# Experimental Study of Reactions of the Buckminsterfullerene Cations $C_{60}^{\bullet+}$, $C_{60}^{2+}$, and $C_{60}^{\bullet 3+}$ with Ammonia and Amines in the Gas Phase

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**Abstract:** Results of SIFT experiments are reported for ion–molecule reactions initiated by $C_{60}^{\bullet+}$, $C_{60}^{2+}$, and $C_{60}^{\bullet 3+}$ in ammonia, methylamine, ethylamine, dimethylamine, and trimethylamine at 294 ● 2 K in helium gas at a pressure of 0.35 ● 0.02 Torr. The main features of the observed reactions can be described in terms of adduct formation and charge transfer and are in line with the known electron recombination energies of these three fullerene cations. Higher order reactions of the adduct ions display both further adduct formation and proton transfer. Addition is the only primary product channel observed with $C_{60}^{\bullet+}$. The apparent bimolecular rate coefficient for adduct formation increases systematically from a low value of less than $1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (with NH$_3$) to a value which appears to saturate at about $1 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, the collision rate coefficient, with decreasing ionization energy of the added amine. C–N bond formation is proposed for these addition reactions and a model is presented which accounts for the trend in the rate coefficients. Secondary adducts were observed to form rapidly with ammonia and all of the amines except trimethylamine and are attributed to the formation of a proton bond. Charge transfer was observed to compete with addition in the reactions of the $C_{60}^{2+}$ dication with the amines (NH$_3$ reacted exclusively by addition), increasing in relative importance with decreasing ionization energy of the amine. Secondary adduct formation, although observed with ammonia, methylamine, and ethylamine, was seen to occur in competition with a dominant proton-transfer channel. Addition of up to three molecules of ammonia was observed with $C_{60}^{\bullet 3+}$, with each adduct also undergoing proton transfer in a secondary reaction with ammonia. The amines react with $C_{60}^{\bullet 3+}$ exclusively by charge transfer which in the case of ethylamine is largely dissociative. It is proposed that the reactions of $C_{60}^{\bullet+}$ and $C_{60}^{2+}$ provide pathways for nitrogen derivatization of neutral fullerenes in the presence of ionization sources and mechanisms for ion neutralization, as, for example, in interstellar clouds and circumstellar envelopes.

## Introduction

The possible chemical derivatization of Buckminsterfullerene, $C_{60}$, which has been isolated in bulk quantities only recently,[1] continues to capture the imagination of many chemists.[2] Already a substantial number of studies have been reported which explore the chemical derivatization of $C_{60}$, $C_{60}^{\bullet+}$, and $C_{60}^{2+}$ in both the gas and the condensed phase. For example, a "radical-sponge" behavior of neutral $C_{60}$ has now been identified toward the species H•,[3] F•,[4] O,[5,6] OH•,[6] CH$_2$,[6] CH$_3$•,[6–8] CF$_3$•,[8] (CH$_3$)$_3$CO•,[8] C$_6$H$_5$•,[8] C$_6$H$_5$CH$_2$•,[8] C$_6$H$_5$S•,[8] and C(C$_6$H$_5$)$_2$.[9] Several studies have explored the interaction of $C_{60}$ with nitrogen. N(1s) core-level

spectroscopic measurements have found that nitrogen interacts with multimolecular films of $C_{60}$.[10] Mass-spectrometric studies have shown that contact-arc vaporization of graphite in a partial atmosphere of N$_2$, NH$_3$, or CH$_3$NH$_2$ yields nitrogenous products tentatively assigned to species such as $C_{70}N_2$, $C_{59}N_6$, $C_{59}N_4$, and $C_{59}N_2$ involving addition of, or substitution by, nitrogen along with species due to C$_2$ and C$_4$ losses.[10] There was no evidence for C–H or N–H bond formation. On the other hand, primary and secondary amines such as *n*-propylamine, *n*-dodecylamine, *tert*-butylamine, ethylenediamine, and morpholine have been observed to react with neutral $C_{60}$ in solution to give amino addition compounds of the type $C_{60}H_n(NRR')_n$ (predominantly $n = 6$).[11] The chemical reactivity of $C_{60}$ with N$^+$ has been shown to be low in a collision-energy range from 1 to 80 eV, but $C_{60}N^+$ was observed as a product channel driven by C–N bond formation with $C_{60}$.[12] We have previously reported SIFT experiments which demonstrate the addition of $C_{60}^{2+}$ with NH$_3$ in the gas phase at room temperature, presumably by C–N bond formation.[13a] Indirect evidence for this process has also been obtained with a triple-quadrupole mass spectrometer.[13b] Here we report detailed results of a systematic experimental mass-spectrometric study of the reactivities of singly-, doubly-, and triply-ionized $C_{60}$ toward ammonia and several aliphatic amines which further explores fundamental aspects of C–N bond formation with $C_{60}$ in the gas

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phase. We have presented elsewhere results of experimental studies which address the feasibility of C–H, C–C, and C–O bond formation in gas-phase reactions of $C_{60}^{\bullet+}$ and $C_{60}^{2+}$.[14] All of these studies have been motivated in part by the proposed occurrence of $C_{60}$ in space.[15] Ionic mechanisms for the gas-phase derivatization of $C_{60}$ have become of interest in connection with the search for possible chemical signatures of this molecule in interstellar clouds and circumstellar envelopes.[16] Ammonia and methylamine are known space molecules,[17] so their reactions with cations of $C_{60}$ may provide avenues for the derivatization of $C_{60}$ in these stellar environments. Such chemistry would have consequences for the spectroscopic search for signatures of $C_{60}$ in these regions.

## Experimental Section

The experiments were performed with a selected-ion flow tube (SIFT) apparatus which has been described previously.[18] The $C_{60}$ cations were produced in a conventional electron-impact source by electron bombardment of $C_{60}$ vapor entrained in argon carrier gas. Singly- and doubly-charged $C_{60}$ were produced at ca. 70–80 eV, and $C_{60}^{\bullet3+}$ was generated at 105 eV. The fullerene samples were obtained from Strem Chemicals Co. ($C_{60}/C_{70}$ with 2–12% $C_{70}$) and Texas Fullerenes Corp. (mixed fullerene extract, ca. 80% $C_{60}$). After selection with the upstream quadrupole mass filter, the $C_{60}$ cations were allowed to thermalize by collision with helium atoms prior to reaction downstream in the flow tube. The ammonia and aliphatic amines used as reagent gases were of an anhydrous grade (Matheson) with purities greater than 98.0 wt % ($CH_3NH_2$), 98.5 mol % ($C_2H_5NH_2$), 99.0 wt % (($CH_3$)$_3$N), 99.0 mol % (($CH_3$)$_2$NH), and 99.99% ($NH_3$). All but one of the reactions investigated were measured at 294 ± 2 K in helium buffer gas at a pressure of 0.35 ± 0.02 Torr. The reaction between $C_{60}^{\bullet+}$ and methylamine was investigated at several pressures between 0.205 and 0.601 Torr.

## Results and Discussion

**Reactions of $C_{60}^{\bullet+}$.** $C_{60}^{\bullet+}$ was observed to react with ammonia and all of the amines investigated in this study exclusively by adduct formation as illustrated in reaction 1. Figure 1 shows

$$C_{60}^{\bullet+} + M \rightarrow C_{60}M^{\bullet+} \qquad (1)$$
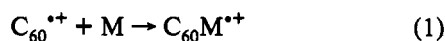
data obtained for the reaction of $C_{60}^{\bullet+}$ with dimethylamine, ($CH_3$)$_2$NH. The apparent bimolecular rate coefficients which were measured as summarized in Table I. The rate coefficient for the reaction with ammonia was immeasurably small, but adduct formation was observed to occur. It should be noted that the measured rate coefficients in Table I are somewhat lower than those reported previously in our study of the derivatization of doubly-charged fullerene ions (although observed trends in reactivity are consistent with our earlier study).[14] In repeating the measurements, we have found that the amines, particularly ($CH_3$)$_3$N, which reacts rapidly, are very difficult to remove completely from the capillaries and influence the performance of the pressure transducers used to measure their flow.

Table I shows a clear trend in the rate coefficient for adduct formation: the rate coefficient increases dramatically (by a factor of 1000!) with increasing aliphatic substitution. Also, there is a correlation with the ionization energy of the adduct molecule. Elsewhere[14] we have noted that the observed trend in reaction efficiency is *not* consistent with changes in the polarizabilities or dipole moments of the neutral reagents: for $NH_3$, $CH_3NH_2$,

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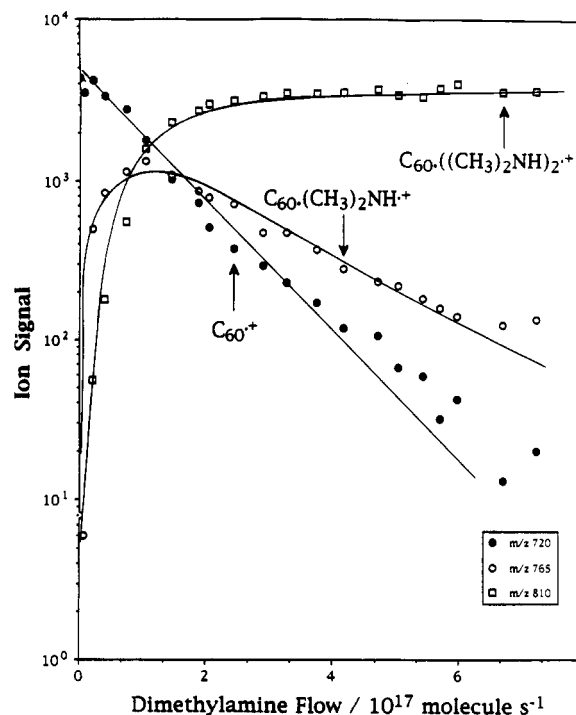


**Figure 1.** Variation in ion signals recorded for the addition of dimethylamine into the reaction region of the SIFT apparatus in which $C_{60}^{\bullet+}$ has been established as the dominant ion in helium buffer gas. $P$ = 0.357 Torr, He velocity = 7.4 × 10³ cm s⁻¹, reaction length = 47 cm, and $T$ = 294 K. $C_{60}^{\bullet+}$ is derived from the vapor of $C_{60}$ by electron impact at 80 eV.

**Table I.** Products and Rate Coefficients[a] Determined Using the SIFT Technique for Reactions of $C_{60}^{\bullet+}$ with Ammonia and Various Amines at 294 ± 2 K in Helium at 0.35 ± 0.2 Torr

| neutral[b] | product | $k_{obs}$ | $k_c$ |
|---|---|---|---|
| $NH_3$ (10.16) | $C_{60}\cdot NH_3^{\bullet+}$ | <0.001 | 1.69 |
| $CH_3NH_2$ (8.97) | $C_{60}\cdot CH_3NH_2^{\bullet+}$ | 0.015 | 1.44 |
| $CH_3CH_2NH_2$ (8.86) | $C_{60}\cdot CH_3CH_2NH_2^{\bullet+}$ | 0.050 | 1.34 |
| ($CH_3$)$_2$NH (8.23) | $C_{60}\cdot(CH_3)_2NH^{\bullet+}$ | 0.85 | 1.22 |
| ($CH_3$)$_3$N (7.82) | $C_{60}\cdot(CH_3)_3N^{\bullet+}$ | 1.0 | 1.05 |

[a] Rate coefficients are in units of 10⁻⁹ cm³ molecule⁻¹ s⁻¹. The measured rate coefficients, $k_{obs}$, have an absolute uncertainty estimated to be ±40%; relative accuracies are less than ±20%. $k_c$ is the ADO collision rate coefficient calculated according to the method of: Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347. [b] Ionization energies (in eV) are given in parentheses.

$CH_3CH_2NH_2$, ($CH_3$)$_2$NH, and ($CH_3$)$_3$N, the polarizabilities have values of 2.18, 4.35, 7.10, 6.37, and 8.15 Å³ and the dipole moments have values of 1.47, 1.31, 1.22, 1.03, and 0.61 Debye.[19]

We attribute the formation of the adduct ions of $C_{60}^{\bullet+}$ with $NH_3$ and the amines to the formation of a covalent C–N bond with the fullerene cation through donation of an electron pair from the nitrogen atom to the site of charge concentration on the surface of the fullerene ion in the manner illustrated in reaction 2. It is interesting to note that this reaction requires a transition
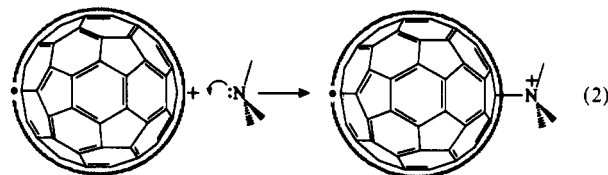


from a reactant ion with extreme charge delocalization (each carbon atom in $C_{60}^{\bullet+}$ carries $^1/_{60}$th of the total charge) to a product ion in which the charge is extremely localized (on the nitrogen

(19) *CRC Handbook of Chemistry and Physics*, 67th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1986.
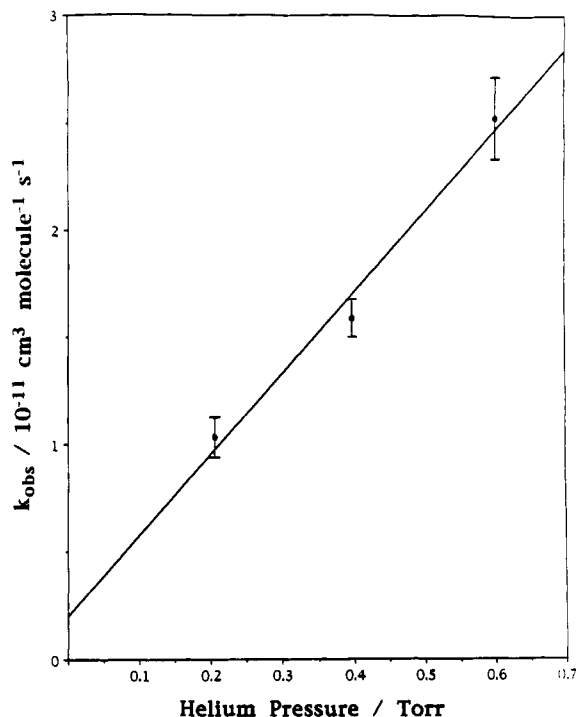
**Figure 2.** Pressure dependence of the apparent bimolecular rate coefficient measured for the reaction of $C_{60}^{\bullet+}$ with methylamine. The rate coefficient was determined from repeated measurements at helium buffer gas pressures of 0.205, 0.399, and 0.601 Torr. The solid line represents a least-squares fit to the data, and the error bars represent the standard deviation. $T = 294 \pm 2$ K.

atom). This mechanism of C–N bond formation may be contrasted with that proposed for the addition of amines to neutral $C_{60}$ in solution, which involves two steps: namely, single-electron transfer to a $\pi$-bond, followed by covalent bond formation and proton transfer.[11] With ionized $C_{60}$, the reactant site is formally a carbocation featuring a vacant bonding orbital which permits bond formation by electron-pair donation.

The apparent bimolecular rate coefficients for the addition reactions listed in Table I were measured at a pressure of 0.35 $\pm$ 0.02 Torr. A study of the pressure dependence of the apparent bimolecular rate coefficient for the reaction of $C_{60}^{\bullet+}$ with methylamine suggests that all of the addition reactions occur in a termolecular, rather than a bimolecular, fashion under our experimental conditions. Figure 2 shows that the apparent bimolecular rate coefficient for the reaction between $C_{60}^{\bullet+}$ and methylamine is linearly dependent on the pressure and that the intercept has no measurable bimolecular component within the experimental uncertainty.

How can one account for the observed trend of increasing rate of association of $C_{60}^{\bullet+}$ with increasing aliphatic substitution of the amine involved? The termolecular association may be described in terms of two steps which involve the formation of a collision complex and its stabilization by collision with the He atoms of the buffer gas. The collisional stabilization

$$(C_{60}\cdot NR_3^{\bullet+})^* + He \rightarrow C_{60}\cdot NR_3^{\bullet+} + He^* \qquad (3)$$

proceeds in competition with unimolecular dissociation
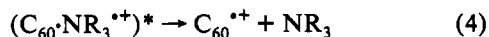
$$(C_{60}\cdot NR_3^{\bullet+})^* \rightarrow C_{60}^{\bullet+} + NR_3 \qquad (4)$$

of the collision complex $(C_{60}\cdot NR_3^{\bullet+})^*$. Application of the steady-state assumption to the concentration of the collision complex leads to a termolecular rate constant given by the expression $k(3) = k_c k_s \tau_d$, in which $k_c$ and $k_s$ are the rate constants for the formation of the collision complex and its collisional stabilization and $\tau_d$ is the lifetime for unimolecular dissociation. The large increase in the rate constant for association with aliphatic substitution is expected to be due primarily to changes in $\tau_d$ since $k_c$ and $k_s$

should not be very sensitive to aliphatic substitution. Statistical theories lead to various expressions for $\tau_d$, of which the simplest, but qualitatively useful, is that given in (5),[20] where $\tau_0$ is a collision

$$\tau_d = \tau_0((D + 3RT)/3RT)^{s-1} \qquad (5)$$

lifetime (corresponding to the frequency of vibration along the reaction coordinate), $D$ is the dissociation energy of the collision complex, $s$ is the number of effective degrees of freedom available in the complex for energy transfer, and $R$ is the gas constant. We have stated previously[14] that, owing to the large size of $C_{60}$, there should be little difference in the expected lifetimes for unimolecular dissociation of collision complexes of fullerene cations with neutrals having the same functional groups but differing levels of molecular complexity: we now believe that this assumption needs refinement. It should be noted that, although $C_{60}$ contains 60 atoms, it has no internal modes of rotation and, given its highly rigid structure, the vibrational modes are widely spaced and will not allow for a great degree of energy dispersal within the collision complex. Trimethylamine contains substantially fewer degrees of freedom than $C_{60}$; however, three of these degrees are methyl group rotational modes which have a much higher energy density than the vibrational modes of $C_{60}$. Bending vibrational modes of trimethylamine will also have a comparatively high energy density, suggesting that they may aid in energy dispersal within the collision complex and thus in promoting the complex lifetime. We propose, therefore, that the lifetime of the collision complex $(C_{60}\cdot NR_3^{\bullet+})^*$ may depend strongly upon the molecular complexity of the neutral $NR_3$. This proposal is consistent with the observed trend in efficiency of association. The role of the bond dissociation energy of the collision complex, which also influences its lifetime, is less certain. The bond dissociation energies of the species $C_{60}\cdot NR_3^{\bullet+}$ are not known. If the bonds are formed by nucleophilic addition of the ammonia or the amine to $C_{60}^{\bullet+}$, i.e. by electron-pair donation from the molecule to the fullerene cation, the observed trend in rate coefficients is consistent with the relative Lewis base strengths of ammonia and the series of amines employed. Alternatively, bond formation may proceed according to the mechanism proposed by Grützmacher et al.[21] adapted from the reactivity model of Shaik and Pross[22] to account for the observed reactivity of ionized halobenzenes and dihalobenzenes with $NH_3$. In this model, the reaction features a transition state involving single-electron transfer (effectively, charge transfer) from ammonia to the aromatic radical cation and formation of a C–N bond by coupling of the unpaired electron of the radical cation $NH_3^{\bullet+}$ with one of the $\pi$-electrons of the neutral halogenated benzene in a second step. An activation energy is predicted for the nucleophilic addition of ammonia to the radical cation of a benzene derivative which should be quite large and decrease with decreasing IE. Such a model suggests that ammonia, with its relatively high ionization energy, should react less efficiently, and amines with lower ionization energies should react more efficiently with $C_{60}^{\bullet+}$, which is consistent with our observations.

The ion chemistry initiated by $C_{60}^{\bullet+}$ with methyl-, ethyl-, and dimethylamine also showed secondary reactions leading to the formation of the adduct ions $C_{60}\cdot(CH_3NH_2)_2^{\bullet+}$, $C_{60}\cdot(C_2H_5NH_2)_2^{\bullet+}$, and $C_{60}\cdot((CH_3)_2NH)_2^{\bullet+}$, but further addition leading to formation of tertiary adduct ions was not observed. The secondary reaction with dimethylamine can be seen in Figure 1. In sharp contrast, the secondary adduct ion with trimethylamine, $(CH_3)_3N$, was noticeably absent. We attribute these results to the formation

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**Table II.** Products and Rate Coefficients[a] Determined Using the SIFT Technique for Reactions of $C_{60}^{2+}$ with Ammonia and Various Amines at $294 \pm 2$ K in Helium at $0.35 \pm 0.2$ Torr

| neutral | products[a] | branching ratio | $k_{obs}$ | $k_c$ |
|---------|-------------|-----------------|-----------|-------|
| $NH_3$ | $C_{60}\cdot NH_3^{2+}$ | 1.00 | 1.2 | 3.37 |
| $CH_3NH_2$ | $C_{60}\cdot CH_3NH_2^{2+}$ | 0.90 | 2.6 | 2.88 |
| | $C_{60}^{\cdot+} + CH_3NH_2^{\cdot+}$ | 0.10 | | |
| $CH_3CH_2NH_2$ | $C_{60}\cdot CH_3CH_2NH_2^{2+}$ | 0.70 | 2.6 | 2.68 |
| | $C_{60}^{\cdot+} + CH_3CH_2NH_2^{\cdot+}$ | 0.30 | | |
| $(CH_3)_2NH$ | $C_{60}\cdot(CH_3)_2NH^+$ | 0.10 | 2.9 | 2.44 |
| | $C_{60}^{\cdot+} + (CH_3)_2NH^{\cdot+}$ | 0.90 | | |
| $(CH_3)_3N$ | $C_{60}^{\cdot+} + (CH_3)_3N^{\cdot+}$ | 1.00 | 2.2 | 2.10 |

[a] Rate coefficients are in units of $10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The measured rate coefficients, $k_{obs}$, have an absolute uncertainty estimated to be $\pm40\%$; relative accuracies are less than $\pm20\%$. $k_c$ is the ADO collision rate coefficient calculated according to the method of: Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347.

of proton-bound adducts of type I which are possible with methyl-, ethyl-, and dimethylamine but not with trimethylamine.

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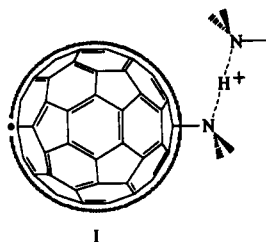
We have also observed that, while the primary addition reactions of $C_{60}^{\cdot+}$ with methylamine and ethylamine are comparatively inefficient, secondary adduct formation in these reactions is considerably more efficient. On the basis of the comparative intensity of primary and secondary adduct signal intensities at low amine flows, we estimate that the rate coefficient for secondary adduct formation exceeds the corresponding rate of primary adduct formation by at least a factor of 10; the reactions

$$C_{60}\cdot NH_2R^{\cdot+} + RNH_2 \rightarrow C_{60}\cdot(NH_2R)_2^{\cdot+} \qquad (6)$$
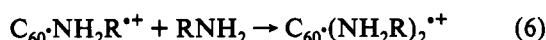
(R = $CH_3$, $C_2H_5$) occur, therefore, at an appreciable fraction (>10% and >30%, respectively) of the ADO collision rate coefficient. The enhanced rate coefficients for these secondary reactions may reflect the greater number of degrees of freedom available for energy dispersal in the adduct $C_{60}\cdot(NH_2R)_2^{\cdot+}$ than in $C_{60}\cdot NH_2R^{\cdot+}$; alternatively, other factors such as a difference in the potential well depths for the primary and secondary adducts might also be expected to influence the relative rates for these reactions.

**Reactions of $C_{60}^{2+}$.** As is evident from the summary presented in Table II, the doubly-charged $C_{60}$ cation reacted quite differently from the singly-charged cation in that adduct formation was observed to compete with charge transfer. Charge transfer is endothermic in the reactions of $C_{60}^{\cdot+}$ monocation with ammonia and the amines investigated in this study, but it is exothermic for the reactions with the $C_{60}^{2+}$ dication and so potentially may compete with adduct formation. However, Coulombic repulsion between the monocations produced in the charge-transfer process introduces a barrier to charge transfer with a height of up to 1.80 $\pm$ 0.16 eV, as we have discussed previously.[23,24] Consequently, charge transfer should be observable at room temperature only for reactions which are sufficiently exothermic to overcome this barrier.[23]

The best current value for the ionization energy of $C_{60}^{\cdot+}$, IE-
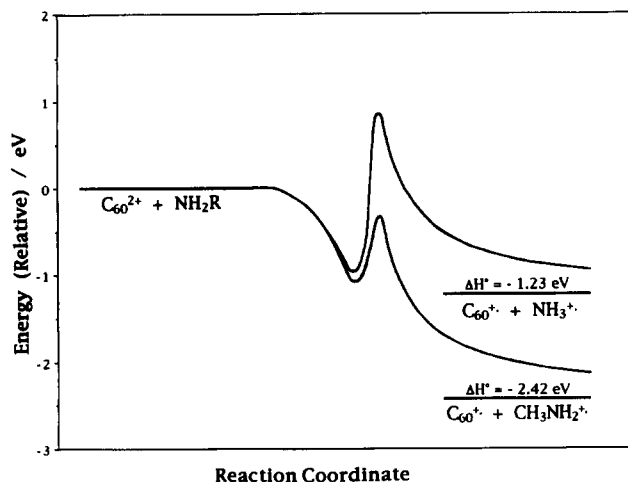


**Figure 3.** Hypothetical potential energy/reaction coordinate profiles which account for the occurrence and nonoccurrence of charge transfer in the reactions of $C_{60}^{2+}$ with amines (methylamine has been used as an example) and ammonia, respectively. The interaction between the product ions is assumed to be dominated by Coulombic repulsion.

($C_{60}^{\cdot+}$), is $11.39 \pm 0.05$ eV.[25] This makes charge transfer between $C_{60}^{2+}$ and all of the amines investigated in this study exothermic by more than 2 eV. Indeed, charge transfer was observed to compete with association in all the reactions with the amines (IE($CH_3NH_2$) = 8.97 eV, IE($C_2H_5NH_2$) = 8.86 eV, IE(($CH_3$)$_2$-NH) = 8.23 eV)[27] and, according to the branching ratios given in Table II, does so increasingly as it becomes more exothermic until it becomes the only observed channel in the reaction with trimethylamine which has the lowest ionization energy (IE-(($CH_3$)$_3$N = 7.82 eV)[27] of the amines investigated.

In contrast, ammonia (IE($NH_3$) = 10.16 eV)[27] was observed to react with $C_{60}^{2+}$ exclusively by association; there was no evidence for a significant occurrence of charge transfer, even though this channel is exothermic.[13a] The exothermicity of charge transfer in this case is only 1.23 eV, which is well below the contribution to the barrier height of 1.80 $\pm$ 0.16 eV which arises from Coulombic repulsion at a separation of 1.0 $\pm$ 0.7 Å, at which charge transfer is thought to take place.[23,24,28] However, this barrier must be regarded as an upper limit, in part because of the possibility of charge transfer at longer range but also because of the presence of other (attractive) interactions which act to reduce the reverse activation energy. Nevertheless, the failure to observe charge transfer with ammonia appears to indicate a barrier to charge transfer greater than 1.23 eV.

Figure 3 presents hypothetical potential energy/reaction coordinate profiles which account for the occurrence and nonoccurrence of charge transfer in the reactions of $C_{60}^{2+}$ with amines (methylamine has been used as an example) and ammonia, respectively.

We attribute the adduct formation observed with $NH_3$, $CH_3$-$NH_2$, $C_2H_5NH_2$, and ($CH_3$)$_2$NH again to electron-pair donation from the N atom as shown in reaction 7.

Table II shows that the reactions of ammonia and all the amines proceed close to, or at, the collision limit and that the trend in the rate coefficient with increasing aliphatic substitution observed for the reactions with the monocation $C_{60}^{\cdot+}$ is absent for the

(23) Petrie, S.; Javahery, G.; Wang, J.; Bohme, D. K. *J. Phys. Chem.* **1992**, *96*, 6121.

(24) Petrie, S.; Wang, J.; Bohme, D. K. *Chem. Phys. Lett.* **1993**, *204*, 473.

(25) The ionization energy for the direct double ionization of $C_{60}$ has been reported to be 19.00 $\pm$ 0.03 eV: Steger, H.; de Vries, J.; Kamke, B.; Kamke, W.; Drewello, T. *Chem. Phys. Lett.* **1992**, *194*, 452. The value for IE($C_{60}^{\cdot+}$) is derived using IE($C_{60}$) = 7.61 $\pm$ 0.02 eV reported in ref 26.

(26) Lichtenberger, D. L.; Jareko, M. E.; Nebesny, K. W.; Ray, C. D.; Huffman, D. R.; Lamb, L. D. *Mater. Res. Soc. Symp. Proc.* **1991**, *206*, 673.

(27) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1.

(28) Javahery, G.; Wincel, H.; Petrie, S.; Bohme, D. K. *Chem. Phys. Lett.* **1993**, *204*, 467.

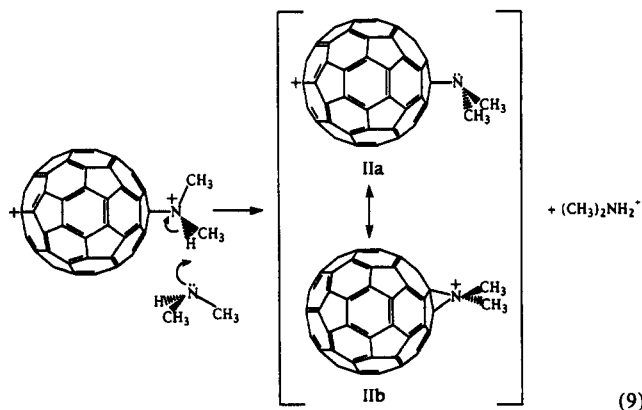$$+ \quad + \cap : N \quad \longrightarrow \quad + \quad + N \qquad (7)$$
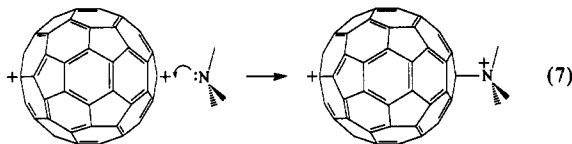
reactions with the dication $C_{60}^{2+}$.[29] The large increase (by a factor of ca. 1000!) in the effective bimolecular rate coefficient for addition of ammonia to the singly- and doubly-charged $C_{60}$ is particularly noteworthy. Since there is no change in molecular complexity (i.e. degrees of freedom), the increase in the rate of association is presumably to be attributed to an increase in the bond strength of the adduct (which leads to an increase in the lifetime of the collision complex). The bond strength of $C_{60} \cdot NH_3^{2+}$ is not known, but one may expect an enhancement over that of the singly-charged adduct due to a smaller loss of charge-delocalization energy and the occurrence of Coulombic relaxation in its formation. Similar considerations should apply to the adduct formation observed with methyl-, ethyl-, and dimethylamine, but for these reactions the increasing contribution due to a charge-transfer channel will contribute to an increase in the measured reaction rate coefficient.

Since molecules can interact with both sites of charge on the $C_{60}$ surface, a second covalent bond can be expected to form according to reaction 8. Indeed, secondary association reactions



$$N^+ \quad + \cap : N \quad \longrightarrow \quad N^+ \quad + N \qquad (8)$$
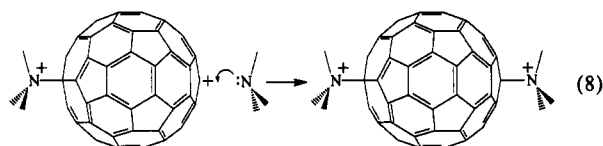
were observed, but in this case the formation of the adduct was seen to compete with proton transfer as we have already shown for the reaction with $NH_3$, with proton transfer actually being favored by a ratio of approximately 9 to 1.[13a] With the amines, secondary adduct formation was observed only with methylamine and ethylamine accounting for <10% of secondary product channels in each case. In our preliminary study of the reaction with ammonia, we incorrectly assigned charge transfer as the dominant product channel for the secondary reactions of the dicationic adducts with the amines $CH_3NH_2$, $(CH_3)_2NH$, and $C_2H_5NH_2$.[13a] We have since reexamined the reaction with dimethylamine and have determined that the dominant secondary reaction of $C_{60}(CH_3)_2NH^{2+}$ is in fact proton transfer as shown in reaction 9. The fullerene product ion, II, from this proton-



$$(9)$$

transfer reaction was observed not to react further with dimethylamine, in contrast to the product III, which would result from charge-transfer from the dicationic adduct. The ion III is

Table III. Products and Rate Coefficients[a] Determined Using the SIFT Technique for Reactions of $C_{60}^{\cdot 3+}$ with Ammonia and Various Amines at $294 \pm 2$ K in Helium at $0.35 \pm 0.2$ Torr

| neutral | products | braching ratio | $k_{obs}$ | $k_c$ |
|---|---|---|---|---|
| $NH_3$ | $C_{60} \cdot NH_3^{\cdot 3+}$ | 1.00 | 3.9 | 5.04 |
| $CH_3NH_2$ | $C_{60}^{2+} + CH_3NH_2^{\cdot +}$ | 1.00 | 3.8 | 4.32 |
| $CH_3CH_2NH_2$ | $C_{60}^{2+} + CH_3^{\cdot} + CH_2NH_2^{+}$ | >0.90 | 3.4 | 4.02 |
| | $C_{60}^{2+} + CH_3CH_2NH_2^{\cdot +}$ | <0.10 | | |
| $(CH_3)_2NH$ | $C_{60}^{2+} + (CH_3)_2NH^{\cdot +}$ | 1.00 | 3.5 | 3.66 |
| $(CH_3)_3N$ | $C_{60}^{2+} + (CH_3)_3N^{\cdot +}$ | 1.00 | 2.8 | 3.15 |

[a] Rate coefficients are in units of $10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The measured rate coefficients, $k_{obs}$, have an absolute uncertainty estimated to be $\pm 40\%$; relative accuracies are less than $\pm 20\%$. $k_c$ is the ADO collision rate coefficient calculated according to the method of: Su, T.; Bowers, M. T. Int. J. Mass Spectrom. Ion Phys. 1973, 12, 347.

formed as the primary product in the reaction of $C_{60}^{\cdot +}$ with dimethylamine and is seen to undergo further addition to form, as we have proposed, a proton-bound species IV. The lack of
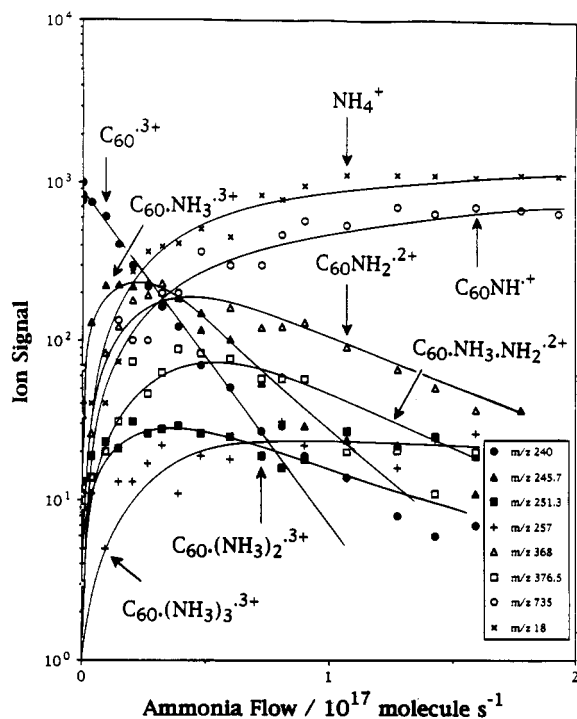


III          IV
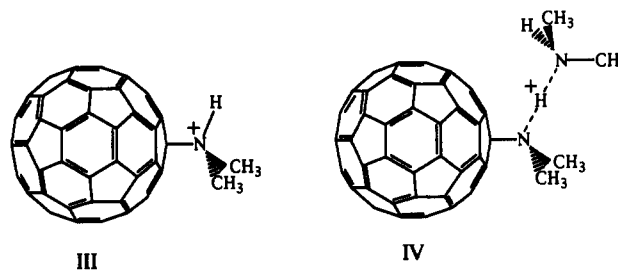
further addition of dimethylamine to II suggests a rearranged structure different from IIa; for example, the isomer IIb, in which charge is localized upon the nitrogen, is unable to form either a proton-bound adduct or a "double-handled" adduct (arising from nucleophilic attack by dimethylamine of a charge site upon the fullerene framework). Structure IIa possesses a positive charge distributed over the fullerene cage, in much the same manner as in $C_{60}^{\cdot +}$, and might therefore be expected to display a similar tendency to undergo further addition with dimethylamine by analogy with the efficient addition reaction observed with $C_{60}^{\cdot +}$. Since such addition does not occur with II, we favor IIb as the most likely structure for this product ion.

Since the ionization energy of dimethylamine is substantially lower than those of methylamine and ethylamine, the reaction of $C_{60}^{2+}$ with dimethylamine represents the thermodynamically most favorable case for charge transfer from the dication adduct. While proton transfer was the dominant reaction of this adduct with dimethylamine, a minor channel (<25%) leading to charge transfer could not be excluded due to the formation of the same product ion ($C_{60} \cdot (CH_3)_2NH^{\cdot +}$) initiated by the primary charge-transfer reaction channel which leads to $C_{60}^{\cdot +}$.

Reactions of $C_{60}^{\cdot 3+}$. Table III provides a summary of the products and specific reaction rates determined for the reactions of $C_{60}^{\cdot 3+}$ with ammonia and the amines. Ammonia was observed to react rapidly with triply-charged $C_{60}$ by association; there was no measurable contribution due to charge transfer. This result is somewhat surprising in that previous charge-transfer bracketing measurements have indicated thresholds for charge transfer from $C_{60}^{\cdot 3+}$ at ionization energies of $11.09 \pm 0.09$[28] and $11.2 \pm 0.2$ eV.[30] The ionization energy of ammonia is 10.16 eV, which means that the barrier for charge transfer should be superseded by almost 1 eV. Presumably, the high efficiency of adduct formation is a reflection of the strong C–N bond which is formed between $C_{60}^{\cdot 3+}$ and $NH_3$. We have observed previously reactions with $C_{60}^{2+}$ in which adduct formation competes effectively with charge transfer. For example, the initial energy in the charge-transfer reaction between $C_{60}^{2+}$ and butadiene supersedes the barrier by ca. 0.5 eV

(29) The rate coefficients in Table II supersede those reported earlier.[14] The earlier measurements were influenced by the difficulty in removing the amines from the capillaries and pressure transducers used to measure their flow.
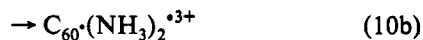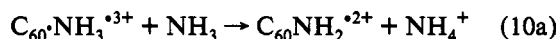
(30) McElvany, S. W.; Bach, S. B. H. ASMS Conf. Mass Spectrom. Allied Top. 1991, 39, 422.

**Figure 4.** Variation in ion signals recorded for the addition of ammonia into the reaction region of the SIFT apparatus in which $C_{60}^{\bullet 3+}$ has been established as the dominant ion in helium buffer gas. $P = 0.365$ Torr, He velocity $= 6.8 \times 10^3$ cm s$^{-1}$, reaction length $= 47$ cm, and $T = 294$ K. $C_{60}^{\bullet 3+}$ is derived from the vapor of $C_{60}$ by electron impact at 105 eV.

but charge transfer occurs only in 20% of the collisions and adduct formation predominates. Similar situations arise in the reactions of $C_{60}^{2+}$ with methylamine, ethylamine (see Table II), and (Z)-2-butene,[23] for which the initial energy overcomes the barrier by approximately 0.6, 0.7, and 0.35 eV, respectively.

Figure 4 shows the sequential chemistry which is initiated by $C_{60}^{\bullet 3+}$ in ammonia. The first $C_{60}\cdot NH_3^{\bullet 3+}$ adduct ion is seen to react rapidly with ammonia primarily by proton transfer but also by further adduct formation as indicated by reaction 10. The

$$C_{60}\cdot NH_3^{\bullet 3+} + NH_3 \rightarrow C_{60}NH_2^{\bullet 2+} + NH_4^+ \quad (10a)$$

$$\rightarrow C_{60}\cdot(NH_3)_2^{\bullet 3+} \quad (10b)$$

data provide a branching ratio of about 8 to 2. The second adduct reacts further, still quite rapidly, to form the third adduct $C_{60}\cdot(NH_3)_3^{\bullet 3+}$. Presumably, proton transfer is a competing channel also in this reaction. Indeed, the product ion $C_{60}\cdot NH_3\cdot NH_2^{\bullet 2+}$ is observed to be formed, but this ion may also arise from the addition of $NH_3$ to $C_{60}NH_2^{\bullet 2+}$ formed in reaction 10a. Va/Vb and VIa/VIb are likely structures for the second and third adducts formed in this sequence of addition reactions initiated by $C_{60}^{\bullet 3+}$. Structures Va and VIa involve direct bonding to the fullerene surface and minimize Coulombic repulsion.[24] It is interesting to note the structural difference between the triply-charged double-ammonia adduct of $C_{60}$ (Va), in which the two ammonia molecules are at an angle of 120° to each other, and the doubly-charged double-ammonia adduct shown in reaction 7, in which the two ammonia molecules are bonded to $C_{60}$ opposite each other. Structures Vb and VIb allow for the formation of a proton bond between the incoming ammonia molecule and an ammonia molecule already bonded to the $C_{60}$. However, the apparent failure of $C_{60}\cdot(NH_3)_3^{\bullet 3+}$ to form a proton-bound adduct would seem to make the formation of structures Vb and VIb unlikely.

Also noteworthy is the proton-transfer reaction sequence manifested in Figure 4 and illustrated in reaction 11. The sequence appears to terminate with the production of $C_{60}NH^{\bullet +}$, presumably
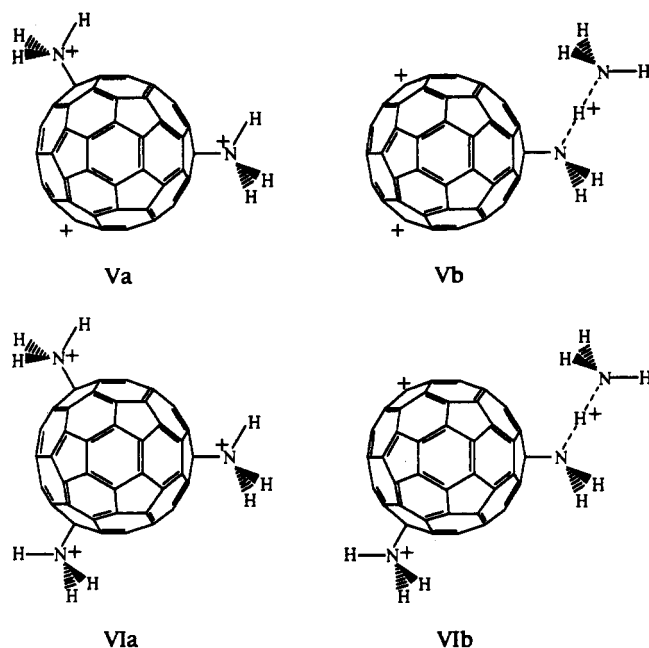


because delocalization of the single remaining charge on $C_{60}NH^{\bullet +}$ can lead to a higher value for $PA(C_{60}N^\bullet)$. This delocalization leads to a much lower degree of charge concentration upon the nitrogen atom in $C_{60}NH^{\bullet +}$ than in $C_{60}NH_2^{\bullet 2+}$ and $C_{60}\cdot NH_3^{\bullet 3+}$. The nature of the further reaction of $C_{60}\cdot NH_3\cdot NH_2^{\bullet 2+}$, apparent from the data in Figure 4, is not clear; proton transfer is perhaps most likely. $C_{60}\cdot(NH_3)_3^{\bullet 3+}$ appears to be quite unreactive.
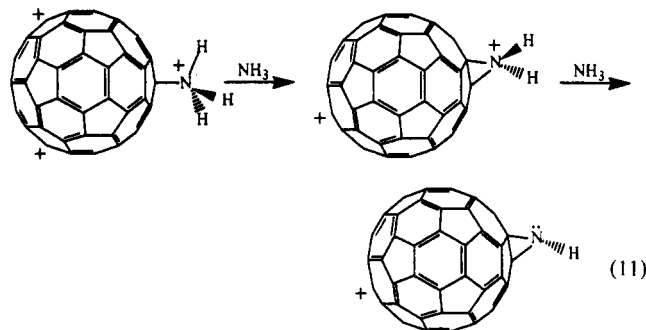


Charge transfer is the only product channel observed in the reactions of $C_{60}^{\bullet 3+}$ with methyl-, dimethyl-, and trimethylamine. In contrast, the primary product channel in the reaction with ethylamine, for which data is shown in Figure 5, is the dissociative charge-transfer channel (12), where the low-mass product, $m/z$

$$C_{60}^{\bullet 3+} + CH_3CH_2NH_2 \rightarrow C_{60}^{2+} + CH_3^\bullet + CH_2NH_2^+ \quad (12)$$
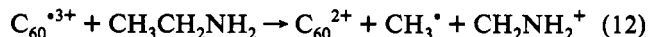
30, is assigned as $CH_2NH_2^+$ (arising from methyl group loss); formation of $C_2H_6^{\bullet +} + NH$ is considerably less exothermic and requires a greater degree of rearrangement. It is surprising that methyl group loss is observed in the reaction with ethylamine while no fragmentation (including loss of H or $CH_3$) is seen with trimethylamine, since the lowest-energy fragmentation process for $(CH_3)_3N^{\bullet +}$ is calculated to require less energy (14 kcal mol$^{-1}$) than the lowest-energy fragmentation process for $CH_3CH_2NH_2^{\bullet +}$ (20 kcal mol$^{-1}$). Also, the charge-transfer reaction (13) is more
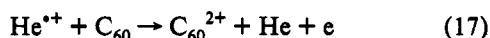
$$C_{60}^{\bullet 3+} + NRR'R'' \rightarrow C_{60}^{2+} + NRR'R''^{\bullet +} \quad (13)$$
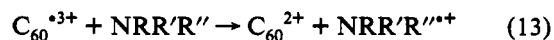
exothermic for $NRR'R'' = (CH_3)_3N$ ($\Delta H° = -179$ kcal mol$^{-1}$) than for $CH_3CH_2NH_2$ ($\Delta H° = -155$ kcal mol$^{-1}$), so a greater amount of internal energy should be initially deposited in the $(CH_3)_3N^{\bullet +}$ product ion. However, at least one factor may mitigate against fragmentation of ionized trimethylamine. $(CH_3)_3N$ has more internal modes of energy dispersal than $CH_3CH_2NH_2$, and

so the probability of enough internal energy becoming localized in a vibrational mode of the weakest bond is therefore reduced.

The secondary chemistry of $C_{60}^{2+}$ produced in the charge-transfer reactions of $C_{60}^{\bullet 3+}$ with the amines was observed to be identical to that identified in the experiments in which $C_{60}^{2+}$ was produced directly by electron impact of $C_{60}$, as discussed in the previous section. The ionized amine which accompanies the production of $C_{60}^{2+}$ in the initial charge-transfer reaction was observed to transfer a proton to the parent amine molecule, and subsequent formation of the proton-bound dimer of the amine was generally observed. Also, the $CH_2NH_2^+$ ion produced by dissociative charge transfer from ethylamine was observed to react further with this amine to generate $C_2H_5NH_3^+$, as can be seen in Figure 5.

**Implications for Space Chemistry.** The Buckminsterfullerene molecule, $C_{60}$, has been proposed to be present in circumstellar and interstellar environments,[15] where it may be ionized both by physical (e.g. photoionization) and by chemical means. As an example of the latter, we have shown elsewhere that $He^{\bullet+}$ ionizes $C_{60}$ by charge transfer to produce $C_{60}^{\bullet+}$ and by charge-transfer electron detachment to produce $C_{60}^{2+}$.[31] The results presented here indicate that subsequent chemical reactions of $C_{60}^{\bullet+}$ and $C_{60}^{2+}$ in these environments with ammonia and methylamine will act to chemically derivatize these ions through the formation of C–N bonds. Subsequent neutralization by proton transfer and electron/ion recombination reactions will then produce derivatized neutral $C_{60}$. The overall result is that *neutral* $C_{60}$ becomes derivatized through an *ionic* mechanism. For example, the following two reaction sequences will derivatize $C_{60}$ to produce $C_{60}NH$ and $C_{60}NH_2^\bullet$:

$$He^{\bullet+} + C_{60} \rightarrow C_{60}^{\bullet+} + He \qquad (14)$$

$$C_{60}^{\bullet+} + NH_3 \rightarrow C_{60}NH_3^{\bullet+} + h\nu \qquad (15)$$

$$C_{60}NH_3^{\bullet+} + e(M) \rightarrow C_{60}NH_2^\bullet + H^\bullet(MH^+) \quad (16a)$$

$$\rightarrow C_{60}NH + H_2 \qquad (16b)$$

$$He^{\bullet+} + C_{60} \rightarrow C_{60}^{2+} + He + e \qquad (17)$$

$$C_{60}^{2+} + NH_3 \rightarrow C_{60}NH_3^{2+} + h\nu \qquad (18)$$

$$C_{60}NH_3^{2+} + NH_3 \rightarrow C_{60}NH_2^+ + NH_4^+ \qquad (19)$$

$$C_{60}NH_2^+ + e(M) \rightarrow C_{60}NH + H^\bullet(MH^+) \qquad (20)$$
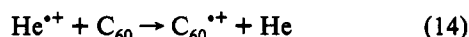
Here it is assumed that the addition reactions with ammonia proceed by radiative association rather than termolecular collisional association, which is improbable in interstellar environments because of the low densities but could contribute in circumstellar environments, where densities can be much higher.[17] Analogous schemes with the other amines studied here would produce $C_{60}NR$, $C_{60}NRH^\bullet$, and $C_{60}N(CH_3)_2^\bullet$, where R = $CH_3$ or $C_2H_5$.

## Conclusions

We have shown that $C_{60}^{\bullet+}$, $C_{60}^{2+}$, and $C_{60}^{\bullet 3+}$ can be derivatized in the gas phase by addition reactions with ammonia at room temperature in helium at 0.35 Torr. The number of molecules of ammonia which add to these fullerene cations appears to be determined by the number of charges on the fullerene surface. In contrast, aliphatic amines were observed to add to $C_{60}^{\bullet+}$ and

(31) Javahery, G.; Petrie, S.; Wang, J.; Bohme, D. K. *Chem. Phys. Lett.* **1992**, *196*, 7.
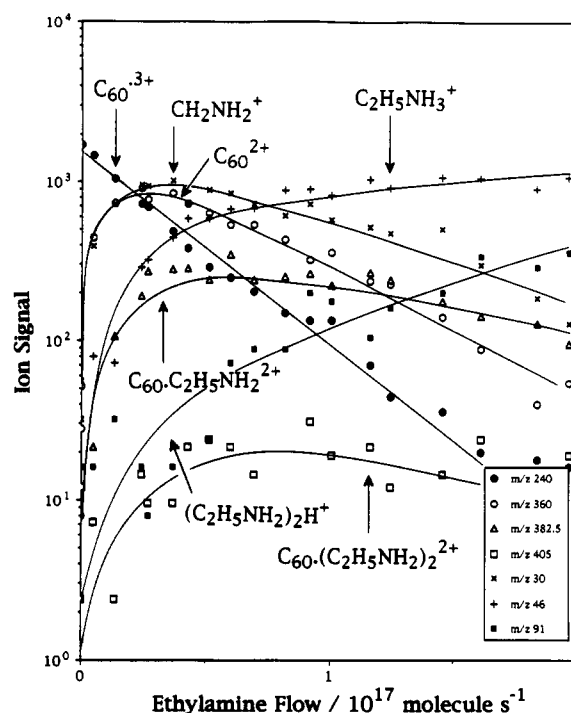


**Figure 5.** Variation in ion signals recorded for the addition of ethylamine into the reaction region of the SIFT apparatus in which $C_{60}^{\bullet 3+}$ has been established as the dominant ion in helium buffer gas. $P = 0.37$ Torr, He velocity $= 6.8 \times 10^3$ cm s$^{-1}$, reaction length $= 47$ cm, and $T = 294$ K. $C_{60}^{\bullet 3+}$ is derived from the vapor of $C_{60}$ by electron impact at 105 eV.

$C_{60}^{2+}$ but not to $C_{60}^{\bullet 3+}$, which reacts exclusively by charge transfer with all of the amines investigated, in accordance with the lower ionization energies of the amines. The amine-addition reactions of $C_{60}^{2+}$ were observed to compete with charge transfer which predominates in the reactions with $(CH_3)_2NH$ and $(CH_3)_3N$, which have relatively low ionization energies. The addition reactions with $C_{60}^{\bullet+}$ show an increasing rate with increasing aliphatic substitution. This trend is consistent with expected binding energies and collision-complex lifetimes.

The derivatization is proposed to proceed by covalent C–N bond formation via donation of the lone pair of electrons on the nitrogen atom to a charge site on the fullerene cation. This is in contrast to the mechanism which has been proposed for amine addition to neutral $C_{60}$ in solution.

The derivatized $C_{60}M^{\bullet+}$ ions appear to form proton-bound adducts with M = $CH_3NH_2$, $C_2H_5NH_2$, and $(CH_3)_2NH$. $C_{60}M^{2+}$ ions can add a second molecule of M, but addition competes with proton transfer for M = $NH_3$ and amines. $C_{60}M^{\bullet 3+}$ is formed only with M = $NH_3$, but this adduct adds a second and a third molecule of $NH_3$ in a sequential fashion. It also loses two protons to ammonia in a sequential fashion.

The observations that multiply-charged adducts react by proton transfer and that singly-charged adducts form proton-bound secondary adducts, where feasible, indicate a tendency for charge(s) to concentrate on the nitrogen atom(s) rather than upon the fullerene cage, as shown in the structures which we have proposed for these species.

The reactions of $C_{60}^{\bullet+}$ and $C_{60}^{2+}$ with ammonia and with amines provide pathways for the derivatization of fullerenes in the presence of ionization sources and mechanisms for ion neutralization, as, for example, in interstellar clouds and circumstellar envelopes.