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Intramolecular S_N2 Reaction Caused by Photoionization of Benzene Chloride−NH_3 Complex: Direct ab Initio Molecular Dynamics Study

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Ionization processes of chlorobenzene−ammonia 1:1 complex (PhCl−NH_3) have been investigated by means of full dimensional direct ab initio molecular dynamics (MD) method, static ab initio calculations, and density functional theory (DFT) calculations. The static ab initio and DFT calculations of neutral PhCl−NH_3 complex showed that one of the hydrogen atoms of NH_3 orients toward a carbon atom in the para-position of PhCl. The dynamics calculation for ionization of PhCl−NH_3 indicated that two reaction channels are competitive with each other as product channels: one is an intramolecular S_N2 reaction expressed by a reaction scheme $[PhCl-NH_3]^+ \rightarrow$ S_N2 intermediate complex $\rightarrow PhNH_3^+ + Cl$, and the other is ortho-NH_3 addition complex (ortho complex) in which NH_3 attacks the ortho-carbon of $PhCl^+$ and the trajectory leads to a bound complex expressed by $(PhCl-NH_3)^+$. The mechanism of the ionization of PhCl−NH_3 is discussed on the basis of the theoretical results.

1. Introduction

The reactions in clusters and hydrogen-bonding networks have received much attention from both experimental and theoretical points of view because they have the potential ability to open a new reaction channel that does not usually occur in the gas phase.[1−5] In particular, the reaction caused by photoionization is important because it can be easily controlled by photoirradiation.

In the case of a weakly bound complex composed of an aromatic molecule (denoted by A) and a hydrogen donor molecule (HB), three reaction channels expressed by the following reaction scheme

$$
\begin{aligned}
A\cdots HB \xrightarrow[-e^-]{h\nu} [A\cdots HB]^+ &\rightarrow (A^+)-HB \quad \text{(complex formation)}\\
&\rightarrow A^+H + B \quad \text{(hydrogen/proton transfer)}\\
&\rightarrow A^+ + HB \quad \text{(dissociation)}
\end{aligned}
$$

are mainly competitive after the photoionization, where H is a hydrogen. The first channel is a complex formation channel where HB molecule adducts to A^+ ion after the ionization. In the second channel, a hydrogen atom or a proton transfer takes place between A and HB. The third channel is a dissociation channel where HB dissociates from A^+ after the ionization.

Maeyama and Mikami[6,7] investigated the ionization dynamics of halogenated benzene−NH_3 1:1 complex (denoted by PhX−NH_3, where X = F or Cl) by means of the trapped ion photodissociation (TIP) technique. They found for the first time that intramolecular nuclear substitution (S_N2) reaction takes place after the ionization of PhX−NH_3. The reaction is expressed as follows:

$$
PhX-NH_3 + Ip \rightarrow [PhX-NH_3^{\ +}]_{ver} + e^-
$$

$$
\begin{aligned}
[PhX-NH_3^{\ +}]_{ver} &\rightarrow [PhX-NH_3^{\ +}] \quad \text{(complex)}\\
&\rightarrow PhNH_3^{\ +} + X \quad (S_N2 \text{ reaction})
\end{aligned}
$$

Ionization of PhX−NH_3 leads to the formation of the intermediate complex, and then S_N2 reaction product ($PhNH_3^+ + X$) is formed. Also, the other ions ($PhX-NH_3^+$ (intermediate complex), $C_6H_5X^+$ (parent cation), and $PhX^+(NH_3)_2$) are found as products. A similar reaction is also observed in a reaction of dihalobenzene radical cation with ammonia.[8] This type of S_N2 reaction is a new channel which has not been observed previously. However, reaction mechanisms may be also clearly understood by carefully designed experiments and not by theoretical calculations alone. For example, it has been also considered that first photodissociation of PhX occurs ($PhCl + h\nu \rightarrow Ph + Cl$) and then ionized benzene radical reacts with NH_3: $C_6H_6 + Ip \rightarrow C_6H_6^+ + e^-$, and $C_6H_6^+ + NH_3 \rightarrow C_6H_6-NH_3^+$. Thus, the reaction mechanism is still disputing it.

In the present study, we investigate theoretically the ionization dynamics of the chlorobenzene−ammonia 1:1 complex (PhCl−NH_3) by means of the direct ab initio molecular dynamics (MD) method. The main purposes of this study are (1) to elucidate qualitatively the ionization dynamics of PhCl−NH_3 and (2) to predict the reaction channels after the ionization of $PhNH_3$. In particular, we focus our attention on the question of whether the intramolecular S_N2 reaction takes place after the ionization PhCl−NH_3.

Benzene (C_6H_6) is a typical aromatic molecule that forms π-type hydrogen-bonded complexes with several hydrogen donor molecules such as HF,[9] HCl,[10] NH_3,[11] and H_2O.[12] Zwier and co-workers measured resonant two-photon ionization (R2PI)

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time-of-flight mass spectra of $C_6H_6(H_2O)_n$ complex ($n = 1$ and 2). They found that the $PhH-H_2O^+$ complex is formed by the photoionization of the $C_6H_6(H_2O)_n$ complex.[2] Courty et al. investigated the ionization process of the size-selected benzene−water cluster $C_6H_6(H_2O)_n$ by means of the resonance-enhanced multiphoton ionization technique,[13,14] and a similar conclusion is derived from their experiment.

In previous papers, we applied full dimensional direct ab initio MD calculations to ionization processes of $C_6H_6-H_2O$,[15] C_6H_6-HF,[16] ethylene−HF,[17] formanilide−H_2O,[18] and $C_6H_6-(NH_3)$[19] complexes. It was found that two reaction channels, namely, the direct dissociation and complex formation channels, are concerned with the photoionization of the complexes. Also, it was found that the vibrational frequencies of H_2O are remarkably shifted by the formation of a complex with $C_6H_6{}^+$.[20] In the present study, we apply the full dimensional direct ab initio MD method to the ionization dynamics of $PhCl-NH_3$, which was observed by Maeyama and Mikami using the TIP technique.[6,7]

2. Computational Methods

In general, a classical trajectory calculation can be made on an analytically fitted potential energy surface (PES). However, it is not appropriate to predetermine the reaction surface of the present system due to the large number of degrees of freedom ($3N - 6 = 42$, where N is the number of atoms in the system). Therefore, in the present study, we applied direct ab initio MD calculations[21,22]with all degrees of freedom to the ionization dynamics of the $PhCl-NH_3$ system.

Direct ab initio MD calculation was carried out at the HF/3-21G(d) level of theory throughout. The neutral complex $PhCl-NH_3$ was fully optimized by the energy gradient method. Next, several geometries were generated around the equilibrium point of $PhCl-NH_3$ by ab initio MD calculation at 10 K. The trajectories for $PhCl-NH_3{}^+$ were run from these generated points. We considered an electronic state, expressed schematically by $(PhCl)^+(NH_3)$ in the trajectory calculations. The electronic state of the system was monitored during the simulation. We confirmed carefully that the electronic state and charge on each atom are retained during the reaction. The velocities of atoms at the starting point were assumed to be zero (i.e., the momentum vector of each atom is zero). The equations of motion for n atoms in a molecule are given by

$$\frac{\mathrm{d}Q_j}{\mathrm{d}t} = \frac{\partial H}{\partial P_j}$$

$$\frac{\partial P_j}{\partial t} = -\frac{\partial H}{\partial Q_j} = -\frac{\partial U}{\partial Q_j}$$

where $j = 1 - 3N$, H is the classical Hamiltonian, Q_j is the Cartesian coordinate of the jth mode, and P_j is the conjugated momentum. These equations were numerically solved by the Runge−Kutta method. No symmetry restriction was applied to the calculation of the energy gradients. The time step size was chosen as 0.10 fs, and a total of 10 000 or 20 000 steps were calculated for each dynamics calculation. The drift of the total energy is confirmed to be less than 10^{-3}% throughout at all steps in the trajectory. The momentum of the center of mass and the angular momentum are assumed to zero. Static ab initio molecular orbital (MO) calculations were carried out using Gaussian 03.[23]

It should be noted that structures and the shape of the potential energy surface of $PhCl-NH_3{}^+$ obtained at the HF/3-21G(d) level agree qualitatively with those of the B3LYP/6-311G(d,p) level, as will be shown in a later section, so this level of theory should be adequate to discuss the qualitative features of the ionization dynamics of $PhCl-NH_3$.

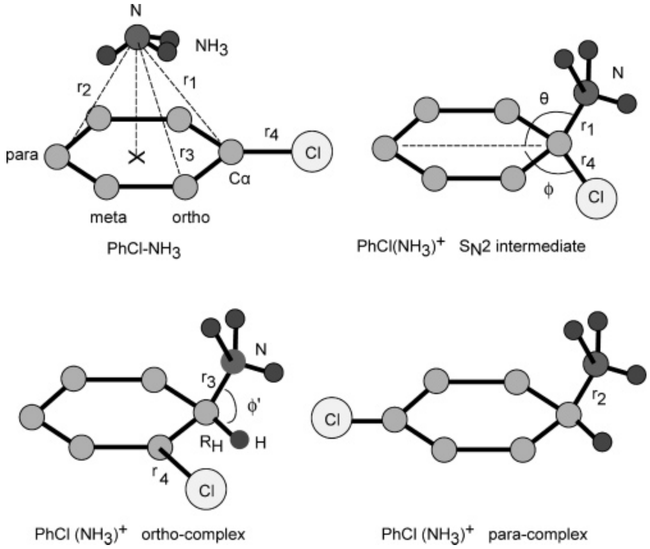

Figure 1. Schematic illustrations of structures and geometric parameters of complexes.

3. Results

A. Structures of Neutral Complex $PhCl-NH_3$. The structure of a $PhCl-NH_3$ complex is fully optimized at several levels of theory. On the basis of a structure of the $C_6H_6-NH_3$ complex,[24−27] it is assumed that an ammonia molecule interacts with the π-orbital of PhCl in an initial structure of geometric optimization. Using this initial arrangement, geometric optimizations were carried out for the $PhCl-NH_3$ neutral complex. The optimized structure shows that one of the hydrogens of NH_3 interacts with a carbon atom of PhCl (in the para position of PhCl). The definitions of geometric parameters are illustrated in Figure 1, and the optimized parameters are given in Table 1. The distance between the N atom of NH_3 and Cα carbon atom of PhCl (denoted by r_1) was calculated to be 3.9709 Å at the B3LYP/6-311G(d,p) level. The NH_3 molecule is located 3.7361 Å above the benzene ring. The binding energy was calculated to be 1.30 kcal/mol. The details of structures and energetics will be discussed in a later section. A similar structural feature is obtained at the HF/3-21G(d) and CAS(6,6)/6-311G(d,p) levels of theory.

To elucidate the electronic states of $PhCl-NH_3{}^+$ at a vertical ionization point from the neutral state, Hartree−Fock (HF) and B3LYP/6-311G(d,p) calculations were carried out for the optimized structure. The calculations show that a positive charge is mainly distributed on the $PhCl^+$ moiety of $PhCl-NH_3$, while a spin is slightly diffused into the NH_3 molecule. The spin densities on α-, ortho-, meta-, and para-carbon atoms were calculated to be 0.28, 0.08, −0.02, and 0.39, respectively, indicating that the spin density is larger on Cα and C(para) atoms of PhCl. Similar features were obtained by the HF/3-21G(d) level.

B. Ionization Dynamics of $PhCl-NH_3$. To generate the initial geometries of $[PhCl-NH_3]^+$ at vertical ionization points, ab initio MD calculations were carried out for neutral complex $PhCl-NH_3$ under a constant temperature condition (10 K). The geometric configurations of neutral complex are generated around its equilibrium structure. A total of 40 points around the equilibrium geometry of $PhCl-NH_3$ are generated using ab

TABLE 1: Selected Optimized Geometric Parameters of Neutral Complex PhCl−NH$_3$[a]

	HF/3-21G(d)	CAS(6,6)/6-311G(d,p)	B3LYP/6-311G(d,p)	B3LYP/6-311++G(d,p)	MP2/cc-pVDZ	MP2/6-311G(d,p)
r_1	4.0477	3.9667	3.9709	4.2771	3.4917	3.4431
r_2	4.1428	4.5714	3.9353	4.3050	3.9746	3.8716
r_3	3.9423	4.1967	3.9041	3.9409	3.6275	3.6905
r_4	1.7503	1.7829	1.7611	1.7604	1.7466	1.7370
θ^b	72.2	83.6	70.2	71.7	77.5	76.0
ϕ^c	179.8	179.7	179.8	179.8	179.1	178.9

[a] Bond lengths and angles are in angstroms and degrees, respectively. [b] Angle of N−Cα−C(para). [c] Angle of Cl−Cα−C(para).

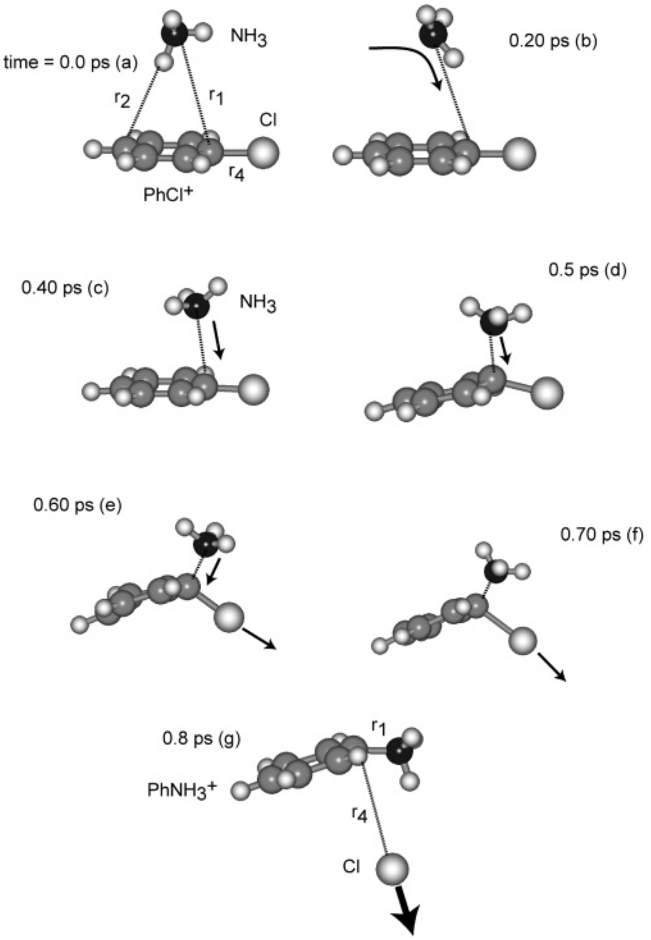

Figure 2. Snapshots for intramolecular S$_N$2 reaction channel of PhCl−NH$_3^+$ after the ionization of its neutral complex calculated by direct ab initio MD method.

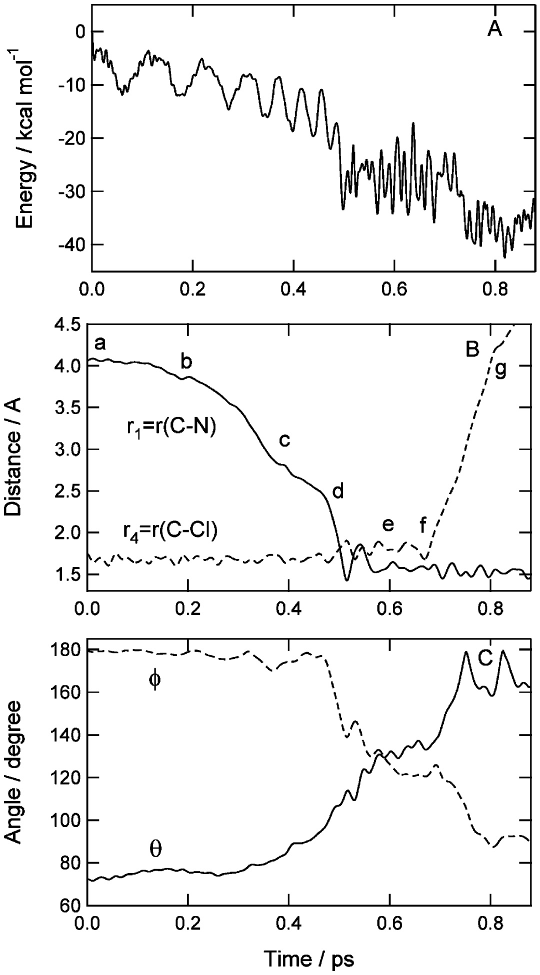

Figure 3. Time propagations of potential energy (A), distances (r_1 and r_2) (B), and angles (θ and ϕ) (C) for intramolecular S$_N$2 reaction.

initio MD calculations at 10 K. The ab initio MD calculations for the ionization dynamics gave two reaction channels as main products: S$_N$2 reaction channel and complex formation channel. Details for these channels will be discussed as follows.

S$_N$2 Reaction Channel. Snapshots of the geometric configurations of [PhCl−NH$_3$]$^+$ after the vertical ionization of PhCl−NH$_3$ are illustrated in Figure 2. Before the ionization, one of the hydrogen atoms of NH$_3$ orients to a carbon atom in the para-position of PhCl. The NH$_3$ molecule is located 3.875 Å above the benzene ring (r_1 = 4.063 and r_2 = 4.163 Å). At time zero, the trajectory of [PhCl−NH$_3$]$^+$ starts from the vertical ionization point. An electron of the neutral complex is removed from the π-orbital of PhCl by the ionization, while a hole is localized on the PhCl ring (the ionization potentials of PhCl and NH$_3$ are measured to be 9.07 and 10.16 eV, respectively).[28]

The interaction between the PhCl ring and NH$_3$ is suddenly changed to a repulsive interaction between the positive charge on the benzene ring and hydrogen atoms of NH$_3$ in (PhCl$^+$)-NH$_3$. Hence, an umbrella mode of NH$_3$ is inverting, and then the NH$_3$ molecule moves to a more stable position. At 0.2 ps, NH$_3$ is located near the C−Cl carbon atom (Cα carbon) (r_1 = 3.866 and r_2 = 4.159 Å). As NH$_3$ gradually approaches the Cα carbon, the distance of the C−Cl bond increases: for example, r_1 = 3.866 Å, r(C−Cl) = r_4 = 1.668 Å at 0.20 ps; r_1 = 2.745 Å, r_4 = 1.656 Å at 0.40 ps; and r_1 = 1.848 Å, r_4 = 1.801 Å at 0.50 ps. At 0.60 ps, the complex for the S$_N$2 reaction is formed and then the S$_N$2 reaction is completed at 0.80 ps. The bond distances of C−Cl at time = 0.80, 0.90, and 1.0 ps are r_4 = 4.034, 5.517, and 7.077 Å, respectively, indicating that the Cl atom leaves PhNH$_3^+$.

To elucidate the dynamics in more detail, the profile of the potential energy and geometric parameters calculated as a function of reaction time are plotted in Figure 3. Figure 3A shows the potential energy of the reaction system (PE) plotted as a function of time. Parts B and C, respectively, of Figure 3 show the distances (r_1 and r_4) and angles (θ and ϕ). The zero level of the PE corresponds to an energy at the vertical ionization point from PhCl−NH$_3$. After the ionization, the PE decreases

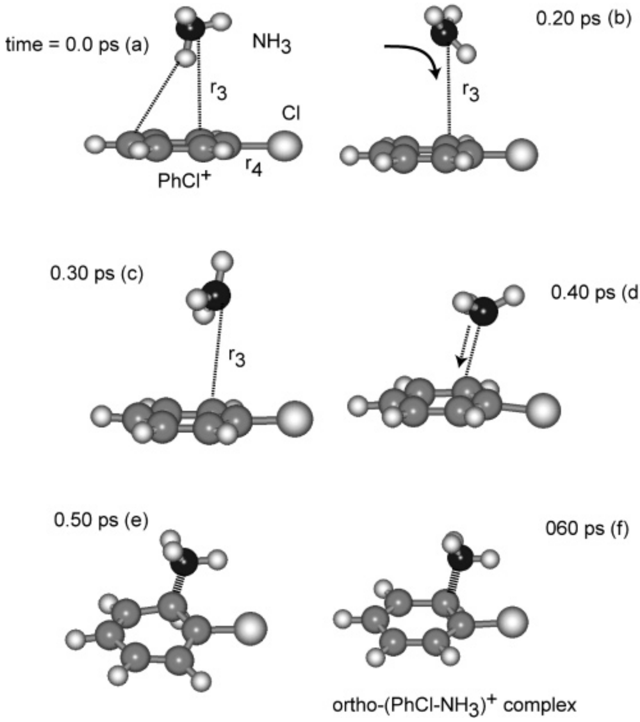

Figure 4. Snapshots for ortho complex formation channel.

rapidly by up to −5.0 kcal/mol due to the Jahn−Teller deformation of the benzene ring at the cationic state.[29] After that, the PE changes periodically in the time range 0−0.4 ps: if a hydrogen atom of NH_3 orients to PhCl, PE decreases, but the orientation of the N atom of NH_3 causes instability. The PE decreases gradually in time range 0−0.4 ps due to an approach of NH_3 to $PhCl^+$. At 0.5 ps, NH_3 attaches to the Cα atom and the complex of the S_N2 reaction is formed. The S_N2 reaction is completed after several collisions at 0.80 ps. Finally, the Cl atom leaves $PhNH_3^+$. Time propagations of angles (θ and ϕ) indicate that the structural deformation of $PhCl^+$ suddenly takes place around the complex formation region.

Ortho Complex Formation Channel. Snapshots for the ortho complex formation channel are illustrated in Figure 4. The structural parameters of the neutral complex are $r_1 = 4.201$, $r_2 = 4.434$, $r_3 = 3.882$, $r_4 = 1.7497$ Å, $\theta = 76.1°$, and $\phi = 179.9°$ at time zero. The NH_3 molecule is located at $R = 4.078$ Å above the benzene ring. The trajectory of $PhCl^+(NH_3)$ starts from the vertical ionization point, and a hole is localized on the benzene ring. After the ionization, NH_3 moves on the benzene ring and approaches a C−Cl part of PhCl (time = 0.0−0.30 ps). However, NH_3 falls to a carbon atom in the ortho-position before arriving at the C−Cl carbon at 0.40 ps. The distance parameter (r_3) is suitable for expressing the approach of NH_3 to the ortho-position: the values at 0.2, 0.3, and 0.4 ps are calculated to be 3.733, 3.432, and 2.477 Å, indicating that NH_3 gradually approaches the ortho-carbon atom, and the ortho complex is formed at 0.50 ps ($r_3 = 1.473$ Å). The lifetime of this complex is longer than 2.0 ps, and the complex exists as a long-lived complex.

Figure 5 shows the time propagation of the potential energy of the reaction system (PE), the distances (r_3 and r_4), and the angle (ϕ) for the ortho complex formation channel. The time profile of the PE is very similar to that of the S_N2 reaction channel. Addition of NH_3 occurs at 0.41 ps, while the energy of the system suddenly decreases to −40 kcal/mol. The time propagation of the distance (r_3) indicates that NH_3 is gradually approaching and the addition of NH_3 rapidly takes place. The C−Cl distance of PhCl is hardly changed during the reaction.

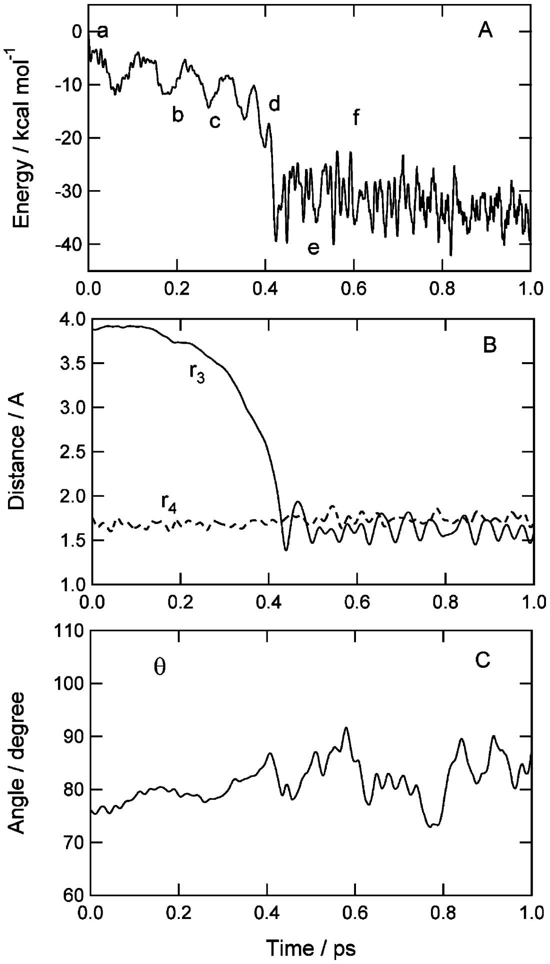

Figure 5. Time propagations of potential energy (A), distances (r_3 and r_4) (B), and angles (θ) (C) for ortho complex formation channel.

TABLE 2: Summary of Direct ab Initio MD Calculations for Ionization of $PhCl-NH_3$

	no. of trajectories	branching ratio
S_N2 reaction[a]	18	0.45
ortho complex	20	0.50
meta complex	0	0
para complex	0	0
dissociation[b]	1	0.02
dipole complex[c]	1	0.02
total	40	1.0

[a] Products are both S_N2 reaction product ($PhNH_3^+$ + Cl) and S_N2 intermediate $(PhCl-NH_3)^+$. [b] Dissociation channel: products are $PhCl^+$ + NH_3. [c] Dipole orientation complex is formed.

C. Summary of Direct ab Initio MD Calculations. In the previous section, the results for two main reaction channels are introduced as sample trajectories. Actually, the structure of the neutral complex fluctuates around the equilibrium point because of its flexibility. To elucidate the effects of initial structures on ionization dynamics, we carried out direct ab initio MD calculations from several selected points. A total of 40 trajectories were calculated, and product channels are analyzed in detail.

The results are summarized in Table 2. It is found that four product channels are available from the vertical ionization of $PhCl-NH_3$. Major product channels are both the S_N2 reaction channel (including an S_N2 reaction intermediate, namely, α-position adduct complex) and ortho-position adduct complex.

TABLE 3: Selected Optimized Geometric Parameters of S$_N$2 Reaction Intermediate and Complexes of (PhCl−NH$_3$)$^+$ [a]

	HF/3-21G(d)	B3LYP/6-311G(d,p)
	S$_N$2 Intermediate	
r_1	1.5800	1.5563
r_4	1.7921	1.8850
θ	120.6	134.4
ϕ	136.1	125.6
	Ortho Complex	
r_1	1.5922	1.61124
r_H	1.0813	1.09497
θ	119.0	121.4
ϕ	103.6	101.2
	Meta Complex	
r_1	1.6049	1.6250
r_H	1.0804	1.0949
θ	115.1	119.4
ϕ	103.2	100.8
	Para Complex	
r_1	1.6063	1.6434
r_H	1.0804	1.0936
θ	114.6	117.7
ϕ	103.2	100.2

[a] Bond lengths and angles are in angstroms and degrees, respectively.

The latter complex is not dissociated into the S$_N$2 reaction product (PhNH$_3^+$ + H). The branching ratios for S$_N$2 and ortho-positions are 0.45 and 0.50, respectively. As a minor channel, dissociation channel, leading to PhCl$^+$ + NH$_3$, is found. Also, a weakly bound complex where NH$_3$ molecule binds to two hydrogen atoms of PhCl$^+$ is formed; all heavy atoms are located on the same molecular plane. However, these channels are significantly minor. The S$_N$2 reaction and ortho complex channels preferentially occur. Thus, selectivity of the product channels is clearly shown in the dynamics calculation.

D. Structures of the Intermediate Complexes. As mentioned above, direct ab initio MD calculations showed that two reaction complexes are mainly formed as products: S$_N$2 intermediate and ortho complexes. In this section, the structures of the complexes are calculated by static ab initio and DFT calculations to obtain more detailed structural characteristics of the complexes. The optimized geometric parameters for S$_N$2 intermediate and ortho complexes are listed in Table 3 together with those of meta and para complexes for comparison. In the S$_N$2 intermediate complex, the nitrogen atom of NH$_3$ is bonded to the α-carbon atom of PhCl$^+$. By addition of NH$_3$, the C−Cl bond of PhCl is elongated from 1.7611 to 1.8850 Å (B3LYP/6-311G(d,p) level), and the position of the Cl atom deviates from the molecular plane of benzene because of sp^3 hybrid orbital formation. A similar structural change (but a hydrogen atom in the ortho-position deviates from the plane) is found in the ortho complex, indicating that the ortho complex is an intermediate in an S$_N$2 reaction NH$_3$ + C$_6$H$_5$Cl$^+$ → PhCl(NH$_3$)$^+$ + H. The geometric optimizations are also carried out for meta and para complexes. Similar structural characteristics are obtained.

The activation barrier for Cl atom dissociation from S$_N$2 intermediate, (PhNH$_3^+$)Cl → TS → PhNH$_3^+$ + Cl, is calculated to be 2.9 kcal/mol (B3LYP/6-311G(d,p) level) without zero-point energy (ZPE). This energy barrier is changed to 2.4 kcal/mol including a ZPE correction. The barrier height is significantly lower in energy than the reaction energy.

The ortho complex is the most stable in energy of these complexes. The relative energies for the S$_N$2, meta, and para complexes are +2.8, +0.4, and +3.1 kcal/mol (B3LYP/6-311G(d,p) level), respectively, and +3.2, +2.2, and +3.0 kcal/mol (HF/3-21G(d) level), respectively, with respect to the ortho complex. This means that the HF/3-21G(d) calculation gave reasonable structural and energetics features for the (PhClNH$_3$)$^+$ system. The basis set superposition error (BSSE) is less than 0.8 kcal/mol at the HF/3-21G(d) level.

TABLE 4: Harmonic Vibrational Frequencies of S$_N$2 Reaction Intermediate (PhCl−NH$_3$)$^+$ Calculated at HF/3-21G(d) and B3LYP/6-311G(d,p) Levels of Theory

		HF/3-21G(d)			
3618(a′)	3615(a″)	3520(a′)	3401(a′)	3384(a″)	3381(a′)
3365(a′)	3364(a″)	1822(a′)	1813(a″)	1669(a′)	1620(a′)
1617(a″)	1576(a′)	1530(a″)	1442(a″)	1379(a″)	1282(a′)
1254(a″)	1232(a′)	1164(a″)	1086(a′)	1077(a′)	1069(a′)
1036(a″)	1014(a′)	938(a)	898(a′)	864(a′)	818(a″)
728(a′)	693(a′)	636(a″)	591(a′)	488(a′)	467(a″)
393(a)	366(a″)	309(a′)	246(a″)	230(a″)	78(a′)
		B3LYP/6-311G(d,p)			
3467(a′)	3465(a″)	3370(a′)	3217(a′)	3201(a″)	3198(a′)
3179(a′)	3179(a″)	1647(a′)	1634(a″)	1601(a′)	1543(a″)
1490(a′)	1452(a′)	1420(a″)	1351(a″)	1314(a″)	1216(a′)
1170(a″)	1114(a″)	1100(a′)	1008(a′)	1002(a′)	998(a″)
994(a)	972(a″)	919(a′)	873(a′)	774(a″)	756(a′)
692(a)	628(a′)	585(a″)	505(a′)	431(a′)	429(a″)
350(a′)	345(a″)	262(a′)	243(a″)	202(a″)	81(a)

To elucidate the shape of the potential energy surface (PES) around the equilibrium points of the S$_N$2 intermediate complex, vibrational frequencies were calculated. The results are listed in Table 4. Three frequencies in the higher energy region (3467, 3465, and 3370 cm^{-1}) are assigned to the N−H stretching modes of the NH$_3$ moiety of PhNH$_3^+$. The corresponding frequencies of free NH$_3$ were calculated to be 3586 and 3466 cm^{-1}. The frequencies of NH$_3$ are red-shifted by the formation of an S$_N$2 complex. The frequencies calculated at the HF/3-21G(d) level are in reasonable agreement with those of B3LYP/6-311G(d,p). From the calculations, it seems that the HF/3-21G(d) calculation gives a reasonable PES around the equilibrium points of the complex. At least, one can discuss a qualitative feature of ionization dynamics of PhCl−NH$_3$ using the results of HF/3-21G(d) level of theory.

4. Discussion

A. Summary of the Present Calculation. In the present study, the ionization dynamics of (PhCl−NH$_3$)$^+$ was investigated by means of direct ab initio MD method. The reaction scheme obtained in the present study is given in Figure 6. The electronic states are schematically expressed by (PhCl)$^+$(NH$_3$) at the vertical ionization point (time zero in trajectory calculation). It was found that two product channels are mainly available from the vertical ionization of PhCl−NH$_3$, and these channels are competitive to each other: an S$_N$2 intermediate (including α-position adduct complex) and an ortho-position adduct complex. The branching ratios for S$_N$2 intermediate and ortho complex channels are 0.45 and 0.50, respectively. Thus, selectivity of the product channels is clearly shown in the dynamics calculation.

B. Effects of Halogen Substitution on the Product Channels. In a previous work, we investigated theoretically ionization dynamics of benzene−ammonia 1:1 complex (C$_6$H$_6$−NH$_3$).[19] It was found that two reaction channels compete with each other:

$$(\mathrm{C_6H_6{-}NH_3})^+ \rightarrow \mathrm{C_6H_6}^+ + \mathrm{NH_3} \qquad \text{(dissociation channel)}$$

$$\rightarrow \mathrm{C_6H_6}^+\mathrm{NH_3} \qquad \text{(complex formation channel)}$$

In the first channel, NH$_3$ is dissociated from C$_6$H$_6^+$ because of

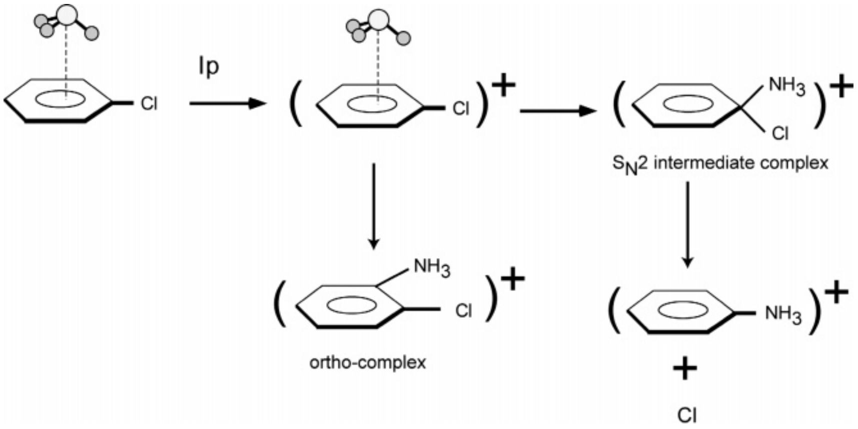

Figure 6. Reaction model for the ionization dynamics of PhCl−NH$_3$.

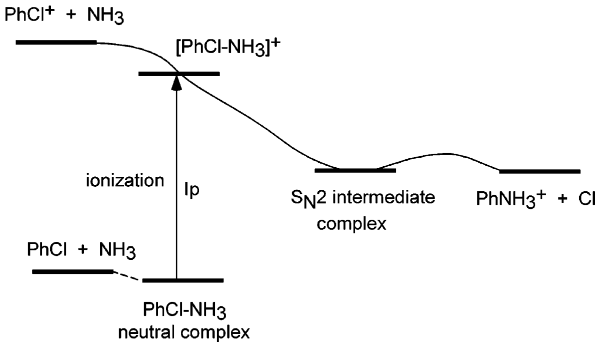

Figure 7. Schematic representation of intramoelcular S$_N$2 reaction in PhCl−NH$_3$ system.

repulsive interaction between the hydrogen of NH$_3$ and the positive charge of C$_6$H$_6$$^+$. In the second channel, NH$_3$ is added to one of the carbon atoms of the benzene ring, but the S$_N$2 reaction product (C$_6$H$_5$−NH$_3$$^+$ + H) is not found in the benzene−NH$_3$ system without a halogen atom. Hence, the S$_N$2 reaction can occur in the case of halogenated benzene.

The dynamics calculation in the present study gives two product channels of (PhCl−NH$_3$)$^+$: S$_N$2 intermediate complex (α-position) and ortho-position addition complex. The meta and para complexes are not formed. The selectivity is clearly shown in the present system. This selection is due to the fact that the nonbonding orbital of NH$_3$ interacts strongly with a singly occupied molecular orbital (SOMO) of PhCl$^+$. The spin densities on α-, ortho-, and para-positions of PhCl$^+$ are larger than that of the meta-position. Hence, the NH$_3$ reacts preferentially with these sites.

A schematic illustration of reaction model derived from the present calculation is given in Figure 7. By the ionization of the PhCl−NH$_3$ neutral complex, the electronic state is vertically changed from the neutral to ionic states. This point corresponds to the collision region on the surface of the S$_N$2 reaction, PhCl$^+$ + NH$_3$. The trajectory is stagnant in the S$_N$2 intermediate region. After several collisions, some trajectories pass into the product region.

C. Comparison with Experiments. Maeyama and Mikami investigated the ionization dynamics of C$_6$H$_5$Cl−NH$_3$ and C$_6$H$_5$F−NH$_3$ complexes by means of the trapped ion photodissociation (TIP) technique.[6,7] They showed that the ionization of PhX−NH$_3$ complexes (X = F and Cl) leads to the complex formation of PhX−NH$_3$$^+$ and S$_N$2 products, C$_6$H$_5$−NH$_3$$^+$ + X, via complex formation. The present calculation indicates that the formations of both PhX−NH$_3$$^+$ complex and the S$_N$2 intermediate are main channels for the ionization of PhCl−NH$_3$. This result is consistent with their experimental findings. The present study also predicts that NH$_3$ is added to the ortho-position of PhNH$_3$$^+$ complex.

D. Additional Comments. We have introduced several approximations to calculate the potential energy surface and to treat the reaction dynamics. First, we have assumed that [PhNH$_3$]$^+$ has no excess energy at the initial step of the trajectory calculation (time = 0.0 ps). Also, we neglected zero-point vibrational energies in the dynamics calculation because these energies were close to each other in the present system (difference was less than 3 kcal/mol). Therefore, this approximation is enough to describe the dynamics of the present system. Inclusion of these effects on the dynamics calculations may cause a slight change of lifetime of the S$_N$2 intermediate. In the case of higher excess energy, the lifetime of the intermediate complex will become shorter.

Second, we assumed an HF/3-21G(d) multidimensional potential energy surface in the dynamics calculations throughout. In previous papers, we investigated the ionization dynamics of benzene−H$_2$O and benzene−HF using the HF/3-21G(d) level of theory. The results obtained at the HF/3-21G(d) calculation gave a reasonable description of the ionization dynamics of the complexes. Therefore, the level of theory used in the present calculation (HF/3-21G(d)) is adequate to discuss qualitatively the ionization dynamics of PhCl−NH$_3$. However, more accurate wave functions may provide deeper insight into the dynamics. Despite the several assumptions introduced here, the results enable us to obtain valuable information on the mechanism of the ionization of PhCl−NH$_3$.

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