2011). Up to now, many experimental investigations on its quantum chemical parameters (Irgibaeva, 2004) and spectroscopic properties (Baek et al., 2003a, 2003b; Naganathappa & Chaudhari, 2010) have been reported. Several theoretical studies have been devoted also to the reaction of CH_3NH_2 with OH (Tian et al., 2009), HNO_2 (Tiwary & Mukherjee, 2009), Cl (Rudić et al., 2003), H (Kerkeni & Clary, 2007), and so forth (Lv et al., 2010; Kua et al., 2011; Liu et al., 2010) using the density functional theory or the ab initio methods.

Smith et al. (1981) reported the reactions of H_nS^+ ions with several molecular gases, such as CH_3NH_2, NO, NH_3, etc., using a SIFT apparatus. Their results indicated that the charge transfer does not necessarily imply a long range electron transfer, but rather that a charge transfer channel is often just one of the exit channels resulting from the interaction. It was postulated that the reaction of HS^+ with CH_3NH_2 can afford various products as illustrated in Fig. 1 (products distribution is given in brackets).

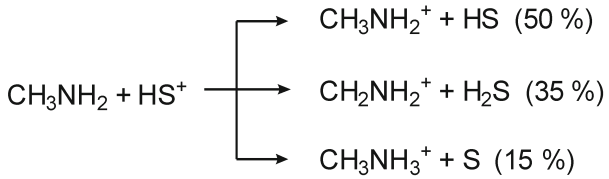

Fig. 1. Possible products of the reaction of HS^+ with CH_3NH_2.

In the present article, a detailed theoretical study on the reaction of CH_3NH_2 with HS^+ was carried out to investigate the reaction mechanism. This investigation can help to explain the experimental results and understand the mechanism of this series of reactions.

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