Gas-Phase Ion−Molecule Reactions of Neutral C_{60} With the Plasmas of Alkyl Methyl Ethers and Primary Alcohols

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Received: January 13, 1999; In Final Form: June 15, 1999

The gas-phase ion−molecule reactions of C_{60} with the methoxymethyl ion $[CH_3O{=}CH_2]^+$ and the 1-hydroxyethyl ion $[CH_3CH{=}OH]^+$ generated under the self-chemical-ionization (self-CI) conditions of alkyl methyl ethers and primary alcohols were studied in the ion source of a mass spectrometer. The adduct ions $[C_{60}C_2H_5O]^+$ and protonated molecules $[C_{60}H]^+$ were observed as the major products of C_{60} with the plasma of alkyl methyl ethers. On the contrary, the reactions of C_{60} with the plasmas of primary alcohols produced few corresponding adduct ions. The AM1 semiempirical molecular orbital calculations were carried out on 14 possible structures. The calculated results showed that the most stable structure among the possible isomers of $[C_{60}C_2H_5O]^+$ is the [3+2] cycloadduct. According to experimental and theoretical results, the pathway for the formation of the adduct was presented.

Introduction

The studies on the fascinating structures and properties of fullerenes continue to be an active area of research in both the condensed- and gas-phase since the first observations of C_{60} and C_{70} were made using mass spectrometry by Smalley and Kroto in 1985.[1] The success in macroscopic fullerene synthesis and isolation pushes the research on fullerenes forward.[2] Of particular interests for us are the addition reactions to C_{60}, which as a strained, electron-deficient polyalkene with rather localized double bonds can undergo many kinds of additions including mono- and multiadditions. The additions of molecules to C_{60} in the condensed-phase have been extensively studied, e.g., the additions of azides to C_{60},[3]: the multiply regiochemical additions to the fullerene core,[4] the addition of silylene to C_{60},[5] the photocycloaddition of cyclic 1,3-diones to C_{60},[6] etc. In parallel with the condensed-phase fullerene chemistry, considerable progress has been made toward gas-phase ion−molecule reactions of fullerenes. For example, the charge-transfer reactions of $C_{60}{}^{2+}$ with several neutral compounds and the reactions of $C_{60}{}^{+}$ with metals have been studied using an FT-ICR (Fourier transform-ion cyclotron resonance) apparatus:[7,8] the gas-phase reactions of fullerene ions $C_{60}{}^{+}$, $C_{60}{}^{2+}$, $C_{60}{}^{3+}$ with water, alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, nitriles, etc., have been systematically investigated using SIFT (the selected-ion flow tube) technique, in which $C_{60}{}^{+}$ was unreactive with most of neutral species studied, but $C_{60}{}^{2+}$ and $C_{60}{}^{3+}$ had very rich chemical reactions with wide range of reactivity.[9−13] In contrast to the results of these studies, we have previously reported the reactions of neutral C_{60} with the plasmas of small organic compounds using a triple-quadrupole mass spectrometer and found that C_{60} could react with variety of kinds of fragment and/or molecular ions of small organic compounds generated under the chemical ionization conditions.[14−18] All of the above-mentioned studies in the gas-phase provide insight into investigations on the reactivity of fullerenes and their further applications in the condensed phase.

Here we report the results of the gas-phase ion−molecule reactions of C_{60} with the plasmas of alkyl methyl ethers and primary alcohols derived under the self-CI conditions, and the results of AM1[19] calculations.

Experimental and Theoretical Methods

All reactions were performed on a VG-Quattro triple-quadrupole mass spectrometer (Fisons instruments, Manchester, UK). Methyl ethyl ether, methyl *n*-propyl ether, methyl *n*-butyl ether, ethanol, and propanol were injected into the ion source through the reference gas inlet, and C_{60} was introduced into the ion source via a desorption chemical ionization (DCI) probe. The solution of C_{60} was deposited on the DCI filament, which was ramped up to 1200 mA manually while operating. The electron energy was 100 eV, the ion source was maintained at 473 K, and a unit-mass resolving power at *m*/*z* 1000 was used for the recording mass spectra. Fullerenes were synthesized by use of an arc-discharge device set up in our laboratory and separated using column chromatography. Alkyl methyl ethers were synthesized according to literature methods.[20] Primary alcohols are commercially available with analytical grade purity and were used without further purification.

Full geometry optimizations without symmetry restrict for the adduct ions at the restricted Hartree−Fock level were carried out using the AM1 semiempirical method as implemented in the MOPAC 7.0.[19]

Results and Discussions

Gas-Phase Reactions. Figure 1a−c show the self-CI mass spectra of methyl ethyl ether, methyl *n*-propyl ether, and *n*-butyl ether at a source pressure of 1.2×10^{-2} Pa, respectively. It can be seen that the $[CH_3O{=}CH_2]^+$ ion (*m*/*z* 45), $[M{+}H]^+$ ions (*m*/*z* 61, 75, or 89), and $[M{-}H]^+$ ions (*m*/*z* 59, 73, or 87) are predominant ionic products under the self-CI conditions. With the increase of carbon chain length, the relative abundance of $[CH_3O{=}CH_2]^+$ (*m*/*z* 45) is enhanced. As is well-known,

10.1021/jp990191w CCC: $18.00

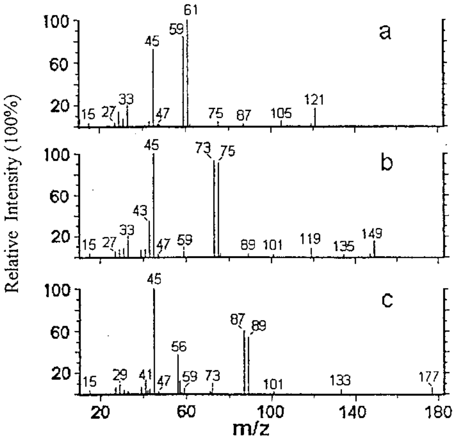


Figure 1. Mass spectra for the self-CI (a) methyl ethyl ether, (b) methyl *n*-propyl ether, (c) methyl *n*-butyl ether.

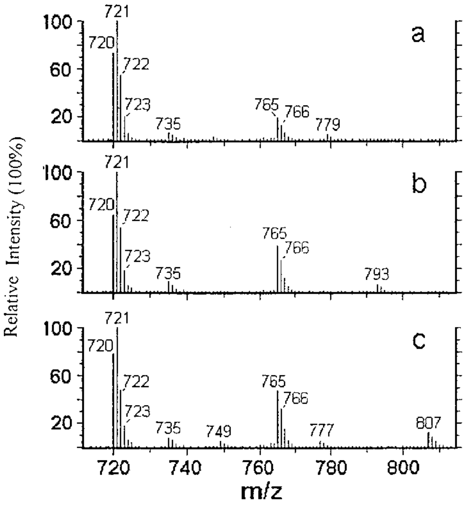


Figure 2. Mass spectra for the reactions of C_{60} with the plasmas of **a**, **b**, and **c**, respectively.

$[CH_3O{=}CH_2]^+$ is a typical fragment ion produced by α-cleavage of alkyl methyl ethers in mass spectrometry, and the increase of carbon chain benefits the α-cleavage of ethers. In addition, a series of ions at higher *m/z* due to the ion−molecule reactions in the ion source are also observed.

After C_{60} was introduced into the ion source, it reacted with the plasmas mentioned above to form adduct cations and protonated molecule. Mass spectra are shown in Figure 2. It is a common characteristic that the adduct ions $[C_{60}C_2H_5O]^+$ at *m/z* 765 and $[C_{60} + M-H]^+$ at *m/z* 779, 793, or 807 are formed by the reactions of C_{60} with the fragment ion $[C_2H_5O]^+$ and $[M-H]^+$ ions, respectively. In addition, the adduct ion $[C_{60}CH_3]^+$ at *m/z* 735 between C_{60} and the methyl ion CH_3^+ is also observed as a minor peak while C_{60} reacts with the plasma of methyl butyl ether.

It can be seen from Figure 2a−c that the relative abundances of adduct ions $[C_{60}C_2H_5O]^+$, which are consistent with those in their self-CI spectra, increase from methyl ether to *n*-butyl methyl ether. These relationships between the relative abundances of adduct ions and reagent ions indicate that the neutral C_{60} rather than C_{60}^+ involves the gas-phase ion−molecule reactions to form the adduct ions, contrast to the experiments of Bohme's group.[9−13] It is unlikely for two main reasons that the adduct cations are produced by the reactions of the C_{60}^+ ion with neutral radicals in the experiments. First, there are few neutral radicals with the formula $CH_2OC_nH_{2n+1}$ which can react with C_{60}^+ to form the corresponding adduct ions because the α-cleavages of alkyl methyl ether molecular ions, which produced $[CH_2OC_nH_{2n+1}]^+$ ions and alkyl radicals, are exclusively the fragmentation channel. Second, the studies of FT-ICR,[7,8] SIFT[9−13] and DCI mass spectrometry[18] experiments have shown that C_{60}^+ was unreactive to most neutral compounds.

There are few addition reactions, except proton-transfer reactions between C_{60} and $[M+H]^+$ of alkyl methyl ethers, although $[M+H]^+$ is one of the major ions. The factor that the reactions between C_{60} and $[M+H]^+$ ions preferred proton transfer to generate the protonated molecule $[C_{60}H]^+$ may be rationalized by the highly saturated properties of $[M+H]^+$ ions. The proton affinity(PA) of methyl ethyl ether (196.4 kcal mol^{-1}) is significantly lower than that of C_{60} (205.5 kcal mol^{-1})[21] determined previously by Bohme and co-workers,[13] so the proton transfer to C_{60} from the protonated ethers is more facile than the addition.

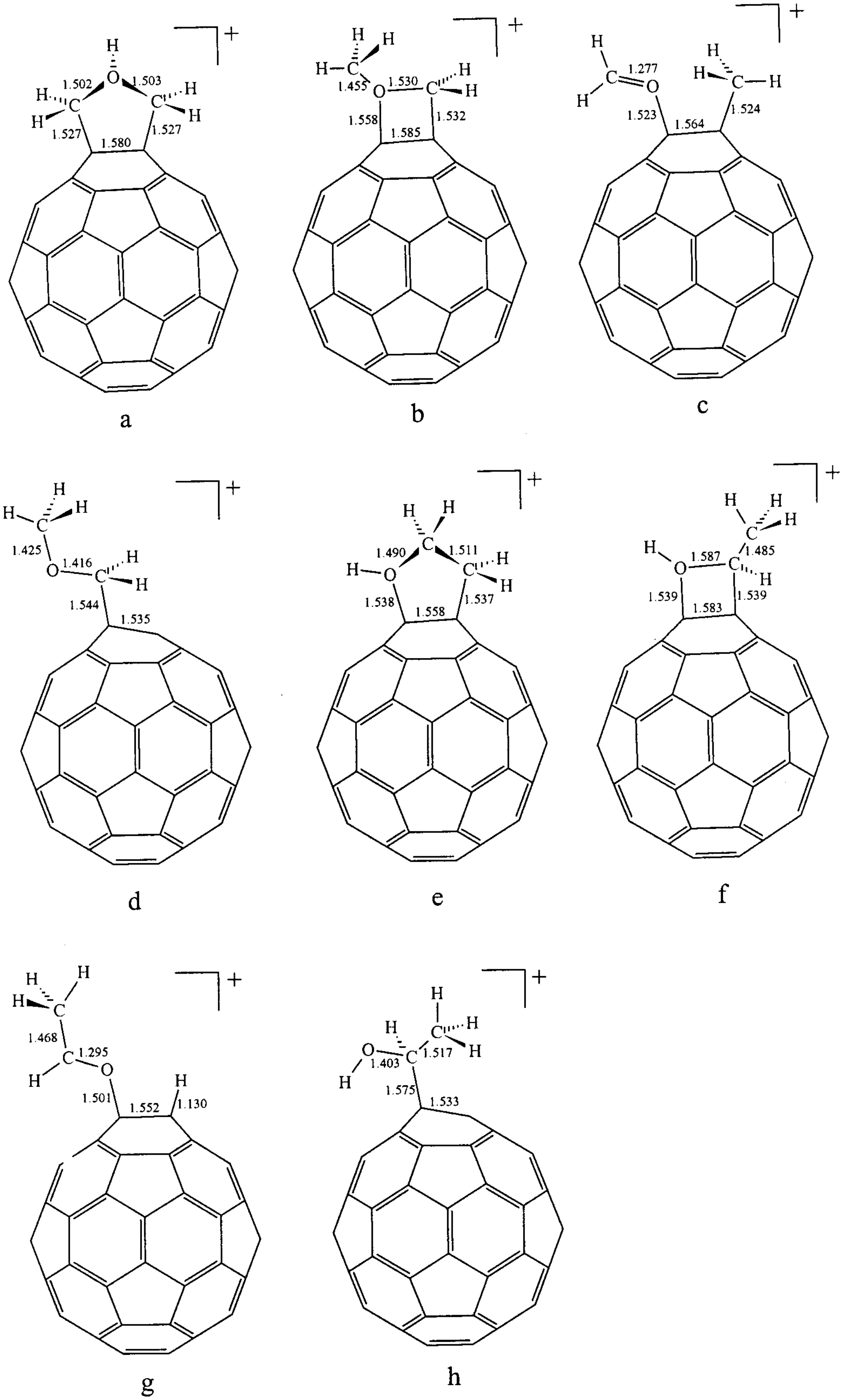
It is of great interest to compare our experimental results with Bohme's. In our experiment, the single additions of fragment ion of alkyl methyl ether to C_{60} were the unique reaction channel, but in Bohme's experiment, polyfunctionalizations by sequential additions often took place as predominant reactions for both of C_{60}^{2+} and C_{60}^{3+}. The reaction characteristics of the former will provide valuable information for preparing the single addition products of C_{60} in the condensed phase, which will simplify the separation procedure of the aimed products. Bohme has pointed out that the reactions of charged C_{60} with neutrals were typical nucleophilic reactions which involved the attack of neutrals to the charge site of multi-charged C_{60}. In contrast to Bohme's mechanism, it is suggested that the reactions of neutral C_{60} with the fragment ions of alkyl methyl ethers are similar to of electrophilic reactions and resulted in delocalizing the positive charge from the fragment ions to some extent to neutral C_{60} to stablize the addition products because C_{60} can play a role in providing electron donator under some conditions. This is consistent with the ionization potential of 7.61 eV of C_{60}, which is similar to that of benzene for which the electrophilic reaction is facile.

Theoretical Studies

The experimental results have shown that the fragment ion $[CH_3O{=}CH_2]^+$ derived from alkyl methyl ethers can react readily with C_{60} to form adduct cations, but the fragment ion $[CH_3CH{=}OH]^+$ generated from primary alcohols has little reactivity with C_{60}, although the experiments were performed under the same conditions. The difference in the reactivity of these two ions to C_{60} may be attributed to the difference of the structures and stabilities of the precursor ions, methoxymethyl ion $[CH_3O{=}CH_2]^+$ and the 1-hydroxyehtyl ion $[CH_3CH{=}OH]^+$. The possible isomers of the ion $[C_2H_5O]^+$ derived from a variety of organic compounds have been the subject of extensively experimental and theoretical investigations.[22−26] It has been proved that there were four energetically low-lying stable isomers of $[C_2H_5O]^+$ ions, viz., the 1-hydroxyethyl ion $[CH_3CH{=}OH]^+$ (protonated acetaldehyde), the methoxymethyl ion $[CH_3O{=}CH_2]^+$, the vinyloxonium (the protonated vinyl alcohol) $[CH_2{=}CHOH_2]^+$, and the O-protonated oxirane $[CH_2CH_2OH]^+$.[23,25] The ion $[CH_3O{=}CH_2]^+$ produced by the fragmentation of alkyl methyl ethers lies 20.3 kcal mol^{-1} higher in energy than the ion $[CH_3CH{=}OH]^+$, the most stable isomer derived from the fragmentation of primary and secondary alcohols lies.[27,28]

To elucidate the structures of the adduct ions of C_{60} with $[CH_3O{=}CH_2]^+$ and $[CH_3CH{=}OH]^+$, semiempirical quantum

CHART 1: Optimized Geometries of $[C_{60}C_2H_5O]^+$ Obtained by AM1 Method



a b c d e f g h

chemistry calculations at HF level were performed on the 14 possible geometries of the $[C_{60}C_2H_5O]^+$ including 8 isomers arising from the reactions of $[CH_3O{=}CH_2]^+$, with C_{60} and 6 isomers formed by the addition reactions of $[CH_3CH{=}OH]^+$ to C_{60}. All of the structures of the C_{60} adduct ions can be divided into three groups according to the linking types of these two moieties in the adduct ions. The first two types are the additions of the $[C_2H_5O]^+$ ions across to 6−6 and 6−5 bonds of C_{60}, respectively, and the third type is the single σ addition of the $[C_2H_5O]^+$ ions with any carbon atom of C_{60}. The optimized geometries and main parameters of the adduct ions are shown in Charts 1 and 2 and the corresponding calculated results

CHART 2: Optimized Geometries of $[C_{60}C_2H_5O]^+$ Obtained by AM1 Method

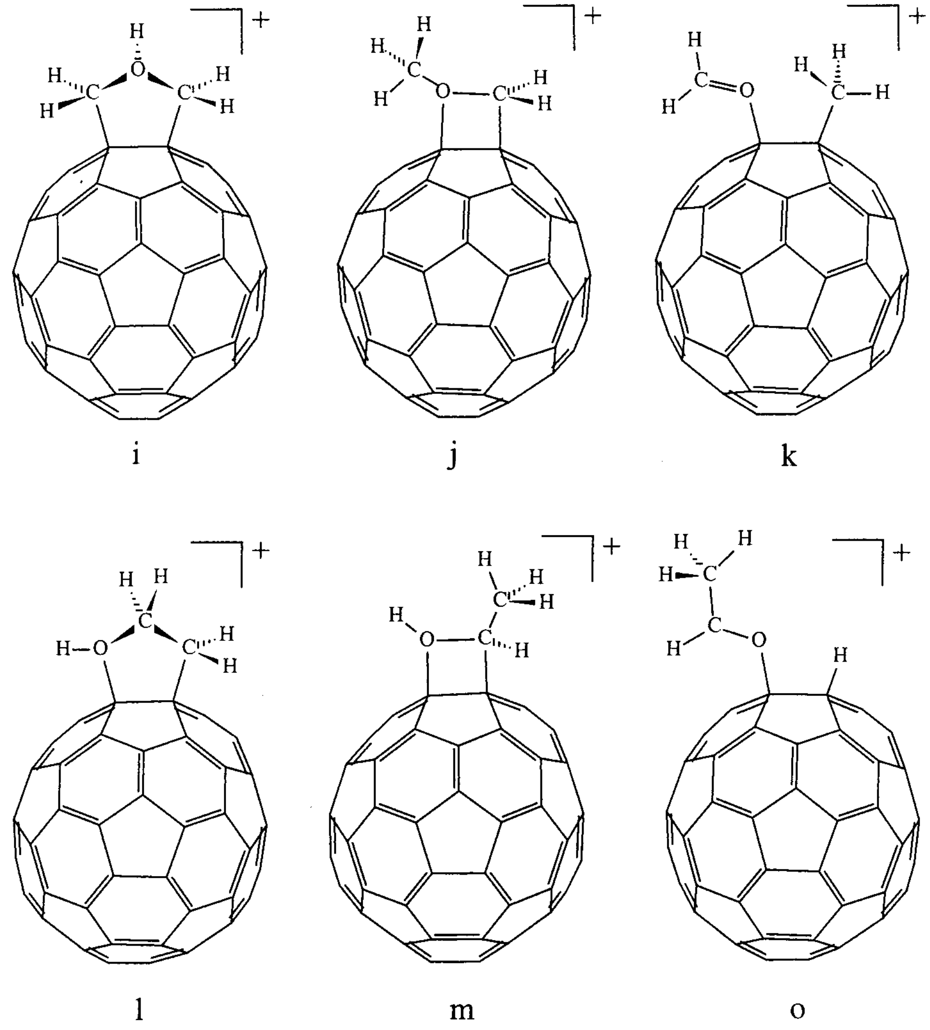


TABLE 1: Results of AM1 Calculations on the Adducts of $[C_2H_5O]^+$ to a 6-6 Bond

adduct cation	precursor ion	addition type	ΔH_f^0 at standard temperature and pressure (kcal mol^{-1})	charge location C_{60}	charge location C_2H_5O	cage strength (Å)
a	$[CH_3O{=}CH_2]^+$	[3+2]	1088.8	+0.10	+0.90	0.305
b	$[CH_3O{=}CH_2]^+$	[2+2]	1120.7	+0.40	+0.60	0.274
c	$[CH_3O{=}CH_2]^+$	σ	1109.3	+0.27	+0.73	0.334
d	$[CH_3O{=}CH_2]^+$	σ	1110.5	+0.82	+0.18	0.275
e	$[CH_3CH{=}OH]^+$	[3+2]	1089.5	+0.36	+0.64	0.114
f	$[CH_3CH{=}OH]^+$	[2+2]	1109.2	+0.38	+0.62	0.277
g	$[CH_3CH{=}OH]^+$	σ	1092.8	+0.19	+0.81	0.292
h	$[CH_3CH{=}OH]^+$	σ	1102.8	+0.76	+0.24	0.274

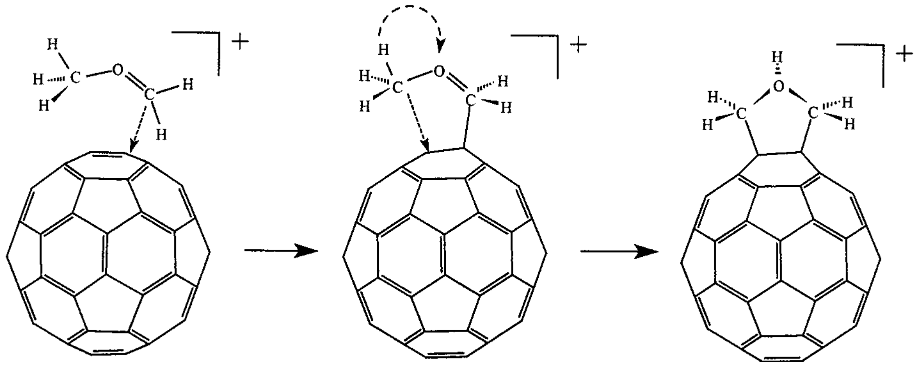
TABLE 2: Results of AM1 Calculations on the Adducts of $[C_2H_5O]^+$ to a 6-5 Bond

adduct cation	precursor ion	addition type	ΔH_f^0 at standard temperature and pressure (kcal mol^{-1})	charge location C_{60}	charge location C_2H_5O	cage strength (Å)
i	$[CH_3O{=}CH_2]^+$	[3+2]	1105.9	+0.09	+0.91	0.326
j	$[CH_3O{=}CH_2]^+$	[2+2]	1137.6	+0.41	+0.59	0.293
k	$[CH_3O{=}CH_2]^+$	σ	1125.4	+0.29	+0.71	0.336
l	$[CH_3CH{=}OH]^+$	[3+2]	1106.0	+0.39	+0.61	0.324
m	$[CH_3CH{=}OH]^+$	[2+2]	1126.7	+0.42	+0.58	0.199
n	$[CH_3CH{=}OH]^+$	σ	1109.3	+0.21	+0.79	0.262

gathered in Tables 1 and 2, respectively. It can been seen from the tables that the standard heats of formation of all of 6−5 adduct cations are much greater than those of the corresponding 6−6 adduct cations with the same addition fashion. These results indicate that the reactivity of the additions of $[C_2H_5O]^+$ to the 6−6 bond of C_{60} is more favorable than that to the 6−5 bond and are identical with the theoretical and experimental results so far accumulated.[25−35] Therefore, the following discussions on the structures of the adduct cations will be mainly focused on the 6−6 adduct cations.

Among the 6−6 adduct cations (**a**−**c**, **e**−**g**) and the single σ adduct cations (**d**, **h**), listed in Tables 1 and 2, there are three common characteristics: the π bond breakage of 6−6 bond of C_{60}, the delocalization of the positive charge from C_2H_5O moiety to the C_{60} cage, and the stretch of the C_{60} sphere. The $C_1{-}C_2$ bond of reaction sites has been pulled away from

CHART 3: Possible Pathway of Formation of [3+2] Cycloadduct of $[C_{60}C_2H_5O]^+$



the remaining part of the C_{60} sphere in 6−6 adduct cations with a little longer bond distance than that of ordinary single σ bond, 1.552−1.585 Å. However, the C_1-C_2 bond lengths in the single σ adducts are the typical values of single σ bond, 1.535 and 1.533 Å. Moreover, the hybridization of C_1 and C_2 changes from $sp^{2.2}$ into near sp^3 judged from the bond angles and twist angles of the carbon atoms of reaction site center in all adduct cations. Other bond lengths and bond angles of the C_{60} skeleton in the adducts are changed slightly compared with the changes around C_1 and C_2. The single bonds and double bonds in the C_{60} sphere away from the reaction regions are not much distorted from the C_{60} original bonds. These are in good agreement with the results reported by Matsuzawa that the influence of interactions upon the geometries was limited to the local area in the addition of H_2 and X_2 (X = F, Cl, Br, and I).[34]

It can be seen from Tables 1 and 2 that the charge redistribution from C_2H_5O moiety to the C_{60} sphere is remarkable feature during the formations of adduct cations. About 0.1−0.4 unit of positive charge is delocalized to the C_{60} cage for 6−6 adduct cations, but the higher values of 0.82 and 0.76 are obtained from the single σ adduct cations. The aforementioned charge transfer is likely to reflect that the reactions between C_{60} and $[C_2H_5O]^+$ occurred in a fashion of electrophilic additions, which contrasted to the gas-phase nucleophilic additions studied by Bohme and co-workers. It is well-known that C_{60} reacted as an electron acceptor with a number of reagents. However, it is little reported that C_{60} reacted as an electron donator in the condensed phase reactions. Our results demonstrate that excellent property of electron donation for C_{60}'s can be understood by the gas-phase reactions of C_{60} with alkyl methyl ether plasmas generated under the self-chemical ionization conditions.

The distortion of the C_{60} sphere occurs during the additions of $[C_2H_5O]^+$ to the C_{60} cage, and the sphere stretches around 0.3 Å, which is mainly attributed to the changes of bond angle, twist angle, and hybridization of reaction site atoms.

The structures of adducts of the methoxymethyl ion $[CH_3O{=}CH_2]^+$ with C_{60} are shown in Chart 1. The [3+2] cycloadduct cation **a** has the C_s symmetry and the lowest standard heat of formation. Each of the bond angles for the newly formed five-membered ring is near 107°, which indicates that there is low degree of ring strain for the cycloadduct cation. The most unstable isomer is the structure **b** with the [2+2] cycloaddition across to the 6−6 bond of C_{60}. The four atoms involving the formation of four-membered ring lie in a same planar, and the bond angles in the ring are all close to 90°. As is well-known, the four-membered ring has always high degree of ring strain, so the heat of formation of the [2+2] cycloadduct cation **b** is the highest among adduct cations, which agrees with the previous conclusions on these kinds of structures. The standard heat of formation of isomer **c** is 11.4 kcal mol^{-1} lower than that of the isomer **b**. The isomer **d** seems different from the isomers **a**−**c**, in which only one σ bond between the two moieties of adduct cation is formed. It is the remarkable features for the isomer **d** that positive charge is mainly distributed on the C_{60} cage. The standard heat of formation of the isomer **d** is 1110.5 kcal mol^{-1}, relatively higher than that of the isomers **a** and **b**, which is consistent with the fact that only one bond is formed in the adduct ion.

As for the geometries **e**−**h**, the proposed adducts generated from the reaction C_{60} with the 1-hydroxyethyl cation, the calculated results show the same trend as that of reactions C_{60} with the methoxymethyl cation, the most stable isomer is the [3+2] cycloadduct cation **e** with the standard heat of formation of 1089.5 kcal mol^{-1}, and the most unstable isomer is the [2+2] cycloadduct cation **f**.

Among the possible isomeric structures of the adducts of C_{60} with the methoxymethyl cation, the [3+2] cycloadduct cation, in which there is a hydrogen migration from carbon to oxygen during the formation of the five-membered ring with lower ring strain, is the most stable one. Taking into account the factor that cycloaddition should not be hindered by hydrogen migration, which is a common phenomenon with small active energy in organic and gas-phase ion chemistry,[37,38] we conclude that the most possible structure for the adducts of neutral C_{60} with the methoxymethyl cation is the [3+2] cycloaddition isomer. The pathway for the formation of the [3+2] cycloadduct is presented in Chart 2. This conclusion is consistent with this from our previous investigations on the adducts of C_{60} with $[C_2H_3O]^+$ generated from acetone and vinyl acetate.[14] Moreover, the conclusion is also supported by the experimental results in which C_{60} can readily undergo the [3+2] cycloaddition under suitable conditions in the condensed phase as well.[29]

The experimental results of gas-phase ion−molecule reactions show that the methoxymethyl cation derived from α-cleavage of alkyl methyl ethers can readily react with C_{60} to form adducts, but the 1-hydroxyethyl cation has little reactivity. These two kinds of reactions were carried out under almost same kinetic conditions including the concentration of C_{60}, the same ion source pressure, viz., the same concentration of reagent fragment ions. Therefore, the different behaviors of these two ions reacting with C_{60} are probably attributed to thermodynamic and energy barrier factors during the adduct formation. The following thermodynamic reaction equations describe the reaction enthalpies for the reactions of C_{60} with the methoxymethyl cation, 1-hydroxyethyl cation, and the ethoxymethyl cation, respectively.

$$C_{60} + [CH_3O{=}CH_2]^+ \rightarrow [C_{60}C_2H_5O]^+ \quad \Delta H^\circ = -42.8 \text{ kcal mol}^{-1} \quad (1)$$

$$C_{60} + [CH_3CH{=}OH]^+ \rightarrow [C_{60}C_2H_5O]^+ \quad \Delta H^\circ = -24.5 \text{ kcal mol}^{-1} \quad (2)$$

$$C_{60} + [CH_3CH_2O{=}CH_2]^+ \rightarrow [C_{60}C_3H_7O]^+ \quad \Delta H^\circ = -38.8 \text{ kcal mol}^{-1} \quad (3)$$

It is obvious that the reaction enthalpy of the eq 1 is much lower than that of the eq 2 with -24.5 kcal mol^{-1}, which mainly arises from the different stability of the precursor $[C_2H_5O]^+$ ions, in which the 1-hydroxyethyl cation is the most stable isomer, and its standard heat of formation calculated by the AM1 method is 16.6 kcal mol^{-1} lower than that of the methoxyethyl cation.[23−25,27,28] In view of the thermodynamics, the remarkable different reactivity of these two kinds of fragment ions with C_{60} can be rationalized by considering the great difference of the reaction enthalpy. However, the factor that reaction 2, which was calculated to be exothermic, was not observed may be rationalized by taking account of presence of barriers of reaction. The barrier for reaction 2 may lie above the initial reactant energy, but that for the more exothermic reaction 1 lies below the initial reactant energy. Such barriers are considered to arise from the energetic requirement to distort the fullerene surface in order to achieve sp^3 hybridization at the carbon atom involved in bond formation. The higher barriers of reaction 2 is expected to result from the formation of carbon oxygen bond between C_{60} and $[CH_3CH{=}OH]^+$ ion, which causes more distortions of the carbon atoms lactated in the reaction sites. This is consistent with Bohme's investigations on the reactions of fullerene cations.[39]

Conclusion

We have investigated the gas-phase ion−molecule reactions of C_{60} with the ion systems of alkyl methyl ethers and primary alcohols in the chemical source of the mass spectrometer. $[C_{60}C_2H_5O]^+$ and $[C_{60}H]^+$, together with other minor adduct ions were observed as the reaction products of the plasma of alkyl methyl ethers with C_{60}. However, there were few reaction products between C_{60} and the ion systems of primary alcohols except the protonated molecule C_{60}. The AM1 semiempirical calculations on the 14 possible adduct isomers of the $[C_{60}C_2H_5O]^+$ ion demonstrate that a 6−6 bond is more reactive than a 6−5 bond. The C_{60} sphere has been stretched up, and the positive charge has been delocalized from C_2H_5O moiety to the C_{60} cage in the adducts, which indicates that the reactions studied in this experiment are the electrophilic reactions. Among the calculated possible isomers, the most stable structure is **a**, the [3+2] cycloadduct with C_s symmetry, and during its formation a hydrogen migration occurred. The formation pathway of **a** is presented in Chart 3. From both thermodynamics and energy barrier points of view, the different reactivity of the methoxymethyl cation and the 1-hydroxyethyl cation toward neutral C_{60} is likely to attribute to much difference of reaction enthalpy and hybridization of reaction site carbon atoms.

Acknowledgment. This work was performed with the support of the National Natural Science Foundation of P. R. China and Changchun Applied Chemistry Research Center for financial support. We appreciate Dr. V. G. Voinov for his helpful discussions.

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