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A DFT study of the reactions of the Cu^+ ion with methylamine and dimethylamine

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ABSTRACT

The fragment ions $Cu^+(CH_3N)$ and $Cu^+(C_2H_5N)$ have been detected in the recent experiment from the products of the ion-molecule reactions of the Cu^+ ion with methylamine (MA, CH_3NH_2) and dimethylamine (DMA, $(CH_3)_2NH$) using the time-of-flight mass spectrum technology. Their forming mechanisms and the structural characteristics, however, are still not clear. Here, we show a detailed DFT study for the potential energy surfaces relevant for the reactions of the Cu^+ ion with MA and DMA to address the concerned issues. We find that the ion-molecule reactions are driven by a large energy gain upon the association of the Cu^+ ion with MA or DMA. A general dehydrogenation mechanism of MA and DMA promoted by the Cu^+ ion has been shown, and the preponderant structures contributing to the recorded mass spectra for the product ions $Cu^+(CH_3N)$ and $Cu^+(C_2H_5N)$ have been formulized as Cu^+–CH_2NH and Cu^+–CH_2NHCH_2. The present study represents a prototype of the reaction of the Cu^+ ion with amine, and the conclusion drawn out from this work is expected to provide a consistent view on the reactivity of this kind of reactions.

1. Introduction

Ion-molecule or atom-molecule complexes between transition metals and a number of well defined ligands (neutral or anionic non-metal species), have been extensively applied in chemistry and chemical engineering, and attracted a lot of attentions for a long time [1–5]. It is important to investigate in detail the structures and properties of transition metal complexes in order to understand the interactions between transition metals and ligands. The copper is one of the most well known transition metals, which plays important roles in many important biochemical processes, such as the enzymatic catalysis and dioxygen transport [6–10]. In the last years, particular attentions have been focused on the reactivity of the Cu^+ ion with various organic compounds [11–15].

The complexes of the Cu^+ ion with amine molecules are one kind of the most important transition metal complexes. As far as we know, not much is known about the intrinsic reactivity of the Cu^+ ion with amine, although some experimental and theoretical efforts have been devoted to the study for the reactions of the Cu^+ ion with many inorganic and organic molecules in past decades [16–18]. Recently, Hu et al. [19] reported the reactions of the Cu^+ ion with methylamine (MA, CH_3NH_2) and dimethylamine (DMA, $(CH_3)_2NH$) by using the laser ablation—molecular beam method. In the time-of-flight mass spectra, the product ions $Cu^+(CH_3N)$ and $Cu^+(C_2H_5N)$ were detected. These fragmentations are formally dehydrogenation products from the ion-molecule complexes of the Cu^+ ion with CH_3NH_2 and CH_3NHCH_3, as indicated in Eqs. (1) and (2).

$$Cu^+ + CH_3NH_2 \rightarrow Cu^+(CH_3N) + H_2 \quad (1)$$

$$Cu^+ + (CH_3)_2NH \rightarrow Cu^+(C_2H_5N) + H_2 \quad (2)$$

However, it is not clear why those complex ions were produced in experiments, and what the structural characteristics of these recorded fragment ions are. From an experimental point of view, a complete elucidation for the concerned issues is very difficult [20] owing to the lack of the detailed information on the structural characterization of these species involved in the ion-molecule reactions. Alternatively, this kind of information source can be supplemented by performing quantum chemical calculations, which together with experimental data can provide a complete understanding towards the aims. In this work, we carry out a systematic theoretical study for the reactions of the Cu^+ ion with MA and DMA, and show their energetics and kinetics by performing density functional theory (DFT) [21,22] calculations. As a consequence, we can understand the forming mechanism and structural details of dehydrogenated products from the reactions of the Cu^+ ion with MA and DMA.

2. Computation details

The present DFT calculations are carried out with Gaussian 03 [23] program package. The geometries are optimized at the hybrid

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functional B3LYP [24,25] level using the 6-311+G(d, p) basis set. Previous studies show that the B3LYP functional is quite reliable for describing metal cation–neutral complexes [21,26]. The combination of the B3LYP functional with the large 6-311+G(d, p) basis set (for Cu this basis set corresponds to the (14*s*9*p*5*d*/9*s*5*p*3*d*) basis of Watchers-Hay supplemented with a set of (1*s*2*p*1*d*) diffuse functions and with a set of *f* polarization functions) provides a good compromise between the computational cost and the accuracy of computational results.

The Geometries of the reactants, products, intermediates and transition states involved in the reactions of the Cu^+ ion with MA and DMA are fully optimized without imposing symmetry constraints. All stationary points are searched on the singlet potential energy surface (PES) since the Cu^+ ion (d^{10}), MA and DMA molecules are all closed-shell species. Optimized transition states and minima have been confirmed by performing analytical vibration frequency calculations. The intrinsic reaction coordinate (IRC) pathways have been traced in order to verify that each saddle point link connects the proper reactant and product. Zero-point vibrational energy corrections have been taken into account in all cited energies. The electronic properties and bonding characteristics for the relevant stationary points were illustrated based on the natural population analysis (NPA) [27].

3. Results and discussion

3.1. Calibration

To assess the reliability of the theory method used in this work for describing the systems at hand, we performed the benchmark calculations for several species, which are either involved in the reactions considered or closely relevant to the present systems.

3.1.1. Atomic asymptotes for Cu^+ ion

The Cu^+ ion has a $^1S_0$ (d^{10}) ground-state and its lowest energy excited state is the $^3D_3$ ($3d^9 4s^1$) atomic state. At the employed level of theory, the separation of these two states are calculated to be 2.98 eV, which is in good agreement with the corresponding experimental value of 2.72 eV [28].

3.1.2. Dissociation energies

Table 1 summarizes calculated dissociation energies from the present B3LYP/6-311+G(d, p) calculations along with the available experimental data and those obtained in the framework of G2 molecular orbital theory [29], which shows a very promising performance at predicting many thermochemical properties such as bond dissociation energies with an error normally less than 2 kcal mol^{-1}. It can be observed that there is a good agreement between our calculated results and the corresponding experimental/G2 values [30–31].

3.1.3. Geometries

Fig. 1 compares optimized geometrical parameters for CH_3NH_2, H_2, and NH_3 using the present DFT method with the available experimental findings [32–33]. Clearly, the experimental results are well reproduced by our theoretical calculations.

Table 1
Calculated and experimental bond dissociation energies (in kcal mol^{-1}).

Species	This work	G2[a]	Expt.[b]
$Cu^+–NH_3$	57.31	52.3	60.0
$Cu^+–NH_2CH_3$	61.0	59.0	–
$Cu^+–NHCH_2$	59.92	55.1	–

[a] Results obtained in the framework of G2 theory from Ref.[30].

[b] Experimental estimation from Ref. [31].

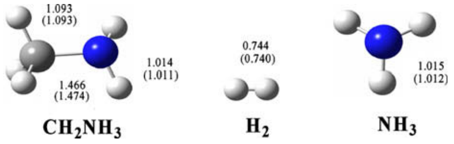

Fig. 1. Calculated and experimental (in parentheses) geometrical parameters for CH_3NH_2, H_2, and NH_3.

All above results clearly indicate that the DFT approach described in the present work provides a satisfying reliability to describe Cu^+–amine complex systems.

3.2. Reaction of the Cu^+ ion with methylamine

We first consider the interaction of the Cu^+ ion with CH_3NH_2. To explore dehydrogenation mechanism of Eq. (1) to form the observed product $Cu^+(CH_3N)$, we have scanned the details of the PES relevant for this reaction. Fig. 2 shows the optimized geometries of minima ($IM1_{MA}$–$IM5_{MA}$) and transition states ($TS1_{MA}$–$TS3_{MA}$) located on the PES. By combining the structural information with the indication obtained from our IRC calculations, two general reaction pathways I_{MA} and II_{MA} clearly emerge, as shown in Fig. 3. Pathway I_{MA} involves two consecutive elementary steps, while pathway II_{MA} corresponds to a concerted process.

$IM1_{MA}$ is an initial ion-molecular complex when the Cu^+ ion and MA approach each other. The calculated energy gain for binding the Cu^+ ion to MA is 61.0 kcal mol^{-1}, which is much lager than that resulting from the pure electrostatic interaction. The released energy for forming the covalent complex is expected to be an intrinsic drive for the succeeding reaction.

As seen in Fig. 3, this complex is found to a global minimum on the PES. From Fig. 2, it is clear that in $IM1_{MA}$ the Cu^+ ion binds to the N atom of MA with a distance of 1.956 Å. NPA analysis shows the natural charge and natural configuration for the Cu^+ atom in $IM1_{MA}$ are 0.597 and 4 s(0.22)3d(9.92), respectively. All these facts indicate that this initial complex involves a remarkable covalent contribution, which arises from the a sizable charge transfer from the lone pair orbital of the N atom to the 4s empty orbital of the Cu^+ ion owing to the efficient overlay between the two orbitals with the matching symmetry and the close energy level.

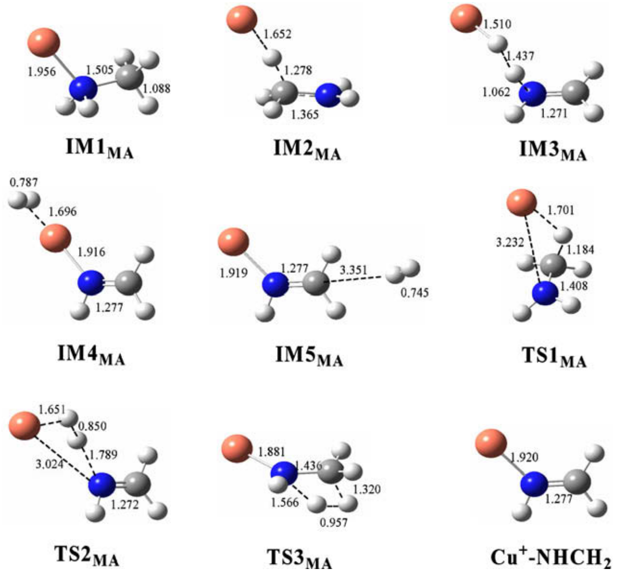

Fig. 2. Optimized geometries for the intermediates, transition states, and product involved in the reaction of the Cu^+ ion with MA. Distances are in Å.