Proton Transfer of NH_3−HCl Catalyzed by Only One Molecule

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The proton transfer in NH_3−HCl by only one molecule of catalyst was studied by using the MP2 method with the large 6-311++G(2d,2p) basis set. The 18 structures are obtained for the smallest units, NH_3−HCl−A trimers, for which the proton transfer maybe occurred. The final results show that the proton transfers have occurred in the 15 cyclic shape structures for A = H_2SO_4, H_2SO_3, HCOOH (a), HF, H_2O_2, HNO_3, HNO_2 (a), CH_3OH, HCl, HNC, H_2O, HNO_2 (b), NH_3, HCOOH (b), and HCHO, and not occurred in another 3 trimer structures for A = HCN, H_2S, and PH_3. These results show that the proton transfer occurs from HCl to NH_3 when catalyst molecule A (acidic, neutral, or basic) not only as a proton donor strongly donates the proton to the Cl atom but as an acceptor strongly accepts the proton from the NH_3 molecule in the cyclic H-bond structure. In this work, a proton circumfluence model is proposed to explain the mechanism of the proton transfer. We find that, for the trimer, when the sum of two hydrogen bond lengths ($R = R_1 + R_2$) is shorter than 5.0 Å, molecule A has the ability to catalyze the proton transfer. In addition, we also find that the interaction energy E_{int} between NH_3−HCl and A is nearly related to the extent (R_{H1-Cl}) of proton transfer, that is, the interaction energy E_{int} increases with the proton transfer.

Introduction

The possibility of proton transfer between acid and base subunits in a system plays a crucial role in a wide range of chemical and biological reactions.[1−6] Hydrogen chloride and ammonia provide us with a simple, prototypical acid−base pair for studying the proton-transfer reactions. Chemists have puzzled over the following questions: What is the detailed mechanism of proton transfer and what is the stable form of NH_3−HCl in the gas phase? Mulliken[7,8] speculated that gas-phase NH_3−HCl might exist as an ion pair ($NH_4^+\cdots Cl^-$) just as in the aqueous solution. Early ab initio calculation by Clementi[9−11] indeed showed the strong ion-pair character for the system. This seems to corroborate with the well-known observation that a white fog of solid ammonium chloride particles appears in the interdiffusion of the vapors from concentrated ammonia and hydrochloric acid.[12,13] However, microwave experiments by Legon and co-workers[14,15] concluded that the system exists as a simple hydrogen-bonded system with HCl as the proton donor and NH_3 as the acceptor rather than an ion pair form resulting from complete proton transfer. This experimental result is supported by several higher level ab initio calculations[16−22] and by matrix isolation studies.[23]

It seems that water as catalyst may play a critical role in assisting the proton transfer in NH_3−HCl.[24−26] Latajka[25] found a minimum structure, NH_3−HCl−$(H_2O)_2$ (tetramer) complex, containing an ion pair formed by a proton transfer from HCl to NH_3. Tao[26] found out that the minimum structure containing two ion pairs is the tetramer $(NH_3{-}HCl)_2$ in the solid state. Recently, using larger basis functions, our group[27] and co-workers obtained the minimum structure of proton transfer occurring to be NH_3−HCl−H_2O trimer, in which the NH_3−HCl subunit becomes an ion pair $NH_4^+\cdots Cl^-$ resulting from a proton transfer from HCl to NH_3. Then an interesting question appeared: Are there other molecules as single molecule catalysts to promote proton transfer in NH_3−HCl besides the H_2O molecule?

In this paper, we study the structures of the interaction between NH_3−HCl and only one A molecule(A = H_2SO_4, H_2SO_3, HCOOH, HF, H_2O_2, HNO_3, HNO_2, CH_3OH, HCl, HNC, H_2O, NH_3, HCHO, HCN, H_2S and PH_3), discuss the mechanism of proton transfer from HCl to NH_3 with the catalyst effect of only one A molecule, propound a condition of proton transfer occurring from HCl to NH_3 in the NH_3−HCl−A trimer, and contribute new knowledge to proton transfer in hydrogen bond complexes.

Computational Methods

To choose suitable basis set, the basis set effects were studied at the MP2 level (NH_3−HCl−HCl, NH_3−HCl−NH_3, and NH_3−HCl−H_2O as examples) with 6-311++G(d,p), 6-311++G(2d,p), 6-311++G(2d,2p), and 6-311++G(2df,2p) basis sets.

Using the selected basis set 6-311++G(2d,2p), the structures of NH_3−HCl−A (A = H_2SO_4, H_2SO_3, HCOOH, HF, H_2O_2, HNO_3, HNO_2, CH_3OH, HCl, HNC, H_2O, NH_3, HCHO, HCN, H_2S, and PH_3) were optimized at the MP2 level. To confirm the MP2/6-311++G(2d,2p) result of three structures (A = HCN, H_2S, and PH_3) without proton transfer, the larger basis set 6-311++G(2df,2p) was used to further optimize the three structures at the MP2 level.

To understand the electron correlation effect, two levels of theory [SCF, MP2] with the 6-311++G(2d,2p) basis set were used in the calculations of the interaction energies between the A and NH_3−HCl (A = H_2SO_4, H_2SO_3, HCOOH, HF, H_2O_2, HNO_3, HNO_2, CH_3OH, HCl, HNC, H_2O, NH_3, HCHO, HCN, H_2S, and PH_3). The counterpoise (CP) method[28] was used to correct the basis set superposition error (BSSE).

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To research the influence of molecule A on NH_3-HCl and the interaction energy between the A and NH_3-HCl, NH_3-HCl is regarded as a unit, and the interaction between A and NH_3-HCl is treated as two-body interaction. The interaction energy corrected by the CP method can be written as

$$E_{\mathrm{int}} = E_{\mathrm{NH_3-HCl-A}} - E_{\mathrm{NH_3-HCl-X}} - E_{\mathrm{X-A}}$$

Here, A = H_2SO_4, H_2SO_3, HCOOH, HF, H_2O_2, HNO_3, HNO_2, CH_3OH, HCl, HNC, H_2O, NH_3, HCHO, HCN, H_2S, and PH_3. $E_{\mathrm{NH_3-HCl-X}}$ is the energy of subsystem NH_3-HCl in the presence of the ghost orbitals of subsystem A. $E_{\mathrm{X-A}}$ is the energy of subsystem A in the presence of the ghost orbitals of subsystem NH_3-HCl.

The electron correlation correction for the interaction energies E_{int} is defined as

$$E_{\mathrm{corr}} = E_{\mathrm{MP2}} - E_{\mathrm{SCF}}$$

where E_{MP2} is the energy calculated by the MP2 method and E_{SCF} is the value by the HF method.

To show bond properties in $NH_3-HCl-A$, the AIM (atom in molecule) method is used. The Laplacian of the electron density at a bond critical point, $\nabla^2\rho(r)$, is also calculated with the 6-311++G(2d,2p) basis set. Popelier[29,30] proposed that, for covalent bonds, the value of the $\nabla^2\rho(r)$ is negative. For ionic bonds, hydrogen bonds, and van der Waals interactions, the value of the $\nabla^2\rho(r)$ is positive. Among them, the hydrogen bond value of the $\nabla^2\rho(r)$ lies in the proposed range of 0.024−0.139 au

All the calculations were performed with the Gaussian98 program.[31]

Results and Discussion

What is the proton transfer between NH_3 and HCl? It is the process in which the hydrogen bond complex NH_3-HCl unit becomes an ion pair $NH_4^+\cdots Cl^-$, that is, the bond between Cl and H_1 changes from a covalent bond ($R_{\mathrm{H1-Cl}}$ =1.322 Å[22]) to an ionic bond and NH_3 accepts a proton from HCl to form NH_4^+. It is shown that the length $R_{\mathrm{H1-Cl}}$ is nearly related to the extent of proton transfer. So the $R_{\mathrm{H1-Cl}}$ value is used to represent the extent of proton transfer from HCl to NH_3. It is observed that proton transfer occurred for $R_{\mathrm{H1-Cl}} > 1.60$ Å in $NH_3-HCl-A$ (A = H_2SO_4, H_2SO_3, HCOOH (a), HF, H_2O_2, HNO_3, HNO_2 (a), CH_3OH, HCl, HNC, H_2O, HNO_2 (b), NH_3, HCOOH (b), and HCHO).

1. Choice of Basis Set. The choice of basis set is important in accurate quantum chemistry calculations. In the $NH_3-HCl-A$ complex, we select three kinds of A molecules (acidic HCl, neutral H_2O, and basic NH_3) as examples to study basis set effects at the MP2 level with 6-311++G(d,p), 6-311++G(2d,p), 6-311++G(2d,2p), and 6-311++G(2df,2p) basis sets. Results are shown in Table 1.

For the $NH_3-HCl-HCl$ complex, with the 6-311++G(d,p) basis set, the $R_{\mathrm{Cl-H1}}$ value is only 1.338 Å ($R_{\mathrm{H1\cdots N}}$ = 1.691 Å). With the 6-311++G(2d,p) basis set (increasing 15 basis functions), the $R_{\mathrm{Cl-H1}}$ value only increases by 0.036 Å to be 1.374 Å ($R_{\mathrm{H1\cdots N}}$ = 1.580 Å). Further, from 6-311++G(2d,p) to 6-311++G(2d,2p), also increasing 15 basis functions, the $R_{\mathrm{Cl-H1}}$ value dramatically increases by 0.360 Å to be 1.734 Å, which shows that proton transfer occurs (the $R_{\mathrm{H1-N}}$ value of 1.130 Å shows that a covalent bond is formed). But from 6-311++G(2d,2p) to 6-311++G(2df,2p), increasing 21 basis functions, the $R_{\mathrm{Cl-H1}}$ value is almost unchanged ($R_{\mathrm{H1-N}}$ is fixed).

TABLE 1: Optimized Structural Parameters for $NH_3-HCl-A$ (A = HCl, NH_3, and H_2O) at the MP2 Level

	basis set	N	$R_{\mathrm{H1-Cl}}$ (Å)	$R_{\mathrm{N\cdots H1}}$ (Å)
$NH_3-HCl-HCl$	6-311++G(d,p)	117	1.338	1.691
	6-311++G(2d, p)	132	1.374	1.580
	6-311++G(2d,2p)	147	1.734	1.130
	6-311++G(2df,2p)	168	1.735	1.130
$NH_3-HCl-H_2O$	6-311++G(d,p)	116	1.361	1.611
	6-311++G(2d,p)	131	1.698	1.159
	6-311++G(2d,2p)	149	1.724	1.137
	6-311++G(2df,2p)	170	1.718	1.141
$NH_3-HCl-NH_3$	6-311++G(d,p)	123	1.355	1.629
	6-311++G(2d,p)	138	1.687	1.164
	6-311++G(2d,2p)	159	1.714	1.141
	6-311++G(2df,2p)	180	1.710	1.144

TABLE 2: Total Energies (E, kcal/mol) and Interaction Energies (E_{int}, kca/mol) for MP2/6-311++G(d,p) and MP2/6-311++G(2d,2p) Geometries of $NH_3-HCl-A$ (A = H_2O, NH_3, and HCl) by CCSD(T)/6-311++G(2d,2p)

	MP2/6-311++G(d,p)		MP2/6-311++G(2d,2p)	
	E	E_{int}	E	E_{int}
$NH_3-HCl-H_2O$	−372159.28	−6.80	−372160.42	−14.03
$NH_3-HCl-NH_3$	−359699.51	−6.63	−359700.05	−13.54
$NH_3-HCl-HCl$	−613108.89	−4.31	−613108.93	−11.67

Dissimilarly, for the $NH_3-HCl-H_2O$ complex, from the 6-311++G(d,p) to the 6-311++G(2d,p) basis set, the $R_{\mathrm{Cl-H1}}$ value dramatically increases by 0.337 Å from 1.361 to 1.698 Å (proton transfer occurred), while from 6-311++G(2d,p) to 6-311++G(2d,2p) the change (0.026 Å) of $R_{\mathrm{Cl-H1}}$ is small.

For $NH_3-HCl-NH_3$, the basis set effect is similar to that for $NH_3-HCl-H_2O$.

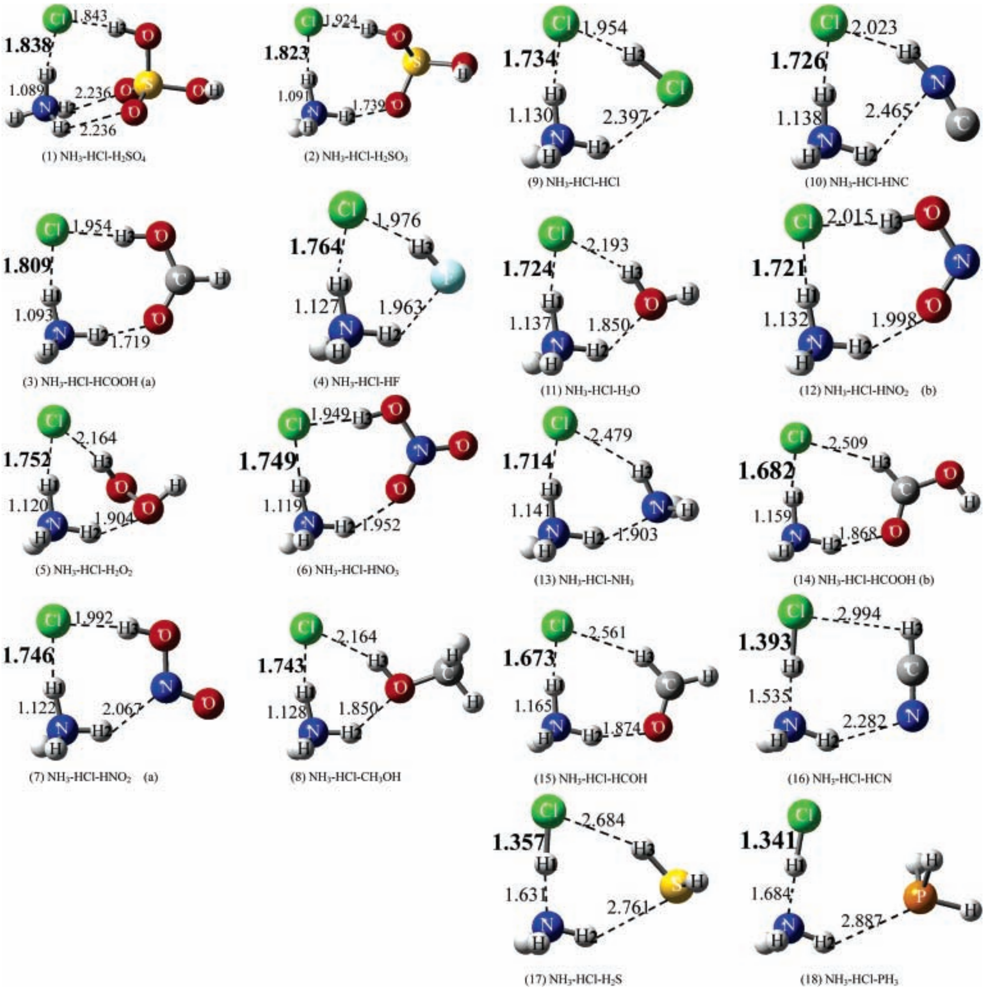
As stated above, when the basis set is larger than that of 6-311++G(2d,p), the $R_{\mathrm{Cl-H1}}$ values can converge.

The calculated results show that when we performed the computations with the 6-311++G(d,p) basis set, the proton transfer does not occur in the three complexes $NH_3-HCl-HCl$, $NH_3-HCl-NH_3$, and $NH_3-HCl-H_2O$. But with the 6-311++G(2d,2p) and larger basis sets, the proton transfer can be displayed in the three complexes.

Therefore, the 6-311++G(2d,2p) basis set is selected to study the proton transfers in the $NH_3-HCl-A$ trimers.

In a recent article,[32] it has been found that, for the NH_3-HX complex, the optimized structure at the MP2/6-311++G(d,p) level is closer to that of the structure at the CCSD(T)/6-311++G(2df,2dp) level than that at the MP2/6-311++G(2df,2dp) level. To confirm our result, total energies and interaction energies are calculated for MP2/6-311++G(d,p) and MP2/6-311++G(2d,2p) geometries of $NH_3-HCl-A$ (A = H_2O, NH_3, and HCl) at the CCSD(T)/6-311++G(2d,2p) level. The results are shown in Table 2. For each MP2/6-311++G(d,p) geometry, its energy is slightly higher than that of the MP2/6-311++G(2d,2p) geometry. It is shown that the MP2/6-311++G(d,p) geometry is not better than the MP2/6-311++G(2d,2p) geometry. For each MP2/6-311++G(2d,2p) geometry, the absolute value of its interaction energy is much larger than that of the MP2/6-311++G(d,p) geometry. It is shown that, on the more reliable interaction energy surface, the MP2/6-311++G(2d,2p) geometry is closer to that of the geometry at the global minimum of the counterpoise-corrected potential energy surface by CCSD(T)/6-311++G(2d,2p). This means that the MP2/6-311++G(2d,2p) geometry optimization for $NH_3-HCl-A$ complexes should be suitable.

In addition, an interesting case is observed that acidic, neutral, or basic molecule A all may catalyze the proton transfer from HCl to NH_3.



(1) NH_3-HCl-H_2SO_4
(2) NH_3-HCl-H_2SO_3
(9) NH_3-HCl-HCl
(10) NH_3-HCl-HNC
(3) NH_3-HCl-HCOOH (a)
(4) NH_3-HCl-HF
(11) NH_3-HCl-H_2O
(12) NH_3-HCl-HNO_2 (b)
(5) NH_3-HCl-H_2O_2
(6) NH_3-HCl-HNO_3
(13) NH_3-HCl-NH_3
(14) NH_3-HCl-HCOOH (b)
(7) NH_3-HCl-HNO_2 (a)
(8) NH_3-HCl-CH_3OH
(15) NH_3-HCl-HCOH
(16) NH_3-HCl-HCN
(17) NH_3-HCl-H_2S
(18) NH_3-HCl-PH_3

Figure 1. Optimized structures of NH_3−HCl−A for A = H_2SO_4, H_2SO_3, HCOOH, HF, H_2O_2, HNO_3, HNO_2, CH_3OH, HCl, HNC, H_2O, NH_3, HCHO, HCN, H_2S, and PH_3 at the MP2/6-311++G(2d,2p) level. **1**−**15** are proton-transfer structures; **16**−**18** are hydrogen bond structures (without proton transfer).

2. Characteristics of Proton Transfer. The optimized structures of the NH_3−HCl−A complexes (A = H_2SO_4, H_2SO_3, HCOOH, HF, H_2O_2, HNO_3, HNO_2, CH_3OH, HCl, HNC, H_2O, NH_3, HCHO, HCN, H_2S, and PH_3) are obtained at the MP2/6-311++G(2d,2p) level and shown in Figure 1 and Table 3. The (a) and (b) in Figure 1 and Table 3 are used to differentiate two isomers of NH_3−HCl−HCOOH and NH_3−HCl−HNO_2. The frequencies are all real for the optimized NH_3−HCl−A structure. The smallest frequency value of each structure is shown in Table 3.

From Figure 1 and Table 3, the proton transfer appears in almost all the trimers except in three complexes as NH_3−HCl−H_2S, NH_3−HCl−PH_3, and NH_3−HCl−HCN. To confirm the results above, the three structures without proton transfer are reoptimized with the larger basis set 6-311++G(2df,2p) by the MP2 method. From 6-311++G(2d,2p) to 6-311++G(2df,2p), each structure is almost unchanged (for example, the R_{H1-Cl} change is smaller than 0.006 Å) for the three complexes. The 6-311++G(2df,2p) results are R_{H1-Cl} = 1.393 Å and $R_{N\cdots H1}$ = 1.532 Å for NH_3−HCl−HCN, R_{H1-Cl} = 1.358 Å and $R_{N\cdots H1}$ = 1.626 Å for NH_3−HCl−H_2S, and R_{H1-Cl} = 1.343 Å and $R_{N\cdots H1}$ = 1.679 Å for NH_3−HCl−PH_3, respectively. Thus the results from 6-311++G(2d,2p) are credible, namely, no proton transfers occurred in the three complexes.

In NH_3−HCl−A complexes, the extent of proton transfer occurring is nearly related to the length of R_{H1-Cl}. So the R_{H1-Cl} value is used to represent the extent of proton transfer from HCl to NH_3. The order of the extent of proton transfer from HCl to NH_3 is as follows: NH_3−HCl−H_2SO_4 > NH_3−HCl−H_2SO_3 > NH_3−HCl−HCOOH (a) > NH_3−HCl−HF > NH_3−HCl−H_2O_2 > NH_3−HCl−HNO_3 > NH_3−HCl−HNO_2(a) > NH_3−HCl−CH_3OH > NH_3−HCl−HCl > NH_3−HCl−HNC > NH_3−HCl−H_2O > NH_3−HCl−HNO_2 (b) > NH_3−HCl−NH_3 > NH_3−HCl−HCOOH (b) > NH_3−HCl−HCHO. This order is based on the length of R_{H1-Cl}.

According to the extent of proton transfer, the 18 structures can be classified into three classes. The first class is strong proton-transfer complexes, in which the R_{H1-Cl} is larger than 1.80 Å, including NH_3−HCl−H_2SO_4 (R_{H1-Cl} = 1.838 Å), NH_3−HCl−H_2SO_3 (R_{H1-Cl} = 1.823 Å), and NH_3−HCl−HCOOH (a) (R_{H1-Cl} = 1.809 Å). The second class is generic proton-transfer complexes, in which the R_{H1-Cl} is larger than 1.60 Å, including NH_3−HCl−HF (R_{H1-Cl} = 1.764 Å), NH_3−HCl−H_2O_2 (R_{H1-Cl} = 1.752 Å), NH_3−HCl−HNO_3(R_{H1-Cl} = 1.749 Å), NH_3−HCl−HNO_2 (a) (R_{H1-Cl} = 1.746 Å), NH_3−HCl−CH_3OH (R_{H1-Cl} = 1.743 Å), NH_3−HCl−HCl (R_{H1-Cl} = 1.734 Å), NH_3−HCl−HNC (R_{H1-Cl} = 1.726 Å), NH_3−HCl−H_2O (R_{H1-Cl} = 1.724 Å), NH_3−HCl−HNO_2 (b) (R_{H1-Cl} = 1.721 Å), NH_3−HCl−NH_3 (R_{H1-Cl} = 1.714 Å), NH_3−HCl−HCOOH (b) (R_{H1-Cl} = 1.682 Å), and NH_3−HCl−HCHO (R_{H1-Cl} = 1.673 Å). For the above 15 structures in which proton transfer occurs, the structures are cyclic with a strong hydrogen bond. The third class is weak hydrogen bond complexes without proton transfer, in which the HCl acts as the proton donor and NH_3 as the

TABLE 3: Optimized Structural Parameters, Smallest Values of Vibrational Frequencies, Laplacian of the Electron Densities at a Bond Critical Point $\nabla^2\rho(r)$, and the Interaction Energies between NH_3−HCl and A at the MP2/6-311++G(2d,2p) Level

			bond lengths (Å)				$\nabla^2\rho(r)$ (au)				
	A	υ_{min} (cm^{-1})	R_{H1-Cl}	$R_{N\cdots H1}$	$R_{N\cdots Cl}$	$R_1 + R_2$	H_1−Cl	N···H_1	A···H_2	Cl···H_3	E_{int} (kcal/mol)
1	H_2SO_4	52.6	1.838	1.089	2.919	*a*	0.055	−1.457	0.051	0.048	−31.69
2	H_2SO_3	37.4	1.823	1.091	2.901	3.663	0.054	−1.426	0.125	0.062	−27.62
3	HCOOH (a)	59.9	1.809	1.093	2.880	3.673	0.053	−1.403	0.062	0.128	−25.37
4	HF	159.7	1.764	1.127	2.867	3.939	0.031	−1.137	0.089	0.061	−17.58
5	H_2O_2	77.7	1.752	1.120	2.859	4.068	0.033	−1.175	0.068	0.102	−17.87
6	HNO_3	33.1	1.749	1.119	2.860	3.901	0.033	−1.195	0.092	0.063	−20.58
7	HNO_2 (a)	66.4	1.746	1.123	2.855	4.058	0.031	−1.156	0.072	0.064	−18.05
8	CH_3OH	31.0	1.743	1.128	2.852	4.014	0.027	−1.111	0.066	0.114	−15.67
9	HCl	121.2	1.734	1.130	2.852	4.351	0.024	−1.099	0.055	0.057	−13.30
10	HNC	97.6	1.726	1.138	2.861	4.488	0.018	−1.046	0.068	0.040	−15.67
11	H_2O	162.8	1.724	1.137	2.846	4.043	0.019	−1.042	0.105	0.065	−14.49
12	HNO_2 (b)	45.6	1.721	1.132	2.847	4.013	0.021	−1.080	0.080	0.064	−15.78
13	NH_3	120.1	1.714	1.141	2.854	4.382	0.015	−0.982	0.090	0.048	−14.02
14	HCOOH (b)	64.3	1.682	1.159	2.835	4.377	−0.001	−0.883	0.044	0.100	−12.27
15	HCHO	87.4	1.673	1.165	2.834	4.435	−0.006	−0.842	0.040	0.098	−11.58
16	HCN	68.4	1.393	1.535	2.928	5.276	−0.419	0.043	0.027	0.046	−6.37
17	H_2S	82.6	1.357	1.631	2.985	5.445	−0.509	0.074	0.028	0.031	−3.90
18	PH_3	46.6	1.337	1.700	3.022	b	−0.550	0.082	0.022		−2.87

[a] There are two H-bonds between two H atoms of NH_3 and two O atoms of the H_2SO_4 molecule in the NH_3−HCl−H_2SO_4 complex. This shows the H_2SO_4 molecule has a very strong ability to form H-bonds with NH_3−HCl, which is not represented by $R_1 + R_2$. [b] In the NH_3−HCl−PH_3 complex, the PH_3 molecule has a very weak ability to form H-bonds with NH_3−HCl, and the distances between the Cl atom and H atoms of PH_3 are very long at 3.616 Å, out of the range of the H-bond length.

acceptor rather than an ion pair form resulting from complete proton transfer. They are NH_3−HCl−HCN (R_{H1-Cl} = 1.393 Å), NH_3−HCl−H_2S (R_{H1-Cl} = 1.357 Å), and NH_3−HCl−PH_3 (R_{H1-Cl} = 1.337 Å).

In addition, the hydrogen bridge (N−H···Cl or N···H−Cl) distances $R_{N\cdots Cl}$ are shown in Table 3. The biggest $R_{N\cdots Cl}$ value is 3.022 Å (NH_3−HCl−PH_3) and the smallest $R_{N\cdots Cl}$ value is 2.834 Å (NH_3−HCl−HCOH). The hydrogen bridge distances $R_{N\cdots Cl}$ of NH_3−HCl−A (A = H_2SO_4, H_2SO_3, HCOOH, HF, H_2O_2, HNO_3, HNO_2, CH_3OH, HCl, HNC, H_2O, NH_3, HCHO, HCN, H_2S, and PH_3) are all shorter than that of the NH_3−HCl ($R_{N\cdots Cl}$ = 3.136 Å[33,34]). Among the complexes with proton transfer, the bond length R_{H1-Cl} of NH_3−HCl−H_2SO_4 is the biggest (1.838 Å, the strongest proton transfer), and the corresponding hydrogen bridge distance $R_{N\cdots Cl}$ (2.919 Å) is the biggest, too. Similarly, the bond length R_{H1-Cl} of NH_3−HCl−HCHO is the smallest (1.673 Å, generic proton transfer), and the corresponding hydrogen bridge distance $R_{N\cdots Cl}$ (2.834 Å) is also the smallest. However, in the complexes without proton transfer, with the bond length R_{H1-Cl} decreasing, the corresponding hydrogen bridge distance $R_{N\cdots Cl}$ increases.

3. Mechanism of the Proton Transfer. From above section, we know that each proton-transfer complex has a cyclic hydrogen bond structure with a strong hydrogen bond interaction between NH_3−HCl and catalyst molecule A. In the cyclic hydrogen bond structure of NH_3−HCl−A, catalyst molecule A is not only a proton donor, strongly donating a proton to the Cl atom, but also an acceptor, strongly accepting a proton from the NH_3. When the H_1−Cl covalent bond is broken and one new N−H_1 covalent bond is formed the proton transfer (ion part $NH_4^+\cdots Cl^-$ is formed) occurs from HCl to NH_3. For the cyclic H-bond structure, a visual depiction is that catalyst molecule A pushes one of its protons to the Cl atom and simultaneously pulls a proton from the NH_3. Finally, the proton of HCl is pulled to the N atom of NH_3 to perform the proton transfer. As a result, the proton circumfluence model is proposed to explain the mechanism for proton transfer (the proton from A to Cl, from Cl to N, and from N to A) and shown in Figure 2. This model is similar to an electric circumfluence model.

If the ability to form the hydrogen bond between the catalyst molecule A and NH_3−HCl is too weak to form the strong proton circumfluence, proton transfer from HCl to NH_3 does not occur. While molecule A connecting with NH_3−HCl forms a strong proton circumfluence, proton transfer occurs.

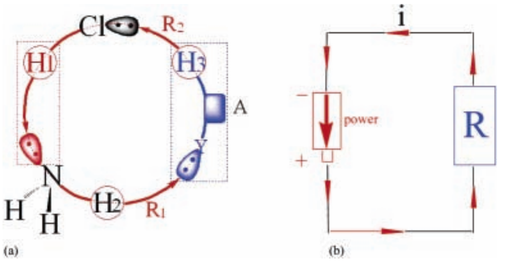


Figure 2. The mechanism of proton transfer: (a) the proton circumfluence model is similar to (b) the electric circumfluence model. The H of molecule A is pulled to the Cl atom, the H_1 of HCl is pulled to the N atom of NH_3, and the H_2 of the NH_3 is pulled to molecule A. R_1 is the length of the H-bond between the H_2 atom of NH_3 and the Y atom of molecule A and R_2 is the length of the H-bond between the Cl atom of HCl and the H_3 atom of molecule A.

Obviously, for catalyst molecule A, its ability to form a hydrogen bond with HCl and NH_3 in a cyclic hydrogen bond structure decides the extent (R_{H1-Cl}) of proton transfer in NH_3−HCl−A. For molecule A, the order of its ability in catalyzing proton transfer is as follows: H_2SO_4 > H_2SO_3 > HCOOH (a) > HF > H_2O_2 > HNO_3 > HNO_2 (a) > CH_3OH > HCl > HNC > H_2O > HNO_2 (b) > NH_3 > HCOOH (b) > HCHO > HCN > H_2S > PH_3. It is noted that molecule A sometimes has different modes in forming a hydrogen bond with HCl and NH_3. For example, for HCOOH there are two modes: (a) and (b). For mode (a), the acidic H atom of the H−O bond forms a hydrogen bond with the lone pair of the Cl atom. For mode (b), the acidic H atom of the H−C bond forms a hydrogen bond with the lone pair of the Cl atom (see **3** and **14** in Figure 1). For molecule A, the ability to form a hydrogen bond with HCl and NH_3 depends on the mode used to form the hydrogen bond.

For catalyst molecule A, its ability to form a hydrogen bond with HCl and NH_3 increases with the sum $R = R_1 + R_2$ shortening. So the sum R may be used to represent the ability of molecule A as a catalyst (R_1 is the length of the H-bond

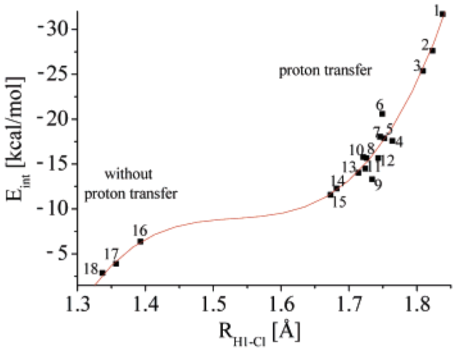


Figure 3. The interaction energy E_{int} (between NH_3−HCl and A) for the bond length R_{H1-Cl} in the NH_3−HCl−A: 1 for A = H_2SO_4, 2 for A = H_2SO_3, 3 for A = HCOOH (a), 4 for A = HF, 5 for A = H_2O_2, 6 for A = HNO_3, 7 for A = HNO_2 (a), 8 for A = CH_3OH, 9 for A = HCl, 10 for A = HNC, 11 for A = H_2O, 12 for A = HNO_2 (b), 13 for A = NH_3, 14 for A = HCOOH (b), 15 for A = HCHO, 16 for A = HCN, 17 for A = H_2S, and 18 for A = PH_3.

between the H_2 atom of NH_3 and the Y atom of the A molecule, R_2 is the length of the H-bond between the Cl atom of HCl and the H_3 atom of the A molecule, see Figure 2).

One can notice that when the hydrogen bond length sum R is shorter than 5.0 Å, A has the ability to catalyze proton transfer. While the sum is longer than 5.0 Å, molecule A does not have the ability to catalyze proton transfer.

4. Interaction Energies between NH_3−HCl and A. In section 3, it was mentioned that the stronger the hydrogen bond interactions between A and NH_3−HCl are, the bigger is the extent of proton transfer from HCl to NH_3.

The interaction energies E_{int} between the NH_3−HCl and A (A = H_2SO_4, H_2SO_3, HCOOH, HF, H_2O_2, HNO_3, HNO_2, CH_3OH, HCl, HNC, H_2O, NH_3, HCHO, HCN, H_2S, and PH_3) are obtained at the MP2/6-311++G(2d,2p) level, as shown in Table 3. The relationship between the extent (R_{H1-Cl}) of proton transfer and the interaction energy E_{int} is found and shown in Figure 3. For most of the 18 structures, the interaction energy E_{int} increases as the R_{H1-Cl} length increases.

We discuss interaction energies according to three classes of complexes mentioned above. The first class is strong proton-transfer complexes including NH_3−HCl−H_2SO_4 (E_{int} = −31.69 kcal/mol), NH_3−HCl−H_2SO_3 (E_{int} = −27.62 kcal/mol), and NH_3−HCl−HCOOH (a) (E_{int} = −25.37 kcal/mol). Their interaction energies are very large, E_{int} > −25 kcal/mol. The second class is generic proton-transfer complexes including NH_3−HCl−HF (E_{int} = −17.58 kcal/mol), NH_3−HCl−H_2O_2 (E_{int} = −17.87 kcal/mol), NH_3−HCl−HNO_3(E_{int} = −20.58 kcal/mol), NH_3−HCl−HNO_2 (a) (E_{int} = −18.05 kcal/mol), NH_3−HCl−CH_3OH (E_{int} = −15.67 kcal/mol), NH_3−HCl−HCl (E_{int} = −13.30 kcal/mol), NH_3−HCl−HNC (E_{int} = −15.67 kcal/mol), NH_3−HCl−H_2O (E_{int} = −14.49 kcal/mol), NH_3−HCl−HNO_2 (b) (E_{int} = −15.78 kcal/mol), NH_3−HCl−NH_3 (E_{int} = −14.02 kcal/mol), NH_3−HCl−HCOOH (b) (E_{int} = −12.27 kcal/mol), and NH_3−HCl−HCHO (E_{int} = −11.58 kcal/mol). Their interaction energies E_{int} are in the range of −10 to −25 kcal/mol. The third class is weak hydrogen bond complexes without proton-transfer including NH_3−HCl−HCN (E_{int} = −6.37 kcal/mol), NH_3−HCl−H_2S (E_{int} = −3.90 kcal/mol), and NH_3−HCl−PH_3 (E_{int} = −2.87 kcal/mol). Their interaction energies E_{int} are very small, E_{int} < −10 kcal/mol. Obviously, the interaction energies of three classes of complexes lie in different ranges. This also proves that the classification mentioned above for three classes of complexes is reasonable from the point of view of the interaction energy.

TABLE 4: The Contributions of Electron Correlation Effects on the Interaction Energies for NH_3−HCl−A at 6-311++G(2d,2p)

	A	E_{int} (kcal/mol)		E_{corr} (kcal/mol)	$\eta = E_{corr}/E_{MP2} = (E_{MP2} - E_{SCF})/E_{MP2}$
		SCF	MP2		
1	H_2SO_4	−26.31	−31.69	−5.38	16.98%
2	H_2SO_3	−24.06	−27.62	−3.56	12.89%
3	HCOOH (a)	−21.70	−25.37	−3.67	14.47%
4	HF	−15.04	−17.58	−2.54	14.45%
5	H_2O_2	−13.72	−17.87	−4.15	23.22%
6	HNO_3	−18.10	−20.58	−2.48	12.05%
7	HNO_2 (a)	−13.02	−18.05	−5.03	27.87%
8	CH_3OH	−1.49	−15.67	−4.18	26.68%
9	HCl	−7.27	−13.30	−6.03	45.33%
10	HNC	−9.55	−15.67	−6.12	39.06%
11	H_2O	−11.20	−14.49	−2.29	15.80%
12	HNO_2 (b)	−12.18	−15.78	−3.60	22.81%
13	NH_3	−10.28	−14.02	−3.74	26.68%
14	HCOOH (b)	−11.04	−12.27	−1.23	10.02%
15	HCHO	−10.59	−11.58	−0.99	8.55%
16	HCN	−4.32	−6.37	−2.05	32.18%
17	H_2S	−1.27	−3.90	−2.63	67.44%
18	PH_3	−0.90	−2.87	−1.97	68.64%

The contributions of electron correlation effects on the interaction energies are shown in Table 4. From Table 4, the largest value of electron correlation effect is 68.64% for NH_3−HCl−PH_3 and the smallest value is 8.55% for NH_3−HCl−HCHO. It is obvious that the electron correlation contribution is important for the calculation of the interaction energy. As a result, it is necessarily to calculate interaction energy by using a higher level method including electron correlation.

5. "Atoms in Molecules" (AIM) Topological Analysis. The topological analyses of NH_3−HCl−A are calculated by using the atoms in molecules (AIM) theory at the MP2/6-311++G-

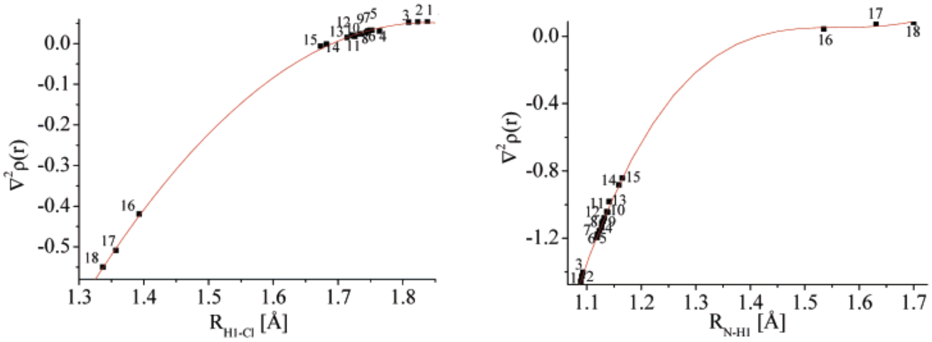


Figure 4. Laplacian of the electron densities for bonds H_1−Cl and N−H_1 in the NH_3−HCl−A: 1 for A = H_2SO_4, 2 for A = H_2SO_3, 3 for A = HCOOH (a), 4 for A = HF, 5 for A = H_2O_2, 6 for A = HNO_3, 7 for A = HNO_2 (a), 8 for A = CH_3OH, 9 for A = HCl, 10 for A = HNC, 11 for A = H_2O, 12 for A = HNO_2 (b), 13 for A = NH_3, 14 for A = HCOOH (b), 15 for A = HCHO, 16 for A = HCN, 17 for A = H_2S and 18 for A = PH_3. For proton-transfer structures **1**−**15**, H_1−Cl is hydrogen bond and N−H_1 is the covalent bond.

(2d,2p) level (see Table 3). For 15 structures of proton transfer occurring, most of the $\nabla^2\rho(r)$ values of bond H_1-Cl are in the typical range for a hydrogen bond (from 0.024 to 0.139 au[25,26]) and $\nabla^2\rho(r)$ values of all $N-H_1$ bonds are in the typical range for a covalent bond ($\nabla^2\rho(r) < 0$). This shows, in the 15 structures, that each original covalent bond H_1-Cl has became a hydrogen bond and the original hydrogen bond $H_1\cdots N$ has became a covalent bond. For the 3 structures without proton transfer, the $\nabla^2\rho(r)$ values of the H_1-Cl bond are from -0.419 to -0.550 au and $\nabla^2\rho(\mathrm{r})$ values of the $N-H_1$ bond are from 0.043 to 0.082 au (see Table 3). It shows that the H_1-Cl bond is still a typical covalent bond and the $N-H_1$ bond is still a typical hydrogen bond. The relationships between $\nabla^2\rho(r)$ and both $R_{\mathrm{H1-Cl}}$ and $R_{\mathrm{N-H1}}$ are illustrated in Figure 4. These structures with proton transfer are located in one area and those without proton transfer are located in another area in Figure 3 and 4. The results of AIM also support the above discussions on proton transfer.

Conclusion

(1) To show the essentials of proton transfer from HCl to NH_3 in a $NH_3-HCl-A$ complex, at least the basis set 6-311++G(2d,2p) must be used in the calculation at the MP2 level.

(2) Fifteen structures, in which proton transfer occurred from HCl to NH_3 by catalysis with only one molecule of A, were obtained.

(3) The order of molecule A catalyzing the proton transfer from HCl to NH_3 in a $NH_3-HCl-A$ complex is dependent on its ability to form a cyclic hydrogen bond with $HCl-NH_3$. The order is the following: $H_2SO_4 > H_2SO_3 >$ HCOOH (a) $>$ HF $> H_2O_2 > HNO_3 > HNO_2$ (a) $> CH_3OH >$ HCl $>$ HNC $> H_2O > HNO_2$ (b) $> NH_3 >$ HCOOH (b) $>$ HCHO $>$ HCN $> H_2S > PH_3$.

(4) The proton circumfluence model (the proton from A to Cl, from Cl to N, and from N to A) is suggested to explain the mechanism of proton transfer. If molecule A is replaced by a suitable hydrogen bond cluster, the mechanism may also hold.

(5) The interaction energy E_{int} between NH_3-HCl and A is nearly related to the extent ($R_{\mathrm{H1-Cl}}$) of proton transfer.

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