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Gas-Phase Reactions of Fullerene Monocations, Dications, and Trications with Nitriles

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Abstract: Results are reported for the reactions of the fullerene ions $C_{60}^{\cdot+}$, $C_{70}^{\cdot+}$, C_{60}^{2+}, C_{70}^{2+}, and $C_{60}^{\cdot3+}$ with the nitriles HCN, CH_3CN, CH_2CHCN, CH_3CH_2CN, CH_2CHCH_2CN, $CH_3CH_2CH_2CN$, $(CH_3)_2CHCN$, C_2N_2, and $CH_2(CN)_2$. The reactions were studied using a selected-ion flow tube (SIFT) at 294 ± 2 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr and exhibited a wide range of chemical behavior. For the monocations $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$, no detectable reaction occurred with any of the nitriles. For the dications C_{60}^{2+} and C_{70}^{2+}, the only primary or secondary product channel evident in all instances was addition: tertiary association was seen to be considerably less efficient than the primary and secondary reactions, and the formation of a quadruple adduct $C_{60}(RCN)_4^{2+}$ was only detected in the reaction with butyronitrile, $CH_3CH_2CH_2CN$. The observed primary rate coefficients show a very clear dependence upon the molecular complexity of the nitrile: association proceeds more efficiently for nitriles with a higher number of hydrogen atoms. This observation is explained in terms of a model which relates the number of C–H bonds—or, alternatively, the number of internal rotational modes—in the collision complex to the lifetime and probability of stabilization of this complex. For the trication $C_{60}^{\cdot3+}$, addition was observed as the main primary product channel for all of the nitriles and was rapid for all nitriles except dicyanogen. Multiple adducts were observed in most instances, although in the reactions of tricationic adducts of acrylonitrile, allyl cyanide, malononitrile, and dicyanogen with the parent neutral, the dominant secondary product channel was a charge-separating ligand-transfer reaction resulting in the formation of a nitrile dimer cation $(RCN)_2^{\cdot+}$. Proton transfer from a multiply-charged nitrile adduct to the parent nitrile was noted only in the case of $C_{60}(NCH)^{\cdot3+}$ + HCN. The consequences of the observed reactivity of $C_{60}^{\cdot+}$ and C_{60}^{2+} for models of interstellar chemical evolution are discussed.

Introduction

A very large number of studies of fullerene chemical and physical properties has been undertaken following the discovery[1] and synthesis[2] of these all-carbon cage molecules. Among the many areas which have been investigated is that of the ion–molecule chemistry of fullerenes, which was recently reviewed.[3] Singly-ionized fullerenes such as $C_{60}^{\cdot+}$ and C_{60}^{-} are of very low reactivity; for this reason and for the comparative scarcity of other experimental data on the bimolecular reactivity of molecular dications, much effort has recently been directed toward studying the ion–molecule chemistry of fullerene dications. McElvany and co-workers[4,5] have studied the charge-transfer reactions of C_{56}^{2+}, C_{60}^{2+}, and C_{70}^{2+} with several neutrals in an FT-ICR (Fourier transform–ion cyclotron resonance) apparatus. We have also studied the charge-transfer reactions of C_{60}^{2+} and C_{70}^{2+} with a wider variety of neutrals[6,7] using a SIFT (selected-ion flow tube), and have used the same apparatus to study addition reactions of C_{60}^{2+} with atomic hydrogen,[8] unsaturated hydrocarbons,[9,10] ammonia and amines,[9,11,12] water, alcohols and ethers,[13] and carbonyl- and carboxyl-containing compounds.[14] We have also discussed the structure[9,15] and gas-phase acidity[16,17] of hydrogenated and derivatized fullerene dications. The reaction of C_{60}^{2+} with NH_3 was also studied recently in a triple-quadrupole (MS/MS/MS) experiment.[18]

Fewer studies of fullerene trication reactivity have been performed. McElvany and Bach have studied the charge-transfer reactions of $C_{56}^{\cdot3+}$, $C_{60}^{\cdot3+}$, and $C_{70}^{\cdot3+}$ with several neutrals in an FT-ICR experiment.[5] We recently also investigated the reactions of $C_{60}^{\cdot3+}$ with several neutrals[12,13,19] and used a model for the charge transfer process to derive IE(C_{60}^{2+}) = 15.6 ± 0.5 eV from the reactions observed.[19,20] Most of the reactions of $C_{60}^{\cdot3+}$ which have been studied to date are dominated by charge transfer.

Our interest in the reactions of multiply-charged fullerenes with nitriles arises, in part, from an interest in the chemical

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processes occurring within dense interstellar clouds and circumstellar shells. Nitriles are known to be comparatively abundant within such environments,[21-23] and fullerenes (including fullerene dications)[24-28] are also expected to be present. It is therefore of considerable interest to explore the possible interstellar chemistry of fullerene cations and nitriles.

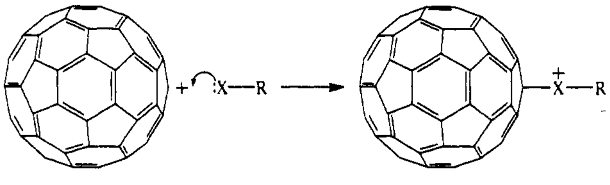
Experimental Section

The results reported here were obtained using a selected-ion flow tube (SIFT) which has been described previously.[29,30] All measurements were obtained at 294 ± 2 K and a helium buffer gas pressure of 0.35 ± 0.01 Torr. The fullerene cations $C_{60}^{\cdot+}$, $C_{70}^{\cdot+}$, C_{60}^{2+}, C_{70}^{2+}, and $C_{60}^{\cdot3+}$ were generated by 50 eV (100 eV for $C_{60}^{\cdot3+}$) electron bombardment upon a vaporized fullerene mixture (C_{60}/C_{70} containing 2–12% C_{70}, obtained from Strem Chemicals Co.) entrained in argon. HCN was synthesized by the action of orthophosphoric acid upon KCN in a manner similar to that described by Melville and Gowenlock.[31] C_2N_2 was obtained from Matheson. Other cyanides were obtained from Aldrich and were of >98% purity. The reactions of fullerene cations with HCN and C_2N_2 were studied using the pure gas RCN; the reaction with malononitrile, $CH_2(CN)_2$, was monitored using helium saturated with malononitrile vapor,[32] in a manner which we have used previously for naphthalene;[33] reactions with other nitriles were studied using dilute mixtures (1–10%) of nitrile vapor in helium.

Results and Discussion

Reactions of $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$. The monocations $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$ were not observed to react detectably with any of the nitriles surveyed. Upper limits to the rate coefficient for reactions of these ions can be set at $<1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for HCN, C_2N_2, CH_3CN, CH_2CHCN, and CH_3CH_2CN and at $<1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for C_3H_5CN, n-C_3H_7CN, i-C_3H_7CN, and $CH_2(CN)_2$. The comparatively high upper limits for the latter reagents reflect their low vapor pressures at 294 K: it was not possible to attain such high concentrations of these reactants within the reaction region as could be achieved for the more volatile nitriles.

The low reactivity of $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$ with these neutrals is in keeping with the results of earlier studies. Aside from the occurrence of charge transfer to neutrals having lower ionization energy (IE(C_{60}) = 7.61 ± 0.02 eV, IE(C_{70}) = 7.47 ± 0.02 eV),[34-36] the only product channel yet reported for reactions of $C_{60}^{\cdot+}$ or $C_{70}^{\cdot+}$ is that of addition, which has been observed only with atomic hydrogen[8] and ammonia and the amines.[11,14] The proposed mechanism for addition of ammonia and amines to $C_{60}^{\cdot+}$ (and of other neutrals featuring electronegative atoms such as N or O, with C_{60}^{2+} and $C_{60}^{\cdot3+}$) is one of nucleophilic attack of a charge site upon the fullerene cation:



(1)

Table I. Observed Reaction Rate Coefficients for the Reaction C_n^{2+} (n = 60, 70) + RCN

RCN	product	k_{60}[a]	k_{70}[b]	k_c[c]
HCN	none	<0.001	<0.001	4.23
CH_3CN	$C_n(NCCH_3)^{2+}$	0.080	0.029	4.68
CH_2CHCN	$C_n(NCC_2H_3)^{2+}$	0.070	0.040	4.51
CH_3CH_2CN	$C_n(NCC_2H_5)^{2+}$	2.5	1.6	4.41
CH_2CHCH_2CN	$C_n(NCC_3H_5)^{2+}$	1.8[d]	0.77	3.87
$CH_3CH_2CH_2CN$	$C_n(NCC_3H_7)^{2+}$	3.9[d]	3.0	4.15
$(CH_3)_2CHCN$	$C_n(NCC_3H_7)^{2+}$	4.3[d]	3.4	3.93
NCCN	$C_n(NCCN)^{2+}$	<0.001	<0.001	1.90
$NCCH_2CN$	none	<0.01	<0.01	3.64

[a] Observed effective bimolecular reaction rate coefficient for C_{60}^{2+} + RCN at 294 ± 2 K and 0.35 ± 0.01 Torr, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [b] Observed effective bimolecular reaction rate coefficient for C_{70}^{2+} + RCN at 294 ± 2 K and 0.35 ± 0.01 Torr, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [c] ADO collision rate coefficient in units of 10^{-9} cm^3 molecule^{-1} s^{-1}, calculated according to the method of Su and Bowers,[37] for the reaction of C_{60}^{2+} + RCN. The ADO collision rate coefficient for C_{70}^{2+} + RCN is not given separately since in all cases this lies between 99% and 100% of the calculated collision rate coefficient for C_{60}^{2+}. [d] These values supersede the values reported previously in ref 15 which were derived from fewer measurements than the present results.

The lack of observable reactivity of the fullerene monocations with the nitriles surveyed is consistent with the relatively poor nucleophilic character of these nitriles.

Reactions of C_{60}^{2+} and C_{70}^{2+}. The reactions of the fullerene dications C_{60}^{2+} and C_{70}^{2+} with various nitriles are summarized in Table I. The only product channel seen in any of these reactions is association, which under our experimental conditions is expected to occur in a termolecular fashion:

$$C_{60}^{2+} + RCN \rightarrow [C_{60}(RCN)^{2+}]^* \qquad (2)$$

$$[C_{60}(RCN)^{2+}]^* + He \rightarrow C_{60}(RCN)^{2+} + He^* \qquad (3)$$

We have elsewhere[9,12] reported the pressure dependence of the association reactions C_{60}^{2+} + CH_2CCH_2 and $C_{60}^{\cdot+}$ + CH_3NH_2 between 0.2 and 0.6 Torr. These studies provide evidence that the predominant mode of stabilization of the collision complex (at 0.35 Torr) is termolecular in these instances, and we anticipate that this is also the case in the association reactions C_{60}^{n+} + RCN reported here. The mechanism for the formation of the initial collision complex $[C_{60}(RCN)^{2+}]^*$ is thought to involve nucleophilic attack of a charge site as in (1). The observed reactivity is illustrated by the data shown in Figure 1, showing the reaction of C_{60}^{2+} with n-C_3H_7CN.

We have calculated, as shown in Table II, the effective bimolecular rate coefficients k_2 for the secondary addition reaction

$$C_{60}(RCN)^{2+} + RCN \rightarrow C_{60}(RCN)_2^{2+} \qquad (4)$$

These values were determined by curve fitting of the primary adduct ion signal versus the reactant neutral flow. The rate coefficients so obtained have an estimated uncertainty of ±50%. In all instances, the reaction rate coefficients k_2 pertaining to the reactivity of $C_{60}(RCN)^{2+}$ were very close to the rate coefficients k_1 for association of C_{60}^{2+}. We have interpreted this observation[15] as indicating that the most probable site of secondary addition

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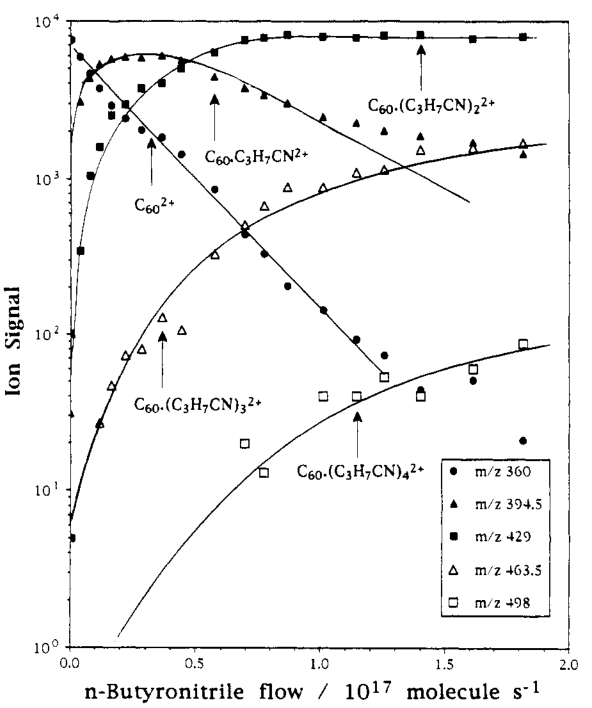


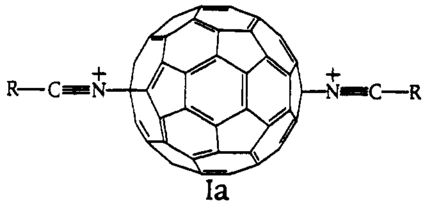
Figure 1. Experimental data for the reaction of $C_{60}{}^{2+}$ with *n*-butyronitrile, $CH_3CH_2CH_2CN$, at 294 ± 2 K and a helium buffer gas pressure of 0.359 ± 0.001 Torr.

Table II. Observed Reaction Rate Coefficients for the Reaction $C_{60}(RCN)_{n-1}{}^{2+} + RCN \rightarrow C_{60}(RCN)_n{}^{2+}$ (n = 1–4)

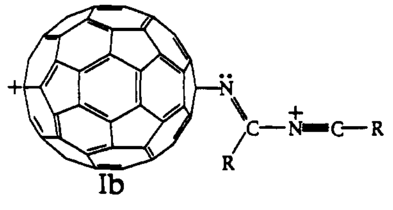
RCN	$k_1{}^{a,b}$	$k_2{}^{a,c}$	$k_3{}^{a,d}$	$k_4{}^{a,e}$
HCN	<0.001			
CH_3CN	0.080	0.12	<0.005	
CH_2CHCN	0.070	0.13	<0.005	
CH_3CH_2CN	2.5	2.2	0.034	<0.05
CH_2CHCH_2CN	1.8	1.9	0.08	<0.05
$CH_3CH_2CH_2CN$	3.9	4.6	0.38	<0.1
$(CH_3)_2CHCN$	4.3	3.6	0.16	<0.1
NCCN	<0.001			
$NCCH_2CN$	<0.01			

[a] All rate coefficients are effective bimolecular reaction rate coefficients obtained from experiments performed at 294 ± 2 K and 0.35 ± 0.01 Torr and are expressed in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [b] Observed rate coefficient for the primary addition reaction, $C_{60}{}^{2+} + RCN$. [c] Calculated rate coefficient for the secondary addition reaction, $C_{60}(RCN)^{2+} + RCN$. [d] Calculated rate coefficient for the tertiary addition reaction, $C_{60}(RCN)_2{}^{2+} + RCN$. [e] Calculated rate coefficient for the quaternary addition reaction, $C_{60}(RCN)_3{}^{2+} + RCN$.

is the back side of the fullerene adduct $C_{60}(RCN)^{2+}$, to produce a "double-handled" adduct **Ia** in which the bonds from the fullerene cage to the N atoms are diametrically opposed (or nearly so), as dictated by the expected charge distribution upon the fullerene dication. A "single handled" isomer **Ib** is also possible and would arise from nucleophilic attack of the charge site localized upon the nitrile moiety of the primary adduct; however, we expect that the single-handled isomer **Ib** accounts for only a small fraction of the observed secondary adducts.[15]



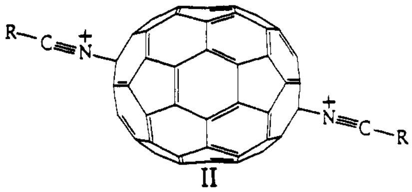
Ia



Ib

Curve fitting of the product ion signals for reactions of $C_{70}{}^{2+} + RCN$ to obtain a quantitative measure of the reactivity of $C_{70}(RCN)^{2+}$ was not attempted: the fullerene sample used in our experiments gave ion signals of $C_{70}{}^{2+}$ (and its product ions) which were typically 1 order of magnitude below the obtainable signals due to $C_{60}{}^{2+}$ (and its product ions), and hence the uncertainty in the interpolated rate coefficients would be substantially higher for $C_{70}(RCN)^{2+}$ than for $C_{60}(RCN)^{2+}$. Nevertheless, the reactivity of $C_{70}{}^{2+}$ and its product ions appeared to be entirely analogous to that of $C_{60}{}^{2+}$, with the general feature that $C_{70}{}^{2+}$ underwent addition at a lower efficiency than did $C_{60}{}^{2+}$. The structure of the double adduct $C_{70}(RCN)_2{}^{2+}$ is dependent upon the charge distribution in $C_{70}{}^{2+}$, since this dictates the sites of nucleophilic attack: unlike C_{60} where all carbon atoms are equivalent, C_{70} possesses five nonequivalent types of carbon atoms. We anticipate that the most likely sites for nitrile addition are those atoms at the "endcaps" of the C_{70} molecule, since these possess the greatest degree of pyramidalization in the unsubstituted species and are thus likely to be deformed least by formation of a fullerene–nitrogen bond. The reduced efficiency of $C_{70}{}^{2+}$ addition reactions (versus those of $C_{60}{}^{2+}$) is consistent with the greater extent of charge delocalization which is possible for $C_{70}{}^{2+}$: if adduct formation is considered to require a localization of charge, such localization will necessitate a greater expenditure of energy for $C_{70}{}^{2+}$ than for $C_{60}{}^{2+}$. The potential well corresponding to collision complex formation will therefore be less deep for $C_{70}{}^{2+}$ than for $C_{60}{}^{2+}$.

The observed occurrence of secondary adduct formation in the reactions initiated by $C_{70}{}^{2+}$ indicates, presumably, formation of a double adduct **II** (showing only the isomer with the greatest charge separation: several other isomers are, of course, also possible). We note that this structure has some similarities to the only neutral, doubly-derivatized C_{70} compound for which a crystallographic structural determination has yet been performed:[38] the compound $[C_{70}\{Ir(CO)Cl(PPhMe_2)_2\}_2]\cdot 3C_6H_6$ has been found to involve η^2-coordination of the 6–6 ring junctions radiating from the opposite endcaps of the fullerene cage. However, as we have noted previously, the factors involved in derivatization of C_{60} or C_{70} via solution chemistry are likely to be substantially different from those influencing the gas-phase ion–molecule chemistry of fullerene ions.[15] The slower rates observed for association reactions of $C_{70}{}^{2+}$ than for $C_{60}{}^{2+}$ may reflect the hypothesis that not all possible charge sites on the larger ion are as well suited to nucleophilic derivatization as the charge sites upon $C_{60}{}^{2+}$.



II

In the reactions of $C_{60}{}^{2+}$ with CH_3CH_2CN, CH_2CHCH_2CN, and C_3H_7CN (both isomers), a tertiary adduct was also detected. The reactivity observed with $CH_3CH_2CH_2CN$, *n*-butyronitrile, is shown in Figure 1; experimental data for the reaction with CH_3CH_2CN, propanenitrile, have been presented previously.[15] Rate coefficients (k_3) for these tertiary addition reactions, and upper limits for the tertiary addition reactions of the other nitriles

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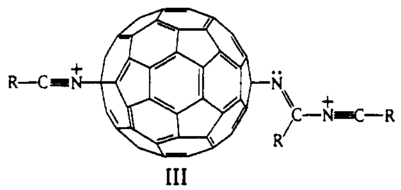
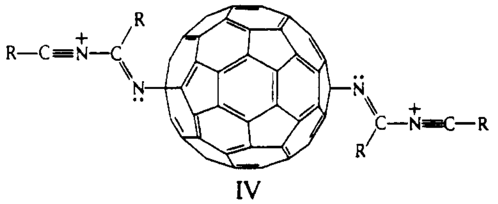
studied, were obtained by curve fitting: these are given in Table II. The very noticeable kinetic break between k_2 and k_3, apparent from the data summarized in Table II, is attributable to the difference in reaction mechanisms for the second and third nitrile additions.[15] While the first two additions are thought to involve nucleophilic attack of the fullerene cage as shown in reaction 1, the third addition will involve nucleophilic attack of one of the charge sites upon the nitrile moieties of **I**. The charges on the double adduct **I** (and **II**) are partially localized upon the nitrogen atoms, which are already participating in four chemical bonds and so cannot reasonably participate in any further bond formation without substantial additional electron rearrangement; therefore they are not readily susceptible to nucleophilic attack. Bond formation *can* occur through nucleophilic attack of the C atom of either cyano group to yield **III**, since the nitrile C atoms must also be considered as bearing some degree of positive charge[15] and have a vacant orbital for bonding. The low efficiency of the tertiary addition reaction (compared to that of the primary and secondary additions) provides support for our contention that the secondary adduct $C_{60}(RCN)_2{}^{2+}$ is formed predominantly in the "double-handled" configuration typified by structure **Ia** and contains little contribution (probably ≤5%) from the "single-handled" structure **Ib**, as would be formed by the (apparently inefficient) attack of the ^{+}NCR moiety of the primary adduct.

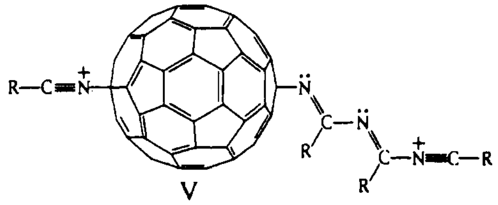


III

As shown in Figure 1, a fourth adduct $C_{60}(RCN)_4{}^{2+}$ was also detectable in the reaction with *n*-butyronitrile. This fourth adduct, for which structures **IV** and **V** appear probable, was formed with low efficiency: $k_4 < 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. In all other cases, no signal due to a quaternary adduct could be detected over the accessible range of reactant neutral concentration within the flow tube.



IV



V

The size dependence of the reaction rates for $C_{60}{}^{2+}$ + RCN (n = H, CH_3, C_2H_5, C_3H_7) is clear from Tables I and II. The tabulated results also show that unsaturated species (CH_2CHCN, CH_2CHCH_2CN) are less prone to addition than the corresponding saturated nitriles CH_3CH_2CN and n-C_3H_7CN. This latter observation was initially rather surprising: in a previous study[9] we found that the occurrence of addition of $C_{60}{}^{2+}$ with unsaturated hydrocarbons was essentially universal, whereas saturated hydrocarbons were not observed to add detectably to $C_{60}{}^{2+}$. The dependence of addition efficiency upon reactant size was also noted in this previous study[9] for the examples of unsaturated hydrocarbons and amines. Our earlier results[9] suggest that unsaturated nitriles might intuitively be expected to react more rapidly than their saturated equivalents, whereas the observed results indicate the opposite.

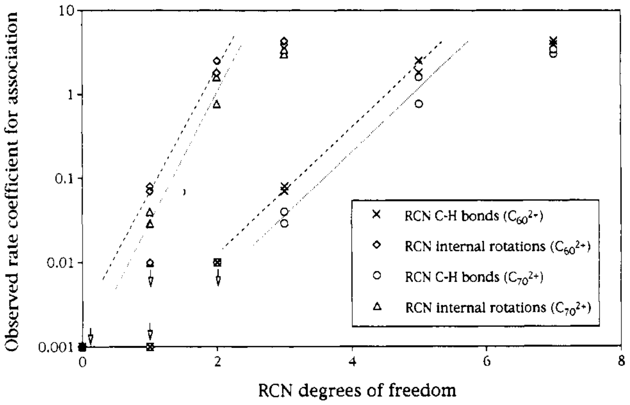


Figure 2. Variation in the observed effective bimolecular rate coefficient for association of $C_n{}^{2+}$ (n = 60, 70) + RCN, plotted versus the number of degrees of freedom (internal rotational modes or number of C–H bonds) of the reactant nitrile RCN. Rate coefficients are expressed in the same units (10^{-9} cm^3 molecule^{-1} s^{-1}) as used in Tables I–III. Interpolated lines ($C_{60}{}^{2+}$, dashed; $C_{70}{}^{2+}$, dotted) are intended merely as an aid in visualizing the data in the range between the experimental detection limit for reaction (10^{-12} cm^3 molecule^{-1} s^{-1}, 10^{-11} for $CH_2(CN)_2$; nonreactions are denoted on the graph by downward-pointing arrows) and the expected onset for saturation of the association reactions (in the vicinity of the collision rate coefficient, $>10^{-9}$ cm^3 molecule^{-1} s^{-1}). The data shown here suggest a correlation between the efficiency of association and the number of C–H bonds or internal rotational modes in RCN; note that, since $C_{60}{}^{2+}$ consistently undergoes association at a somewhat higher efficiency than $C_{70}{}^{2+}$ (which nevertheless has several more vibrational modes than $C_{60}{}^{2+}$), the number of fullerene vibrational modes does not appear to be of much importance in influencing the association efficiency.

We have previously remarked upon the dependence of the observed primary association reaction rate coefficients on neutral reactant size for the reactions of $C_{60}{}^{\cdot+}$ with ammonia and with amines[12] and for the reactions of $C_{60}{}^{2+}$ with nitriles.[15] This dependence is apparent also in Figure 2, which plots the observed rate of association versus the number of C–H bonds, or the number of internal rotations, in the reactant nitrile RCN. We have commented that the trends in reaction efficiency (which apply also to a comparison of the rates of saturated and unsaturated nitriles) can be satisfactorily accounted for by a consideration of the lifetime of the collision complex. The reaction

$$C_{60}{}^{2+} + X \rightarrow (C_{60}X^{2+})^* \tag{5}$$

involves the formation of a collision complex in which the energy of association and the excess thermal energy are distributed among the available rotational, vibrational, and electronic modes of energy dispersal. The complex can be destroyed by fragmentation to reactants and can be stabilized by radiative emission or by subsequent collision. Several theoretical studies have dealt with modeling the lifetime of such collision complexes as a function of the molecular complexity (number of atoms) of the collision complex and the temperature.[39–41] Studies such as that of Herbst and Dunbar[41] suggest that a complex containing 60 or more atoms should (unless the potential well describing complex formation is very shallow) have a lifetime sufficiently long to favor radiative or termolecular stabilization versus complex dissociation, with the efficiency of association increasing only weakly with increasing complex size above this point. However, models of complex lifetime are generally concerned with species having very many

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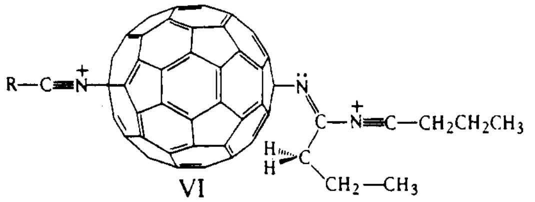
(39) Bates, D. R.; Herbst, E. In *Rate Coefficients in Astrochemistry*; Millar, T. J., Williams, D. A., Eds.; Kluwer: Dordrecht, The Netherlands, 1988; p 17.

(40) Dunbar, R. C. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 423.

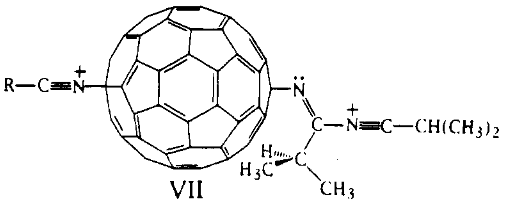
(41) Herbst, E.; Dunbar, R. C. *Mon. Not. R. Astron. Soc.* **1991**, *253*, 341.

degrees of freedom (the "standard hydrocarbon" of Herbst and Dunbar contains more hydrogens than heavy atoms, which is clearly not the case for adducts of C_{60}^{2+} with small neutrals). It is important to note that C_{60} has *no* internal rotational or bending vibrational modes and only 14 different (but highly degenerate) vibrational frequencies comprising 174 stretching vibrational modes. The number of available modes in such a small neutral as CH_3CN (including an internal rotation about the C_3 axis and C–H bending and stretching modes), and the greater energy density of rotational and bending vibrational levels than stretching vibrational levels, suggests strongly that the degrees of freedom of the nitrile, most especially the rotational degrees of freedom of RCN, are important in prolonging the $[C_{60}(RCN)^{2+}]^*$ complex lifetime. It can also be considered that, in a collision of C_{60}^{2+} with RCN, a much larger fraction of the energy liberated by collision complex formation is partitioned into the "recoil" of the less massive nitrile moiety than into the change in translational motion of the more massive fullerene. In this case, the vibrational and rotational degrees of freedom of the nitrile would initially become the repository of most of the energy of collision and would thus be expected to be substantially more important than those of the fullerene in the stabilization of the collision complex. The number of rotational degrees of freedom and the number of C–H bonds (which have bending vibrational modes) in RCN both increase with increasing nitrile size and decrease with unsaturation of the alkyl group. The observed efficiency of association ($k_1(HCN, C_2N_2) < k_1(CH_3CN, CH_2CHCN) < k_1(C_2H_5CN) < k_1(C_3H_7CN)$) suggests a dependence upon the number of rotational and/or C–H bending vibrational modes. Furthermore, this trend in association efficiency has been noted also in the reactions of C_{60}^{2+} with alcohols and ethers[13] and with ketones.[14]

In the present study, it is also apparent that the dependence of k_1 upon reactant complexity is paralleled by the trend in k_2 and k_3, the rates of formation of the secondary and tertiary adducts. It is of interest also to note that k_3 for the reaction involving *n*-butyronitrile is markedly higher than that for the isobutyronitrile reaction, whereas both k_1 and k_2 for each of these compounds are close to the collision rate under our experimental conditions. We attribute the difference in efficiencies of tertiary adduct formation for *n*-C_3H_7CN and for *i*-C_3H_7CN to the difference in the expected structures of these adducts: specifically, the steric interaction between the C_{60} cage and the adjacent alkyl side chain is expected to be less destabilizing for the adduct **VI** from *n*-C_3H_7CN than for the corresponding *i*-C_3H_7CN adduct **VII**.



VI



VII

Reactions of $C_{60}^{\cdot 3+}$. The results of reactions of $C_{60}^{\cdot 3+}$ with RCN are summarized in Table III. Addition was the dominant primary product channel for all of these reactions. We have previously determined that $C_{60}^{\cdot 3+}$ is able to undergo efficient charge transfer with neutrals having IE < 11.09 ± 0.09 eV.[19] With the exceptions of CH_2CHCN (IE = 10.91 eV) and CH_2CHCH_2CN (IE = 10.55 eV),[42] all of the nitriles in the present study have ionization energies higher than this threshold value: therefore, charge transfer is not possible with the majority of these reagents. This is in keeping with the reactivity observed.

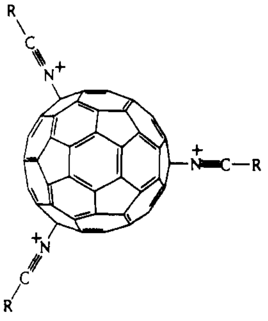
Table III. Observed Reaction Rate Coefficients for the Reaction $C_{60}^{\cdot 3+}$ + RCN

RCN	products[a]		k_{obs}[b]	k_c[c]
HCN	$C_{60}(NCH)^{\cdot 3+}$		2.5	6.35
CH_3CN	$C_{60}(NCCH_3)^{\cdot 3+}$		5.9	7.02
CH_2CHCN	$C_{60}(NCC_2H_3)^{\cdot 3+}$	[0.9]	4.0	6.77
	$C_{60}^{2+} + C_2H_3CN^{\cdot +}$	[0.1]		
CH_3CH_2CN	$C_{60}(NCC_2H_5)^{\cdot 3+}$		4.0	6.62
CH_2CHCH_2CN	$C_{60}(NCC_3H_5)^{\cdot 3+}$	[0.6]	6.6	5.81
	$C_{60}^{2+} + C_3H_5CN^{\cdot +}$	[0.4]		
$CH_3CH_2CH_2CN$	$C_{60}(NCC_3H_7)^{\cdot 3+}$		6.3	6.23
$(CH_3)_2CHCN$	$C_{60}(NCC_3H_7)^{\cdot 3+}$		4.8	5.90
NCCN	$C_{60}(NCCN)^{\cdot 3+}$		0.01	2.85
$NCCH_2CN$	$C_{60}(NCCH_2CN)^{\cdot 3+}$		5.6	5.46

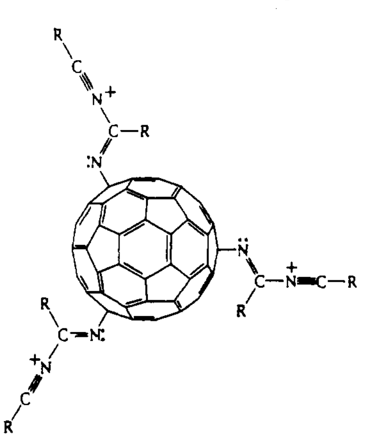
[a] For reactions in which more than one product channel was detected, the branching ratio is given in brackets. [b] Observed effective bimolecular reaction rate coefficient for $C_{60}^{\cdot 3+}$ + RCN at 294 ± 2 K and 0.35 ± 0.01 Torr, in units of 10^{-9} cm³ molecule⁻¹ s⁻¹. [c] ADO collision rate coefficient in units of 10^{-9} cm³ molecule⁻¹ s⁻¹, calculated according to the method of Su and Bowers.[37]

The secondary chemistry of the tricationic fullerene adducts is substantially more varied than that of the dicationic adducts described in the previous section. Further addition is the sole channel seen for the saturated nitriles CH_3CN, C_2H_5CN, and C_3H_7CN (both isomers). In all of these cases, at least four nitriles (at least six for C_2H_5CN and for *i*-C_3H_7CN) are added sequentially to the fullerene trication. Addition of at least four nitriles was also noted in the instances of C_2H_3CN, C_3H_5CN, and $CH_2(CN)_2$, although in these cases addition was not the dominant secondary product channel, as will be discussed below.

By analogy with the mechanism for association of the nitriles with C_{60}^{2+} and C_{70}^{2+}, we anticipate that the first three nitriles are able to add directly to charge sites upon the fullerene trication as in structure **VIII**, with subsequent addition occurring at the C atom of the initial CN groups to form structures as complex as the 6-fold adduct **IX** (most symmetrical isomer shown). However, the kinetic break between the third and fourth addition steps is not so distinct as the analogous break between the k_2 and k_3 steps in the reactions of C_{60}^{2+} + RCN. This is a consequence of the generally greater efficiency of association to the tricationic fullerenes than to the dications, most probably reflecting the greater potential well depth arising from the electrostatic interaction between the trication and the neutral: the lifetime of the collision complex, and the probability of radiative or termolecular stabilization, increases with increasing well depth. A charge-separating ligand transfer reaction



VIII



IX

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[42] Ohno, K.; Matsumoto, S.; Funai, K.; Harada, Y. *J. Phys. Chem.* **1984**, *88*, 206.

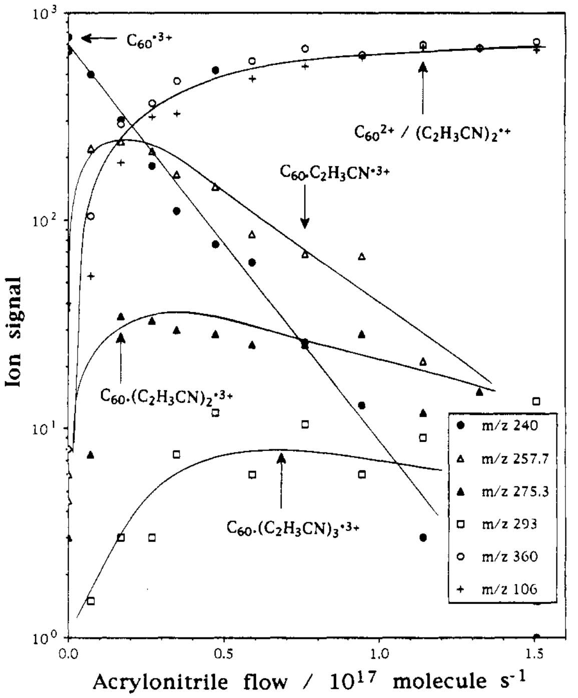


Figure 3. Experimental data for the reaction of $C_{60}^{\bullet 3+}$ with acrylonitrile, CH_2CHCN, at 294 ± 2 K and 0.350 ± 0.001 Torr of helium.

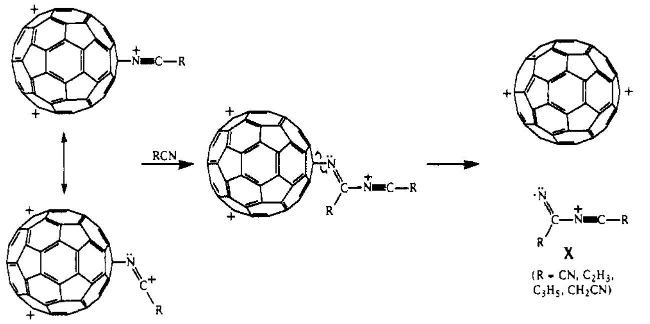


Figure 4. Proposed mechanism for the formation of nitrile dimer cation $(RCN)_2^{\bullet +}$ in the secondary reaction $C_{60}(RCN)^{\bullet 3+}$ + RCN. As with other reactions of nitriles with fullerene cations, the reaction is thought to involve nucleophilic attack by the nitrile RCN.

$$C_{60}(NCR)^{\bullet 3+} + RCN \rightarrow C_{60}^{2+} + (RCN)_2^{\bullet +} \quad (6)$$

is seen to compete with addition in the reactions of CH_2CHCN, CH_2CHCH_2CN, C_2N_2, and $CH_2(CN)_2$, as is illustrated by Figure 3. While the structure of the nitrile dimer cation thus produced is not known, we propose a reaction mechanism as shown in Figure 4, leading, ostensibly, to the series of dimers typified by structure X. The dominant secondary reaction observed in the case of HCN (for which typical experimental data are displayed in Figure 5) is proton transfer from the adduct:

$$C_{60}(NCH)^{\bullet 3+} + HCN \rightarrow C_{60}(NC)^{\bullet 2+} + HCNH^+ \quad (7a)$$

$$\rightarrow C_{60}(NCH)_2^{\bullet 3+} \quad (7b)$$

Channel 7a is observed to account for >90% of the secondary products. Deprotonation results formally in the production of a carbene dication, **XI**: it is possible that isomerization to nitrile dication **XII** occurs, since nitriles are generally more stable than the analogous isonitriles. The deprotonated ion $C_{60}CN^{\bullet 2+}$ was observed to be unreactive with HCN.

Implications for Interstellar Chemistry. Given the comparatively high abundances of the nitriles HCN, CH_3CN, CH_2CHCN, C_2H_5CN, and the cyanopolyynes $H(C{\equiv}C)_nCN$ (n = 1–5) within dense interstellar clouds and circumstellar shells,[21] the expectation that fullerene dications are also present within these environments,[27,28] and the efficiency of addition reactions of the more heavily hydrogenated nitriles with C_{60}^{2+}, it would appear that fullerene dications can act as a sink for such nitriles within interstellar clouds and circumstellar shells.

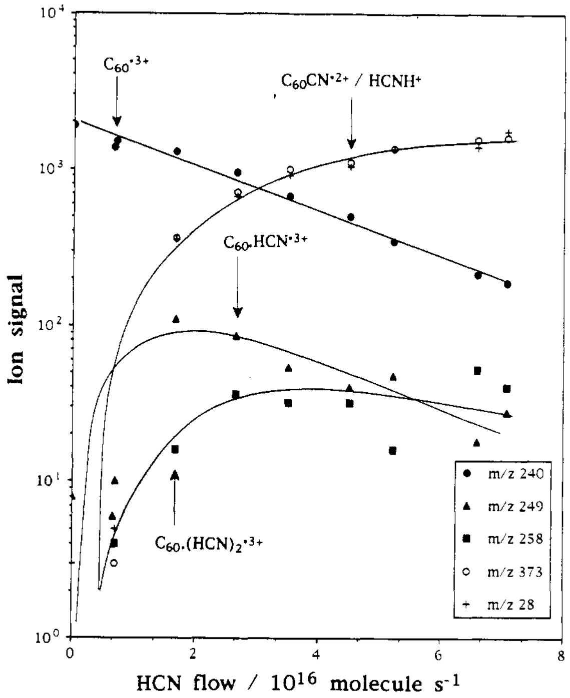
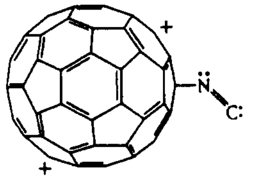
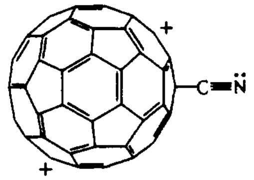


Figure 5. Experimental data for the reaction of $C_{60}^{\bullet 3+}$ with hydrogen cyanide, HCN, at 294 ± 2 K and 0.352 ± 0.001 Torr.



XI



XII

However, several factors mitigate against the possible rôle of fullerene cations in the chemical processing of nitriles. First, the reaction show a strong dependence of association efficiency upon size and upon saturation: the nitriles most likely to undergo efficient association with C_{60}^{2+} are large, saturated nitriles. Within interstellar environments, the most abundant nitriles are the highly unsaturated cyanopolyynes $HC_{2n}CN$ (n = 0–5) which are expected to have a low association efficiency in reactions with C_{60}^{2+} on the basis of the results of this study. It could conceivably be argued that the observed abundances are consistent with high loss rates for saturated nitriles by reaction with C_{60}^{2+}: however, several other factors are thought to influence the degree of saturation of the observed nitriles and other observed interstellar molecules, and we do not contend that the observed abundance ratios for interstellar nitriles are symptomatic of their reactivity with fullerene dications (whose abundance in interstellar environments is expected to be comparatively low).[27] It is also possible, nevertheless, that the association reactions in the present study, many of which are of low efficiency at 294 K, could occur with substantially higher efficiency under cold interstellar cloud conditions ($T \sim$ 10–50 K). Regardless of the possibility of its enhanced efficiency, however, association (which in the SIFT experiments is predominantly termolecular[9,12] but which under interstellar conditions is expected to occur solely as a radiative process)

$$C_{60}^{2+} + RCN \rightarrow C_{60}(NCR)^{2+} + h\nu \quad (8)$$

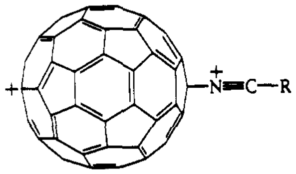
is quite likely to result in the regeneration of the nitrile RCN.

The absence of proton transfer from the adduct $C_{60}(NCR)^{2+}$ to the parent nitrile RCN, in our experiments, suggests that deprotonation of this adduct is an inefficient means of semineutralizing this adduct: the total abundance of interstellar molecules having PA > PA(RCN) is quite small. Other avenues for semineutralization of adduct **XIII** are charge transfer

$$C_{60}(NCR)^{2+} + X \rightarrow C_{60}(NCR)^{\bullet+} + X^{\bullet+} \qquad (9)$$

and dissociative recombination, for example

$$C_{60}(NCR)^{2+} + e \rightarrow C_{60}^{\bullet+} + RCN \qquad (10)$$



XIII

While the reactivity of the adduct $C_{60}(NCR)^{2+}$ with a variety of neutrals has not been assessed, we anticipate that its tendency to undergo charge transfer will not be substantially greater than the tendency of C_{60}^{2+} to undergo charge transfer. C_{60}^{2+} does not transfer a charge to the most abundant interstellar neutrals (H_2, He, CO, N_2, etc),[6] and so reaction 9 is also likely to be inefficient as a semineutralization step for the dicationic adduct under interstellar conditions. The most significant semineutralization step, therefore, is expected to be dissociative recombination, and we would anticipate that neutralization of *either* charge site of a fullerene dication, **XIII**, will most probably result in scission of the single C_{60}–N bond (rather than the three or four bonds required to lose C or C_2 from the fullerene cage, the N≡C bond, or any of the other bonds within the nitrile which lie substantially further from the charge sites). In a sense, since dissociative recombination of a functionalized fullerene dication may be a more efficient process than recombination of an unfunctionalized ion, C_{60}^{2+},[8,28] the reactions of fullerene dications with nitriles may serve as a more effective sink for C_{60}^{2+} than for interstellar nitriles.

Conclusion

The repeated addition of small nitriles to fullerene dications and trications has been observed. In the reactions with dications, a sharp kinetic break is observed after the addition of the second nitrile, which we interpret as indicating that the most reactive sites (the charge centers) of the fullerene dication have been occupied by the first two nitriles. The dependence of reaction efficiency upon the molecular complexity of the nitrile appears to indicate that the fullerene dication has few internal modes for energy dispersal within the collision complex. In the reactions of trications, repeated addition occurred in competition, in several instances, with charge-separating reactions (proton transfer as a secondary reaction with HCN; nitrile dimer cation formation in the secondary reactions of CH_2CHCN, CH_2CHCH_2CN, C_2N_2, and $CH_2(CN)_2$).

The expected presence of fullerene dications and nitriles within dense interstellar clouds and circumstellar shells has implications for the chemical evolution of these objects. However, since the reactivity of C_{60}^{2+} is less with unsaturated nitriles than with the corresponding saturated nitriles, the prospects for derivatization of fullerene ions by cyanopolyynes (which are the most abundant nitriles in these environments) are comparatively poor.

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