Nucleophilic Substitution within the Photoionized van der Waals Complex: Generation of $C_6H_5NH_3^+$ from $C_6H_5Cl-NH_3$

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Received June 21, 1988

The nucleophilic substitution (S_N) of aromatic compounds is one of the fundamental organic reactions which proceeds bimolecularly in condensed phases. The S_N reaction producing $C_6H_5NH_2$ from $C_6H_5Cl + NH_3$, for example, is known to occur under a severe basic condition such as in liquid ammonia.[1] The solvent assistance is essentially important to obtain an efficient yield of the bimolecular reaction. In this respect the S_N reaction in the gas phase may be inefficient because of the absence of solvent molecules assisting the attack of the nucleophilic reagent onto the aromatic ring. However, the situation is expected to be totally different for the gaseous reaction of an aromatic cation and a reagent. Since the positive charge density of the ground-state ion is mostly distributed in the ring, the basic nucleophilic reagent can easily attack the positively charged carbon atom in the aromatic skeleton.

In this communication, we report the efficient generation of $C_6H_5NH_3^+$ as an immediate consequence of the S_N reaction occurring after the selective photoionization of the van der Waals (vdW) complex of $C_6H_5Cl-NH_3$, which is prepared in a supersonic free expansion. Chemical reactions involving ionized molecular clusters which have recently attracted attention[2-5] provide a variety of reaction products as a result of intracluster ion-molecule reactions including not only dissociations but also new bond formations. Most of these studies have been done by electron impact ionization or by photoionization with vacuum UV light which is inappropriate for the selective ionization of particular cluster(s) of interest. We have recently demonstrated that the resonant two-photon ionization via its S_1 state is quite useful for the selective ionization of small-size clusters and for observing their dissociation processes.[6,7] In this work we also employ the two-photon ionization method for ionizing the complex. This allows us to observe the reaction product resulting only from the complex ion. To our knowledge the present result shows for the first time that the S_N reaction takes place within the (1:1) vdW complex ion in its ground state.

Experimental method is the same as that reported elsewhere.[6] Briefly, the $C_6H_5Cl-NH_3$ complex was prepared in a pulsed supersonic free jet with a gaseous mixture of C_6H_5Cl (ca. 10 Torr), NH_3 (ca. 100 Torr), and He (ca. 1900 Torr). The complex was selectively photoionized by the resonant MPI through its S_1 state with the second harmonic of an excimer pumped dye laser (C540A dye). The resulting ionic species are analyzed by a Q-pole mass filter.

Figure 1 shows the MPI spectrum due to the $S_1 \leftarrow S_0$ transition obtained by monitoring the total ion current without mass separation. In addition to the well-known spectrum of the bare molecule of C_6H_5Cl given by Durant et al.,[8] a few bands are newly observed which are assigned to the (1:1) complex, $C_6H_5Cl-NH_3$. The 0,0 transition of the complex occurs at 76 cm^{-1} higher in energy than that of C_6H_5Cl. A vibronic band of the complex corresponding to the $6a_0^1$ band of C_6H_5Cl is also blue-shifted. A weak background is seen and found to be due to clusters having more than two ammonia molecules.

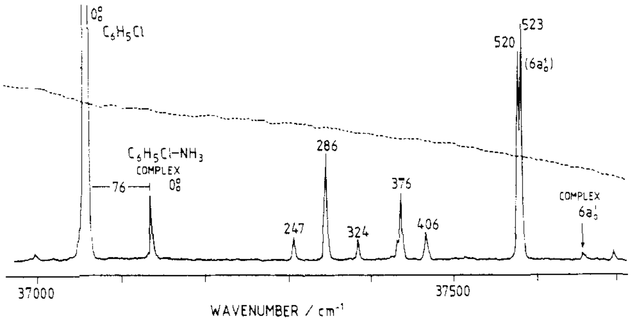

Figure 1. The $S_1 \leftarrow S_0$ transition of jet-cooled $C_6H_5Cl-NH_3$ obtained by MPI with monitoring the total ion. The 0,0 transition of the complex occurs at 37 135 cm^{-1}. The transitions of C_6H_5Cl reproduces the known spectrum (ref 8). The intensities of these bands are not normalized with respect to the laser power spectrum which is shown by a broken line.

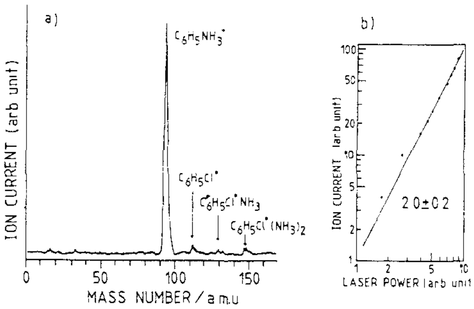

Figure 2. (a) Low resolution mass spectrum obtained by the two-photon ionization of the $C_6H_5Cl-NH_3$ complex. The most intense peak is found to be $M = 94.1 \pm 0.3$ amu in the mass spectrum with a higher resolution of $\Delta M = 0.3$ amu. Weak peaks found at M = 113, 130, and 147 are mostly due to simultaneous excitation of the larger clusters exhibiting a broad background spectrum in Figure 1. (b) Laser power dependence of the $C_6H_5NH_3^+$ yield. The maximum laser power corresponds to 500 $\mu J/cm^2$ at 266.3 nm. The laser beam is not focused.

The mass spectrum obtained after the selective photoionization of the complex is shown in Figure 2a, where the two-photon ionization resonantly enhanced by its 0,0 transition is used. The intense peak at $M = 94.1$ amu is uniquely assigned to $C_6H_5NH_3^+$, and assignments of other weak peaks are given in the figure. In contrast to this, the mass spectrum obtained by the two-photon ionization of bare C_6H_5Cl showed a totally different pattern in which two intense peaks of $C_6H_5Cl^+$ ($M = 112.5$ for ^{35}Cl and 114.5 for ^{37}Cl) and a moderately intense peak of $C_6H_5^+$ ($M = 77.1$) appear.

Two mechanisms for the $C_6H_5NH_3^+$ generation are emerging from the above results: (1) the "bimolecular" S_N reaction occurring within the ionized complex and (2) the unimolecular dissociation yielding $C_6H_5^+$ followed by the bond formation with NH_3. In order to see which is feasible the laser power dependence of the $C_6H_5NH_3^+$ yield was examined. The log-log plot of the yield versus the light intensity shows a slope of 2.0 ± 0.2, as shown in Figure 2b, indicating that the product ion is generated by the two-photon excitation of the neutral complex. Although the ionization threshold of the vdW complex has not been observed, its ionization potential will not be greatly different from that of C_6H_5Cl which is known to be 9.066 eV.[9] The two-photon energy of the incident light ($h\nu$ = 37 135 cm^{-1}), therefore, leads the C_6H_5Cl moiety in the complex to its ground-state ion but not to electronically excited ion. On the other hand, the similar plot of the yield of $C_6H_5^+$ produced from the bare C_6H_5Cl molecule showed a slope of 2.8 ± 0.2, indicating that three photons are required for the generation of $C_6H_5^+$ from C_6H_5Cl. This is in

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0002-7863/88/1510-7238$01.50/0

accord with the fact that the dissociation threshold of the $C_6H_5^+$ generation locates at about 12.3 eV from the neutral C_6H_5Cl, as it was examined by Durant et al.[8] Even higher threshold for the $C_6H_5^+$ generation is expected in the complex because of stabilization of the neutral complex by the vdW interaction. From the observed power dependence, thus, the $C_6H_5NH_3^+$ generation cannot be explained by the formation of $C_6H_5^+$ as a precursor of $C_6H_5NH_3^+$. Therefore, we conclude that $C_6H_5NH_3^+$ is produced by the substitution reaction within the complex ion. Detailed energetics of the present system including the complexes C_6H_5X-ND_3 are now in progress by using two-color photoionization mass spectroscopy.

In conclusion we have found that the "bimolecular" S_N reaction within the (1:1) vdW complex ion $C_6H_5Cl^+$-NH_3 yields the product $C_6H_5NH_3^+$ with a quite high efficiency. The present result demonstrates that the chemical reactivity of mutually stable reagents bound weakly in neutral vdW complexes is altered dramatically upon the ionization which triggers vigorous chemical reactions.

Acknowledgment. We are grateful to Prof. Mitsuo Ito for stimulating discussions and suggestions. We are also indebted to Prof. Hideki Sakurai for his interest in this work.

Reductive Coupling of Nitriles via Formal [2 + 2] Cycloadditions to the Titanium-Carbon Double Bond

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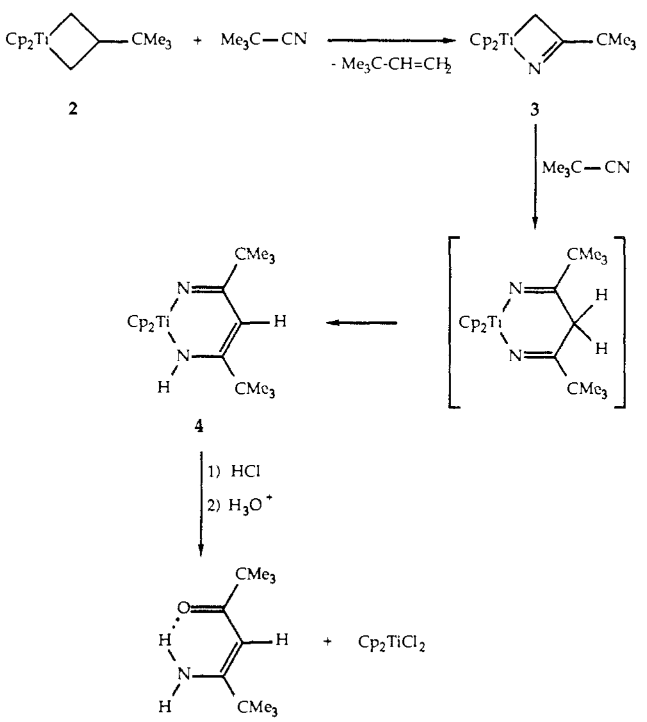
Received May 13, 1988

As part of a broader investigation of the synthesis and reactivity of metallacyclobutenes and related complexes,[1] we have begun an exploration of the reactivity of nitriles with sources of the reactive methylidene complex of bis(cyclopentadienyl)titanium.[2] We have prepared stable metallacyclic complexes resulting from simple formal [2 + 2] cycloaddition and have begun a systematic study of their reactivity and of their utility in synthetic organic transformations. Initial results of these studies are reported here.

Titanacyclobutanes serve as convenient precursors,[12] via metathetic loss of alkene, of either the free methylidene complex, $Cp_2Ti{=}CH_2$ (**1**), or its alkene complex. We have found that treatment of the metallacyclobutane **2** with pivalonitrile provides an azametallacyclobutene, the product of formal [2 + 2] cycloaddition of methylidene complex **1** and the nitrile. Thus, treatment of a C_6D_6 solution of titanacyclobutane **2** with 1 equiv of pivalonitrile at 50 °C for 48 h, following the reaction progress by ^1H NMR, led to formation of metallacycle **3** (Scheme I).[13] Under these conditions, the reaction was quite sluggish, however, and various byproducts were also obtained. Isolation of the pure azametallacyclobutene from this mixture, which contains ca. 50% of **3**, has not yet proved possible. Use of 2 equiv of pivalonitrile accelerated the reaction, and the product was formed in essentially quantitative yield after 1.5 h at 60 °C. The azametallacyclobutene appears to be indefinitely stable under these conditions; no decomposition was observed even after prolonged heating (several days) at 60 °C, though very slow conversion to a follow-up product, **4** (vide infra), occurred (conversion to **4** was essentially complete after ca. 1 month at 60 °C).

Scheme I



Attempted isolation of **3** from the 2:1 reaction mixture via evaporation of solvent and excess pivalonitrile in vacuo led cleanly to formation of a new metallacyclic product, **4**. Apparently, the increase in concentration of pivalonitrile as the more volatile benzene is removed accelerates this insertion over the very slow insertion seen at the lower concentration of the NMR experiment. The presumed initial insertion product was not observed but underwent a tautomerization to afford the conjugated product, **4** (Scheme I). This structure is in full accord with all spectral data.[14]

Compound **4** is stable thermally in both solution (no observable decomposition in C_6D_6 after 1 month at 110 °C) and in the solid state (mp 133-135.5 °C under nitrogen, without apparent decomposition). The solid is also quite air stable, surviving intact in air for at least several hours, though benzene solutions are more air sensitive. Compound **4** proved not only sufficiently robust but also sufficiently volatile in the solid inlet probe of the mass spectrometer to provide a clean parent ion (m/e 358), intensity 18% of that of the 100% peak. The absence of higher mass ions,

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(1) Initially reported at 3rd Chemical Congress of North America and the 195th ACS National Meeting, Toronto, Canada, June 5, 1988.

(2) Previous reports of the reactivity of nitriles with organotransition-metal complexes have suggested insertion,[3-5] cycloaddition,[6-9] and cyclo-oligomerization[10,11] as primary reaction modes. Discreet cycloadducts have not been directly observed but rather inferred as intermediates.

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(13) ^1H NMR spectrum of **3** reported in Table I: ^1H coupled ^{13}C NMR (C_6D_6) δ 28.5 (q, J = 125 Hz, CH_3), 40.2 (s, C-CH_3), 41.3 (t, J = 123 Hz, CH_2), 112.4 (d, J = 173 Hz, Cp), 165.0 (s, —C=N).

(14) ^1H NMR (C_6D_6) δ 1.02 (s, 9 H, *t*-Bu), 1.21 (s, 9 H, *t*-Bu), 4.86 (d, 1 H, J = 1.46 Hz, —CH=), 5.70 (s, 10 H, Cp), 5.9 (br, 1 H, NH); ^{13}C NMR (C_6D_6) δ 29.51 (CH_3), 29.89 (CH_3), 37.10 (*C*—CH_3), 37.64 (*C*—CH_3), 87.70 (—*C*H=), 110.99 (Cp), 175.02 (—*C*=N or =*C*—N), 175.73 (=*C*—N or —*C*=N); IR (C_6H_6) ν = 3371, 3314 cm^{-1} (N—H).

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