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Attaching Handles to C_{60}^{2+}: The Double-Derivatization of C_{60}^{2+}

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Abstract: Polar neutrals featuring an electronegative atom (O or N) are observed to form adducts with C_{60}^{2+} in the gas phase in selected-ion flow tube experiments at 294 ± 3 K and 0.35 ± 0.01 Torr. Addition is ascribed to the donation of an electron pair from the electronegative atom to the site of charge concentration on the fullerene ion's surface, forming a dative bond between the donor atom and a carbon atom of the fullerene shell and resulting in charge localization upon the donor atom. Secondary adducts are observed in many such reactions, but tertiary adducts are absent or are formed with considerably reduced efficiency, in accordance with the proposed method of addition. Observed association trends for $C_{60}^{\bullet+}$ are also in accordance with the model proposed, and some preliminary measurements on association of $C_{60}^{\bullet 3+}$ are reported.

Introduction

The exploration of fullerene chemistry has undergone explosive growth[1-3] since the development[4] of a synthetic route to C_{60}. A notable feature of studies of the chemical derivatization of C_{60} is that the observed derivatives very often feature multiples of 6 or 8 substituents,[5] as a consequence of the symmetry of the fullerene cage and the multiplicity of reactive sites on the carbon framework. Examples of this aspect of fullerene chemical reactivity, generally involving addition to double bonds located formally along the edges of six-membered rings, include hydrogenation by the Birch reduction to yield $C_{60}H_{18}$ and $C_{60}H_{36}$,[6] halogenation yielding $C_{60}F_{36}$,[7] $C_{60}Cl_{24}$,[8] $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$,[9] and arene addition ("fullerination") of benzene and toluene to yield $C_{60}(HAr)_{12}$ ($Ar = C_6H_5, C_6H_4CH_3$).[10] More limited addition, of single moieties, is also possible: the synthesis of $C_{60}O$ by photo-oxidation of C_{60} in benzene has been reported,[11] as have several studies involving carbenoid addition of aryl-containing substituents to produce "fulleroids",[12] expanded fullerenes (e.g. $C_{61}R_2$, from $C_{60} + R_2CNN$) having the same number of π electrons as the parent fullerene, and with similar electronic properties. Construction of bifulleroids, in which two fullerene cages are connected by reaction with a suitable bicarbenoid precursor, is also possible.[12] Multiple addition of the radicals $CH_3^\bullet$ and $C_6H_5^\bullet$ to C_{60} in solution has also been reported,[13] with mass-spectrometric evidence for the addition of up to 34 methyl radicals to the fullerene surface. In the gas phase substantial derivatization of $C_{60}^{\bullet+}$ by hydrogen atoms and alkyl radicals has been observed under chemical-ionization conditions in the ion source of a mass spectrometer.[14,15] Clearly, there are many different ways in which to derivatize or functionalize C_{60}: in the scant couple of years since fullerenes began to become generally available for chemical studies, an impressive collection of new C_{60} derivatives has already been synthesized, analyzed, and reported.

As a component of our studies of gas-phase ion/molecule reactivity of C_{60} and C_{70},[16-31] we have been concerned[17,20,23,24] with the formation of adducts of C_{60}^{n+} (n = 1, 2, 3) with various neutral species. Adduct formation is one of the most commonly-encountered product channels reported for C_{60}^{n+} + X (the others are charge transfer, hydride transfer, and less commonly the transfer of an atomic, molecular, or anionic fragment of the reactant neutral X). Aside from our own measurements made under the comparatively high-pressure conditions of 0.35–0.4 Torr of helium buffer gas, association has also been reported in the Fourier-transform ion cyclotron resonance (FT-ICR) measurements of McElvany et al.[32] for the reactions of $C_{56}^{\bullet 3+}$ and $C_{60}^{\bullet 3+}$

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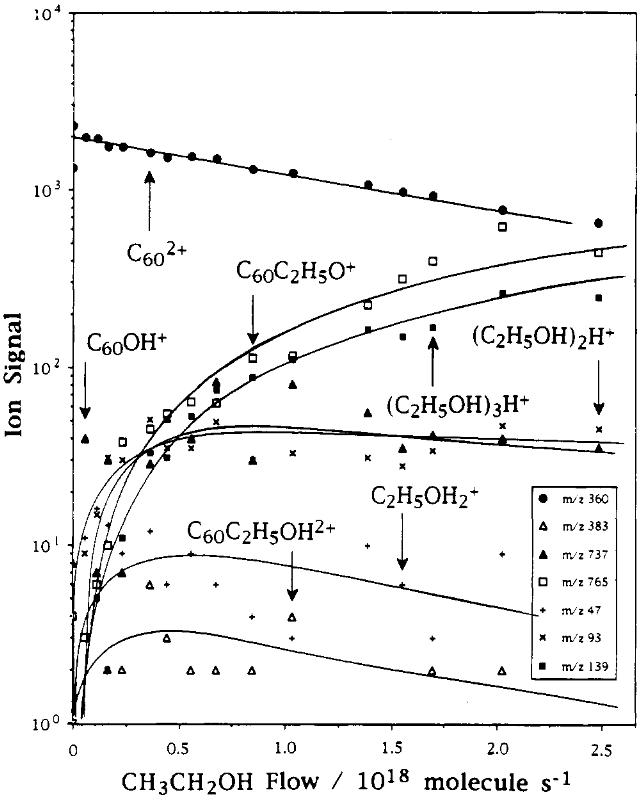

Figure 1. Experimental data for the reaction of C_{60}^{2+} with ethanol, CH_3CH_2OH. In this reaction, the major (90%) primary product is the adduct $C_{60}.C_2H_5OH^{2+}$, but the signal for this adduct is low at all C_2H_5OH flows since the primary rate coefficient ($k = 3.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) is very much lower than the secondary reaction rate coefficient ($k \sim k_c$, for removal of this adduct by proton transfer to ethanol): thus, in essence, a small pseudo-steady-state concentration of the adduct $C_{60}.C_2H_5OH^{2+}$ is established. The secondary adduct $C_{60}.(C_2H_5OH)_2^{2+}$ could not be detected: this is not surprising given the comparative efficiency of the primary adduct formation step and the subsequent proton transfer step. The other primary product channel is the hydroxide transfer reaction $C_{60}^{2+} + C_2H_5OH \rightarrow C_{60}OH^+ + C_2H_5^+$ (note that $C_2H_5^+$ is not detectable because of rapid proton transfer to C_2H_5OH: $PA(C_2H_4) = 162.6$ kcal mol^{-1}, $PA(CH_3CH_2OH) = 188.3$ kcal mol^{-1}).[40] Of the other product ions evident, $C_{60}C_2H_5O^+$ and $C_2H_5OH_2^+$ arise via proton transfer from the primary adduct to ethanol, while $(C_2H_5OH)_2H^+$ and $(C_2H_5OH)_3H^+$ are proton-bound species formed as a result of the association of $C_2H_5OH_2^+$ with ethanol: this is, apparently, a fairly efficient process under the comparatively high pressure conditions (0.35 ± 0.01 Torr of helium buffer gas) used in the SIFT apparatus.

with C_2H_2, and the formation of an adduct $C_{60}.NH_3^{2+}$ has been implicated in the triple-quadrupole experiments of Stry et al.,[33] although they did not directly detect this adduct. (We have already reported elsewhere[19] our own detection of the adduct $C_{60}.NH_3^{2+}$ from the reaction of $C_{60}^{2+} + NH_3$.) Multiple association of unsaturated hydrocarbons with C_{60}^{n+}, which we have reported for the reaction of C_{60}^{2+} with 1,3-butadiene,[23] has also been observed very recently under FT-ICR conditions.[34]

In the present work, we report new kinetic measurements of the reactions of C_{60}^{2+} (and some results for $C_{60}^{\bullet+}$ and $C_{60}^{\bullet 3+}$) with polar neutrals featuring an electronegative atom (O or N). We present evidence that association in such reactions results in the addition of a datively-bonded "handle" protruding from the surface of the fullerene. We have determined that it is possible to place two such "handles" on C_{60}^{2+}, but only one on $C_{60}^{\bullet+}$.

Experimental Section

The results reported here were obtained using a selected-ion flow tube (SIFT) which has been described previously.[35,36] All measurements were performed at 294 ± 3 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr unless otherwise indicated. Fullerene ions were produced in a low-pressure ion source by electron bombardment (50 V for $C_{60}^{\bullet+}$ and C_{60}^{2+}, 100 V for $C_{60}^{\bullet 3+}$) upon fullerene vapor (derived by heating a mixture of C_{60}/C_{70}, containing 2–12% C_{70}, obtained from Strem Chemicals Co.) entrained in argon. Reactant neutrals were admitted to the flow tube either as a pure gas (for neutrals having high vapor pressure, such as $(CH_3)_2O$) or as a dilute (1–10%) mixture in helium. H_2CO was prepared according to the method of Spence and Wild.[37] HCN was synthesized by the method of Melville and Gowenlock.[38] H_2O was distilled and deionized. All other neutrals were commercially obtained and were of high purity (generally >99%). Rate coefficients reported here are estimated to have an uncertainty of ±30%.

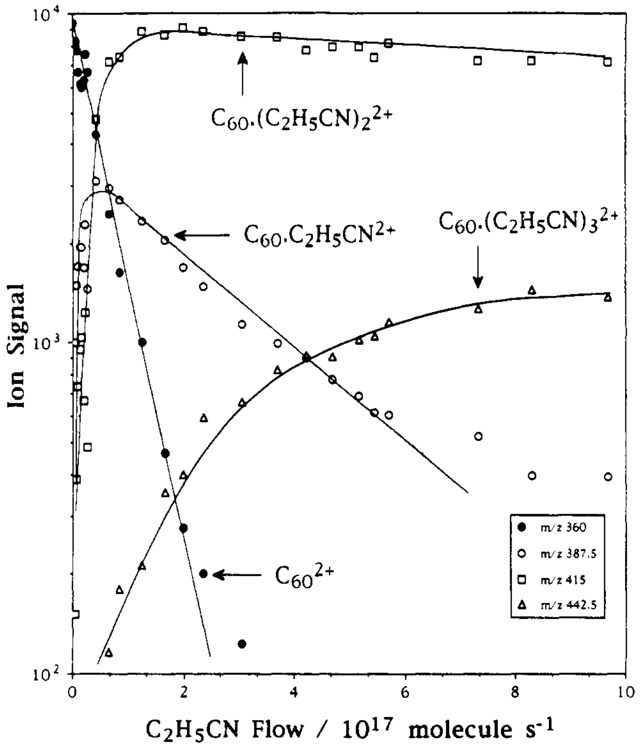

Figure 2. Experimental data for the reaction of C_{60}^{2+} with propanenitrile, C_2H_5CN. In stark contrast to the reaction chemistry of C_{60}^{2+} with ethanol, dicationic adducts are the sole product ions observed in this system. Proton transfer from any of the adducts $C_{60}.(C_2H_5CN)_n^{2+}$ (n = 1, 2, 3) is not detected. The primary ($k_1 = 2.5 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) and secondary ($k_2 = 2.2 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) association rate coefficients, for formation of $C_{60}.C_2H_5CN^{2+}$ and $C_{60}.(C_2H_5CN)_2^{2+}$, respectively, are much higher than the tertiary association rate coefficient ($k_3 = 3.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}). This observation is consistent with the model for nucleophilic addition described in the text.

Results and Discussion

Kinetic measurements related to primary adduct formation in the reactions of C_{60}^{2+} with a variety of polar neutrals are summarized in Table I. Adduct formation is generally the dominant channel of these reactions, and secondary adducts were observed with NH_3, CH_3NH_2, $C_2H_5NH_2$, RCN (R = CH_3, C_2H_3, C_2H_5, C_3H_5, n-C_3H_7 and i-C_3H_7), CH_3COCH_3, $CH_3COCH_2CH_3$, HCOOH, and CH_3COOH. In several cases (NH_3, CH_3NH_2, $C_2H_5NH_2$, CH_3COCH_3, $CH_3CH_2COCH_3$, HCOOH, CH_3COOH), secondary adduct formation was observed to compete with (fast) proton transfer. The absence of observable secondary addition in other systems (CH_3OH, CH_3CH_2OH, and $(CH_3)_2NH$) can be explained by the occurrence of efficient proton transfer from the primary adduct to the neutral in question.

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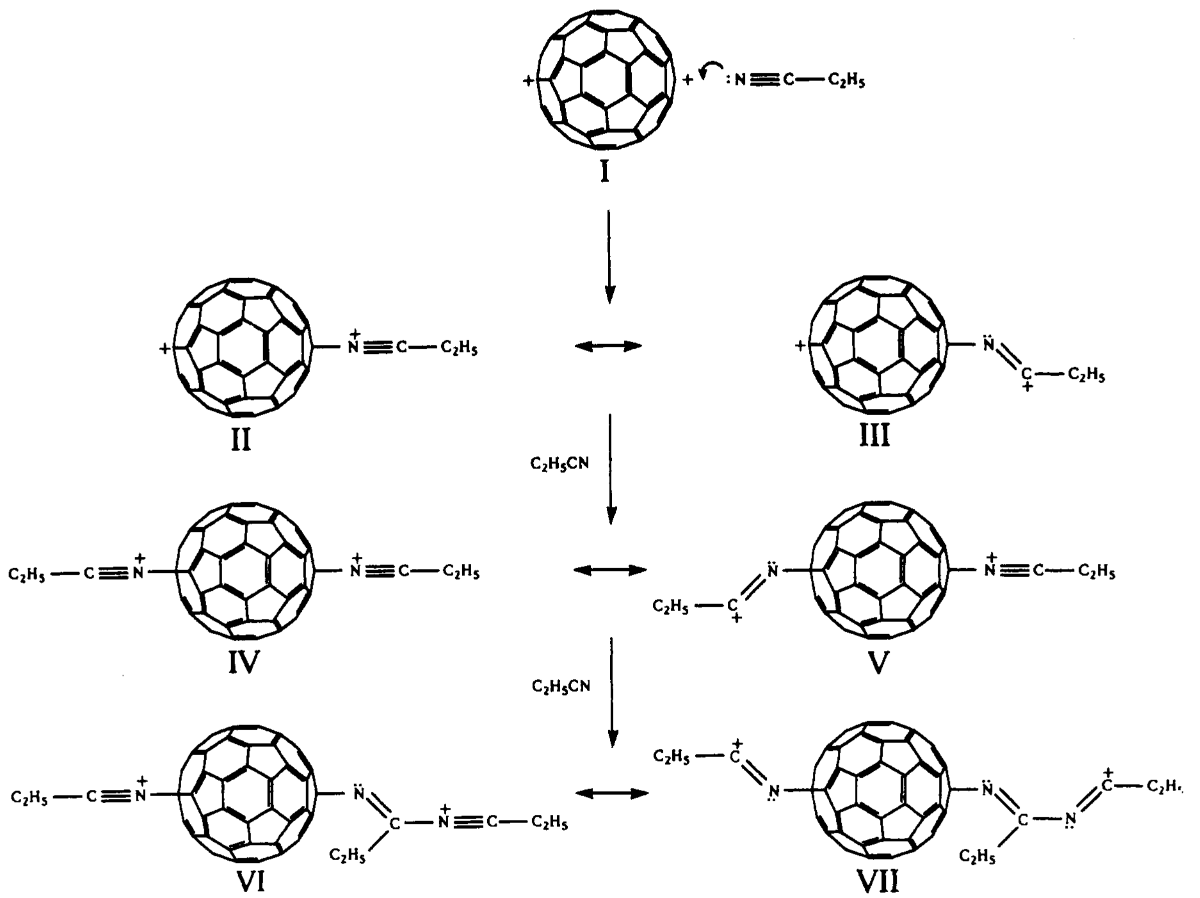


Figure 3. Proposed mechanism for the formation of primary, secondary, and tertiary adducts of ethyl cyanide (and, by analogy, other nitriles listed in Table I) with C_{60}^{2+}. In all instances, the mode of addition proposed is by electron-pair donation from the nitrogen atom of the reactant nitrile to a charge site upon the fullerene or adduct dication. Although structure I is drawn with two diametrically opposed point charges upon the fullerene surface, we expect that neither charge is completely localized: however, ion/dipole and ion/induced dipole interactions will tend to focus one charge at the nitrile's point of closest approach, while Coulombic repulsion between the two charges will constrain the other charge to remain more-or-less opposite this point. Other canonical forms of the secondary (IV and V) and tertiary (VI and VII) adducts are also possible: it is also highly likely that several additional isomers of the secondary and tertiary adducts are formed in the reaction sequence. The isomers shown for $C_{60}.(C_2H_5CN)_2^{2+}$ and $C_{60}.(C_2H_5CN)_3^{2+}$ are those which arise from diametrically opposed addition of the first two nitriles to C_{60}^{2+}: these are likely to be favored on the grounds of minimal Coulombic repulsion and steric interaction, but (by analogy with $C_{60}H_2$)[41] there are 23 different structural isomers possible for structure IV, differing only in the relative site of attachment of the second nitrile upon the fullerene surface, so it seems improbable that any one isomer accounts for a majority of the adducts possessing that stoichiometry.

Typical experimental data are shown in Figure 1 for the reaction of C_{60}^{2+} with CH_3CH_2OH.

Tertiary adduct formation was not detectable except in some reactions of the nitriles, for which it was invariably much less efficient than the primary or secondary addition process, and where proton transfer was not evident as a possible competing process. Figure 2 shows experimental data for the reaction of C_{60}^{2+} with CH_3CH_2CN. Curve fitting indicates that the tertiary addition reaction

$$C_{60}(C_2H_5CN)_2^{2+} + CH_3CH_2CN \rightarrow C_{60}(CH_3CH_2CN)_3^{2+} \quad (1)$$

(which, as with all the other addition reactions under study here, is presumed to be occurring primarily as a termolecular association process within the buffer gas) is approximately two orders of magnitude slower than either the primary or secondary addition reaction. In this instance, as with all of the other reactions of C_{60}^{2+} with nitriles, the rate coefficient for the secondary addition reaction is observed (within the experimental uncertainty) to be equal to that for the primary addition. In none of the reactions studied did the rate coefficient for the tertiary addition process exceed 5% of the rate coefficient for primary or secondary addition.

The observation that tertiary addition of nitriles is very substantially less efficient than primary or secondary addition suggests very strongly to us that the mode of attachment of the third nitrile to the fullerene dication differs in some manner distinct from the mode of attachment of the first two nitriles. This is supported by the general observation that tertiary adducts of other polar neutrals (amines, ketones, carboxylic acids) are not formed detectably, whereas secondary adducts of these species are, in general, formed. This latter observation is less convincing evidence, perhaps, than the break in the efficiency of association in the case of the nitriles, due to the presence of proton transfer as a competing process for polar neutrals other than nitriles.[24] However, it is clear that, at least for the association of C_{60}^{2+} with nitriles, formation of the tertiary adduct is much less efficient than the two preceding association steps. We account for this by a model of nucleophilic addition similar to that which we have proposed[19,20,28] for the reactions of C_{60}^{n+} ($n = 1, 2$) with ammonia and with amines. This model is depicted in Figure 3 for the sequential reactions of C_{60}^{2+} with CH_3CH_2CN.

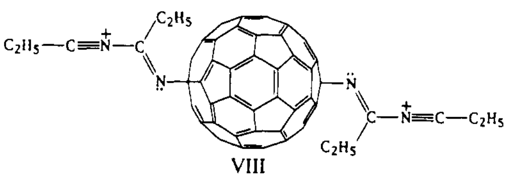
The model indicates that the first two addition steps can be accomodated by direct nucleophilic addition of the nitrile to the charge sites upon C_{60}^{2+}, resulting in the formation of a "double-handled" secondary adduct of type IV (for which several other canonical forms, such as V, are also possible: we stress also that while all the structures of these and other double-handled adducts throughout this paper possess the first two groups attached diametrically opposite upon the fullerene surface, there are many other isomers possible differing in the relative locations of these two groups upon the fullerene surface). The third addition step cannot involve nucleophilic addition to the fullerene surface since, in structures IV and V, the charges are expected to be effectively localized upon the CN group of the nitrile moiety: thus the third addition is anticipated to involve addition to one or the other of

Table I. Reactions of C_{60}^{2+} with Polar Neutrals

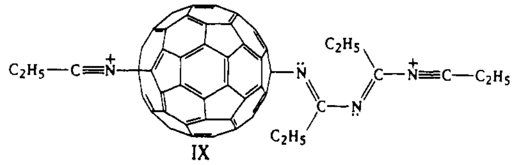
neutral	products[a]		k_{obs}[b]	k_c[c]	secondary reaction[d]
X[e]	none		<0.001		
NH_3	$C_{60}{\cdot}NH_3^{2+}$		1.2[f]	3.36	A, P
CH_3NH_2	$C_{60}{\cdot}N(CH_3)H_2^{2+}$	[0.9]	2.6[f]	2.88	A, P
	$C_{60}^{\cdot+} + CH_3NH_2^{\cdot+}$	[0.1]			A
$(CH_3)_2NH$	$C_{60}{\cdot}N(H)(CH_3)_2^{2+}$	[0.1]	2.9[f]	2.44	P
	$C_{60}^{\cdot+} + (CH_3)_2NH^{\cdot+}$	[0.9]			A
$(CH_3)_3N$	$C_{60}^{\cdot+} + (CH_3)_3N^{\cdot+}$		2.2[f]	2.10	A
$CH_3CH_2NH_2$	$C_{60}{\cdot}N(C_2H_5)H_2^{2+}$	[0.7]	2.6[f]	2.68	A, P
	$C_{60}^{\cdot+} + C_2H_5NH_2^{\cdot+}$	[0.3]			A
CH_3CN	$C_{60}{\cdot}NCCH_3^{2+}$		0.08	4.68	A
CH_2CHCN	$C_{60}{\cdot}NCCHCH_2^{2+}$		0.07	4.51	A
CH_3CH_2CN	$C_{60}{\cdot}NCCH_2CH_3^{2+}$		2.5	4.41	A
CH_2CHCH_2CN	$C_{60}{\cdot}NCCH_2CHCH_2^{2+}$		2.0	3.87	A
$CH_3CH_2CH_2CN$	$C_{60}{\cdot}NCCH_2CH_2CH_3^{2+}$		4.9	4.15	A
$(CH_3)_2CHCN$	$C_{60}{\cdot}NCCH(CH_3)_2^{2+}$		4.7	3.93	A
CH_3OH	$C_{60}{\cdot}O(H)CH_3^{2+}$		0.007	2.92	P
CH_3CH_2OH	$C_{60}{\cdot}O(H)C_2H_5^{2+}$	[0.9]	0.037	2.77	P
	$C_{60}OH^+ + C_2H_5^+$	[0.1]			N
CH_3COCH_3	$C_{60}{\cdot}OC(CH_3)_2^{2+}$		0.27	3.42	A, P
$CH_3COC_2H_5$	$C_{60}{\cdot}OC(CH_3)C_2H_5^{2+}$		1.2	3.06	A, P
HCOOH	$C_{60}{\cdot}OC(H)OH^{2+}$		0.015	2.27	A, P
CH_3COOH	$C_{60}{\cdot}OC(OH)CH_3^{2+}$		0.40	2.47	A, P

[a] Where more than one product channel was detected, branching ratios are given in square brackets. [b] Observed effective bimolecular rate coefficient, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}, at 294 ± 3 K and 0.35 ± 0.01 Torr unless otherwise indicated. [c] ADO collision rate coefficient, calculated according to the method of Su and Bowers,[39] in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [d] Observed secondary reaction attributable to reaction of the fullerene product ion shown with the neutral concerned. A = adduct formation, P = proton transfer, N = no reaction observed. [e] No reaction was observed for C_{60}^{2+} with H_2O, H_2CO, CH_3CHO, or HCN. [f] The value of the rate coefficient supersedes the value previously reported in ref 20. The results for amines reported in this earlier study were subject to a discrepancy thought to arise from the adsorption of amines upon the pressure transducers and capillaries used in the flow measurements.[28]

the cyano groups in structure IV/V, to produce a species of type VI ↔ VII (with several other canonical forms also possible). A subsequent addition to the remaining "handle" upon VI/VII is also possible, producing VIII and/or its structural isomer IX: however, we could not detect such a species in our experiments.

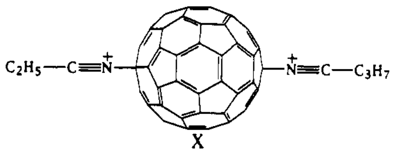


VIII



IX

The two "handles" may differ: we have added sequentially propanenitrile (CH_3CH_2CN) and butanenitrile ($CH_3CH_2CH_2C$-N) to the flow tube and have detected a product at *m/z* 422 corresponding to the species X. Since appreciable concentrations



X

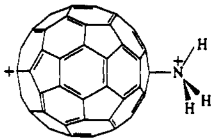
of both the nitriles were present in the flow tube, it was not possible to determine whether the persistence of *m/z* 422 (which was one of the most abundant products over the range of C_3H_7CN flows employed) resulted from the ligand-switching equilibria,

$$C_{60}(C_2H_5CN)_2^{2+} + C_3H_7CN \rightleftharpoons C_{60}{\cdot}C_2H_5CN{\cdot}C_3H_7CN^{2+} + C_2H_5CN \quad (2)$$

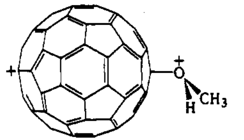
$$C_{60}(C_3H_7CN)_2^{2+} + C_2H_5CN \rightleftharpoons C_{60}{\cdot}C_2H_5CN{\cdot}C_3H_7CN^{2+} + C_3H_7CN \quad (3)$$

or whether the double-handled adduct X, once formed, is unreactive against such ligand-switching. We expect that a reasonably strong C–N bond is formed by nucleophilic addition of a nitrile to the dicationic fullerene surface, in which case ligand switching should not be facile.

"Handle" formation by sequential nucleophilic addition to C_{60}^{2+} can also account for the observed single and double adducts of the other classes of polar neutrals featured in Table I: lone-pair donation from O or N would result in the formation of adducts such as structures XI to XIV shown for ammonia, ethanol, and acetone. We have explored elsewhere[24] the factors underlying the tendency of these adducts to proton transfer to their parent neutral (whereas nitrile adducts do not proton transfer). Two canonical forms XIII and XIV of the adduct with acetone can be drawn: we note that Coulombic repulsion will favor the location of charge upon the more distant C atom as in XIV, although other effects may favor structure XIII. This consideration applies also to the other adducts featuring carbonyl or carboxyl groups.



XI



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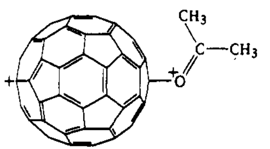
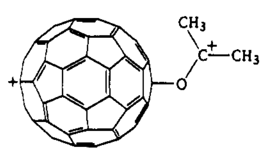


XIII

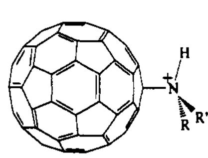


XIV

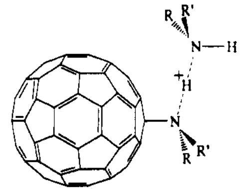
Another general observation, evident from the rate coefficients listed in Table I, is that species of greater molecular complexity are seen to add more efficiently. This is evident in a comparison of the rate coefficients for CH_3OH/CH_3CH_2OH, HCHO/$CH_3CHO/CH_3COCH_3/CH_3COC_2H_5$, and HCOOH/$CH_3COOH$, and for the series of nitriles studied; the series of amines does not display such a trend, but this can be understood in terms of competition between association and increasingly exothermic charge transfer in a series of reactions which occur with a high rate even for ammonia ($k = 1.2 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}).

We have recently argued[28] that the trend in increasing efficiency with size, for reactions of $C_{60}^{\bullet+}$ with ammonia and amines, can be rationalized in terms of the increasing number of rotational degrees of freedom in the collision complex $(C_{60}.M^{n+})^*$, and the consequent increase in the lifetime of this collision complex with increasing molecular complexity of the neutral species M. Due to the exceptionally rigid structure of the fullerene skeleton, C_{60}^{2+} is not expected to possess any internal rotational modes, and if it is assumed that the vibrational modes of the fullerene skeleton are not easily excited in the formation of the collision complex, then the remaining modes available for energy dispersal are the vibrational and internal rotational degrees of freedom possessed by the neutral species M, a rotational mode corresponding to rotation of C_{60} relative to M about the axis described by extension of the C_{60}–M bond, and the vibration of this C_{60}–M bond. There is a very good correlation between the number of internal modes of rotation possessed by M and the efficiency of the primary addition step for any class of compounds featured in Table I: there is also a strong correlation between the efficiency of addition and the number of C–H bonds, which is especially apparent for the series of nitriles studied.

If our model of nucleophilic addition of polar neutrals to fullerene cations is valid, then it should be possible to extend this model to explain the observed addition to fullerene charge states other than C_{60}^{2+}. We have observed addition behavior for C_{70}^{2+} with nitriles which is entirely analogous to that which is observed for C_{60}^{2+} (i.e., the first two addition steps are consistently much more efficient than the third addition). The monocation $C_{60}^{\bullet+}$ is of low reactivity—of more than fifty neutrals which we have surveyed to date,[18,20,31] the only molecular species which have been observed to add efficiently to $C_{60}^{\bullet+}$ are the amines $(CH_3)_2NH$, $CH_3CH_2NH_2$, and $(CH_3)_3N$. Nucleophilic addition to $C_{60}^{\bullet+}$ should be capable of producing only a "single-handled" adduct such as structure XV. In fact, efficient secondary addition is observed for $(CH_3)_2NH$ and $C_2H_5NH_2$ with $C_{60}^{\bullet+}$: we have interpreted[28] this as the formation of the proton-bound species XVI, since $(CH_3)_3N$ (which has no hydrogen atoms attached to nitrogen and so cannot form a proton-bound species of this type) forms only a primary adduct. Thus, the information available concerning addition to $C_{60}^{\bullet+}$ is consistent with the nucleophilic addition model presented here.



XV



XVI

We have recently begun an investigation of the chemistry of $C_{60}^{\bullet 3+}$.[26,31] Since charge transfer is observed to be efficient for

$$C_{60}^{\bullet 3+} + M \rightarrow C_{60}^{2+} + M^{\bullet+} \quad (4)$$

neutrals M having IE(M) < 11.1 eV,[26,32] sequential addition of $C_{60}^{\bullet 3+}$ is not likely to be evident with many of the neutrals featured in Table I. The nitriles featured in Table I do, however, generally have IE > 11.1 eV:[42] for this reason, nitriles form a useful probe of the addition behavior of $C_{60}^{\bullet 3+}$. Figure 4 shows the observed reactivity of $C_{60}^{\bullet 3+}$ with CH_3CH_2CN: in this case, addition of up to six propionitrile molecules is noted. Due to the comparatively small signals obtainable in this experiment, curve fitting to derive rate coefficients has not been attempted: however, the observation that the tertiary adduct is seen to dominate the product signals at the highest flows used strongly suggests that the quaternary addition step

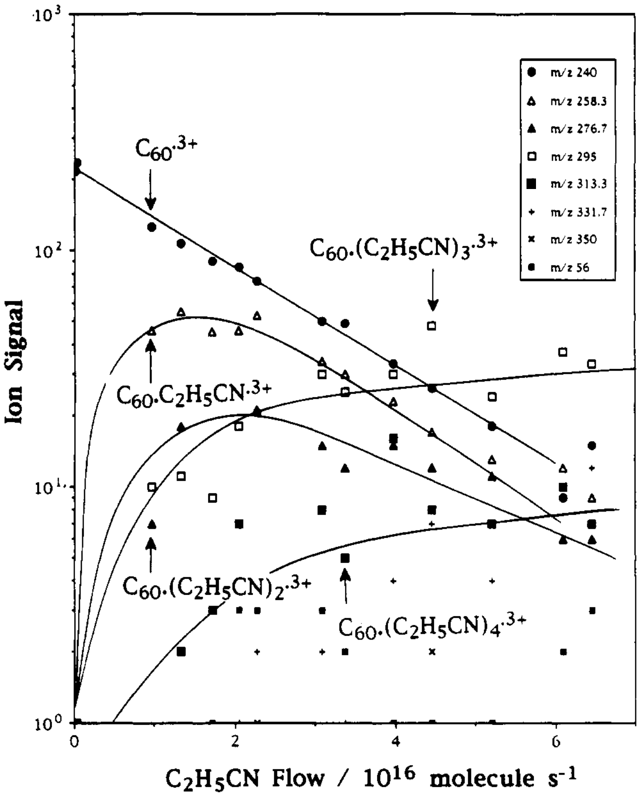
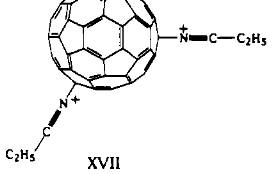


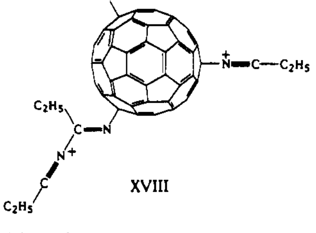
Figure 4. Experimental data for the reaction of $C_{60}^{\bullet 3+}$ with propanenitrile, CH_3CH_2CN. Under our experimental conditions, the observed reaction rate coefficient for the primary addition reaction was 4.0×10^{-9} cm^3 molecule^{-1} s^{-1}: secondary and tertiary addition reactions appear to be similarly efficient, while subsequent reactions are of lower efficiency. The small signal of protonated propanenitrile ($CH_3CH_2CNH^+$, *m/z* 56) evident at higher flows may arise from (inefficient) proton transfer from one or several of these tricationic adduct with CH_3CH_2CN; alternatively, this signal could be due to proton transfer from a minor contaminant ion such as H_3O^+.

$$C_{60}(C_2H_5CN)_3^{\bullet 3+} + C_2H_5CN \rightarrow C_{60}\bullet(C_2H_5CN)_4^{\bullet 3+} \quad (5)$$

is substantially less efficient than the first three addition reactions in this system: subsequent reactions, to form a fifth and possible sixth adduct, also appear to be comparatively inefficient. Structures XVII and XVIII show the tertiary and quaternary adducts expected: as with previous adduct structures, we have shown only those whose bond connectivity to the fullerene surface minimizes the Coulombic repulsion, and many other isomers are possible. Similarly, several different canonical forms of XVII and XVIII also exist.



XVII



XVIII

The proposed mechanism of adduct formation is thus in accord with the results observed to date for addition of polar neutrals to $C_{60}^{\bullet+}$, C_{60}^{2+}, and $C_{60}^{\bullet 3+}$. We note that the factors influencing nucleophilic addition may not apply when dealing with the addition of radicals[17] or of unsaturated, nonpolar species[20,23] to fullerene

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cations: we have observed the addition of up to six molecules of 1,3-butadiene to C_{60}^{2+}[23] (although in this reaction also, the proposed mechanism involves direct attachment of only two C_4H_6 molecules to the fullerene surface itself) and addition of several $H^\bullet$ atoms to both $C_{60}^{\bullet+}$ and C_{60}^{2+}.

The reaction mechanisms discussed here for reactions of fullerene cations with various neutrals are unlikely to correspond closely to those operating in the liquid or solid phase, since C_{60} is more likely to exist as an anion than as a cation under most circumstances in solution.

Conclusion

Kinetic data for the addition of a wide variety of polar neutrals to the fullerene dication C_{60}^{2+} in the gas phase are consistent with a model of nucleophilic addition involving the formation of "double-handled" secondary adducts by electron-pair donation to the charge sites upon the fullerene surface. The strongest support for this model is seen in the reactions of C_{60}^{2+} with various nitriles: in these reactions no other channels are observed to compete with association, and the rate coefficient for the tertiary addition step is invariably substantially lower than the rate coefficients for primary and secondary adduct formation.

Results for adduct formation involving $C_{60}^{\bullet+}$, and initial results for the reactivity of $C_{60}^{\bullet 3+}$, provide additional support for our model of nucleophilic addition. It appears possible, by gas-phase ion–molecule reactions, to add one "handle" to $C_{60}^{\bullet+}$, two to C_{60}^{2+}, and three to $C_{60}^{\bullet 3+}$. Neutralization of these cationic adduct species, perhaps by repeated proton transfer to an appropriate base, is capable of generating an array of novel derivatized neutral fullerenes. We have already suggested elsewhere[24] the notion that the polycationic fullerene adducts may form a useful model for polyprotonated proteins and other large molecules which have recently become accessible through the technique of electrospray ionization.[43]

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The Intrinsic Basicity of 4(5)-2′-Aminoethylimidazole (Histamine)[†]

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Abstract: The gas-phase basicity (GB) of histamine (**1**) relative to ammonia (defined as the standard Gibbs energy change for reaction 1) has been measured by means of Fourier transform ion cyclotron resonance spectroscopy (FT-ICR): $\mathbf{1}H^+(g) + NH_3(g) \rightleftharpoons \mathbf{1}(g) + NH_4^+(g)$. The various tautomer/conformers of $\mathbf{1}H^+(g)$ were studied by means of ab initio SCF–LCAO–MO calculations at the 6-31G//6-31G level. The calculated proton affinity agrees well with that estimated from FT–ICR results. Ring protonation is slightly preferred over side-chain protonation. Chelation provides a major contribution to the stability of $\mathbf{1}H^+(g)$. Comparison of these results with aqueous solution data reveals dramatic differences due to solvation.

1. Introduction

The title compound (**1**)[1], Figure 1, is a key molecule occurring in animal as well as in plant tissues. Free histamine produces in the organism diverse biological effects by interacting with three different biological receptors, namely, H_1, H_2, and H_3. When histamine interacts with H_2 receptors, gastric secretion is stimulated, resulting in serious clinical consequences.

The acid–base properties of the *N*-amino and *N*-imidazolyl groups and the conformational properties of the monocation are involved in all models of H_2 receptors.[2–4] Furthermore, the protonation of the imidazole group is essential for the storage of histamine in the granules of the mast cell.[5] On purely chemical grounds, it is an interesting bifunctional base. In the solid state, histamine monocation is found as the N_3–H tautomer,[6a] and histamine free base as the N_1–H one.[6b] In the monocation form, histamine forms dimers in a configuration with an intermolecular hydrogen bond between one of the hydrogen atoms of the ammonium terminal group and the N_1 atom of the imidazole ring of the nearest protonated molecule. At variance with this, in the neutral form, histamine molecules appear linked in chains through hydrogen bonds between the nitrogen atom of the amine terminal groups and the hydrogen atom bonded to the N_3 atoms. Intermolecular hydrogen bonds thus determine the crystalline structure of this compound under both the neutral and the protonated forms.

[†] Dedicated to Professor Robert W. Taft on his 70th birthday.

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[§] Estación Experimental de Zaidín.

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(1) As pointed out by Vogelsanger, Godfrey, and Brown,[7] the standard nomenclature for histamine is 1*H*-imidazole-4(5)-ethanamine, but the name (2-aminoethyl)imidazole and β-(4-imidazolyl)ethylamine (following Ganellin[2]) are widely used in theoretical and biological studies.

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