Rapid Communication

Unprecedented proton transfer to ammonia from fullerene dications derivatized with ammonia

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ABSTRACT

Results of selected-ion flow tube experiments are reported for ion/molecule reactions initiated by C$_{60}^+$ and C$_{70}^+$ in ammonia which show unprecedented proton-transfer reactions with ammonia when these cations are derivatized with ammonia. C$_{60}$NH$_3^+$ and C$_{70}$NH$_3^+$ transfer a proton to NH$_3$ with rate coefficients $\geq$ 1.2 $\times$ 10$^{-9}$ and 0.7 $\times$ 10$^{-9}$ cm$^3$ molecule$^{-1}$ cm$^{-1}$ respectively, at 294 K in helium at 0.35 Torr. Analogous reactions were observed with C$_{60}$(NH$_3$)$_2^+$ and C$_{70}$(NH$_3$)$_2^+$. Possible structures are given for the derivatized ions C$_x$NH$_2^+$ and C$_x$NH$_3^+$ ($x = 60, 70$) and the ions C$_x$NH$_2^+$ and C$_x$N$_2$H$_4^+$ formed from them by proton transfer.

Keywords: fullerenes; dications; proton transfer; ion/molecule reactions; selected-ion flow tube.

INTRODUCTION

Recent experimental investigations in our laboratory of the chemistry initiated by doubly-charged C$_{60}$ and C$_{70}$ cations in ammonia have revealed the occurrence of unprecedented proton-phase reactions. When C$_{60}$ and C$_{70}$ dications were derivatized with ammonia they were observed to rapidly transfer a proton to ammonia in helium carrier gas at 0.35 Torr and 294 K. Reactions 1 and 2

\[
C_{60}^+ + NH_3 \rightarrow C_{60}NH_3^+ \quad (1)
\]

\[
C_{60}NH_3^+ + NH_3 \rightarrow C_{60}NH_2^+ + NH_4^+ \quad (2a)
\]

\[
\rightarrow C_{60}(NH_3)_2^+ \quad (2b)
\]

show the observed chemistry initiated by C$_{60}^+$. A minor channel (reaction 2b), leading to the association of a second ammonia molecule, was observed to

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compete with the proton-transfer channel (reaction 2a). Similar reactions were observed for $C_{70}^2^+$. Reactions of type 2a have been reported previously, but only for chemistry initiated by atomic metal dications [1,2].

Protonated molecular cations of the general type $XH^2^+$ are often thermodynamically unstable but kinetically stable towards unimolecular deprotonation, owing to the presence of an energy barrier. This has been shown to be the case by quantum-chemical calculations and by charge stripping mass spectrometry experiments which have been used to generate a large variety of doubly-charged molecular cations which are stable on the microsecond time scale of a mass spectrometer (see e.g. ref. 3). Nevertheless, protonated molecular cations have generally proven to be difficult to establish and isolate in sufficiently large amounts for investigations of their chemistry. In contrast, recent selected-ion-bow tube (SIFT) experiments in our laboratory have shown that the fullerene dications $C_{60}^2^+$ and $C_{70}^2^+$ may be derivatized to form a variety of protonated cations of the type $C_{60}XH^2^+$ and $C_{70}XH^2^+$, which are kinetically stable against unimolecular deprotonation and produced in sufficient amounts for chemical studies. For example, we have now observed adducts of $C_{60}^2^+$ with ammonia, several aliphatic amines and many unsaturated hydrocarbons [4]. These adduct ions exhibit a variety of interesting chemistry but the proton-transfer reactions of $C_{60}NH_3^+$ and $C_{70}NH_3^+$ with ammonia are unique in this chemistry in that they result in proton transfer. Ammonia as a reactant molecular favours proton transfer because of its relatively high proton affinity, $PA(NH_3) = 204.0 \text{ kcal mol}^{-1}$ [5], and its relatively high ionization energy, $IE(NH_3) = 10.16 \text{ eV}$ [6], discourages competition with charge transfer [7].

EXPERIMENTAL

The SIFT apparatus used in these experiments to measure reaction kinetics has been described previously [8]. The original two quadrupoles which had a mass range of only about 250 u were replaced with ones which have a mass range well beyond $m/z$ 1000. The fullerene dications were produced in a conventional electron impact source by electron bombardment (at 50 eV) of $C_{60}$ and $C_{70}$ vapours entrained in argon carrier gas. The fullerene sample was obtained from Strem Chemicals Co. and was a mixture of $C_{60}$ and 2–12% $C_{70}$. The ammonia had a minimum purity of 99.99% (Matheson, Anhydrous Grade). All the kinetic measurements were performed at 294 ± 2 K in helium buffer gas at a pressure of 0.35 ± 0.01 Torr.

RESULTS AND DISCUSSION

The experimental results which indicate the occurrence of reactions 1 and 2a are shown in Fig. 1. $C_{60}NH_3^+$ was established by reaction 1 for which we
Fig. 1. Observed variations in ion signals recorded for the addition of ammonia into the reaction region of the SIFT apparatus in which $C_{60}^{2+}$ has been established as the dominant ion in helium buffer gas. ($P = 0.35$ Torr, $\bar{v} = 7.0 \times 10^4$ cm s$^{-1}$, $L = 47$ cm, $T = 294$ K.) The $C_{60}^{2+}$ was derived from electron impact of C$_{60}$ vapour at 50 eV.

have measured an apparent bimolecular rate coefficient of $(1.2 \pm 0.4) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in helium at $0.40 \pm 0.01$ Torr. Presumably the helium acts to collisionally stabilize the $C_{60}NH_3^+$ after its initial formation, although radiative stabilization cannot be ruled out. The occurrence of the proton-transfer reaction (2a) is rate-limited by the production of $C_{60}NH_3^+$ from reaction 1, so that the rate coefficient for the proton transfer is $\geq 1.2 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The experiments provided a branching ratio for reaction 2a: reaction 2b of greater than 9:1.

The apparent bimolecular rate coefficient for reaction 1 is quite large and this is indicative of the formation of a strong bond between $C_{60}^{2+}$ and NH$_3$, presumably with a substantial chemical character, although it also may have a significant electrostatic component owing to the interaction between the double charge and the polar ammonia molecule. For this adduct of $C_{60}^{2+}$ with ammonia we propose the structure I given below in which the two charges are divided between the $C_{60}$ substituent and the nitrogen atom. The removal of a proton from this ion presumably results in a derivatized fullerene monocation
of structure II or perhaps even III, a protonated aziridine, or other less strained nitrogen ring analogues.

![Diagram of structures I, II, and III](image)

The small amounts of the second ammonia adduct, \( \text{C}_{60}(\text{NH}_3)_2^+ \), observed to be produced in the chemistry initiated by \( \text{C}_2^+ \) were seen to generate the ion \( \text{C}_{60}\text{N}_2\text{H}_5^+ \) at high flows of ammonia and this is indicative of the occurrence of reaction 3

\[
\text{C}_{60}(\text{NH}_3)_2^+ + \text{NH}_3 \rightarrow \text{C}_{60}\text{N}_2\text{H}_5^+ + \text{NH}_4^+
\]

which is also formally a proton-transfer reaction. If the second ammonia adduct has the symmetrically "winged" structure given by IV, removal of a proton could yield the derivatized fullerene cation given by structure V. The winged structure would be produced if the second ammonia molecule bonds to the fullerene structure I in the manner in which ammonia is thought to bond to fullerene monocations [4].

![Diagram of structures IV and V](image)

As might be expected, the chemistry initiated by \( \text{C}_70^+ \) was observed to be completely analogous to that initiated by \( \text{C}_2^+ \), although the initiation reaction analogous to reaction 1 occurs more slowly with a rate coefficient of \( 7.0 \times 10^{-10} \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \). The rate coefficient for the proton-transfer reaction between \( \text{C}_{70}\text{NH}_3^+ \) and \( \text{NH}_3 \) is therefore \( \geq 7.0 \times 10^{-10} \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \).

Our observations of the proton-transfer reactions of type 2a imply values for \( \text{PA}(\text{C}_{60}\text{NH}_2^+, \text{C}_{70}\text{NH}_2^+, \text{C}_{60}\text{N}_2\text{H}_5^+, \text{C}_{70}\text{N}_2\text{H}_5^+) \leq 204.0 \text{ kcal mol}^{-1} \), while our failure to observe secondary proton-transfer reactions of ammonia with \( \text{C}_{60}\text{NH}_2^+, \text{C}_{70}\text{NH}_2^+, \text{C}_{60}\text{N}_2\text{H}_5^+ \) and \( \text{C}_{70}\text{N}_2\text{H}_5^+ \) implies values for \( \text{PA}(\text{C}_{60}\text{NH}, \text{C}_{70}\text{NH}, \text{C}_{60}\text{N}_2\text{H}_4^+ \text{ and } \text{C}_{70}\text{N}_2\text{H}_4^+) > 204.0 \text{ kcal mol}^{-1} \).

Other experiments in our laboratory have indicated \( \text{C}_{60}^+ \) derivatization reactions analogous to reaction 1 with the related amine molecules \( \text{CH}_3\text{NH}_2, \text{C}_2\text{H}_3\text{NH}_2 \) and \( (\text{CH}_3)_2\text{NH} \). However, for these adduct ions the observed secondary reactions are dominated by charge transfer rather than proton transfer, as might be expected from the much lower ionization energies of the amines compares with that of ammonia. These results will be reported in detail elsewhere [9].
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REFERENCES