Pergamon

Tetrahedron, Vol. 52, No. 14, pp. 5191-5206, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00124-X

Reactions of $C_{60}^{\bullet +}$, C_{60}^{2+} and $C_{60}^{\bullet 3+}$ with C_2H_2 and C_2H_4 in the Gas Phase: Polymerization Initiated by $C_{60}^{\bullet 3+}$.

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Abstract: Reactions of the C_{60} cations $C_{60}^{\bullet +}$, C_{60}^{2+} and $C_{60}^{\bullet 3+}$ have been investigated with C_2H_2 and C_2H_4 in the gas phase using the Selected-Ion Flow Tube (SIFT) technique at 295±2 K and 0.35±0.02 Torr of helium. Although $C_{60}^{\bullet +}$ was found to be unreactive ($k < 1x10^{-12}$ cm^3 molecule^{-1} s^{-1}), and C_{60}^{2+} reacted only slowly ($k \leq 2x10^{-12}$ cm^3 molecule^{-1} s^{-1}) by adduct formation, $C_{60}^{\bullet 3+}$ reacted rapidly with C_2H_2 by adduct formation ($k = 6.6x10^{-11}$ cm^3 molecule^{-1} s^{-1}) and with C_2H_4 by adduct formation (30%) and electron transfer (70%) ($k = 1.7x10^{-9}$ cm^3 molecule^{-1} s^{-1}). $C_{58}^{\bullet 3+}$, which was present as an impurity ion, was observed to react 10 times faster than $C_{60}^{\bullet 3+}$ with C_2H_2, $k = 6.0x10^{-10}$ cm^3 molecule^{-1} s^{-1} and this was attributed to a greater sp^3 character of the reacting C site. Higher-order addition reactions were observed with $C_{60}^{\bullet 3+}$ and $C_{58}^{\bullet 3+}$ and these were interpreted as the first example of cation-induced "ball-and-chain" polymerization by triply-charged fullerene cations. Mechanisms have been proposed for this polymerization without and with an intramolecular hydride shift in the derivatized fullerene cation. Also, $C_{60}C_2H_4^{\bullet 3+}$ was observed to undergo proton transfer with C_2H_4 and this is the first example of such a reaction with a triply-charged C_{60} derivative.

Introduction

One of the many remarkable features of the buckminsterfullerene molecule, C_{60}, is its stability as a multiply-charged cation against Coulombic explosion. To date it has been possible to remove up to 7 electrons from C_{60} by electron impact in the gas phase.[1] Previous gas-phase studies of ion/molecule reactions of C_{60}^{n+} (n=1,2,3) in our laboratory, using the Selected-Ion Flow Tube (SIFT) technique at 294±3 K and 0.35 Torr helium, have indicated that the reactivity of these cations is highly dependent on their charge state. For example, fullerene monocations, $C_{60}^{\bullet +}$, were observed to be unreactive towards most neutral molecules we surveyed. The important exceptions include H-atoms,[2] ammonia and several aliphatic amines,[3] the conjugated cyclodienes 1,3-cyclopentadiene and 1,3-cyclohexadiene,[4] anthracene[5] and corannulene.[6] The low electron recombination energy of $C_{60}^{\bullet +}$, $IE(C_{60}) = 7.64 \pm 0.02$ eV,[7] limits its electron-transfer reactivity to only a few neutral molecules. In sharp contrast, the fullerene dications, C_{60}^{2+}, and trications, $C_{60}^{\bullet 3+}$, exhibited a much greater reaction efficiency under our experimental conditions. Apparently the stronger electrostatic interaction between multiply-charged C_{60} and an incoming molecule is sufficient to overcome the barrier associated with chemical-bond formation with C_{60}.[8] Also, as the electron-recombination energy increases with increasing charge state, electron transfer becomes more exothermic. However, the rate of electron transfer is controlled by the energy barrier which arises from the Coulombic repulsion between product ions.[9]

The presence of multiple charges on C_{60} has another important consequence. It gives rise to intramolecular Coulombic repulsion which can lead to intramolecular charge separation in molecular adducts of multiply-charged C_{60} cations. Several years ago we proposed that such intramolecular charge separation promotes (polymeric) chain-growth away from the C_{60} surface in the sequential formation of multiple adducts of multiply-charged C_{60} cations. Such a "ball-and-chain" mechanism became evident in a comparative study of reactions of the monocations and dications of the fullerenes C_{60} and C_{70} with 1,3 butadiene[10] and ethylene oxide.[11] While fullerene monocations were found to be unreactive, the fullerene dications C_{60}^{2+} and C_{70}^{2+} reacted efficiently to add at least 6 and 3 molecules of butadiene, respectively. Also, 6 molecules of ethylene oxide were observed to add to C_{60}^{2+} and an observed discontinuity in the rate of addition at $n=5$ was interpreted in terms of the occurrence of cylization.[11] These results suggest that multiply-charged C_{60} cations generally may be suitable as initiators of polymerization in the gas phase.

Here we explore the occurrence of reactions of acetylene and ethylene with $C_{60}^{\cdot +}$, C_{60}^{2+}, and $C_{60}^{\bullet 3+}$ with a particular view to the possible role of these ions as initiators of polymerization.

Experimental

The reactions of C_{60}^{n+} (n = 1,2,3) with acetylene and ethylene were investigated using a Selected-Ion Flow Tube (SIFT) apparatus.[12,13] The fullerene cations were produced in a conventional low-pressure ion source by electron impact of C_{60} vapour at an electron energy of 50 eV for $C_{60}^{\bullet +}$, 80 eV for C_{60}^{2+}, and 100 eV for $C_{60}^{\bullet 3+}$, higher energies being required for the higher charge states. The fullerene powder was a mixture of C_{60} and C_{70} containing 2-12% C_{70} (Strem Chemical Co.). The C_{60} cations produced in the source were selected with a quadrupole mass filter and injected into the flow tube where they were thermalized by collisions (ca. 4×10^4) with helium buffer gas at 295 ± 2K and 0.35 ± 0.02 Torr. The neutral reagents, acetylene and ethylene, were introduced into the flow tube downstream. These gases were obtained commercially and were of high purity (Matheson, >99.5%). The acetylene was passed through a cold trap at dry ice temperature followed by an activated charcoal trap to remove acetone. The progress of the reaction was monitored with a second quadrupole mass filter and detector as a function of the flow of the neutral reagent. The data was analyzed in the usual manner. The rate coefficients for the observed primary reactions reported here are estimated to have an uncertainly of ±30%. Higher-order rate coefficients were obtained by fitting the experimental data to the solution of the system of differential equations for a chain of successive reactions. The accuracy for these procedures of fitting depends on many parameters and is reported separately for every calculated high-order rate coefficient in the text.

Results and Discussion

Table 1 provides a summary of the experimental results obtained for rate coefficents and product distributions associated with the primary reactions which were observed. Similar details for the higher-order reactions are indicated in the text.

Reactions of $C_{60}^{\bullet+}$: $C_{60}^{\bullet+}$ was found to be unreactive towards both acetylene and ethylene, $k < 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The failure of electron transfer can be explained thermodynamically on the basis of the relative ionization energies of C_{60} (7.64±0.02 eV) and acetylene and ethylene (11.42 and 10.51 eV, respectively)[14] which make electron transfer endothermic. We do not know whether C-C bonding of C_2H_2 and C_2H_4 with $C_{60}^{\bullet+}$ is exothermic, but if it is, the association reaction appears to involve an energy barrier. An energy barrier between the electrostatically-bound collision complex and the covalently-bound adduct may arise from the transition required from largely sp^2 hybridization to sp^3 hybridization at the C atom on C_{60} which becomes bonded.[8]

Table 1: Measured products and rate coefficients for the reactions of C_{60}^{n+} (n=1,2,3) and $C_{58}^{\bullet 3+}$ with C_2H_2 and C_2H_4 at 295±2 K and 0.35±0.02 Torr of helium.

Reactants	Products	B.R.[a]	k_{obs}[b]	k_c[c]
$C_{60}^{\bullet +}$				
C_2H_2	none		<0.001	0.85
C_2H_4	none		<0.001	0.93
C_{60}^{2+}				
C_2H_2	$C_{60}C_2H_2^{2+}$	1	<0.001	1.71
C_2H_4	$C_{60}C_2H_4^{2+}$	1	0.0016	1.86
$C_{60}^{\bullet 3+}$				
C_2H_2	$C_{60}C_2H_2^{\bullet 3+}$	1	0.066	2.56
C_2H_4	$C_{60}C_2H_4^{\bullet 3+}$	0.3	1.7	2.79
	$C_{60}^{2+} + C_2H_2^{\bullet +}$	0.7		
$C_{58}^{\bullet 3+}$				
C_2H_2	$C_{58}C_2H_2^{\bullet 3+}$	1	0.60	2.56

[a] Branching ratio. [b] Apparent bimolecular rate coefficient in units of 10^{-9} cm^3 molecule^{-1} s^{-1} with an uncertainty of ±30%. [c] Collision rate coefficient in units of 10^{-9} cm^3 molecule^{-1} s^{-1} calculated with the Langevin model described by Gioumousis, G.; Stevenson, D.P. *J. Chem. Phys.* **1958**, *29*, 294. This model assumes a point charge for the colliding ion which is a poor approximation for the ions investigated. As a consequence, the k_c values tabulated must be regarded only as approximate. The polarizabilities of C_2H_2 and C_4H_4 were taken from Hirschfelder, J.O.; Curtiss, C.F.; Bird, R.B. *Molecular Theory of Gases and Liquids*, John Wiley and Sons, New York, **1954**.

Reactions of C_{60}^{2+}: C_{60}^{2+} was observed to react slowly with acetylene and ethylene to form exclusively adduct ions according to reaction (1) with rate coefficients of $< 1\text{x}10^{-12}$ and 1.6

$$C_{60}^{2+} + X \rightarrow C_{60}X^{2+} \quad (X = C_2H_2 \text{ and } C_2H_4) \qquad (1)$$

$\text{x}10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. Electron transfer was not observed. Electron transfer is slightly endothermic by 0.06 eV (with acetylene) and exothermic by 0.85 eV (with ethylene) in this case, given an ionization energy of 11.36±0.05 eV for $C_{60}^{+\cdot}$.[9] However, the energy barrier, 1.80±0.16 eV, which arises from Coulombic repulsion between the product ions impedes the electron transfer reaction.[15] The low rate coefficients for the association reactions are consistent with the presence of an energy barrier associated with rehybridization of the bonding C atom on C_{60} and a more facile traversal of this barrier as a consequence of the higher charge on C_{60}^{2+} which results in an stronger electrostatic interaction.[8] Adduct formation presumably occurs via the collision stabilization of the chemically-bonded intermediate complex by helium atoms.

Reactions of $C_{60}^{\bullet 3+}$: $C_{60}^{\bullet 3+}$ was found to be very reactive with ethylene and moderately reactive with acetylene. As shown in Figure 1, addition was the only primary channel observed with acetylene. This is indicated by reaction (2). The measured rate coefficient for the primary

$$C_{60}^{\bullet 3+} + C_2H_2 \rightarrow C_{60}C_2H_2^{\bullet 3+} \qquad (2)$$

reaction was $6.6\text{x}10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Electron transfer between C_2H_2 and $C_{60}^{\bullet 3+}$ is exothermic by 4.2 eV since $IE(C_{60}^{2+}) = 15.6 \pm 0.5$ eV but the barrier arising from Coulombic repulsion between the product ions is slightly larger.[9]

Figure 1 also provides evidence for the sequential addition of 6 molecules of acetylene (at least 8 were actually observed). However, the interpretation of the results displayed in

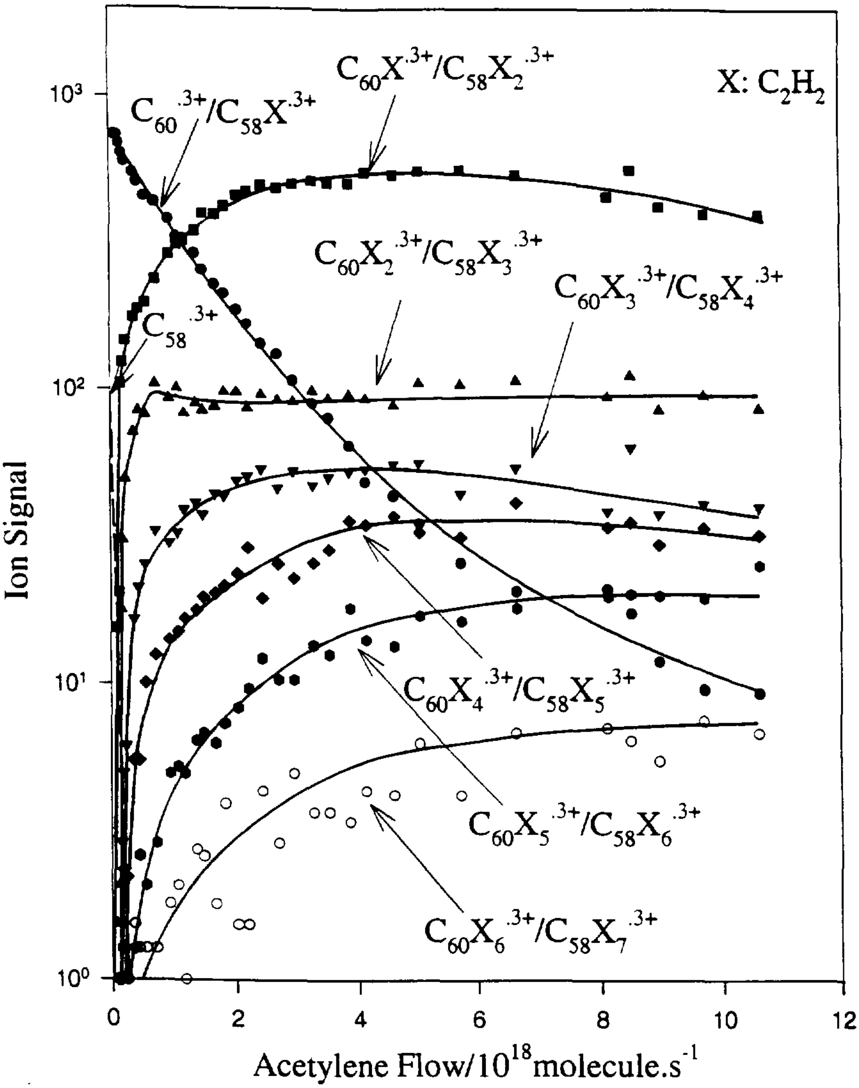


Fig. 1. Variation in the ion signals recorded for the addition of acetylene into the reaction region of the SIFT apparatus in which $C_{60}^{\bullet 3+}$ has been established as the dominant ion in helium buffer gas at 0.34±0.01 Torr and 295±2 K. $C_{58}^{\bullet 3+}$ is initially present as an impurity ion. The fullerene cations are produced from C_{60} vapour by electron impact at 100 eV.

Figure 1 is complicated by the presence initially of (ca. 10%) $C_{58}^{\bullet 3+}$ (which could not be resolved from $C_{60}^{\bullet 3+}$ with the upstream quadrupole) and the failure to resolve $C_{60}(C_2H_2)_n^{\bullet 3+}$ and $C_{58}(C_2H_2)_{n+1}^{\bullet 3+}$ cations with the downstream quadrupole. The data indicate that $C_{58}^{\bullet 3+}$ itself adds C_2H_2 about 10 times faster, k=6.0 x 10^{-10} cm^3 molelcule^{-1} s^{-1}, than $C_{60}^{\bullet 3+}$ and then adds more C_2H_2 in higher order reactions. For example, while the $C_{60}(C_2H_2)^{\bullet 3+}/C_{58}(C_2H_2)_2^{\bullet 3+}$ signal is dominated by $C_{60}(C_2H_2)^{\bullet 3+}$, the fast rise and early hump of the $C_{60}(C_2H_2)_2^{\bullet 3+}/C_{58}(C_2H_2)_3^{\bullet 3+}$ signal must be attributed to the fast reaction of $C_{58}(C_2H_2)_2^{\bullet 3+}$ with C_2H_2. Thus, the observations recorded in Figure 1 can be accounted for by reactions of type (3). The slow decay in the $C_{60}(C_2H_2)_2^{\bullet 3+}$ signal suggests that the combined $C_{60}(C_2H_2)_n^{\bullet 3+}/C_{58}(C_2H_2)_{n+1}^{\bullet 3+}$ signals for $n>2$

$$C_{58,60}(C_2H_2)_n^{\bullet 3+} + C_2H_2 \rightarrow C_{58,60}(C_2H_2)_{n+1}^{\bullet 3+} \quad (n = 0\text{-}8) \qquad (3)$$

are mainly $C_{58}(C_2H_2)_{n+1}^{\bullet 3+}$. Because of these complexities, it was not possible to derive rate coefficients for the sequential addition reactions by curve fitting.

The observed experimental data for the reaction of $C_{60}^{\bullet 3+}$ with C_2H_4 are given in Figure 2. Two product channels are evident for the primary reaction as indicated by equation (4).

$$C_{60}^{\bullet 3+} + C_2H_4 \rightarrow C_{60}C_2H_4^{\bullet 3+} \qquad (4a)$$

$$\rightarrow C_{60}^{2+} + C_2H_4^{\bullet +} \qquad (4b)$$

The branching ratio for these two channels, adduct formation and electron transfer, was determined to be 3:7. The overall reaction (4) is faster and more efficient than the reaction with acetylene. The total rate coefficient measured for reaction (4), $k = 1.7\text{x}10^{-9}$ cm^3 molecules^{-1} s^{-1}, corresponds to reaction in nearly every two collisions when it is compared with the collision rate coefficient for this reaction calculated using ADO theory (see Table 1). The occurrence of electron transfer in this case is not surprising. The relatively low ionization energy of C_2H_4, 10.51 eV,[14] and the relatively high ionization energy of C_{60}^{2+}, 15.6±0.5 eV,[8] makes electron

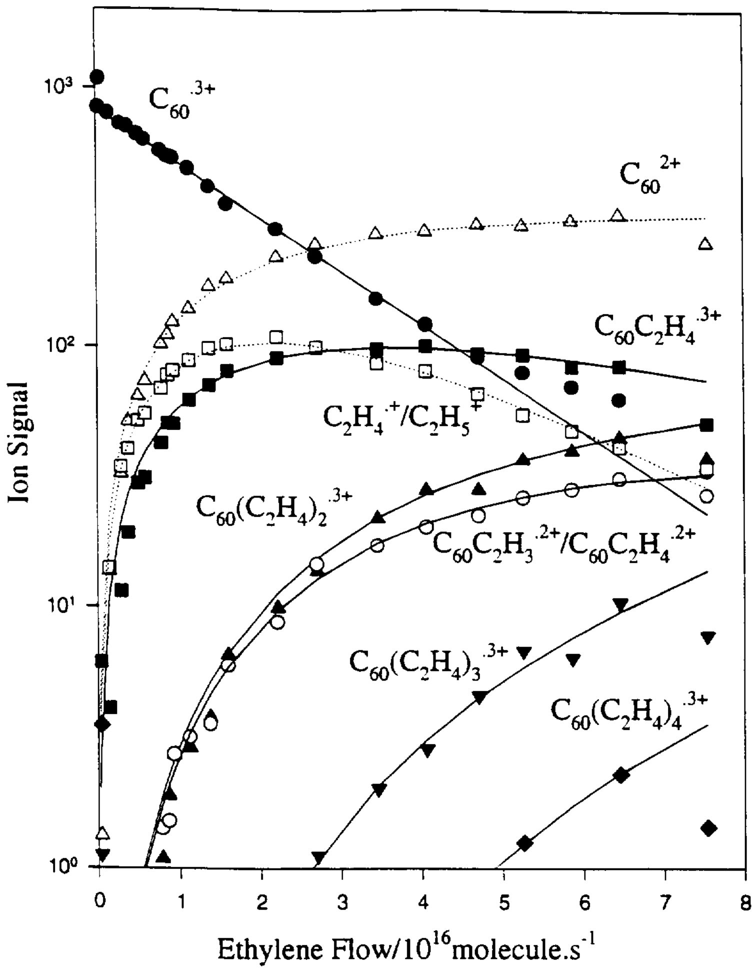


Fig. 2. Variation in the ion signals recorded for the addition of ethylene into the reaction region of the SIFT apparatus in which $C_{60}^{\cdot 3+}$ has been established as the dominant ion in helium buffer gas at 0.33±0.01 Torr and 295±2 K. $C_{60}^{\cdot 3+}$ was produced from C_{60} vapour by electron impact at 100 eV. The dotted lines represent the primary electron transfer products. Products observed for the further well-known reaction of $C_2H_4^{\cdot +}$ with C_2H_4 are not included for clarity. The profiles for the five largest ion signals represent a computer fit with the solutions of differential equations appropriate for the observed reactions.

transfer exothermic by 5.1 eV and this exceeds the 4.5 eV estimated for the barrier due to Coulombic repulsion.[15]

It is evident from Figure 2 that the primary adduct ion, $C_{60}C_2H_4^{\bullet 3+}$, reacts further predominantly by the sequential addition of at least 3 more molecules of ethylene as represented by reaction (5).

$$C_{60}(C_2H_4)_n^{\bullet 3+} + C_2H_4 \rightarrow C_{60}(C_2H_4)_{n+1}^{\bullet 3+} \quad (n = 0\text{-}3) \qquad (5)$$

A fit to the profiles for the first and second adduct ions provided rate coefficients for their reactions with C_2H_4 of $(5.5\pm40\%)\times10^{-10}$ and $(1.5\pm60\%)\times10^{-10}$ cm^3 molecule^{-1} s^{-1}. Clearly, the rate of sequential addition decreases with n.

The first adduct ion produced in reaction sequence (5) also reacts to produce bimolecular products in about 50% of the reactive collisions. This is illustrated by reaction (6).

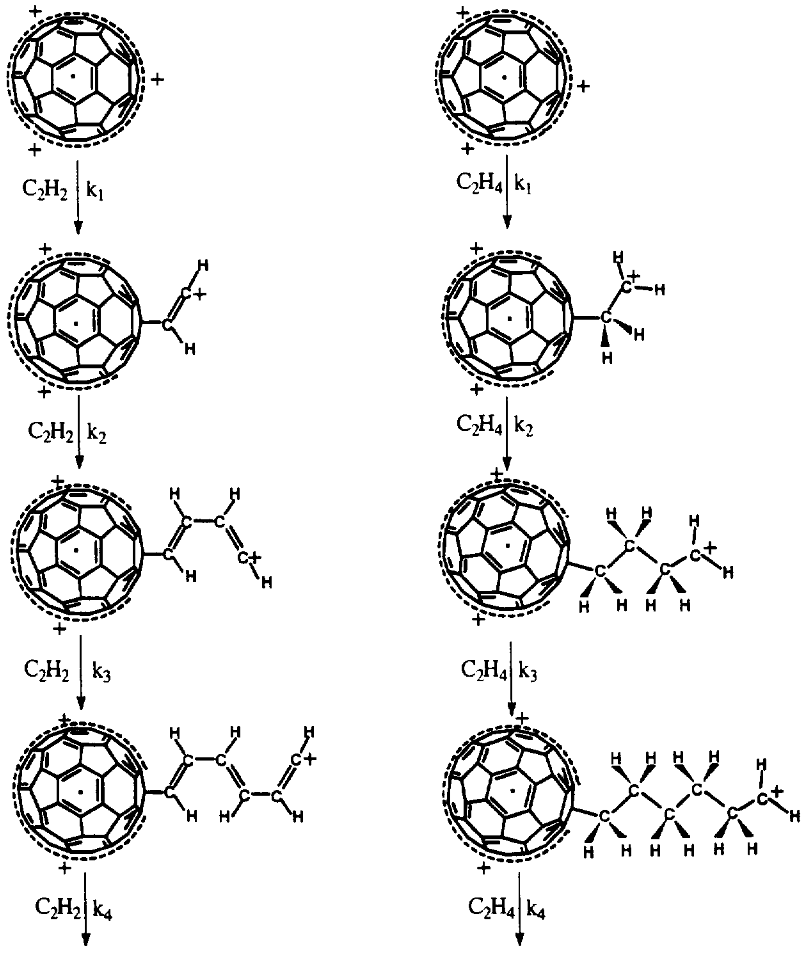
$$C_{60}(C_2H_4)^{\bullet 3+} + C_2H_4 \rightarrow C_{60}(C_2H_4)_2^{\bullet 3+} \qquad (6a)$$

$$\rightarrow C_{60}C_2H_3^{\bullet 2+} + C_2H_5^{+} \qquad (6b)$$

$$\rightarrow C_{60}(C_2H_4)^{2+} + C_2H_4^{\bullet +} \qquad (6c)$$

Channels (6b), proton transfer, and (6c), electron transfer, were not easy to separate mass spectrometrically. The mass spectrometer could not resolve $C_{60}C_2H_3^{\bullet 2+}$ and $C_{60}C_2H_4^{2+}$. Both $C_2H_5^+$ and $C_2H_4^{\bullet +}$ were observed and resolved in a high-resolution spectrum at low mass, but $C_2H_4^{\bullet +}$ is produced in large amounts by the primary reaction. So it appears that $C_{60}C_2H_4^{\bullet 3+}$ reacts by proton transfer in a manner which we have previously observed for a large variety of derivatized fullerene dications,[16] but this is the first example of such a reaction involving a derivatized fullerene trication. Nevertheless, the occurrence of electron transfer could not be completely excluded. Both $C_2H_4^{\bullet +}$ and $C_2H_5^+$ react further with C_2H_4 leading to known products under SIFT conditions,[17] but these are not shown in Fig. 2.

Mechanism of Addition: The sequential addition of C_2H_2 and C_2H_4 observed with $C_{58}^{\bullet 3+}$ and $C_{60}^{\bullet 3+}$ can be envisaged to proceed either on the surface of the fullerene cation or in a manner directed away from the surface. We propose here that these addition reactions proceed via a "ball-and-chain" mechanism in a manner which we have previously proposed for the reactions of C_{60}^{2+} with 1,3-butadiene[10] and ethylene oxide[11], and which is illustrated in Scheme 1.

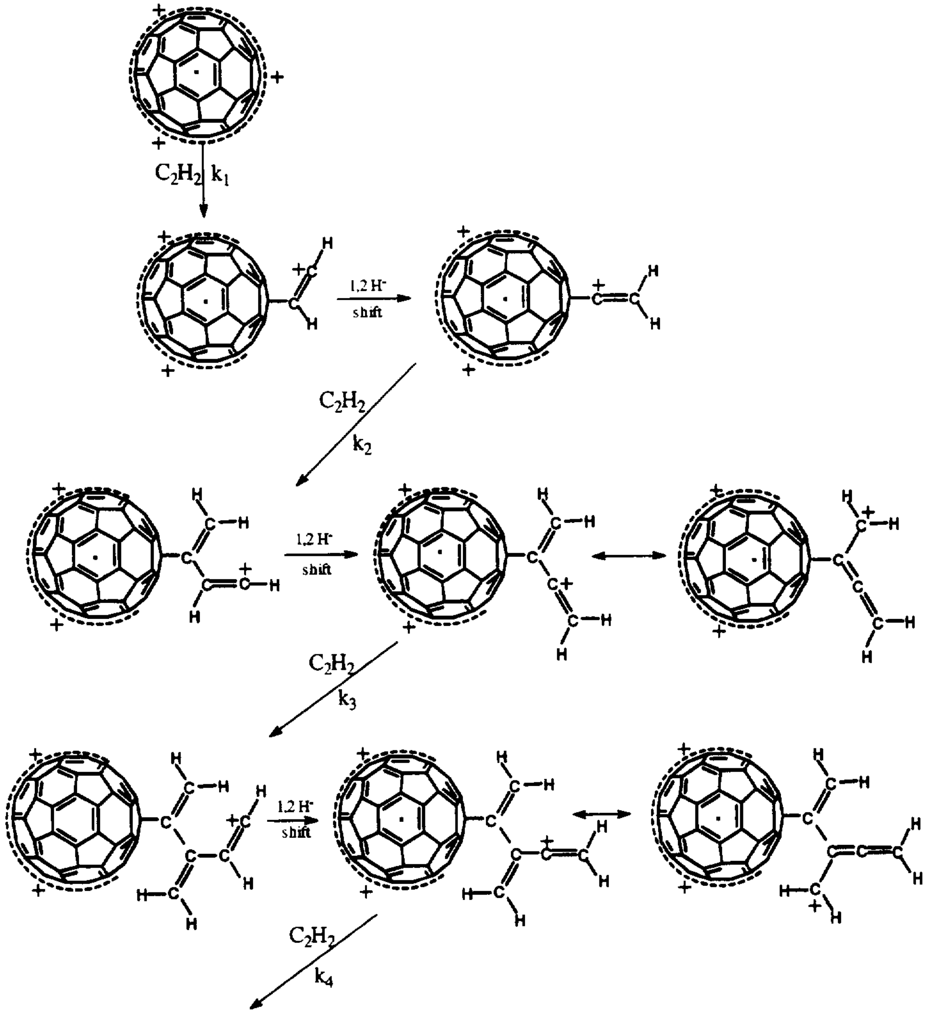


Scheme 1

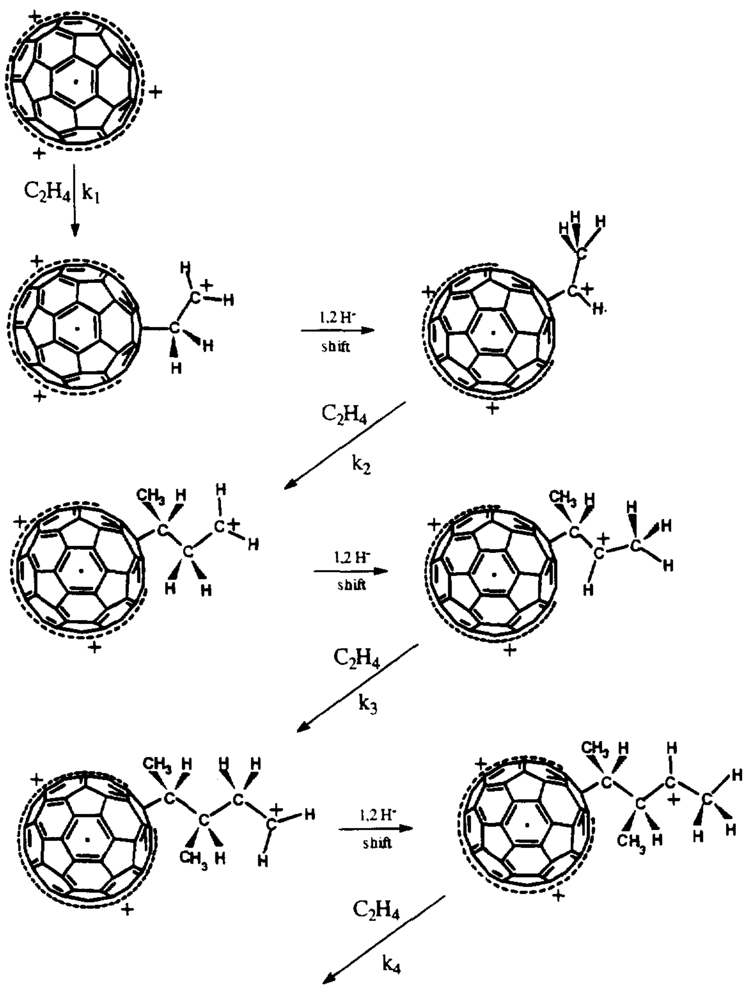
In this mechanism the initial C-C bond is formed by nucleophilic addition to the fullerene surface and a positive charge is shifted to the terminal C of the C_2H_2 or C_2H_4 substituent. Coulombic repulsion between the charge which is propagated along the growing chain substituent and the charges on the fullerene then drives the addition away from the surface of the fullerene.[10,11] In each step the charge is propagated to the terminal C atom.

The higher rate for the first addition of C_2H_2 to $C_{58}^{\bullet 3+}$ is of special interest. We have previously observed a 20-fold difference in the rates of addition of C_2H_4 to C_{60}^{2+} and C_{58}^{2+} and have attributed this difference to the presence of adjacent pentagons in C_{60}^{n+} cations.[18] A greater sp^3 character is associated with the carbon atoms at the shared edge of adjacent pentagons than at the shared edge of an adjacent pentagon and hexagon. Thus it should be easier for C_{58}^{n+} cations to achieve the tetrahedral coordination required in the bonding of a fullerene carbon atom with a carbon atom on the reactant molecule such as C_2H_2 or C_2H_4. After the initial bond formation between C_2H_2 and $C_{58}^{\bullet 3+}$, further addition of C_2H_2 may proceed in a manner analogous to the higher-order addition to $C_{60}^{\bullet 3+}$. However, we cannot exclude the possibility of isomerization of the first adduct, $C_{58}(C_2H_2)^{\bullet 3+}$, to the triply-ionized dihydride of C_{60}, $C_{60}H_2^{\bullet 3+}$, after the initial bond formation.

One other mechanistic aspect deserves attention. Since secondary carbonium ions are more stable than primary carbonium ions, it is necessary to consider the possibility of the occurrence of a 1,2-hydride shift in the various adduct ions observed. Such a shift would be counterbalanced by an increase in Coulombic repulsion, but the magnitude of the latter would decrease with chain length. Although the magnitude of the Coulombic repulsion can be estimated, the difference in carbonium-ion stability is not known and the energetics of the hydride shift cannot be assessed. The occurrence of a hydride shift can have consequences for the nature of the chain growth away from the fullerene surface in that it can lead to branched chains. This is illustrated in Schemes 2 and 3 for acetylene and ethylene, respectively.



Scheme 2



Scheme 3

Conclusions

It is evident that from the results of the experiments reported here that the rate and nature of the reactions of fullerene ions, C_{60}^{n+} (n=1,2,3), with acetylene and ethylene are highly dependant on the charge state of C_{60}. The rate of addition increases with charge state and this is consistent with a double-potential well model in which the increasing electrostatic interaction between the reactants with the charge state of the fullerene cation leads to a decrease in the effective energy barrier associated with the rehybridization required for bond formation. The emergence of electron transfer as a competing product channel with increasing charge state in the reactions of C_{60}^{n+} with C_2H_4 can be understood in terms of known ionization energies and a model which includes an energy barrier in the reaction profile arising from Coulombic repulsion between product ions.

The observation of the rapid addition of C_2H_2 to $C_{58}^{\bullet 3+}$ raises the possibility of formation of the ionized fullerene dihydride $C_{60}H_2^{\bullet 3+}$.

Higher-order sequential addition, previously reported only for fullerene dications, has been observed with a triply-charged fullerene cation for the first time. The observed addition of C_2H_2 to $C_{60}^{\bullet 3+}$ and $C_{58}^{\bullet 3+}$ and of C_2H_4 to $C_{60}^{\bullet 3+}$ is consistent with a "ball-and-chain" polymerization mechanism in which Coulombic repulsion drives chain growth away from the surface of the fullerene. A branched chain may result in the presence of hydride shifts. Proton transfer has been observed to compete with chain growth in the ethylene chemistry and this represents the first example of proton transfer from a derivatized fullerene trication.

Acknowledgment. D.K.B. is grateful to the Natural Sciences and Engineering Research Council of Canada for the financial support of this research.

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(*Received* 24 *July* 1995)