Evidence for the $HCl^+(A)$ Formation in the Reaction of $Ne(^3P)$ with the Size-Selected HCl Dimer Using an Electrostatic Hexapole Field

Kohei Imura,[†,††] Hiroshi Ohoyama,[†] and Toshio Kasai*[†,††]
[†]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043*
[††]*Institute for Molecular Science, 38 Nishigonaka, Myodaiji, Okazaki 444-8585*

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Penning ionization of $Ne(^3P)$ metastable atom with size-selected HCl dimer was studied by using an electrostatic hexapole field and chemiluminescence detection. We found that the HCl dimer can also produce $HCl^+(A)$ ions in the reaction with $Ne(^3P)$ just like its corresponding monomer reaction. The internal energy distribution of $HCl^+(A)$ in the dimer reaction is cooler than that in the monomer reaction, reflecting the third-body effect due to the other HCl in the dimer.

There has been no evidence so far that the reaction of $Ne(^3P)$, in short Ne* hereafter, with the HCl dimer produces $HCl^+(A)$, though the corresponding HCl monomer reaction produces $HCl^+(A)$ in the vibrational states $v' = 0$, 1, and 2.[1–4] Recently, Naaman and co-workers pointed out that chemical reactivity of monomers and clusters strongly depends on species of reactant atom. In the case of $O(^3P)$, the reactivity with the HCl cluster increases by more than two orders of magnitude as compared with the monomer reaction.[5] In the case of $O(^1D)$, on the other hand, the reaction rate and the internal energy distribution of the product are not so affected by the change to cluster reaction. In theory, McCoy and co-workers have done the quasiclassical trajectory calculations on the above-mentioned reactions, and they observed the cooling effect in rotational and vibrational distributions of the product if a long-lived van der Waals complex is formed during collision.[6] In contrast, the internal energy distribution of the product is not so affected if van der Waals complex does not survive long and dissociates fast. For the $Ne^*+(HCl)_2$ reaction, there are many exit channels open such as electronic excitation, Penning ionization, and dissociation from an energetic point of view. In this work, we study the Penning ionization reaction of Ne* with the size-selected HCl dimer using a non-destructive size-selection technique with an electrostatic hexapole field.

A molecular beam reaction apparatus consists of five differentially pumped chambers. A beam of metastable Ne* atoms was generated by a glow discharge operated between a pulse valve and a beam skimmer. Ionic species in the Ne* beam was removed by ion deflector plates in a buffer chamber. For the measurement of product chemiluminescence spectrum, we prepared an intense HCl beam with either 40 or 70 Torr of neat HCl at the pulse valve. Product chemiluminescent spectrum was measured in 310–380 nm wavelength range at 2-nm stepwise by a gated photon-counting system with a monochromator. The chemiluminescence signal was accumulated for several hundreds of the beam pulses on each measured wavelength. To select and confirm the cluster size in the HCl beam, which is responsible for the chemiluminescence, we installed a 60-cm long electrostatic hexapole field and prepared the size-selected HCl dimer beam. In this setup, we collected only total emission from the beam intersection using an optical filter in place of using the monochromator for spectral measurement.

We first measured an emission spectrum in the reaction at 40 Torr of HCl stagnation pressure in order to confirm the emissive product as $HCl^+(A)$. At this low pressure, the HCl beam consists of mostly the monomer, since the observed spectrum was well reproduced by a spectral simulation with reported internal energy distribution of emissive product $HCl^+(A)$.[3] We next measured the spectrum at 70 Torr of HCl as shown in Figure 1. At this pressure, we prepare the HCl cluster instead of monomer. We then performed the spectral simulation again and found that the vibrational and rotational distributions of $HCl^+(A)$ in the cluster reaction were less excited than that in the monomer reaction. Table 1 lists the internal state distribution of $HCl^+(A)$ in both monomer and cluster reactions.

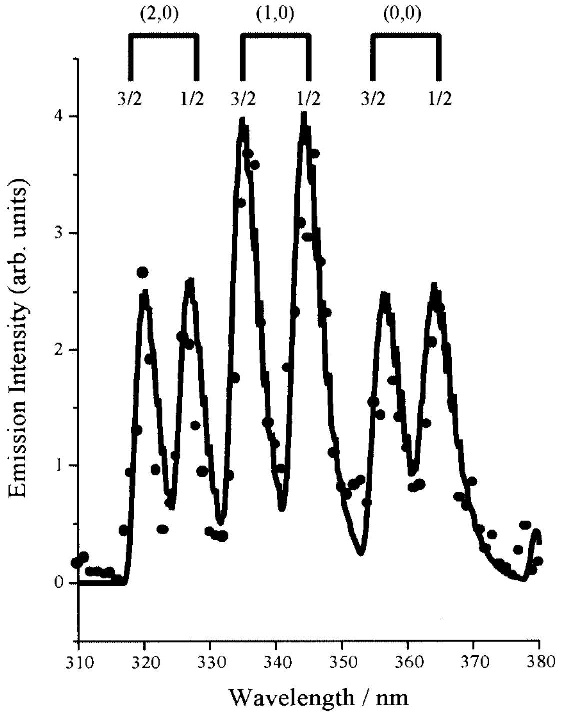

Figure 1. Emission spectrum for the reaction of Ne* with HCl. The spectrum was measured at 70 Torr of neat HCl gas.

Figure 2 shows the signal enhancement of the HCl^+ (A) chemiluminescence when the hexapole field is activated to 12 kV. We have shown in the previous works that only the HCl dimer responds to the Stark effect in the hexapole field, and it

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Table 1. Vibrational populations and rotational temperatures of $HCl^+(A)$ in the monomer reaction at 40 Torr and the cluster reaction at 70 Torr of HCl with Ne*

Emitter (Pressure)	Vibrational Population			Rotational Temperature[a] / K		
	v'=0	1	2	v'=0	1	2
HCl (40 Torr)	0.55	1.0	0.85	800	750	450
$(HCl)_n$ (70 Torr)	0.70	1.0	0.80	500	450	350

[a]Estimated independently for each vibrational state. The statistical errors in vibrational population are estimated to be 20 % and that in rotational temperature for each vibrational level is 30%, respectively.

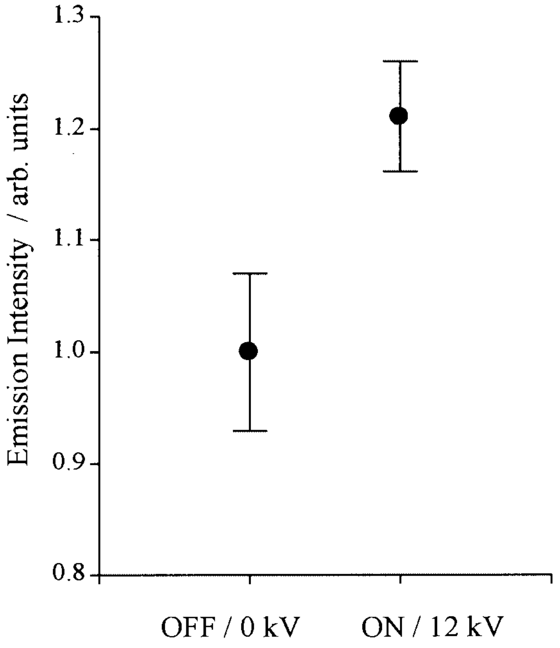

Figure 2. Signal enhancement of $HCl^+(A)$ chemiluminescence upon the hexapole field activation.

gives the enhancement in the dimer beam intensity.[7] Therefore it is clear that the HCl dimer is responsible for the enhancement of $HCl^+(A)$ chemiluminescence in the reaction with Ne* at 12 kV.

Castleman and co-workers recently studied the $(HCl)_2$ photodissociation by three-photon regime with 13.81 eV excitation energy.[8] They observed only HCl^+ in channel (2), even though channel (1) was expected to be major.

$$(HCl)_2^+ \rightarrow (H_2Cl)^+ + Cl \qquad (1)$$
$$\rightarrow (HCl)^+ + HCl \qquad (2)$$

In the Penning ionization, we observed only HCl^+ again, where the available energy of Ne^* is larger than that in the photo-dissociation by 3 eV. Therefore, we may expect that the Penning ionization proceeds in a similar way to the photoionizaiton from an energetic point of view. The reaction scheme is shown as follows.

$$(HCl)_2 + Ne^* \rightarrow [HCl\cdot HCl^+(A)\cdots Ne] + e^- \qquad \text{(step 1)}$$
$$\rightarrow [HCl\cdots HCl^+(A)] + Ne + e^- \qquad \text{(step 2)}$$
$$\rightarrow HCl + HCl^+(A) + Ne + e^- \qquad \text{(step 3)}$$

In Penning ionization and He-I ultraviolet photoelectron spectroscopy of simple molecules, it is suggested that the probability of Penning ionization is related to the degree of overlap between the exterior electron density of molecular orbital and the unfilled atomic orbital of a metastable atom (specifically, 2p orbital for Ne*).[9] If this is the case, $HCl^+(A)$ should be produced by an electron ejection from 3pσ orbital, whose electron density is localized mainly along the H–Cl bond axis.

In step 1, one HCl in the dimer is ionized by Ne* and it is excited to the A state, while the other HCl remains unexcited. When this ionization is occurring, interaction between $HCl^+(A)$ and adjacent Ne atom would become repulsive and therefore Ne and $[HCl\cdots HCl^+(A)]$ begin to separate from each other as indicated in step 2. In step 3, $[HCl\cdots HCl^+(A)]$ continues to dissociate further and forms two separate species, i.e. $HCl^+(A)$ and HCl. In the last step, it is likely that the adjacent HCl would pick up some excess energy from $HCl^+(A)$. In this way, adjacent HCl plays a role as the third body within the dimer. We find that the rotational energy of the $HCl^+(A)$ produced in the dimer reaction is smaller than that in the monomer reaction. The reason for this may be that free rotational motion of $HCl^+(A)$ in the dimer is spatially restricted by the presence of adjacent HCl. Therefore the reaction scheme presented above would be consistent with the scheme suggested by McCoy and co-workers, in which the presence of a long-lived reaction complex would lead to internal energy relaxation of the product in the dimer reaction.[6]

References and Notes

1 A. A. Navarro, B. Brunetti, S. Falcinelli, M. Gonzalez, and F. Vecchiocattivi, *J. Chem. Phys.*, **96**, 433 (1992).

2 B. Brunetti, R. Cambi, S. Falcinelli, J.M. Farrer, and F. Vecchiocattivi, *J. Phys. Chem.*, **97**, 11877 (1993).

3 H. L. Snyder, B. T. Smith, and R. M. Martin, *Chem. Phys. Lett.*, **94**, 90 (1983).

4 M. Tsuji, J. P. Maier, H. Obase, and Y. Nishimura, *Chem. Phys. Lett.*, **110**, 17 (1986).

5 Y. Hurwitz, P. S. Stern, R. Naaman, and A. B. McCoy, *J. Chem. Phys.*, **106**, 2627 (1997).

6 A. B. McCoy, M. W. Lufaso, M. Veneziani, S. Atrill, and R. Naaman, *J. Chem. Phys.*, **108**, 9651 (1998).

7 K. Imura, T. Kasai, H. Ohoyama, and R. Naaman *J. Chem. Phys.*, **110**, 355 (1999).

8 Q. Zhong, L. Poth, J. V. Ford, and A. W. Castleman Jr., *Chem. Phys. Lett.*, **286**, 305 (1998).

9 a) K. Ohno, H. Mutoh, and Y. Harada, *J. Am. Chem. Soc.* **105**, 4555 (1983). b) K. Ohno and Y. Harada, in "Theoretical Models of Chemical Bonding," ed. by Z. B. Maksic̀, Springer-Verlag, Berlin (1991), p 199.