Gas-Phase Halo Alkylation of C_{60} -Fullerene by Ion-Molecule Reaction Under Chemical Ionization*

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Chemical ionization (CI) mass spectra of C_{60} -fullerene were studied using 1,2-dibromoethane and 1,2-dichloroethane as CI reagents. The ion-molecule reaction between C_{60} and $C_2H_4X^+$ ($X = Br$ and Cl) leads to the formation of $(C_{60} + C_2H_4X)^+$ adducts. The collision-induced dissociation of the adducts reveal gas phase halo alkylation of C_{60} -fullerene involving the $C-C$ bond formation. (*J Am Soc Mass Spectrom* 1993, 4, 894-897)

Over the past few years, study of the chemical and physical properties of fullerenes has attracted the attention of several research groups, since the method for producing macroscopic quantities of Buckminsterfullerene, C_{60} , was made available by Kratschmer et al. [1]. Mass spectrometry has played a vital role in the identification and characterization of fullerenes [2]. The molecular ions of fullerenes generated by electron-impact ionization are quite stable. The selected ion flow tube (SIFT) experiments showed that C_{60}^+ and C_{70}^+ are unreactive toward several molecules [3]. However, incorporation of noble gas atoms like He and Ne into the cavity of singly and multiply charged C_n^{n+} fullerene molecules ($X = 60, 70$; $n = 1 - 3$) cage during high-energy collision has been reported by different groups [4, 5]. Chemical ionization (CI) mass spectrometry of fullerenes using various CI reagent gases such as H_2 , CH_4 , H_{20} , CH_3OH , $i-C_4H_{10}$, and NH_3 [6, 7] is also reported. The proton affinity of C_{60} was estimated to be fairly high, and it lies between 204 and 207 kcal mole $^{-1}$ based on ion-molecule reactions in a Fourier transform mass spectrometer. Hence, it forms $C_{60}H^+$ with all the above CI reagents invariably. The noteworthy aspect is the adduct formation with $C_2H_5^+$ and $C_4H_9^+$ under methane and isobutane CI conditions, respectively [7]. Based on the low-energy and high-energy collision-induced dissociation (CID) studies, it was proposed that the $C_{60}(t-C_4H_9)^+$ adduct is a proton bound complex of the type $C_{60} \cdots H^+ \cdots C_4H_8$.

We recently reported the stereoselectivity of

$C_2H_4Br^+$ toward the geometrical isomers of some unsaturated dicarboxylic acids and esters and cinnamates [8]. The structure and energetics of $C_2H_4X^+$ ($X = F, Cl, Br$) are of considerable theoretical and experimental importance [9]. Hence, we have undertaken the CI study of C_{60} -fullerene with 1,2-dibromoethane (DBE) and 1,2-dichloroethane (DCE) as reagents. Herein, we report the results of ion-molecule reactions of $C_2H_4Br^+$ and $C_2H_4Cl^+$ with pure C_{60} under high-pressure CI conditions, which provide evidence for the formation of covalently bound halo alkyl C_{60} -fullerene.

Experimental

The DBE and DCE CI mass spectra were run on a VG-70-70H mass spectrometer at the following conditions. Source temperature, 340 °C; electron energy, 50 eV; emission current, 1000 μA ; acceleration voltage, 3 kV. The spectra were recorded using a strip-chart recorder. DBE was introduced through the liquid inlet reservoir kept at 250 °C to get a source housing pressure of 10^{-4} mbar. DCE was introduced through the CI gas manifold. The C_{60} sample was introduced through the solid probe. It is worth mentioning that the probe needed no heating to get enough sample pressure. The preparation and purification of the C_{60} sample were reported elsewhere [10]. The sample used in the present investigation is free from C_{70} . The CID spectra in the first field-free region were taken using Ar as the collision gas.

Results and Discussion

The DBE CI mass spectrum (Figure 2) of C_{60} displays an abundant ion at m/z 827 corresponding to the addition of $C_2H_4Br^+$ with C_{60} . The adduct ion is

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distinctly clear due to the presence of bromine isotopes. It is also unique that the adduct ion is very well separated from the molecular ion region as compared with the CH₃⁺ adducts observed under isobutane CI [7]. That the adduct (C₆₀ + C₂H₄Br)⁺ formation occurs due to ion-molecule reaction between C₂H₄Br⁺ and C₆₀ is supported by the following arguments: (1) DBE CI plasma contains mainly C₂H₄Br⁺ and very weakly abundant C₂H₄Br₂⁺ (< 1%) (Figure 1a), (2) the favorable reaction between C₆₀ and C₂H₄Br₂⁺ could be charge exchange reaction leading to C₆₀⁺ (I.P. = 7.61) [6] because of the relatively high I.P. of C₂H₄Br₂⁺ (10.37 eV) [11], (3) the formation of the adduct by the ion molecule between C₆₀ and C₂H₄Br₂⁺ is less favorable by about 4 kcal mole⁻¹ as compared with the addition of C₂H₄Br⁺ with C₆₀

(Δ_fH values are taken from reference 11) and (4) at low pressures of C₂H₄Br₂ (< 5 × 10⁻⁶ mbar), the

Figure 1. (a) DBE/CI mass spectrum; (b) DCE/CI mass spectrum.

spectrum resembles the electron-impact ionization spectrum of C₆₀ with no adduct ions, which explains that C₆₀⁺ is unreactive. Further, the abundance of adduct ion (C₆₀ + C₂H₄Br)⁺ increases with the increase in the pressure of C₂H₄Br₂ (Figure 2a and b).

Figure 2. (a) DBE CI mass spectrum of C₆₀ at source housing pressure of 1 × 10⁻⁴ mbar; (b) DBE CI mass spectrum of C₆₀ at a source housing pressure 5 × 10⁻⁵ mbar.

The DBE CI spectrum also exhibits abundant C_{60}^+ , $C_{60}H^+$ and a weakly abundant ion corresponding to the loss of HBr from $(C_{60} + C_2H_4Br)^+$. The formation of C_{60}^+ can be attributed to a charge-transfer reaction between C_{60} and $C_2H_4Br^+$ as the reaction is estimated to be close to thermoneutral since the ionization energies of the $C_2H_4\dot{X}$ radicals [11-13] are close to the first ionization energy of C_{60} (I.P. = 7.61 eV) [6]. Similar results have been very recently reported by Nibbering and co-workers [14] for the ion-molecule reactions of $C_2H_4X^+$ ($X = Br, Cl$) with some alkenes under Fourier transform ion cyclotron resonance mass spectrometry (FT/ICR/MS). The charge-transfer reaction between C_{60} and $C_2H_4Br_2^+$ (I.P. = 10.37 eV) [11] may contribute to the formation of C_{60}^+ only to a minor extent because of the relatively low abundance of $C_2H_4Br_2^+$. Other interesting ions observed in the DBE CI spectrum are m/z 734, 747, and 748, corresponding to the addition of 14, 27, and 28 units to C_{60} , respectively. The formation of these ions cannot be explained by the addition of CH_2 , $\dot{C}_2H_3$ and C_2H_4 by ion-molecule reactions under DBE CI conditions as observed from earlier studies [8]. The only possibility is that the adduct $(C_{60} + C_2H_4Br)^+$ (m/z 827) can give rise to these ions by the loss of Br , HBr , and $\dot{C}H_2Br$, respectively. Loss of HBr is known to occur from the adduct

of benzene with $C_2H_4Br^+$ under DBE CI [8]. Addition elimination reactions are also reported under FT/ICR/MS conditions between $C_2H_4X^+$ and benzene [13]. Loss of Br and $\dot{C}H_2Br$ from the adduct suggest that a new C—C bond is formed between C_{60} and $C_2H_4Br^+$. The abundance of ions m/z 734, 747, and 748 decrease with the increase in the reagent pressure (Figure 2b), which can be attributed to the collisional stabilization of the adduct ion.

The ion-molecule reaction of C_{60} with $C_2H_4Cl^+$ was also studied as an extension of this work. We obtained similar results when the CI mass spectra of C_{60} -fullerene was taken with $C_2H_4Cl_2$ as the CI reagent instead of DBE. The spectrum (Figure 3a and b) shows weakly abundant ions corresponding to $(C_{60} + Cl)^+$ and $(C_{60} + CH_2Cl)^+$ in addition to the ions C_{60}^+ , $(C_{60} + C_2H_4Cl)^+$, $(C_{60} + C_2H_4Cl-HCl)^+$, and $(C_{60} + C_2H_4Cl-Cl)^+$. All the data obtained under DBE and DCE CI of C_{60} suggest C—C bond formation leading to halo alkylation of C_{60} -fullerene in the gas phase. Further evidence is obtained from the CID spectra of both the adduct ions $(C_{60} + C_2H_4Br)^+$ and $(C_{60} + C_2H_4Cl)^+$. Although the major ions observed in the CID spectra are C_{60}^+ and $C_{60}H^+$, ions corresponding to loss of $\dot{X}$, HX , and CH_2X are also seen. Loss of radicals $\dot{X}$ and $\dot{C}H_2X$ from the adduct ion makes us propose

Figure 3. (a) DCE CI mass spectrum of C_{60} at a source housing pressure of 1×10^{-4} mbar; (b) DCE CI mass spectrum of C_{60} at a source housing pressure of 5×10^{-5} mbar.

that C₆₀⁺ is formed from the adduct by the elimination of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{X}$, which is a likely process under high-energy collision conditions. The adduct ion (C₆₀ + C₂H₄X)⁺ has also been confirmed as precursor ion for both C₆₀⁺ and C₆₀H⁺.

In conclusion, we report that C₆₀-fullerene undergoes halo alkylation with C₂H₄Br⁺ and C₂H₄Cl⁺ under high pressure chemical ionization. The CI mass spectra and the CID spectra of the adducts suggest the halo alkylation involving C—C bond formation between C₆₀ and C₂H₄X⁺.

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