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Gas-phase reactions of fullerene cations C_{60}^{x+} ($x = 1$–3) with pyridine and pyrrole: formation of “ball-and-chain” and “spindle” isomers and their interconversion

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Abstract

The chemistry of buckminsterfullerene cations with charge states of +1, +2, and +3 has been investigated with two nitrogen heterocycles, pyridine and pyrrole, in the gas phase at room temperature in helium buffer gas at 0.35 Torr using the selected ion flow tube (SIFT) technique. Adduct formation was observed with pyridine for all three charge states of C_{60}^{x+}, although electron transfer leading to charge separation was the predominant channel with $C_{60}^{\cdot 3+}$. The number of pyridine molecules sequentially added was equal to the number of charges on C_{60}^{x+}. Equilibrium was achieved for the addition of pyridine to $C_{60}^{\cdot +}$ and a bond dissociation enthalpy of 19.5 kcal mol^{-1} was deduced from the measured equilibrium constant. The structures of the derivatized C_{60} cations was explored by multicollision-induced dissociation in mixed He/Ar collision gas. All observed dissociations were heterolytic. With the multiply derivatized C_{60} cations evidence was obtained for both a kinetically favored “ball-and-chain”-like structure and a thermodynamically favored “spindle”-like structure. Experiments with doubly derivatized C_{60}^{2+} indicated the occurrence of a rapid conversion of the ball-and-chain to the spindlelike structure in a bimolecular reaction with pyridine. Only charge-separation reactions driven by electron transfer were observed with pyrrole. The results for the two nitrogen heterocycles are compared with those obtained under similar operating conditions for ammonia and several aliphatic amines. A correlation is presented between the observed reactivity of C_{60}^{x+} and the proton affinity of the adduct molecule. (Int J Mass Spectrom 179/180 (1998) 267–275) © 1998 Elsevier Science B.V.

Keywords: Fullerene ions; Derivatized fullerene ions; Multiply charged ions; Pyridine; Pyrrole; Selected ion flow tube

1. Introduction

The remarkable stability and ready availability of multiply charged fullerene cations afford an opportunity to explore the chemistry of these cations as a function of charge state. We have shown previously in our laboratory that new chemical pathways often become accessible in the gas phase at room temperature (in a helium buffer at 0.35 Torr) to reactions of C_{60}^{x+} cations as the charge state is increased from $x =$ 1 to 2 to 3 [1]. Briefly, we have found monocations of C_{60}^{+} to react with only a few of the molecules that we have investigated and to do so primarily by addition, rather than by the formation of bimolecular products

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Dedicated to Fulvio Cacace for his outstanding contributions to gas-phase ion chemistry.

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as was observed with iron pentacarbonyl [2]. In contrast, C_{60}^{2+} is very reactive towards many molecules and exhibits a rich addition chemistry, although electron transfer becomes an important competitive reaction channel. With $C_{60}^{\cdot 3+}$, also a very reactive cation, this competition often favours electron transfer or even dissociative electron transfer, but addition is still observed.

Here we report the influence of the charge state of C_{60}^{x+} on the rate and mode of its reaction with pyridine and pyrrole. We have chosen these nitrogen heterocycles as reagents because previously we have found ammonia and aliphatic amines [3] to be the most reactive nucleophiles with C_{60}^{x+} ($x = 1$–3) among the various inorganic and organic molecules that we have surveyed, and especially so for $x = 1$. With ammonia, the number of molecules that add to these fullerene cations appeared to be determined by the number of charges on the fullerene surface. In contrast, aliphatic amines were observed to add to $C_{60}^{\cdot +}$ and C_{60}^{2+} but not $C_{60}^{\cdot 3+}$, which reacted exclusively by electron transfer with all the amines investigated, in accordance to the lower ionization energy of the amines. Spindle and starlike structures involving direct bonding to the fullerene surface that minimize Coulombic repulsion have been suggested for the preferred structures of the doubly derivatized C_{60}^{2+} and triply derivatized $C_{60}^{\cdot 3+}$ cations, although other isomers involving proton bonding, for example, are possible [3]. Proton bonding is not likely with pyridine so that the number of possible isomers of the multiply derivatized multiply charged fullerene cations is significantly reduced and their structures become less ambiguous. As a consequence it should be more straightforward to test the correlation between the number of charges and the number of molecules added in nucleophilic addition reactions with C_{60}^{x+} cations.

2. Experimental

The ion/molecule reactions of the fullerene cations C_{60}^{x+} ($x = 1, 2, 3$) with pyridine and pyrrole 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 ± 3 K [4, 5]. The fullerene cations were produced in an ion source by electron impact ionization of the vapour of a sample of fullerene powder (~99.5+% C_{60}, SES Research Inc.): $C_{60}^{\cdot +}$ at ~50 V, C_{60}^{2+} at ~80 V, and $C_{60}^{\cdot 3+}$ 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.

Pyridine and pyrrole were obtained from Aldrich with purities of 99+% and 98%, respectively. They were added into the flow tube as 3–5% mixtures in helium. The collision-induced dissociation (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 [6]. Rate coefficients were measured with pure helium buffer gas in the usual manner [4, 5] and have an uncertainty estimated to be less than ±30%.

3. Results and discussion

3.1. Reactions with pyridine

3.1.1. Reactions initiated by $C_{60}^{\cdot +}$

Kinetic results for the reactions of pyridine with C_{60}^{n+} ($n = 1$–3) are summarized in Table 1.

$$C_{60}^{\cdot +} + C_5H_5N \rightarrow C_{60}(C_5H_5N)^{\cdot +} \qquad (1)$$

The singly charged $C_{60}^{\cdot +}$ undergoes an association reaction with pyridine, reaction (1), to produce the single adduct $C_{60}(C_5H_5N)^{\cdot +}$ with an effective bimolecular rate coefficient of 2.5×10^{-10} cm^3 mol^{-1} s^{-1} in what is presumably a termolecular association reaction. Electron transfer was not observed as a competing channel because of the relatively high ionization energy (IE) of pyridine, IE(pyridine) = 9.26 ± 0.01 eV [7] compared to the recombination energy RE($C_{60}^{\cdot +}$) = 7.64 ± 0.02 eV [8]. Fig. 1 shows that reaction (1) achieves equilibrium under the operating conditions of the SIFT experiment. The measured equilibrium constant is $(6.2 \pm 1.8) \times 10^7$ and corresponds to a standard free-energy change of

Table 1
Effective bimolecular rate coefficients (in units of 10^{-9} cm^3 mol^{-1} s^{-1}) and product channels measured for reactions of C_{60}^{x+} cations with pyridine in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 3 K using the SIFT technique

Reactant ion	Product ion	Branching ratio	k_c[a]	k_{obs}[b]
$C_{60}^{\cdot+}$	$C_{60}(C_5H_5N)^+$	1	1.5	0.25
$C_{60}(C_5H_5N)^{\cdot+}$	Not observed			<0.0005
C_{60}^{2+}	$C_{60}(C_5H_5N)^{2+}$	1	3.1	2.6
	$C_{60}^{\cdot+} + (C_5H_5N)^{\cdot+}$	<0.005		
$C_{60}(C_5H_5N)^{2+}$	$C_{60}(C_5H_5N)_2^{2+}$	1		1.7
$C_{60}(C_5H_5N)_2^{2+}$	Not observed			<0.0005
$C_{60}^{\cdot 3+}$	$C_{60}(C_5H_5N)^{\cdot 3+}$	0.3	4.6	4.6
	$C_{60}^{2+} + (C_5H_5N)^+$	0.7		
$C_{60}(C_5H_5N)^{\cdot 3+}$	$C_{60}(C_5H_5N)_2^{\cdot 3+}$	1		
$C_{60}(C_5H_5N)_2^{\cdot 3+}$	$C_{60}(C_5H_5N)_3^{\cdot 3+}$	1		
$C_{60}(C_5H_5N)_3^{\cdot 3+}$	Not observed			<0.01

[a] k_c represents the collision-rate coefficient calculated according to the method of T. Su and M.T. Bowers in Int. J. Mass Spectrom. Ion. Phys. 12 (1973) 347.

[b] The absolute uncertainties of the observed bimolecular rate coefficients are estimated to be ±30%. Relative accuracies are better than ±10%.

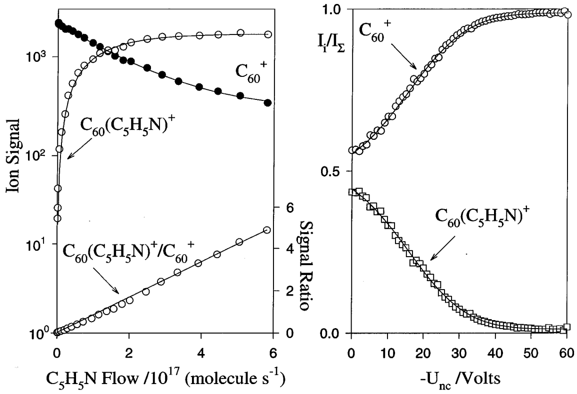


Fig. 1. Top left: Experimental data for the reaction of pyridine with $C_{60}^{\cdot+}$. The solid lines represent a fit to the experimental data with the solution of the system of differential equations appropriate for the observed reversible reaction. Bottom left: Ion-signal ratio plot showing the approach to, and attainment of, equilibrium. Right: Variations in the ion signals recorded as a function of nose-cone voltage, U_{nc}, for ions formed in the reaction of $C_{60}^{\cdot+}$ with pyridine at a flow of pyridine of 1.2×10^{17} mol s^{-1}.

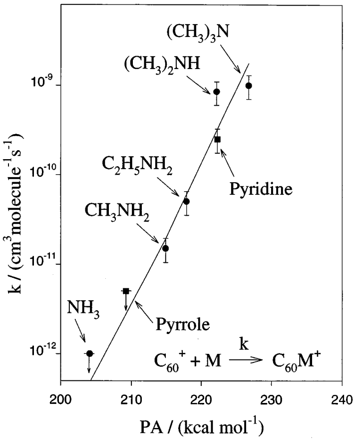


Fig. 2. Correlation of apparent bimolecular rate coefficients for nucleophilic addition to $C_{60}^{\cdot+}$ (measured at 0.35 Torr in helium buffer gas) with the proton affinity of the nucleophile.

−10.6 ± 0.2 kcal mol^{-1}. The standard enthalpy change becomes −19.5 kcal mol^{-1} if the standard entropy change of reaction (1) is taken to be −30 ± 5 e.u. which is typical of ion-molecule association reactions involving the formation of only one new bond [9]. This is a relatively low bond dissociation enthalpy and may be a result of the strain introduced as a consequence of the rehybridization of the bonding C atom from nearly sp^2 to nearly sp^3 that needs to take place upon bonding.

$$C_{60}(C_5H_5N)^{\cdot+} + He/Ar \rightarrow C_{60}^{\cdot+} + C_5H_5N + He/Ar \quad (2)$$

The CID spectrum of $C_{60}(C_5H_5N)^{\cdot+}$ in Fig. 1 shows the occurrence of heterolytic dissociation of the adduct $C_{60}(C_5H_5N)^{\cdot+}$, reaction (2), to produce $C_{60}^{\cdot+}$ ions with a very low, albeit quite broad, dissociation threshold (U_{nc} = 2.5 ± 1 V). This is consistent with the low standard enthalpy of dissociation estimated on the basis of the measured equilibrium constant [6].

It is noteworthy that pyridine adds more rapidly to $C_{60}^{\cdot+}$ than do NH_3 (<1 × 10^{-12} cm^3 mol^{-1} s^{-1}) and CH_3NH_2 (k = 1.5 × 10^{-11} cm^3 mol^{-1} s^{-1}) but less rapidly than do $(CH_3)_2NH$ (k = 8.5 × 10^{-10} cm^3 mol^{-1} s^{-1}) and $(CH_3)_3N$ (k = 1.0 × 10^{-9} cm^3 mol^{-1} s^{-1}) under similar SIFT operating conditions. Fig. 2 shows that the apparent bimolecular rate coefficients for the association reactions of C_{60}^{+} with these five nitrogen-containing molecules correlate with the proton affinities of these molecules as might be expected if the nucleophilic addition mimics protonation. C_{60}^{+} hardly resembles a proton in size and composition, but both have a positive charge and it is known that proton affinities correlate well with affinities for carbon-containing cations such as the methyl cation [we could not correlate with methyl-cation affinities because we are not aware of the methyl-cation affinities of $(CH_3)_2N$ and pyridine] [10].

Our failure to observe the addition of another pyridine molecule to $C_{60}(C_5H_5N)^{\cdot+}$ is consistent with our previous experience with aliphatic amines. We have previously observed secondary reactions with methyl-, ethyl-, and dimethylamine leading to the formation of the adduct ions $C_{60}(CH_3NH_2)_2{}^{\cdot+}$, $C_{60}(C_2H_5NH_2)_2^{\cdot+}$, and $C_{60}[(CH_3)_2NH]_2^{\cdot+}$, respectively [3]. But the secondary adduct with trimethylamine did not form. So we have attributed the secondary reactions with methyl-, ethyl-, and dimethylamine to N–H–N proton-bond formation that is not possible with trimethylamine. It is also unfavorable with pyridine.

Also worthy of comment is a comparison of the reactivity of $C_{60}^{\cdot+}$ with pyridine with reported pyridine reactivities with monocyclic C_n^{+} cations with *n* from 10–24 that have been surveyed with Fourier transform ion cyclotron resonance (FTICR) measurements [11, 12] and for an isomer of C_{24}^{+} for which coronene-like skeleton has been proposed [12]. Interestingly, the monocyclic C_n^{+} (n = 12, 13, 14, 24) ions all were observed to react with the addition of *more than one* pyridine and CID measurements indicated strong "intermingling" (multiple bonding) with the first pyridine molecule [12]. In sharp contrast, the coronene-like isomer of C_{24}^{+} was observed to add only one pyridine molecule as would be expected of single bonding of a localized cabenium ion with the electron lone pair at the nitrogen atom of pyridine [12]. This is also the situation observed in the present study with $C_{60}^{\cdot+}$ for which we have proposed the same chemical interaction.

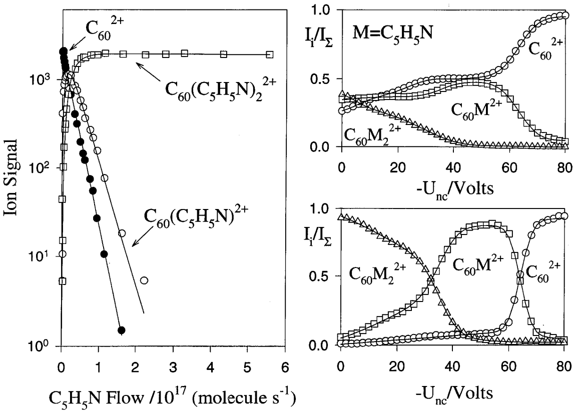
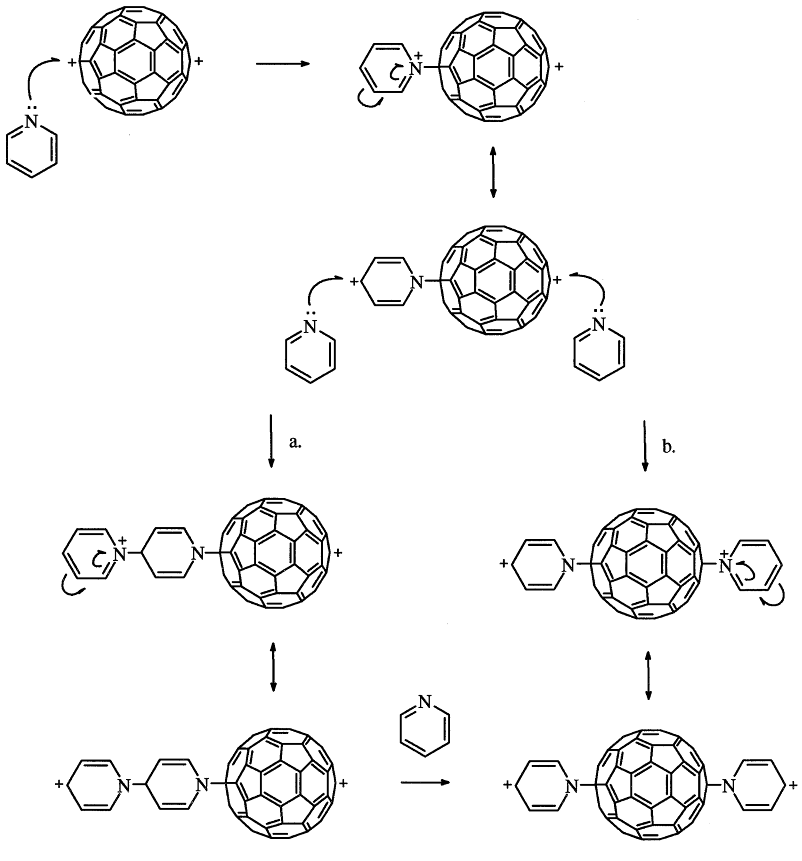


Fig. 3. Left: Experimental data for the reaction of pyridine with C_{60}^{2+}. The solid lines represent a fit to the experimental data with the solution of the system of differential equations appropriate for the observed reversible reaction. Right: Variations in the ion signals recorded as a function of nose-cone voltage, U_{nc}, for ions formed in the reaction of C_{60}^{2+} with pyridine at a flow of pyridine of 2.6 × 10^{16} mol s^{-1} (top) and 9.6 × 10^{16} mol s^{-1} (bottom).

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

The doubly charged C_{60}^{2+} reacted with pyridine sequentially to form the association adducts $C_{60}(C_5H_5N)^{2+}$ and $C_{60}(C_5H_5N)_2^{2+}$ with effective bimolecular rate coefficients of 2.6 × 10^{-9} and 1.7 × 10^{-9} cm^3 mol^{-1} s^{-1}, respectively. The measured ion profiles for this reaction sequence are shown in Fig. 3. There was no evidence for the occurrence of a competing charge-separation reaction due to electron transfer in the first step of this sequence, <0.5%, even though it is exothermic by 2.1 eV since IE(pyridine) = 9.26 ± 0.01 eV [7] and C_{60}^{2+} [RE(C_{60}^{2+}) = 11.36 ± 0.05 eV] [13]. We have shown elsewhere that this result can be understood in terms of a kinetic barrier that arises due to the Coulombic repulsion between product ions [14]. Other investigations in our laboratory have shown that electron transfer competes with direct attachment with neutral molecules having ionization energies below 9.51 eV [13,14]. FTICR measurements have indicated a threshold of 9.48 eV [15]. IE(pyridine) is below, but close to, these threshold values. Competition between adduct formation and electron transfer was clearly apparent in our earlier studies of the reactions of C_{60}^{2+} with ammonia and the aliphatic amines: no electron transfer was observed with ammonia (IE = 10.070 ± 0.020 eV), but an increasing fraction of electron transfer (ET) was observed with decreasing ionization energy for CH_3NH_2 (IE = 8.9 ± 0.1 eV, 10% ET), $C_2H_5NH_2$ (IE = 8.86 ± 0.02 eV, 30% ET), $(CH_3)_2NH$ (IE =



Scheme 1.

8.24 ± 0.08 eV, 90% ET), and $(CH_3)_3N$ (IE $= 7.85 \pm 0.05$ eV, 100% ET) [7]. These results are consistent with the absence of electron transfer with pyridine (IE = 9.26 eV). Addition of a second molecule to the singly derivatized C_{60}^{2+} was observed to compete with proton transfer, the latter predominating in a ratio of 9:1 with ammonia and >10:1 with methyl, ethyl, and dimethylamine [3].

Proposed mechanisms for the two sequential reactions of C_{60}^{2+} with pyridine are shown in Scheme 1. The first adduct $C_{60}(C_5H_5N)^{2+}$ is assumed to be formed by nucleophilic attack of the free electron pair of the nitrogen atom. The second nucleophilic attack can lead to the formation of two isomers: direct bonding to the fullerene surface at the second charge site will lead to a spindlelike bis-adduct structure although bonding to the pyridine already attached to the ring will lead to a "ball-and-chain" structure. The CID spectra in Fig. 3 provide insight into the formation of these two isomers. However, we should note here that only one of eight possible stereoisomeric bis-adducts is indicated in Scheme 1; the trans-1 isomer drawn should be the preferred bis-adduct due to charge repulsion.

The CID spectra of the product ions $C_{60}(C_5H_5N)_n^{2+}$ ($n = 1$–2) show that the primary adduct ion $C_{60}(C_5H_5N)^{2+}$ formed in the reaction of C_{60}^{2+} with pyridine dissociates heterolytically according to reaction (3) at a relatively high onset voltage of 57 ± 5 V

$$C_{60}(C_5H_5N)^{2+} + \mathrm{He/Ar} \rightarrow C_{60}^{2+} + C_5H_5N + \mathrm{He/Ar} \tag{3}$$

The secondary adduct ions $C_{60}(C_5H_5N)_2^{2+}$ appear to dissociate heterolytically to produce *both* C_{60}^{2+} and $C_{60}(C_5H_5N)^{2+}$ ions according to reactions (4a) and (4b)

$$C_{60}(C_5H_5N)_2^{2+} + He/Ar \rightarrow C_{60}^{2+} + (2C_5H_5N) + He/Ar \quad (4a)$$

$$\rightarrow C_{60}(C_5H_5N)^{2+} + C_5H_5N + He/Ar \quad (4b)$$

We did not observe the growth of a $C_{60}^{\cdot+}$ signal with increasing U_{nc} due to homolytic dissociation. The formation of C_{60}^{2+} attributed to the dissociation of $C_{60}(C_5H_5N)_2^{2+}$ has a very low onset voltage close to 0 V and we attribute this early appearance of C_{60}^{2+}, together with what is presumably a pair of pyridine molecules, to the dissociation of a "ball-and-chain" structure for $C_{60}(C_5H_5N)_2^{2+}$. Also, we propose that the observed formation of $C_{60}(C_5H_5N)^{2+}$ from the dissociation of $C_{60}(C_5H_5N)_2^{2+}$ can be attributed to a "spindle"-like structure for $C_{60}(C_5H_5N)_2^{2+}$.

The CID spectra in Fig. 3 show a strong dependence on the flow of pyridine established upstream of the CID region and can be rationalized in terms of a change in the relative proportion of the "spindle" and "ball-and-chain" structures as measured by the relative magnitude of that portion of $C_{60}(C_5H_5N)^{2+}$ produced beyond 57 ± 5 V and that portion of C_{60}^{2+} produced at low CID voltages. The ratio of the "spindle" to the "ball-and-chain" structure at the lower flow of pyridine (2.6×10^{16} mol s^{-1}) is then approximately 1:2 (see Fig. 2, top right) and increases to 3:1 at the higher flow (9.6×10^{16} mol s^{-1}, see Fig. 2, bottom right). We attribute this change in the relative proportion of the "spindle" and "ball-and-chain" structures to the occurrence of the isomerization of the "ball-and-chain" structure to the "spindle" structure by reaction with pyridine as shown in reaction (5) (see Scheme 1). This implies a higher stability for the "spindle" structure.

$$C_5H_5N\text{–}C_5H_5N\text{–}C_{60}^{2+} + C_5H_5N$$
$$\rightarrow C_5H_5N\text{–}C_{60}^{2+}\text{–}NC_5H_5 + C_5H_5N \quad (5)$$

The pyridine flow dependence of the relative proportion of the two isomers suggests that the isomerization reaction (5) is quite rapid, $k > 5 \times 10^{-11}$ cm^3 mol^{-1} s^{-1}, and that the sequential addition of two pyridine molecules leads predominantly to the ball-and-chain structure (path a in Scheme 1), viz. is kinetically favored. The latter result is expected if one of the two charges on the singly derivatized C_{60}^{2+} is localized on the end of the pyridine substituent and more so than the second charge which resides on the C_{60} surface. Coulombic repulsion between the two charges will favor the resonance form in which the charge is localized on the end of the pyridine substituent. Charge localization on the end pyridine due to Coulombic repulsion between the two charges is expected to be diminished in the doubly derivatized adduct because of the greater distance between the two charges. Therefore, attack by the third pyridine molecule may occur preferentially at the charge on the fullerene surface and so lead to the isomerization reaction (5).

Finally, the early "gradual" onset of the dissociation of $C_{60}(C_5H_5N)_2^{2+}$ and the early "gradual" appearance of $C_{60}(C_5H_5N)^{2+}$ in the CID spectra in Fig. 3 (top and bottom), particularly evident at the higher pyridine flow (see Fig. 3, bottom) may be attributed to an enhancement in the rate of that portion of the isomerization reaction (5) occurring in the CID region that could leave the "spindle" isomer sufficiently excited to dissociate. But this interpretation must be considered to be tentative. We have assumed here that the flows of pyridine are sufficiently small so as not to significantly influence the energy deposition in the CID experiments.

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

Fig. 4 shows that the triply charged $C_{60}^{\cdot 3+}$ initiates the sequential formation of the three adducts $C_{60}(C_5H_5N)^{\cdot 3+}$, $C_{60}(C_5H_5N)_2^{\cdot 3+}$, and $C_{60}(C_5H_5N)_3^{\cdot 3+}$ with pyridine. Formation of the fourth adduct was not observed. The primary reaction, reaction (6), is rapid,

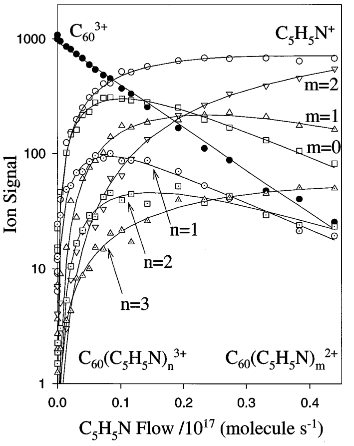


Fig. 4. Experimental data for the reaction of pyridine with $C_{60}^{\cdot 3+}$. The solid lines represent a fit to the experimental data with the solution of the system of differential equations appropriate for the observed reversible reaction.

$k = 4.6 \times 10^{-9}$ cm^3 mol^{-1} s^{-1} and is dominated by electron transfer (70%).

$$C_{60}^{\cdot 3+} + C_5H_5N \rightarrow C_{60}^{2+} + C_5H_5N^{\cdot +} \quad (6a)$$

$$\rightarrow C_{60}(C_5H_5N)^{\cdot 3+} \quad (6b)$$

The kinetic curves for these reactions are shown in Fig. 4. Note from Table 1 that reaction (6) is collision controlled. The occurrence of competing electron transfer is consistent with our previous experience with other reactions of $C_{60}^{\cdot 3+}$. IE(pyridine) is well below the upper limit in the ionization energy of 11.02 eV observed for the occurrence of efficient electron transfer to $C_{60}^{\cdot 3+}$ [RE($C_{60}^{\cdot 3+}$) = 15.6 ± 0.5 eV [16] or 16.6 ± 1 eV [17]] [13, 16]. The observed electron transfer channel (6a) therefore surmounts the kinetic barrier introduced by the Coulombic repulsion between the product ions [18].

The CID spectra of the product ions $C_{60}(C_5H_5N)_n^{\cdot 3+}$ ($n = 1$–3) are shown in Fig. 5 (left). For clarity, the signal decays for the ions $C_{60}(C_5H_5N)_n^{\cdot 3+}$ ($n = 0$–3) are shown separately in Fig. 5 (right). The decay of the $C_{60}(C_5H_5N)_3^{\cdot 3+}$ ions shows two different dissociation onsets at 11.2 ± 2 and 58 ± 2 V. A signal balance analysis shows that approximately 50% of the dissociation of the $C_{60}(C_5H_5N)_3^{\cdot 3+}$ ions is heterolytic leading to the formation of $C_{60}(C_5H_5N)_n^{\cdot 3+}$ ($n = 0$–2) by loss of (nC_5H_5N) units according to channels (7a)–(7c). Channel (7a), loss of pyridine, predominates by at least 4:1

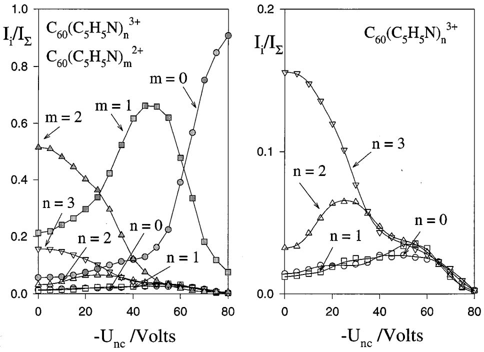


Fig. 5. Variations in the ion signals recorded as a function of nose-cone voltage, U_{nc}, for ions formed in the reaction of $C_{60}^{\cdot 3+}$ with pyridine at a flow of pyridine of 6.2×10^{16} mol s^{-1}. The CID profiles for the triply charged C_{60} $(C_5H_5N)_n^{\cdot 3+}$ ions are shown separately for clarity.

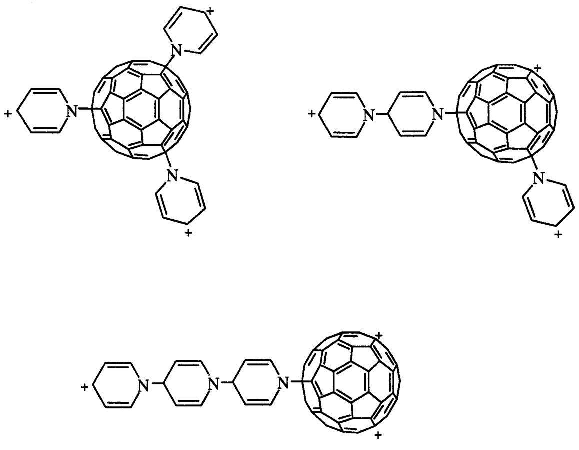
$$C_{60}(C_5H_5N)_3^{\cdot 3+} + He/Ar$$

$$\rightarrow C_{60}(C_5H_5N)_2^{\cdot 3+} + C_5H_5N + He/Ar \quad (7a)$$

$$\rightarrow C_{60}(C_5H_5N)^{\cdot 3+} + (2C_5H_5N) + He/Ar \quad (7b)$$

$$\rightarrow C_{60}^{\cdot 3+} + (3C_5H_5N) + He/Ar \quad (7c)$$

Channels (7b) and (7c) may be accompanied by formation of dimers and trimers of pyridine, respectively. Also, there is evidence for the dissociation of $C_{60}(C_5H_5N)_2^{\cdot 3+}$ to $C_{60}(C_5H_5N)^{\cdot 3+}$ and $C_{60}^{\cdot 3+}$, and of $C_{60}(C_5H_5N)^{\cdot 3+}$ to $C_{60}^{\cdot 3+}$. The ultimate dissociation product, $C_{60}^{\cdot 3+}$, disappears at the higher nose-cone voltages, presumably due to the occurrence of electron transfer, and this may also be happening for a fraction of the singly and doubly derivatized $C_{60}^{\cdot 3+}$ cations. We attribute all of these dissociations to the formation of several isomers of $C_{60}(C_5H_5N)_3^{\cdot 3+}$ in the sequential addition of three molecules of pyridine to $C_{60}^{\cdot 3+}$ prior to the CID region. The three isomers which are proposed for the adduct ions $C_{60}(C_5H_5N)_3^{\cdot 3+}$ are illustrated in Scheme 2. They allow a qualitative explanation of the CID spectra observed for the $C_{60}(C_5H_5N)_n^{\cdot 3+}$ ions in terms of the elimination of one,



Scheme 2.

two, or three units of pyridine but branching ratios for the various possible decompositions could not be resolved.

Finally, it should be noted that the decay of the $C_{60}(C_5H_5N)_2^{2+}$ ion in the CID spectrum shown in Fig. 5 (left) is qualitatively similar to that observed in the experiments in which $C_{60}(C_5H_5N)_2^{2+}$ is formed in a sequential reaction with C_{60}^{2+} in that it exhibits a clear two-component structure. So the "gradual" appearance of C_{60}^{2+} can again be attributed to the heterolytic cleavage of that fraction of the $C_{60}(C_5H_5N)_2^{2+}$ ions with a ball-and-chain structure. The CID spectrum in Fig. 5 was taken at a pyridine flow intermediate between the flows for the two CID spectra in Fig. 3 and the two-component structure in the decay of the $C_{60}(C_5H_5N)_2^{2+}$ ion is also intermediate.

3.2. Reactions with pyrrole

The kinetic results for the reactions of pyrrole with C_{60}^{n+} (n = 1–3) are summarized in Table 2. A reaction of singly charged C_{60}^{+} with pyrrole was not observed under our SIFT conditions, $k < 5 \pm 10^{-12}$ cm^3 mol^{-1} s^{-1}. Electron transfer from pyrrole IE(C_4H_4NH) = 8.207 ± 0.005 eV [7] to $C_{60}^{\cdot+}$ is endothermic. In sharp contrast, both doubly and triply charged C_{60}^{2+} and $C_{60}^{\cdot 3+}$ react with pyrrole *solely* by electron transfer according to the charge-separation reactions (8) and (9)

Table 2
Effective bimolecular rate coefficients (in units of 10^{-9} cm^3 mol^{-1} s^{-1}) and product channels measured for reactions of C_{60}^{x+} cations with pyrrole in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 3 K using the SIFT technique

Reactant ion	Product ion	Branching ratio	k_c[a]	k_{obs}[b]
$C_{60}^{\cdot+}$	Not observed		1.4	<0.005
C_{60}^{2+}	$C_{60}^{\cdot+}$ + $(C_4H_5N)^{\cdot+}$	1	2.9	0.87
	$C_{60}(C_4H_5N)^{2+}$	<0.01		
$C_{60}^{\cdot 3+}$	C_{60}^{2+} + $(C_4H_5N)^{\cdot+}$	1	4.4	1.7
	$C_{60}(C_4H_5N)^{\cdot 3+}$	<0.01		

[a] k_c represents the collision-rate coefficient calculated according to the method of T. Su and M.T. Bowers in Int. J. Mass Spectrom. Ion Phys. 12 (1973) 347.

[b] The absolute uncertainties of the observed bimolecular rate coefficients are estimated to be ±30%. Relative accuracies are better than ±10%.

$$C_{60}^{2+} + C_4H_4NH \rightarrow C_{60}^{\cdot+} + C_4H_4NH^{\cdot+} \quad (8)$$

$$C_{60}^{\cdot 3+} + C_4H_4NH \rightarrow C_{60}^{2+} + C_4H_4NH^{\cdot+} \quad (9)$$

This result was not unexpected, however, as previous measurements in our laboratory have established the occurrence of charge separation due to electron transfer for ionization energies of the neutral reactant less than 9.51 eV [13,14] and 11.02 eV [13, 16] with C_{60}^{2+} and $C_{60}^{\cdot 3+}$, respectively. Finally, we note that the low reactivity of $C_{60}^{\cdot+}$ with pyrrole, viz. our failure to observe an addition reaction, fits nicely on the empirical correlation with proton affinity shown in Fig. 2.

4. Conclusions

The observed chemistry of pyridine and pyrrole nitrogen heterocycles with singly and multiply charged C_{60} cations further advances our understanding of the chemistry of these ions as a function of charge state. Although only charge-separation reactions driven by electron transfer occur with pyrrole because of its relatively low ionization energy, the chemistry of pyridine is dominated by nucleophilic addition. Electron transfer was observed as a predominant competitive reaction channel only with $C_{60}^{\cdot 3+}$. The number of observed sequential addition reactions correlates with the number of the charges on the fullerene ions which is in keeping with our previous measurements with ammonia and aliphatic amines [3]. However, electron transfer is a more predominant competitive channel in the reactions with aliphatic amines than in the reaction with pyridine.

The unexpected equilibrium achieved for the addition of pyridine to $C_{60}^{\cdot+}$ provided, for the first time, a quantitative bond dissociation enthalpy for a derivatized C_{60} cation. Also, an isomerization reaction involving derivatized fullerene cations has been identified for the first time. Finally, the rate coefficient for the derivatization of $C_{60}^{\cdot+}$ has been shown to correlate with the proton affinity of the neutral adduct for the addition of the two nitrogen heterocycles, ammonia, and several aliphatic amines.

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