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Gas-phase reactions of fullerene cations C_{60}^{x+} ($x = 1-3$) with pyrrolidine and piperidine: sequential reactions with C_{60}^+

Jing Sun¹, Diethard K. Böhme**Department of Chemistry and Centre for Research in Earth and Space Science, York University, Toronto, Ontario M3J 1P3, Canada*

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Abstract

Results of selected-ion flow tube experiments are reported that explore the nucleophilic interaction of pyrrolidine and piperidine with C_{60}^+ , C_{60}^{2+} , C_{60}^{3+} at 294 ± 2 K in helium buffer gas at a pressure of 0.35 ± 0.01 Torr. Two efficient sequential addition reactions were observed with C_{60}^+ in analogy with previous results obtained with acyclic amine nucleophiles. Multicollision-induced dissociation experiments suggest the formation and conversion of two isomers of the second adduct ion. As a first step C–N bond formation is proposed to occur with the C_{60} cage with or without ring opening. Subsequent bonding may involve hydrogen bonding or, if ring opening occurs, further C–N bond formation at the terminus of the first substituent. Nucleophilic attack of C_{60}^{2+} and C_{60}^{3+} by pyrrolidine leads to ring cleavage and formation of $C_{60}(NH_3)^{n+}$ ($n = 2, 3$) accompanied by loss of what is likely to be 1,3-butadiene. $C_{60}(NH_3)^{n+}$ effectively donates a proton to pyrrolidine. The ring-cleavage channel dominates competing channels leading to electron transfer and nucleophilic addition. However, ring cleavage is not observed with piperidine which reacts with C_{60}^{2+} and C_{60}^{3+} exclusively by electron transfer because of its lower ionization potential. Further reactions of the proton-transfer product lead to the formation of “mixed” adducts of the type $(NH_2)C_{60}(C_4H_8NH)^{n+}$ ($n = 1, 2$) that may involve two C–N bonds with the C_{60} surface or, alternatively, proton bonding to protonated aziridine. (Int J Mass Spectrom 195/196 (2000) 401–409) © 2000 Elsevier Science B.V.

Keywords: Fullerene ions; Pyrrolidine; Piperidine; Nucleophilic addition; Electron transfer; SIFT

1. Introduction

Among his many interests in ion chemistry, Bob Squires was also fascinated by fullerene ions and his early contribution to our understanding of the gas-phase reactivity of fullerene anions in 1991 [1] is still one of only a small number of reported studies of this kind. In our laboratory we have surveyed the gas-

phase chemistry of fullerene cations [2–5] and we have found that the nucleophilicity of a reacting neutral molecule is particularly important in determining its chemical reactivity with these cations at room temperature, particularly with singly charged fullerene cations. Ammonia, small alkylamines [6], and pyridine [7], all strong nucleophiles because of the availability of two unpaired electrons on the nitrogen, have been found to be particularly reactive, even with the singly charged fullerene cation, C_{60}^+ , which is generally much less reactive than the higher charge states. Strong nucleophiles undergo single association reactions with C_{60}^+ that increase in effi-

* Corresponding author. E-mail: dkbohme@yorku.ca

¹ Present address: Genpharm Inc., 37 Advance Rd., Toronto, Ontario M8Z 2S6, Canada.

Dedicated to Bob Squires in his memory.

ciency with increasing proton affinity of the nucleophile [7]. Electron transfer begins to compete with association in the reactions of these molecules with higher fullerene charge states and more so with increasing charge state [6]. Methyl-, ethyl-, and dimethyl-amine (but not trimethyl-amine) exhibit secondary addition reactions with C_{60}^+ . These have been attributed to the formation of a hydrogen bond with the second amine molecule on the basis of the failure of a similar secondary reaction with trimethyl-amine that is not capable of hydrogen bonding.

The aliphatic nucleophiles that we have investigated so far all have been acyclic. Here we investigate, for the first time, the gas-phase ion–molecule reactions of C_{60}^+ , C_{60}^{2+} or C_{60}^{3+} with two cyclic aliphatic molecules containing nitrogen, viz. piperidine and pyrrolidine. Nucleophilic addition is again expected to occur because of the availability of two unpaired electrons on nitrogen, ring opening now becomes an option upon bonding and hydrogen bonding of a second nucleophile with the C_{60}^+ adduct again is a possibility. Competition between nucleophilic addition and electron transfer is expected with the higher charge states since the ionization energies of pyrrolidine and piperidine are relatively low, 8.80 ± 0.03 and 8.05 ± 0.5 eV, respectively [8].

2. Experimental

The ion/molecule reactions of the fullerene cations C_{60}^{x+} ($x = 1, 2, 3$) with piperidine and pyrrolidine were achieved within the reaction region of a selected-ion flow tube (SIFT) mass spectrometer in helium carrier gas at 0.35 ± 0.01 Torr and 294 ± 2 K [9,10]. The fullerene cations were produced in an ion source by electron impact ionization of the vapour of a sample of fullerene powder ($\sim 99.5\%$ C_{60} , SES Research Inc.): C_{60}^+ at ~ 50 V, C_{60}^{2+} at ~ 80 V and C_{60}^{3+} at ~ 100 V. The desired C_{60} cation was selected with a quadrupole mass filter, injected into the flow tube containing He and then allowed to thermalize by collisions with He ($\sim 4 \times 10^5$ collisions) prior to entering the reaction region further downstream.

Piperidine and pyrrolidine were obtained from

Sigma with purities of 99%. They were added into the flow tube as 3%–5% mixtures in helium.

The CID spectra of the product ions were taken using 10% argon in helium as the buffer/collision gas in the manner reported by Baranov and Bohme [11].

Rate coefficients were measured with pure helium buffer gas in the usual manner [9,10] and have an uncertainty estimated to be less than $\pm 30\%$.

3. Results and discussion

3.1. Reactions with pyrrolidine

The kinetic results for the reactions of pyrrolidine with C_{60}^+ , C_{60}^{2+} , and C_{60}^{3+} are summarized in Table 1. Included here are values for collision rate coefficients calculated with the variational transition-state theory of Su and Chesnavich [12]. The average polarizabilities of pyrrolidine and piperidine were estimated to be 8.91 and 10.75 Å³, respectively, according to the empirical method of Miller and Savchik [13]. The permanent dipole moment of pyrrolidine was taken to be 1.58 D [14] and that of piperidine was taken to be that of the equatorial conformation, 0.82 D [15]. The ratio of the measured reaction-rate coefficient to the calculated collision-rate coefficient, k_{obs}/k_c , provides a measure of reaction efficiency.

3.1.1. Reactions initiated by C_{60}^+

Fig. 1 shows that singly charged C_{60}^+ undergoes sequential addition reactions with pyrrolidine [reaction (1)], ultimately to produce the triple adduct $C_{60}(C_4H_8NH)_3^+$ in



the flow range of pyrrolidine employed in these experiments. The first two additions proceed quite rapidly with effective bimolecular rate coefficients $k \approx 3 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. The third addition is more than 30 times slower, $k < 1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Electron transfer was not observed as a competing primary reaction channel because of the relatively high ionization energy of pyrrolidine, IE(pyrrolidine) = 8.80 ± 0.03 eV [8]

Table 1

Effective bimolecular rate coefficients (in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and product-channel distributions measured for reactions of C_{60}^+ , C_{60}^{2+} , and C_{60}^{3+} cations with pyrrolidine in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 3 K by using the SIFT technique

Reactant ion	Product ion	Branching ratio	k_c^a	k_{obs}^b
C_{60}^+	$\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})^+$	1	1.30	0.27
$\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})^+$	$\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$	1	1.30	0.35
$\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$ C_{60}^{2+}	$\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_3^+$	1	1.29	<0.01
	$\text{C}_{60}(\text{NH}_3)_2^{2+} + \text{C}_4\text{H}_6$	0.80	2.61	1.3
	$\text{C}_{60}^+ + (\text{C}_4\text{H}_8\text{NH})^+$	0.11		
C_{60}^{3+}	$\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^{2+}$	0.09		
	$\text{C}_{60}(\text{NH}_3)_3^{3+} + \text{C}_4\text{H}_6$	0.64	3.91	2.3
	$\text{C}_{60}^{2+} + (\text{C}_4\text{H}_8\text{NH})^+$	0.36		

^a k_c represents the collision-rate coefficient calculated according to the variational transition-state theory [12].

^b The absolute uncertainties of the observed bimolecular rate coefficients are estimated to be $\pm 30\%$. Relative accuracies are better than $\pm 10\%$.

compared to the recombination energy $\text{RE}(\text{C}_{60}^+) = 7.64 \pm 0.02$ eV [16].

The CID spectra in Fig. 1 show the occurrence of heterolytic dissociation of the first two adducts ac-

ording to the following reactions with thresholds at nose-cone voltages:

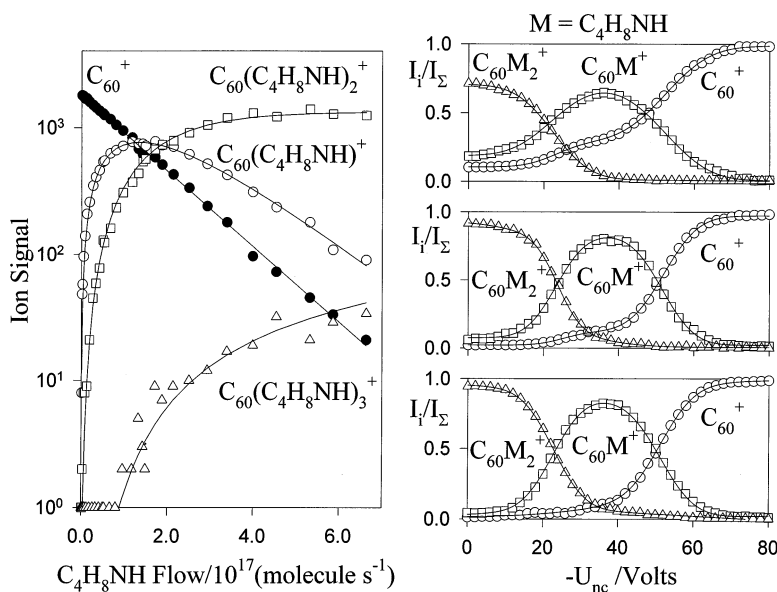
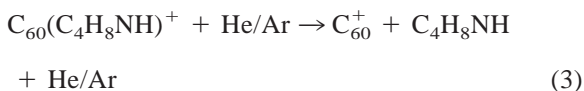


Fig. 1. (Left) Variation in ion signals recorded for the addition of pyrrolidine into the reaction region of the SIFT apparatus in which C_{60}^+ has been established as the dominant ion in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 2 K. (Right) Variation in ion signals recorded as a function of the nose-cone voltage, U_{nc} , for ions formed in the reaction of C_{60}^+ with pyrrolidine at a flow of 3.6 (upper), 5.1 (middle), 6.2 (bottom) $\times 10^{17}$ molecule s^{-1} in a buffer gas of 10% argon in helium.



of 13 ± 2 V for $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$ and 43 ± 2 V for $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})^+$. Channel (2b), which corresponds to the concomitant loss of *two* pyrrolidine molecules, is a minor channel in the dissociation of $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$, but its relative importance was observed to depend on the flow of pyrrolidine. Channel (2b) becomes relatively more important at low flows of pyrrolidine. Such behaviour is indicative of the formation of two isomers [7].

The first addition of pyrrolidine to C_{60}^+ is expected to result in C–N bond formation by nucleophilic addition to the charge site on the C_{60} surface. Bonding with the C_{60} surface could induce ring opening by cleavage of a N–C bond in pyrrolidine or a 1,3 proton shift to form an aminium ion, but these cleavages may require more energy than can be provided by the electrostatic attraction between the reacting ion and molecule. The structures of $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$ and $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_3^+$ are less certain. In analogy to the behaviour proposed for acyclic amines [6], N–H–N hydrogen bonding is possible in the second adduct which also forms rapidly. A further interaction of this kind is less likely and this may account for the slower formation of the third adduct compared to the second adduct. Structures of $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$ involving ring opening of either one or both of the pyrrolidine adduct molecules can be envisaged, as can isomerization reactions involving the switch of an open with a cyclic adduct in a bimolecular switching reaction with pyrrolidine. Such an isomerization reaction may account for the structure observed in the collision induced dissociation (CID) profile of $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$.

3.1.2. Reactions initiated by C_{60}^{2+}

The doubly charged C_{60}^{2+} reacts rapidly with pyrrolidine, $k = 1.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The data in Fig. 2 show the formation of three product ions according to

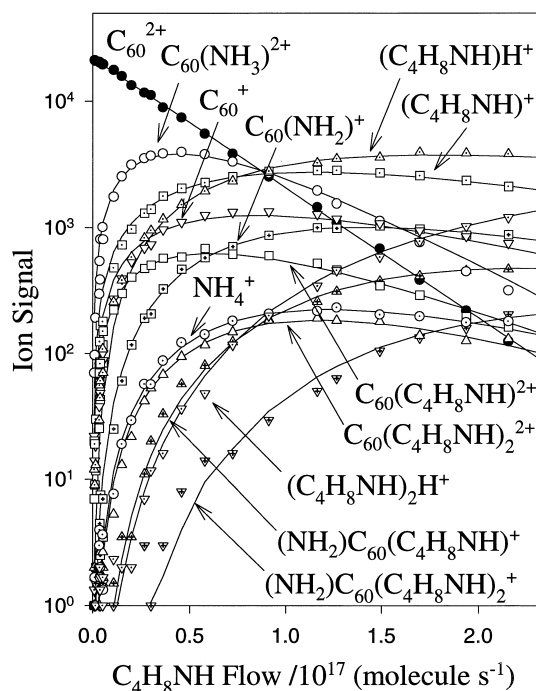


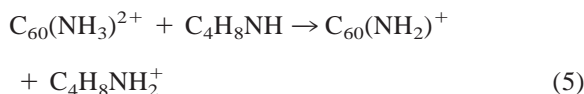
Fig. 2. Variation in ion signals recorded for the addition of pyrrolidine into the reaction region of the SIFT apparatus where C_{60}^{2+} has been established as the dominant ion in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 2 K. Not shown are the ions produced by secondary reactions of C_{60}^+ .



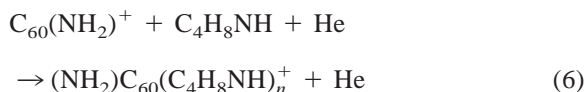
The main channel (80%) of this reaction leads to formation of $\text{C}_{60}(\text{NH}_3)^{2+}$. Minor channels involve electron transfer (11%) and adduct formation (9%).

Electron transfer is expected since $\text{IE}(\text{pyrrolidine}) = 8.80 \pm 0.03$ eV is well within the threshold for efficient electron transfer from C_{60}^{2+} to a neutral (9.59 ± 0.01 eV) [3,17].

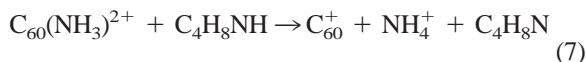
The ionic products for the three channels of reaction (4) all initiate secondary reactions. $\text{C}_{60}(\text{NH}_3)^{2+}$ reacts further with pyrrolidine mainly via proton transfer (80%) to produce $\text{C}_{60}(\text{NH}_2)^+$ and $\text{C}_4\text{H}_8\text{NH}_2^+$ according to



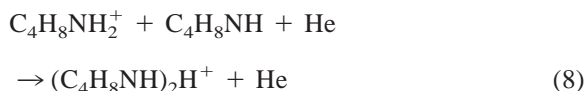
$\text{C}_{60}(\text{NH}_2)^+$ undergoes sequential association reactions with pyrrolidine, producing $(\text{NH}_2)\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_n^+$ with $n = 1$ and 2 according to reactions of type



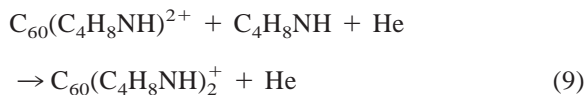
$\text{C}_4\text{H}_8\text{NH}_2^+$ reacts further to form the proton-bound dimer. A minor channel of the reaction of $\text{C}_{60}(\text{NH}_3)^{2+}$ with pyrrolidine is observed to form NH_4^+ ion which cannot be explained easily. One possible reaction path is dissociative hydride transfer as shown in



The C_{60}^+ produced in reactions (4b) and (7) reacts further in the manner established in the separate studies of the chemistry of C_{60}^+ . $\text{C}_4\text{H}_8\text{NH}_2^+$ reacts further to form the proton-bound dimer according to



Finally, the $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^{2+}$ produced in channel (4c) adds a second molecule of pyrrolidine according to



The CID spectrum of the product ions at a relatively high flow of 6.5×10^{17} molecule s^{-1} using 10% argon in helium as buffer gas is shown in Fig. 3 and indicates that the adduct ions $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$ and $(\text{NH}_2)\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$ dissociate heterolytically and sequentially. The dissociation pattern for $\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})_2^+$ is consistent with that observed when this ion is produced directly from sequential reactions of C_{60}^+ with $\text{C}_4\text{H}_8\text{NH}$ at high flows of pyrrolidine.

Channel (4a) was unexpected, although we have observed the formation of the $\text{C}_{60}(\text{NH}_3)^{2+}$ cation previously through the nucleophilic addition of ammonia to C_{60}^{2+} [6]. A possible mechanism for channel

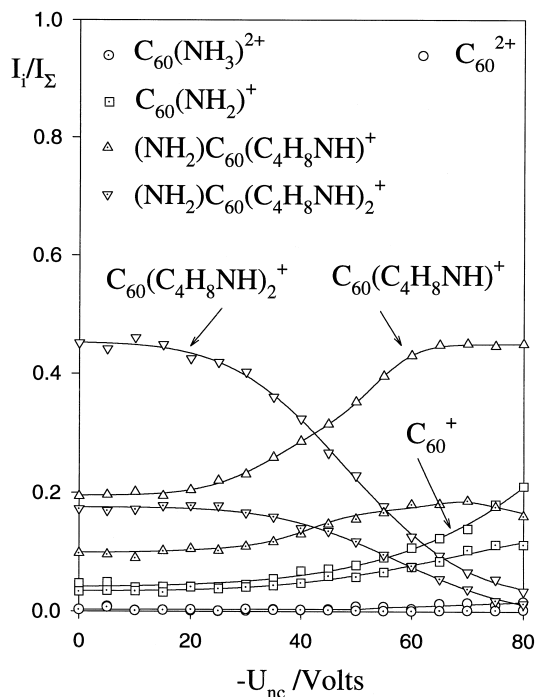


Fig. 3. Variation in ion signals recorded as a function of the nose-cone voltage, U_{nc} , for ions formed in the reaction of C_{60}^{2+} with pyrrolidine at a flow of 6.5×10^{17} molecule s^{-1} in a buffer gas of 10% argon in helium.

(4a) is shown in Fig. 4. The nucleophilic attack of C_{60}^{2+} by pyrrolidine is proposed to lead to ring cleavage accompanied by two 1,2-hydrogen atom shifts and formation of what is likely to be 1,3-butadiene. Once formed, $\text{C}_{60}(\text{NH}_3)^{2+}$ transfers a proton to pyrrolidine, as was the case with ammonia [6], and the proton transfer is followed by a second nucleophilic addition of pyrrolidine. Alternatively, $\text{C}_{60}(\text{NH}_2)^+$ may isomerize to a protonated aziridine structure [6] and then add a pyrrolidine molecule by hydrogen bonding.

3.1.3. Reactions initiated by C_{60}^{3+}

Fig. 5 shows two channels for the rapid reaction of the triply charged C_{60}^{3+} with pyrrolidine. These are indicated in



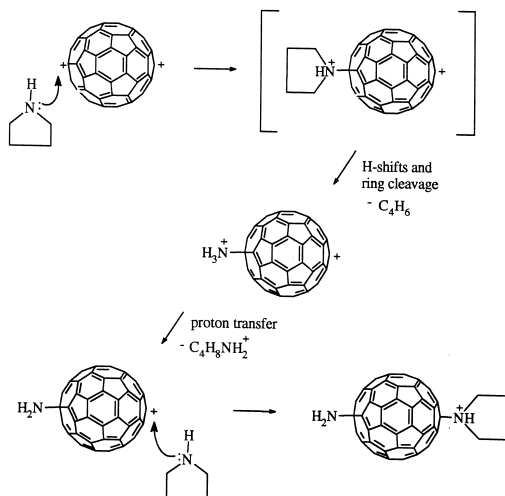


Fig. 4. A possible mechanism for the formation of $(\text{NH}_2)\text{C}_{60}(\text{C}_4\text{H}_8\text{NH})^{+}$ by the sequential reactions of pyrrolidine with C_{60}^{2+} .

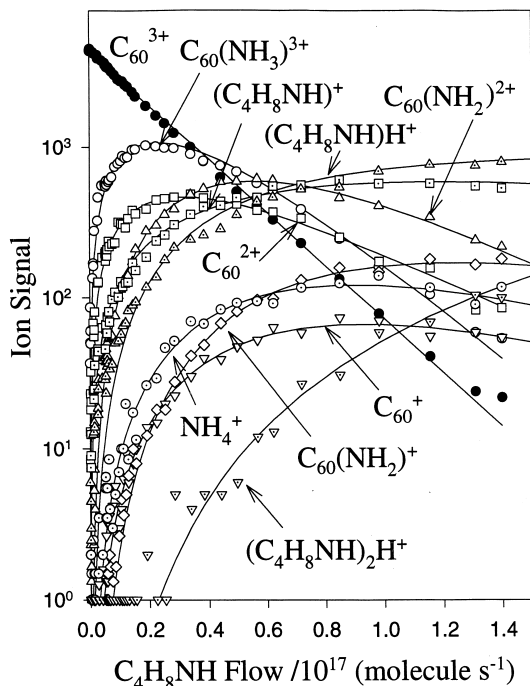
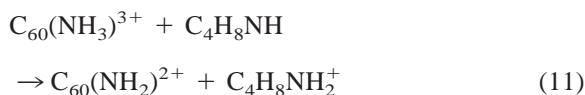


Fig. 5. Variation in ion signals recorded for the addition of pyrrolidine into the reaction region of the SIFT apparatus in which C_{60}^{3+} has been established as the dominant ion in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 2 K.

Channel (10a) is preferred by 0.64/0.36. The ionization energy of pyrrolidine (8.80 ± 0.03 eV) is well within the threshold for efficient electron transfer from C_{60}^{3+} to a neutral (11.02 eV) that we have observed previously [3,18]. Channel (10a) is the analogue of channel (4a) observed with C_{60}^{2+} and, in analogy with reaction (5), $\text{C}_{60}(\text{NH}_3)^{3+}$ reacts further with pyrrolidine by proton transfer according to



The other secondary and higher-order reactions initiated by C_{60}^{3+} are identical to those observed in the separate experiments involving the lower charge states.

3.2. Reactions with piperidine

The kinetic results for the reactions of piperidine with C_{60}^{+} , C_{60}^{2+} , and C_{60}^{3+} are summarized in Table 2.

Table 2

Effective bimolecular rate coefficients (in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) measured for reactions of C_{60}^{+} , C_{60}^{2+} , and C_{60}^{3+} cations with piperidine in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 3 K by using the SIFT technique

Reactant ion	Product ion	k_c^a	k_{obs}^b
C_{60}^{+}	$\text{C}_{60}(\text{C}_5\text{H}_{10}\text{NH})^{+}$	1.02	1.0
$\text{C}_{60}(\text{C}_5\text{H}_{10}\text{NH})^{+}$	$\text{C}_{60}(\text{C}_5\text{H}_{10}\text{NH})_2^{+}$	1.01	0.83
$\text{C}_{60}(\text{C}_5\text{H}_{10}\text{NH})_2^{+}$	$\text{C}_{60}(\text{C}_5\text{H}_{10}\text{NH})_3^c$	1.01	0.07
C_{60}^{2+}	$\text{C}_{60}^{+} + (\text{C}_5\text{H}_{10}\text{NH})^{+}$	2.04	2.4
C_{60}^{3+}	$\text{C}_{60}^{2+} + (\text{C}_5\text{H}_{10}\text{NH})^{+}$	3.05	3.1

^a k_c represents the collision-rate coefficient calculated according to the variational transition-state theory [12].

^b The absolute uncertainties of the observed bimolecular rate coefficients are estimated to be $\pm 30\%$. Relative accuracies are better than $\pm 10\%$.

^c This product was not observable because its mass-to-charge ratio is beyond the mass range of our detection quadrupole mass filter.

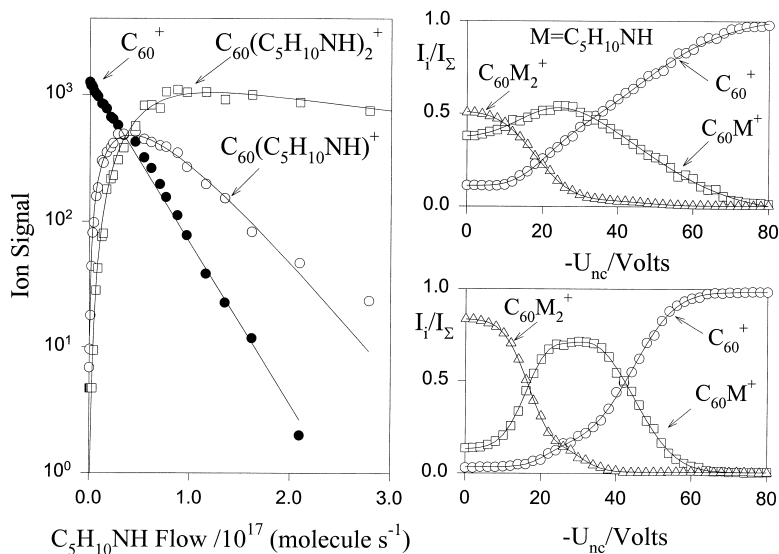
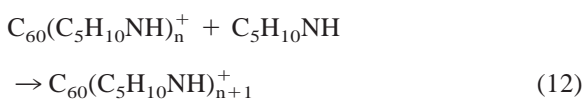


Fig. 6. (Left) Variation in ion signals recorded for the addition of piperidine into the reaction region of the SIFT apparatus where C₆₀⁺ has been established as the dominant ion in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 2 K. (Right) Variation in ion signals recorded as a function of the nose-cone voltage, U_{nc}, for ions formed in the reaction of C₆₀⁺ with piperidine at a flow of 5.0 × 10¹⁶ (upper) and 1.2 × 10¹⁷ molecules s⁻¹ (lower) in a buffer gas of 10% argon in helium.

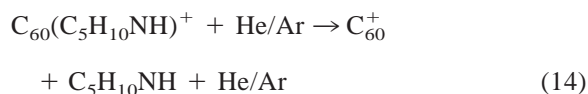
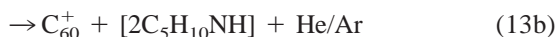
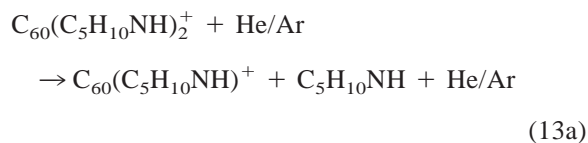
3.2.1. Reactions initiated by C₆₀⁺

Fig. 6 shows that singly charged C₆₀⁺ undergoes sequential addition reactions with piperidine as shown in



The first two additions again are quite rapid, $k \approx 1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The third addition is more than 10 times slower. However, the third adduct was not observable because its mass-to-charge ratio is beyond the mass range of our detection quadrupole mass filter. Electron transfer was not observed as a competing primary reaction channel because of the relatively high ionization energy of piperidine, IE(piperidine) = 8.05 ± 0.5 eV [8] compared to the recombination energy RE(C₆₀⁺) = 7.64 ± 0.02 eV [16].

The CID spectra in Fig. 1 show the occurrence of heterolytic dissociation of the first two adducts according to the following reactions:



with thresholds at nose-cone voltages of 10 ± 2V for C₆₀(C₅H₁₀NH)₂⁺ and 35 ± 2 V for C₆₀(C₅H₁₀NH)⁺. Channel (13b), which corresponds to the concomitant loss of two piperidine molecules is a minor channel in the dissociation of C₆₀(C₄H₈NH)₂⁺ and its relative importance, was observed to depend on the flow of piperidine. Channel (13b) becomes relatively more important at low flows of piperidine.

3.2.2. Reactions initiated by C₆₀²⁺

As shown in Fig. 7, the doubly charged C₆₀²⁺ reacts rapidly with piperidine, $k = 2.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, only by electron transfer,

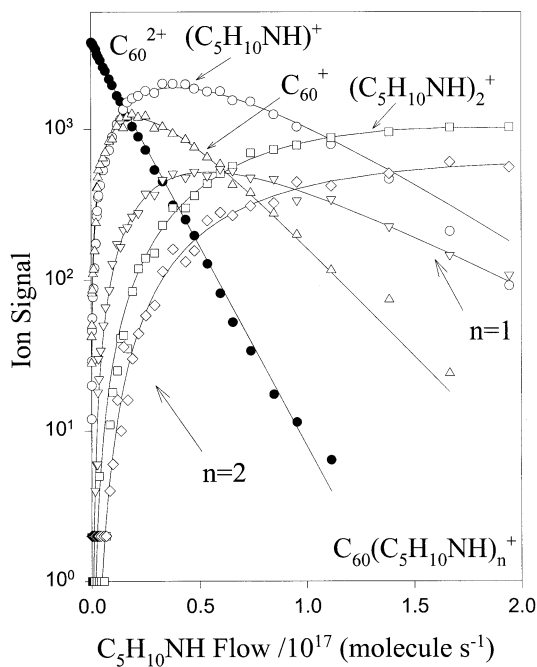
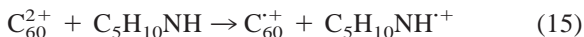


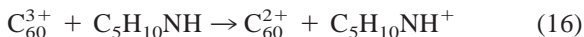
Fig. 7. Variation in ion signals recorded for the addition of piperidine into the reaction region of the SIFT apparatus in which C_{60}^{2+} has been established as the dominant ion in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 2 K.



The ionization energy of piperidine (8.05 ± 0.5 eV) lies below the threshold for electron transfer of 9.51 eV that we have established previously for reactions with C_{60}^{2+} at room temperature [3,17]. C_{60}^{2+} reacts further to add two molecules of piperidine and $C_5H_{10}NH^+$ adds piperidine to form the dimer cation $(C_5H_{10}NH)_2^+$.

3.2.3. Reactions initiated by C_{60}^{3+}

Fig. 8 shows that triply charged C_{60}^{3+} reacts rapidly with piperidine, $k = 3.1 \times 10^{-9}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, only by electron transfer,



IE(piperidine) lies well below the threshold for electron transfer of 11.0 eV that we have established previously for reactions with C_{60}^{3+} at room temperature [3,18]. C_{60}^{2+} reacts further by electron transfer

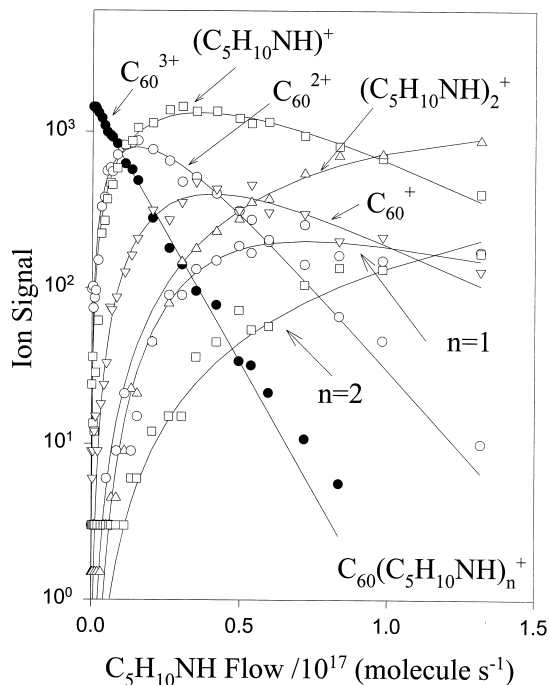


Fig. 8. Variation in ion signals recorded for the addition of piperidine into the reaction region of the SIFT apparatus in which C_{60}^{3+} has been established as the dominant ion in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 2 K.

which is then followed by the chemistry initiated by C_{60}^+ . $C_5H_{10}NH^+$ adds piperidine to form the dimer cation $(C_5H_{10}NH)_2^+$.

4. Conclusion

The singly charged fullerene cation C_{60}^+ efficiently adds two molecules of pyrrolidine or piperidine at room temperature in a helium bath gas at 0.35 Torr, in a manner analogous to that previously identified with acyclic amine nucleophiles. The first step can be viewed as a nucleophilic addition to the carbon cage of C_{60} , with or without ring opening of the nucleophile. Fig. 9 extends the correlation of nucleophilicity with proton affinity reported previously for a series of nitrogen-containing nucleophiles [7]. The second molecule is proposed to add by hydrogen bonding or by nucleophilic addition if ring opening occurs with the first adduct. CID results provide some support for

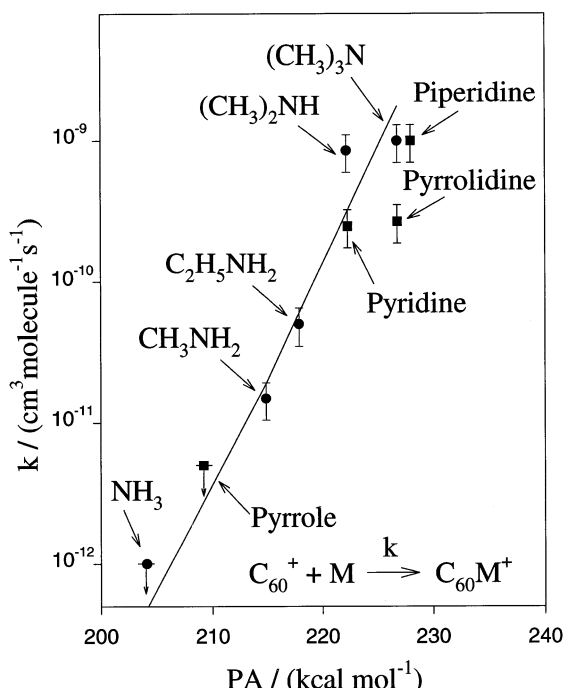


Fig. 9. A correlation of the apparent bimolecular rate coefficients for nucleophilic addition to C_{60}^+ (measured at 0.35 Torr in helium buffer gas) with the proton affinity of the nucleophile.

the formation and interconversion of two different isomers of the double adduct.

Nucleophilic attack of C_{60}^{2+} and C_{60}^{3+} by pyrrolidine leads to ring cleavage and formation of $C_{60}(NH_3)^{n+}$ ($n = 2, 3$) accompanied by loss of what is likely to be 1,3-butadiene. $C_{60}(NH_3)^{n+}$ effectively donates a proton to pyrrolidine. The ring-cleavage channel dominates competing channels leading to electron transfer and nucleophilic addition. However, the ring-cleavage channel is not observed with piperidine which reacts exclusively by electron transfer because of its lower ionization potential. Further reactions of the proton-transfer product leads to the formation of “mixed” adducts of the type $(NH_2)C_{60}(C_4H_8NH)^{n+}$ ($n = 1, 2$) with structures that may involve two C–N bonds with

the C_{60} surface or, alternatively, proton bonding to protonated aziridine.

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References

- [1] L.S. Sunderlin, J.A. Paulino, J. Chow, B. Kahr, D. Ben-Amotz, R. Squires, *J. Am. Chem. Soc.* 113 (1991) 5489.
- [2] S. Petrie, D.K. Bohme, *Can. J. Chem.* 72 (1994) 577.
- [3] D.K. Bohme, *Int. Rev. Phys. Chem.* 13 (1994) 163.
- [4] D.K. Bohme, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*. R.S. Ruoff, K.M. Kadish (Eds.), Electrochemical Society Proceedings Vol. 95-10, Electrochemical Society, Pennington, NJ, 1995, p. 1465.
- [5] D.K. Bohme, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*. R.S. Ruoff, K.M. Kadish (Eds.), Electrochemical Society Proceedings Vol. 97-14, Electrochemical Society, Pennington, NJ, 1997, p. 763.
- [6] G. Javahery, S. Petrie, H. Wincel, J. Wang, D.K. Bohme, *J. Am. Chem. Soc.* 115 (1993) 5716.
- [7] J. Sun, D.K. Bohme, *Int. J. Mass Spectrom.* 179/80 (1998) 267.
- [8] NIST Chemistry Webbook, NIST Standard Reference Database No. 69, 1997, <http://webbook.nist.gov/chemistry>
- [9] G.I. Mackay, G.D. Vlachos, D.K. Bohme, H.I. Schiff, *Int. J. Mass Spectrom. Ion Phys.* 36 (1980) 259.
- [10] A.B. Raksit, D.K. Bohme, *Int. J. Mass Spectrom. Ion Processes* 55 (1983/84) 69.
- [11] V. Baranov, D.K. Bohme, *Int. J. Mass Spectrom. Ion Processes* 154 (1996) 71.
- [12] T. Su, W.J. Chesnavich, *J. Chem. Phys.* 76 (1982) 5183.
- [13] K.J. Miller, J.A. Savchik, *J. Am. Chem. Soc.* 101 (1979) 7206.
- [14] A.C. McClellan, *Tables of Experimental Dipole Moments*, Freeman, San Francisco, 1963.
- [15] J.E. Parker, P.J. Buckley, C.C. Costain, *J. Mol. Spectrosc.* 89 (1981) 465.
- [16] D.L. Lichtenburger, M.E. Rempe, S.B. Gogosha, *Chem. Phys. Lett.* 198 (1992) 454.
- [17] S. Petrie, G. Javahery, J. Wang, D.K. Bohme, *J. Phys. Chem.* 96 (1992) 6121.
- [18] G. Javahery, H. Wincel, S. Petrie, D.K. Bohme, *Chem. Phys. Lett.* 204 (1993) 467.