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Gas-Phase Ion-Molecule Reactions of C_{60} and Theoretical Studies of $[C_{60}C_2H_3O]^+$ Adduct Cations

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Gas-phase ion–molecule reactions of buckminsterfullerene (C_{60}) with the acetyl cation $CH_3{-}^+C{=}O$ (m/z 43) and formylmethyl cation $^+CH_2{-}CH{=}O$ (m/z 43, or oxiranyl cation), generated from the self-chemical ionization of acetone and vinyl acetate, respectively, were studied in the ion source of a mass spectrometer. Adduct cations $[C_{60}C_2H_3O]^+$ (m/z 763) and protonated C_{60}, $[C_{60}H]^+$ (m/z 721), were observed as the major products. AM1 semiempirical molecular orbital calculations on the possible structures, stabilities and charge locations of the isomers of the adducts $[C_{60}C_2H_3O]^+$ were carried out at the restricted Hartree–Fock level. The results indicated that the σ-addition product $[C_{60}\text{–}COCH_3]^+$ is the most stable adduct for the reaction of C_{60} with $CH_3{-}^+C{=}O$ rather than that resulting from the [2 + 2] cycloaddition. The [2 + 3] cycloadduct and the σ-adduct $[C_{60}CH_2CHO]^+$ might be the most possible coexisting products for the reactions of C_{60} with $^+CH_2{-}CH{=}O$ or oxiranyl cation. Other $[C_{60}C_2H_3O]^+$ isomers are also discussed. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

A new and exciting research field, C_{60} derivatization chemistry, began to boom[1–3] after the synthesis and isolation of C_{60} and C_{70} in macroscopic quantities.[4] In the past few years, a number of investigations have focused on the synthesis of fullerene derivatives through condensed-phase reactions involving simple carbon–carbon bond formation as well as through some reactions with heteroatom-containing compounds. Several studies of neutral C_{60} chemistry have dealt with reactions with some unsaturated groups, such as $:CR_2$, $:NCH_2R$, $C{=}C$, $CH_2{=}N^+(R)CH_2^-$ or $C{=}C{-}C{=}C$, to build "organic foundations" on the C_{60} sphere,[1,5] which include three-,[6] four-,[7] five-[5c,8] and six-membered[8c,9] ring systems. Subsequently, a few groups have successfully tried to introduce useful functionalities to these systems[9c,10] in order to obtain some novel derivatives with potentially useful properties. In most of the above-mentioned derivatization reactions, C_{60} behaves as an alkene by taking part in the reactions with a broken carbon–carbon double bond.

Mass spectrometry has played a very important role in the identification and characterization of fullerenes and their derivatives[11] because of advantages such as the need for a small quantity of sample, convenience and speed. Some investigations of the gas-phase ion–molecule reactions of neutral and charged C_{60} have been reported previously. Bohme and co-workers[12] embarked upon extensive studies of the reactions of C_{60}^{2+} and C_{60}^{3+} with a variety of organic molecules and suggested that multiply charged C_{60}^{n+} ($n = 2, 3$) cations are more reactive than C_{60}^{+}.[13] Neutral C_{60} has been found to react with some metal cations.[14] In previous papers[15] we reported the reactions of C_{60} and C_{60}^{+} with the ions and neutrals, respectively, derived from some small organic compounds. These results may be regarded as a supplement to those of Bohme and co-workers.[12–14] We found that neutral C_{60} and C_{60}^{+} could react with fragment ions (or molecular ions) and radicals, respectively, produced under chemical ionization (CI) conditions. In this paper, we report our results on the gas-phase ion–molecule reactions of C_{60} with two fragment cations $C_2H_3O^+$ derived from the self-CI of acetone and vinyl acetate in the ion source of a mass spectrometer. A semiempirical theoretical study of the structures and stabilities of the adduct cations $[C_{60}C_2H_3O]^+$ is also presented.

EXPERIMENTAL

All reactions were performed on a VG-Quattro mass spectrometer (Fisons Instruments, Manchester, UK). Acetone and vinyl acetate were injected into the ion source through the reference gas inlet before C_{60} was introduced. The CI slit was used in order to afford enough pressure to react, and the gauge readings of the ion source pressure were maintained at around 1.2×10^{-2} Pa. The ion gauge is located outside the ionization cell, but the real pressure inside the cell is about 1000 times the readings.[16] C_{60} was introduced into the ion source via the desorption chemical ionization (DCI) probe (the solution of C_{60} was dropped on to the DCI

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filament and the solvent was blown off) and the filament was switched on at 1200 mA while operating. The electron energy was 100 eV. The ion source was operated at 473 K and a resolving power of 1000 was used for recording mass spectra. The fullerenes were produced by the arc-discharge method[4] in our laboratory and separated using column chromatography. UV/visible and mass spectra showed that the purity of C_{60} was better than 99.9%. Acetone and vinyl acetate of analytical grade purity were commercially available.

The AM1 semiempirical molecular orbital calculations[17] were carried out with the MOPAC 5.0 program package on an AST/486 computer at the restricted Hartree–Fock level. The C_{60} geometry with C—C bond lengths of 1.463 and 1.385 Å and with the standard heat of formation of 973.3 kcal mol^{-1} (1 kcal = 4.184 kJ), optimized by the same method as above, was used as the original geometry.

RESULTS AND DISCUSSION

Reactions of C_{60} with the self-CIMS ion system of acetone

Figure 1(a) shows the self-CI mass spectrum of acetone at a source pressure of 1.2×10^{-2} Pa. In comparison with the electron impact (EI) mass spectrum of acetone, there are fewer fragment ions and no molecular ion at *m/z* 58. The protonated molecule at *m/z* 59, the adduct ions at *m/z* 73 and 101 and the protonated dimer at *m/z* 117 corresponding to $CH_3CO^+(H)CH_3$, $(CH_3)_2CO^+CH_3$, $(CH_3)_2CO^+(COCH_3)$ and $^+H(CH_3COCH_3)_2$, respectively, were observed due to ion–molecule reactions.[18] In Fig. 1(a), the ion at *m/z* 117 is the base peak instead of CH_3CO^+ at *m/z* 43, which is the base peak in the EI mass spectrum of acetone.

After C_{60} was introduced into the ion source, it reacted with the ion system mentioned above to form some adduct cations.[19] The mass spectrum is shown in Fig. 1(b). It can be seen that the abundance of *m/z* 721 (about 95% of *m/z* 720) is much higher than that of the expected ^{13}C contribution, which is 66% (1.1% × 60 = 66%) for C_{60}. This indicates that the signal at *m/z* 721 comes partly from the contribution of the protonated molecule $[C_{60}H]^+$ (*m/z* 721) resulting from the proton-transfer reactions of C_{60} with the protonated acetone at *m/z* 59 and the protonated acetone dimer at *m/z* 117.[20] The proton affinity (PA) of acetone is 196.7 kcal mol^{-1},[21] which is obviously lower than that of C_{60}, 205.5 kcal mol^{-1}, which was determined previously by Bohme and co-workers[22] and McElvany and Callahan.[11b] Therefore, the reactions may be described as follows:

$$\underset{m/z\ 59}{C_{60} + CH_3CO^+(H)CH_3} \rightarrow \underset{m/z\ 721}{[C_{60}H]^+} + CH_3COCH_3$$

$$\underset{m/z\ 117}{C_{60} + {}^+H(CH_3COCH_3)_2} \rightarrow \underset{m/z\ 721}{[C_{60}H]^+} + 2CH_3COCH_3$$

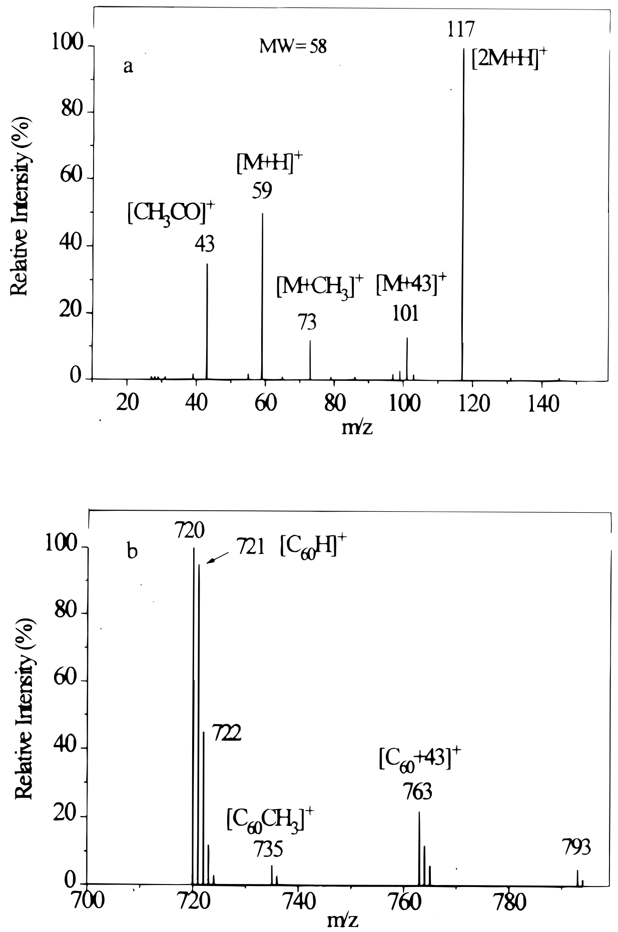


Figure 1. Mass spectra for (a) the self-CI of acetone and (b) reactions of C_{60} with the ion system of (a)

In addition, the proton-transfer reaction of CH_3CO^+ (to yield ketene) with C_{60} could be responsible for $[C_{60}H]^+$ too. Other three major ions at *m/z* 735, 763 and 793, which correspond to $[C_{60} + 15]^+$, $[C_{60} + 43]^+$ and $[C_{60} + 73]^+$ adduct cations, respectively, were observed in Fig. 1(b). The adduct cation at *m/z* 763, $[C_{60}C_2H_3O]^+$, may correspond to the product of the reaction of neutral C_{60} with the predominant fragment ion CH_3CO^+ (*m/z* 43), as might very reasonably have been expected:

$$C_{60} + \underset{m/z\ 43}{CH_3CO^+} \rightarrow \underset{m/z\ 763}{[C_{60}COCH_3]^+}$$

The structure and stability of this ion is discussed below. Our previous work[23] indicated that the ion $[C_{60}CH_3]^+$ at *m/z* 735 had a simple σ-addition structure. On the other hand, the adduct cation, $[C_{60}C_4H_9O]^+$ at *m/z* 793, is due to the reaction of C_{60} with the ion $CH_3CO^+(CH_3)_2$ (*m/z* 73)[18] rather than sequential reactions with CH_3COCH_3 and the CH_3 group and is suggested to have the structure $[C_{60}((CH_3)_2C{=}O{=}CH_3)]^+$ similar to that of the adduct cation of C_{60} with $^+CH_2{=}O{-}CH_3$.[23c] However, the protonated ions $CH_3CO^+(H)CH_3$ (*m/z* 59), $H^+(CH_3COCH_3)_2$ (*m/z* 117) and $(CH_3)_2CO^+(COCH_3)$ (*m/z* 101) are difficult to add to C_{60} cage because of proton transfer to generate $[C_{60}H]^+$.

Reactions of C_{60} with the self-CIMS ion system of vinyl acetate

Figure 2(a) shows the self-CI mass spectrum of vinyl acetate. A very weak molecular ion at *m*/*z* 86, the protonated molecule $[M + H]^+$ at *m*/*z* 87, the protonated dimer $[2M + H]^+$ at *m*/*z* 173, the other adduct ions $[M + 43]^+$ (*m*/*z* 129) and $[2M + 43]^+$ (*m*/*z* 215), as well as the ion at *m*/*z* 155, were observed, but the source of the ions at *m*/*z* 155 was not clear (it may be due to an impurity, but in any case is not very important for the present study.). A striking difference between the self-CI of acetone and that of vinyl acetate is that the protonated ions $[M + H]^+$ and $[2M + H]^+$ dominate the $(C_2H_3O)^+$ at *m*/*z* 43 and the adduct at *m*/*z* 73 in the case of acetone, but the $C_2H_3O^+$ ion, the adduct $[M + C_2H_3O]^+$ at *m*/*z* 129 and $[2M + C_2H_3O]^+$ at *m*/*z* 215 become more abundant in vinyl acetate. These results suggest that the reactivities of the ions $C_2H_3O^+$ derived from acetone and vinyl acetate towards neutral molecules are different and that the structures of the $C_2H_3O^+$ ions might be different also. Scheme 1 shows the possible pathways to generate $C_2H_3O^+$ from acetone and vinyl acetate.

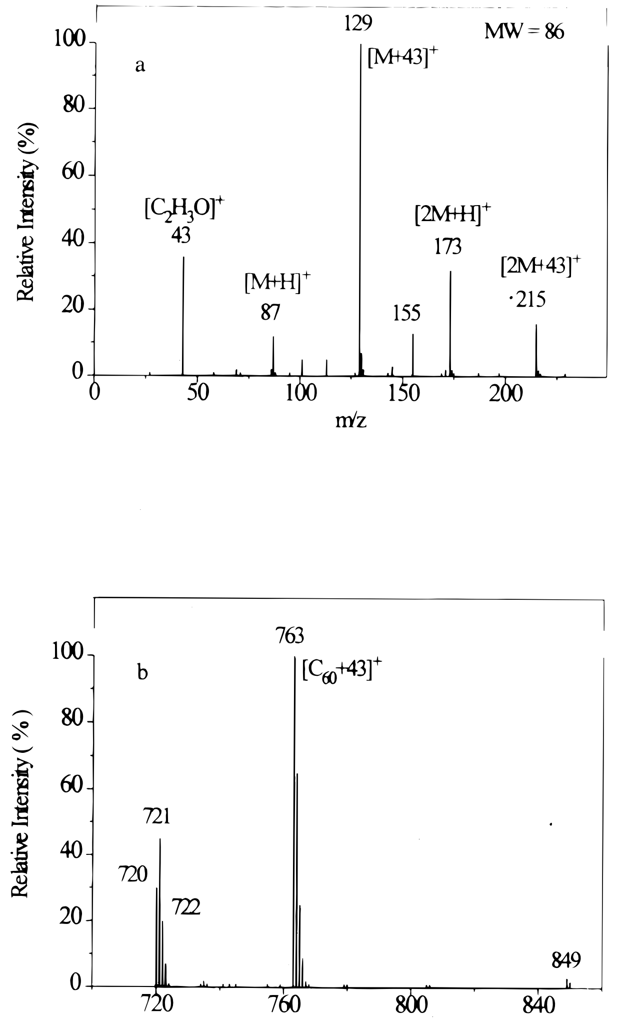
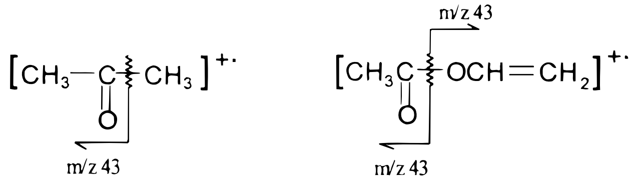


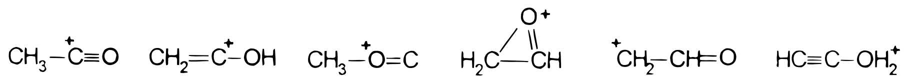
Figure 2. Mass spectra for (a) the self-CI of vinyl acetate and (b) reactions of C_{60} with the ion system of (a)

The mass spectrum resulting from the reactions of C_{60} with vinyl acetate is shown in Fig. 2(b). The abundance of the ion at *m*/*z* 721 is higher than that of C_{60} at *m*/*z* 720. Therefore, except for the contribution of ^{13}C, it is mainly due to the protonated ion $[C_{60}H]^+$ (*m*/*z* 721) generated from proton-transfer processes similar to the reactions with acetone. The peaks at *m*/*z* 763 and 849 are reaction products of C_{60} with the ions $C_2H_3O^+$ (*m*/*z* 43) and $[M + 43]^+$ (*m*/*z* 129), respectively. However, there are no adduct cations corresponding to the reactions of C_{60} with ions $[M + H]^+$, $[2M + H]^+$ and $[2M + 43]^+$ in the system. These results indicate that C_{60} prefers to react with unsaturated rather than saturated ions. It is very interesting that the reaction of C_{60} with $C_2H_3O^+$ (*m*/*z* 43) derived from vinyl acetate shows very high activity compared with that of C_{60} with $CH_3{-}^+C{=}O$ (*m*/*z* 43) derived from acetone, which is similar to the cases of self-CI of acetone and vinyl acetate. This suggests that the two kinds of $C_2H_3O^+$ ions maybe have different structures, especially considering that $C_2H_3O^+$ may have two resources by breaking the C(O)—O bond in vinyl acetate as shown in Scheme 1. Here we focus our attention on the structures of $[C_{60}C_2H_3O]^+$ adduct cations in the gas phase.

The possible isomers of $C_2H_3O^+$ ions derived from a variety of organic compounds have been the subject of extensive experimental and theoretical investigations.[24] The structures of several most stable isomers[24b,25] are illustrated in Scheme 2. The acetyl ion $CH_3{-}^+C{=}O$ (2a), with a standard heat of formation ΔH_f° of 157 kcal mol^{-1}, is the most stable. Generally, measurements of the abundance ratios of the fragment ions at *m*/*z* 29 to that at *m*/*z* 28 in the CAD spectra have been applied as a criterion to differentiate between $C_2H_3O^+$ isomeric structures.[24c,26,27] It has been demonstrated experimentally that in addition to the acetyl ion $CH_3{-}^+C{=}O$ (**2a**) and the 1-hydroxyvinyl cation $CH_2{=}C^+{-}OH$ (**2b**), a third one, which may be presented as either the oxiranyl cation **2d** or $^+CH_2{-}CH{=}O$ (**2e**), exists as a stable species in the gas



Scheme 1.



2a **2b** **2c** **2d** **2e** **2f**

Scheme 2. Possible $C_2H_3O^+$ isomers predicted from theory.

phase.[27,28] Even though some of them can interconvert under certain conditions,[29] the abundance ratio of 0.67 of the ions at *m/z* 29 to that at *m/z* 28 is considered to be a satisfactory criterion for the presence of $CH_3-{}^+C{=}O$.

For example, the ratio of about 0.70, in the CAD spectrum of $C_2H_3O^+$ (*m/z* 43) derived from the self-CI of acetone described in this paper indicates that the $C_2H_3O^+$ ion has the acetyl structure **2a**. However, the ratio of about 10^{30} in the self-CI of vinyl acetate gives clear evidence that the $C_2H_3O^+$ ions derived from vinyl acetate in Fig. 2(a) predominantly have the structure **2d** or **2e**, in which the ions at *m/z* 29 can be produced through direct cleavage, rather than the acetyl structure. On the other hand, the reactions of C_{60} with the self-CI ion system of ethyl acetate gave very weak adducts corresponding to $[C_{60}C_2H_3O]^+$ (*m/z* 763) (spectrum not shown). This is consistent with the conclusion that the $C_2H_3O^+$ ion derived from vinyl acetate does not have the acetyl structure. Therefore, the formation of the adduct cations $[C_{60}C_2H_3O]^+$ from C_{60} follows different pathways in acetone and vinyl acetate and is likely to lead to different adduct structures.

Theoretical studies of $[C_{60}C_2H_3O]^+$ structures

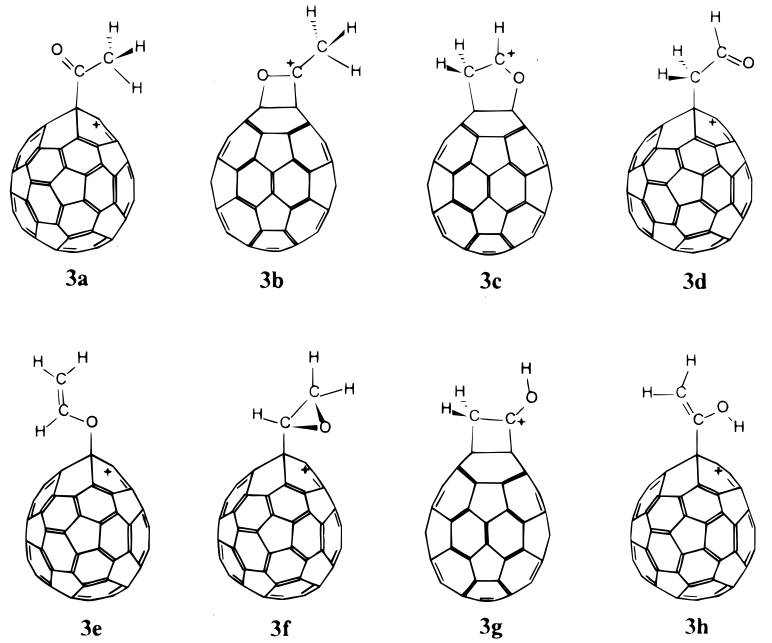
The AM1 semiempirical molecular orbital calculations for the eight possible isomers of $[C_{60}C_2H_3O]^+$ are summarized in Table 1 and the optimized geometries are shown in Scheme 3. According to the differences of the precursor fragment ions, there are three kinds of geometries. First, **3a** and **3b** are possible reaction products of C_{60} with acetyl cation $CH_3-{}^+C{=}O$ (**2a**) derived from acetone. Second, **3c–f** are possible reaction products of the reaction of C_{60} with oxiranyl cation **2d** or ${}^+CH_2-CH{=}O$ **2e**. Third, **3g** and **h**, are perhaps due to the reactions of C_{60} with $CH_2{=}C^+-OH$ (**2b**).

For the first two structures in Scheme **3**, the geometry of **3a**, a simple carbonyl σ-addition product and with the heat of formation of 1127.0 kcal mol^{-1}, is more stable than that of **3b**, which results from a [2 + 2] cycloaddition of carbonyl C=O group to a double bond of C_{60}. Therefore, the adduct cation $[C_{60}C_2H_3O]^+$, at *m/z* 763 in Fig. 1(b), formed from the reaction of C_{60} in the self-CI ion system of acetone predominantly is likely to have the structure **3a**. The newly

Table 1. Comparison of AM1 calculations on $[C_{60}C_2H_3O]^+$ isomers

Adduct cation	Precursor ion	Addition type[a]	ΔH_f° (kcal mol^{-1})	Charge location C_{60}	C_2H_3O	Cage stretch (Å)
3a	$CH_3-{}^+C{=}O$	σ_{C1-}	1127.0	+0.75	+0.25	0.271
3b	$CH_3-{}^+C{=}O$	[2 + 2]	1140.4	+0.42	+0.58	0.213
3c	${}^+CH_2-CH{=}O^b$	[2 + 3]	1109.6	+0.35	+0.65	0.252
3d	${}^+CH_2-CH{=}O^b$	σ_{C2-}	1126.2	+0.86	+0.14	0.286
3e	${}^+CH_2-CH{=}O^b$	σ_{O-}	1157.6	+1.00	0.00	0.304
3f	Oxiranyl ion	σ_{C1-}	1159.8	+0.86	+0.14	0.286
3g	$CH_2{=}C^+-OH$	[2 + 2]	1118.1	+0.20	+0.80	0.240
3h	$CH_2{=}C^+-OH$	σ_{C1-}	1136.8	+0.87	+0.13	0.284

[a] The elemental symbols in subscript following σ indicate the atoms connected to C_{60}.
[b] The oxiranyl cation may behave as the precursor cation also.


3a 3b 3c 3d
3e 3f 3g 3h

Scheme 3. Optimized geometries of $[C_{60}C_2H_3O]^+$ obtained by AM1 calculations.

formed C—C single bond length of 1.560 Å is close to that of the C—C single bond of acetone,[30] but the distance of the two carbon atoms in the C_2H_3O group is only 1.487 Å. The connecting carbon atom in C_{60} is pulled up by 0.271 Å, and the bond lengths, the bond angles and the twist angles of other neighboring carbon atoms are also changed slightly. One unit positive charge delocalizes mainly on C_{60} (about +0.75) from the carbonyl group, and there is + 0.18 unit on the carbon atom that was originally doubly bonded to the connecting atom in C_{60}. Of considerable interest is the possible [2 + 2] cycloaddition product cation of **3b** with a standard heat of formation of 1140.4 kcal mol^{-1}. Only part of the charge (about +0.42) delocalizes on to C_{60}. The bond lengths of the newly formed C—C and C—O bonds are 1.521 and 1.523 Å, respectively, and the distance between the two connecting carbon atoms changes to 1.606 from 1.385 Å. The C_{60} cage has been stretched up by about 0.213 Å along the original C_{2v} axis. The hybridization of the atom in the original carbonyl group remains sp^2 just like that of **3a**. We propose that the two geometries of **3a** and **3b** could convert into each other under certain conditions.

The four geometries **3c–f** are the possible structures for the adduct cations $[C_{60}C_2H_3O]^+$ resulting from the reactions of C_{60} with $^+CH_2—CH=O$ or oxiranyl cation from vinyl acetate. The [2 + 3] cycloaddition adduct cation of **3c**, with a standard heat of formation of 1 109.6 kcal mol^{-1} and C_s symmetry, is obviously the most stable one. The two newly-formed C—C and C—O bond lengths are 1.541 and 1.516 Å and close to those of the single bonds; however, in the C_2H_3O substituent, the bond lengths of C—C and C—O are 1.480 and 1.295 Å, respectively. This means that the character of the original carbonyl group is maintained in the adduct cation. The positive charge is located mainly on the C_2H_3O group (in Table 1) and especially on the carbon atom in the original carbonyl group similar to that in the $C_2H_3O^+$ fragment cation.[30] The C—O—C bond angle of 111.6° is much bigger than that of 93.6° of **3b**, so that the former has less ring strain and it is the most stable structure among the eight geometries. We propose that the structure of **3c**, the [2 + 3] cycloadduct, is the most favorable among the isomeric reaction adducts $[C_{60}C_2H_3O]^+$ of C_{60} with the ion system of vinyl acetate.

As for the other three geometries, **3d–f** resulting from σ-additional reactions, the structure of **3d** with a standard heat of formation of 1 126.2 kcal mol^{-1}, possesses better stability and is even more stable than that of **3a**, the most probable structure for the reaction of C_{60} with the acetyl ion. This indicates that it is possible for the structure to coexist with that of **3c** for the adduct cations of C_{60} with vinyl acetate. One unit positive charge delocalizes dominantly on C_{60} (about +0.86) from the C-2 atom of the $^+CH_2—CH=O$ ion or the oxygen atom of the oxiranyl cation. In addition, the geometry of **3e** has the whole positive charge delocalized on C_{60} because of the conjugative effects between the enol and C_{60}. The connecting carbon atom in C_{60} has been pulled up by 0.304 Å, which is the largest change in C_{60} among the σ-addition isomers described here. The structure of **3f** is the σ-adduct of C_{60} with the oxiranyl cation **2d**. The two structures of **3e** and **3f** are much less stable species so that they may make a negligible contribution to the adduct cations $[C_{60}C_2H_3O]^+$ mentioned above.

Even though the last two structures, **3g** and **h**, are fairly stable, they are difficult to present as possible adduct cations in this study because the precursor 1-hydroxyvinyl cation, $CH_2=C^+—OH$, is not a very reasonable fragment ion in the ion systems of acetone and vinyl acetate and, to some extent, rearranges into acetyl cation or oxiranyl cation prior to reaction.[27] However, the two adducts might be formed by reactions of C_{60} with a suitable ion system that produces predominately the reactive precursor ion $CH_2=C^+—OH$ according to the theoretical calculation. Related investigations are in progress.

CONCLUSION

We have studied the gas-phase ion–molecule reactions of C_{60} with the ion systems of acetone and vinyl acetate produced in the ion source of mass spectrometer under CI conditions. $[C_{60}C_2H_3O]^+$, $[C_{60}H]^+$ and other derivatized C_{60} cations were observed. It is likely that the adduct cations $[C_{60}C_2H_3O]^+$ derived from the two ion systems have different structures. The measurement on the ratios of *m/z* 29 to 28 in the CAD mass spectra of the two $C_2H_3O^+$ (*m/z* 43) ions produced from the different sources gives evidence supporting their different structures, i.e. acetyl cation $CH_3—^+C=O$ and formylmethyl cation $^+CH_2—CH=O$ (or oxiranyl cation), respectively. The AM1 semiempirical molecular orbital calculations on the structures and stabilities of eight possible geometries of $[C_{60}C_2H_3O]^+$ suggest that the simple σ-adduct $[C_{60}—CO—CH_3]^+$ **3a** and the [2 + 3] cycloadduct **3c** are the most probable structures for the two addition reactions, respectively.

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