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# Reaction of $C_{60}^{2+}$ with $BCl_3$ : observation of fullerene cage shrinkage

Robert L. DeLeon, Craig P. Dufresne, Eric F. Rexer, James F. Garvey\*

*Department of Chemistry, NSM Complex, State University of New York at Buffalo, Buffalo, NY 14260-3000, USA*

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## Abstract

The reaction of  $BCl_3$  with  $C_{60}^{2+}$  was studied in a triple quadrupole mass spectrometer. A series of products of the type  $C_{2n}^+$ , with  $2n = 58 - 38$ , is observed. Aside from the  $C_2$  loss products, the only other major product formed is the  $C_{60}Cl^+$  adduct. The experimental data are consistent with a reaction mechanism which has a first step involving charge transfer from the doubly charged fullerene cation to the  $BCl_3 \cdot BF_3$ , whose ionization potential (IP) is too high for such a charge transfer mechanism, produced no such reaction products. The charge transfer step is followed by the loss of from one to 11  $C_2$  units from the  $C_{60}$  cage. A brief discussion of possible  $C_2$  loss mechanisms is presented. (Int J Mass Spectrom 185/186/187 (1999) 149–154) © 1999 Elsevier Science B.V.

*Keywords:* Fullerene; Fragmentation;  $BCl_3$  or boron trichloride;  $C_{60}^{2+}$

## 1. Introduction

The reactions of  $C_{60}$  and other fullerenes have been the subject of a large number of studies [1,2]. In gas phase studies, such as the present, aside from limited adduct formation with some strong nucleophiles [3–5], the  $C_{60}^+$  cation shows little or no reactivity because of the very low first ionization potential (IP), 7.6 eV, of  $C_{60}$  [6]. This present study is no exception, because no reaction products were observed using  $C_{60}^+$  as the reactant. Conversely,  $C_{60}^{2+}$  has a very rich chemistry which has been studied in some detail [7,8]. In the present work,  $C_{60}^{2+}$  has been reacted with the Lewis acid  $BCl_3$ . In anticipation of the results, the  $C_{60}$  cage loses

many  $C_2$  units. It has been demonstrated [9] that after the first removal it takes on the order of 6 eV to remove each successive  $C_2$  unit from  $C_{60}^+$ . This multiple loss of  $C_2$  units process has not been observed previously except in high energy collisions of fullerenes with  $>4$  keV projectiles [10] and in electron impact studies [9].

## 2. Experimental

The reaction of  $BCl_3$  with  $C_{60}^{2+}$  was studied in a VG-TRIO3 triple quadrupole mass spectrometer. This instrument was previously described [7], therefore, only a brief experimental description will be included. The  $BCl_3$  was obtained from Aldrich Chemicals and had a reported purity of 99.9%; it was used directly without further purification. The fullerene extract (SES Research) was introduced by a probe heated to 550 °C. The fullerene mixture used included  $C_{60}$ ,  $C_{70}$

\* Corresponding author.

Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

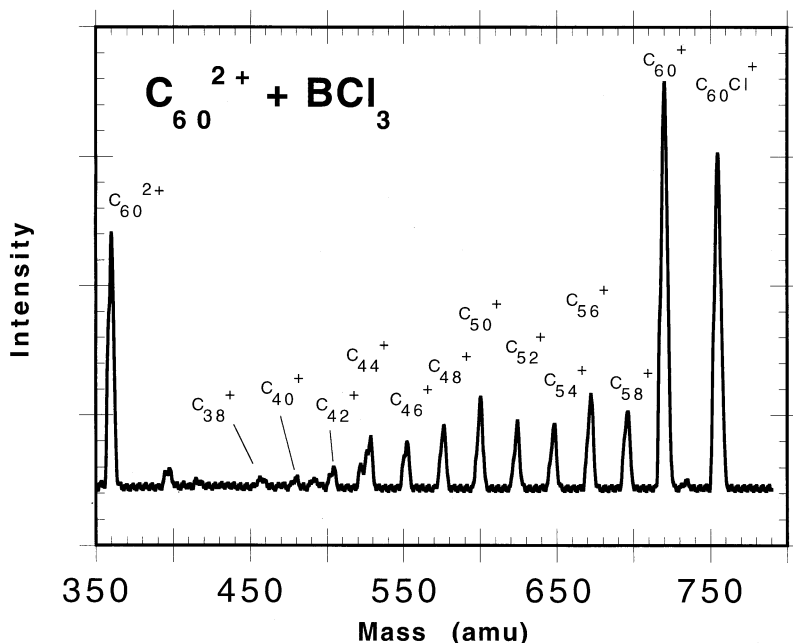


Fig. 1. High pressure (5 mT) survey spectrum of the products of the reaction of  $C_{60}^{2+}$  with  $BCl_3$ . The collision energy was 0.2 eV.

and lesser amounts of the smaller fullerenes. Electron impact ionization was used to produce the singly or doubly charged fullerene cations from their neutral parents with the same formula. The fullerene cations, mainly the  $C_{60}^{2+}$  ion for this study, are mass selected by the first quadrupole. The selected ions are channeled through the second quadrupole, which is radio frequency only, and acts as a collision cell. For the present study, the collision cell contains a 0.01–8 mTorr pressure of  $BCl_3$  gas. Brief studies using  $BF_3$  or  $CCl_4$  as the reaction gas will also be described. The  $C_{60}^{2+}$  undergoes multiple collisions with the  $BCl_3$  reaction gas in the collision cell. The laboratory frame collision energy can be varied from nearly 0–50 eV for doubly charged ions. Reaction products enter the third quadrupole where they are analyzed according to their mass-to-charge ratio. Both the collision energy and the collision cell pressure were systematically varied to deduce information on the reaction kinetics.

### 3. Results

As previously mentioned,  $C_{60}^+$  was found to be unreactive with  $BCl_3$ ,  $BF_3$  and  $CCl_4$  under the condi-

tions of the present study. The results of a high pressure, 5 mT, survey mass spectrum of the reaction of the reagent ion,  $C_{60}^{2+}$ , at 0.2 eV collision energy, with  $BCl_3$  are shown in Fig. 1. The largest product,  $C_{60}^+$ , is generated by direct partial charge transfer to  $BCl_3$ . The second largest product is the addition product  $C_{60}Cl^+$ . Both of these types of products are typical of the reaction of  $C_{60}^{2+}$  with other molecules having IP < 12 eV, such as  $O_2$ ,  $NH_3$  [11,12] and several other species [13] observed in this and other laboratories [8]. Also we note the presence of a series of peaks labeled  $C_{58}^+$ ,  $C_{56}^+$ , ...,  $C_{38}^+$ . These correspond to the formal loss of from 1–11  $C_2$  units from the  $C_{60}$  cage. To the best of our knowledge, this is the first observation of a gas phase chemical reaction which results in extensive loss of multiple  $C_2$  units from the fullerene cage. Typically, under the present experimental conditions with the other above molecules [11–13], a small peak corresponding to the loss of a single  $C_2$  unit is observed. Several small unassigned peaks are seen in Fig. 1 in the 350–500 u region. Other unassigned peaks are also observed below 350 u. A brief study of the reaction of  $C_{58}^{2+}$  and  $C_{70}^{2+}$  with  $BCl_3$  showed results similar to those of  $C_{60}^{2+}$  in that the

loss of a large number of  $C_2$  units from the fullerene cage was also observed similar to that depicted in Fig. 1. It should be pointed out that, with the present mass spectrometric technique, only ionic products will be observable. The presence of neutral products and their potential role in the energetics of the reactions cannot be specifically studied.

High resolution spectra at 5.1 mT and a collision energy of 0.2 eV were taken to confirm the product assignments. Fig. 2(a) shows a high resolution spectrum of  $C_{60}^+$ . The largest peak at 720 u corresponds to the isotope containing 60  $^{12}C$  atoms. Each succeeding peak is produced by replacing one more  $^{12}C$  atom by a  $^{13}C$  atom. The intensity ratios of these peaks are those expected based upon this assignment. Fig. 2(c) is the high resolution spectrum of the  $C_{58}^+$  product. The isotope intensity ratios are those expected for  $C_{58}^+$ . High resolution spectra of products due to the loss of more  $C_2$  units also exhibit the expected isotopic structure. Fig. 2(b) is the high resolution spectrum of the  $C_{60}Cl^+$  product. The observed peaks are explained by the presence of the  $^{35}Cl$  and  $^{37}Cl$  isotopes along with the  $^{12}C$  and  $^{13}C$  isotopes. The relative intensities of the peaks are closely fit by these assignments.

The collision energy dependence of the products was also studied. Fig. 3 shows the normalized intensity of the  $C_{60}^{2+}$  reactant,  $C_{60}^+$ ,  $C_{60}Cl^+$  and the first five  $C_2$  loss products as a function of collision energy at a pressure of 4.5 mT. Each peak is normalized by its maximum intensity for ease in comparison of the laboratory frame energy dependence of the products. In all cases, the intensity maximum occurs at low collision energy, less than 0.5 eV. The product intensities fall off rapidly to zero by 8 eV. We note the similarity of the energy dependence for all of the  $C_2$  loss products. This energy dependence is characteristic of an exothermic reaction with a small or zero exit barrier [14].

The pressure dependence of the reaction was also studied. Fig. 4 shows the normalized total ion current (TIC) of the first five  $C_2$  loss products as a function of the collision cell pressure. The collision energy was 0.2 eV. In order to compare the pressure dependence of these products, the fractional total ion current for

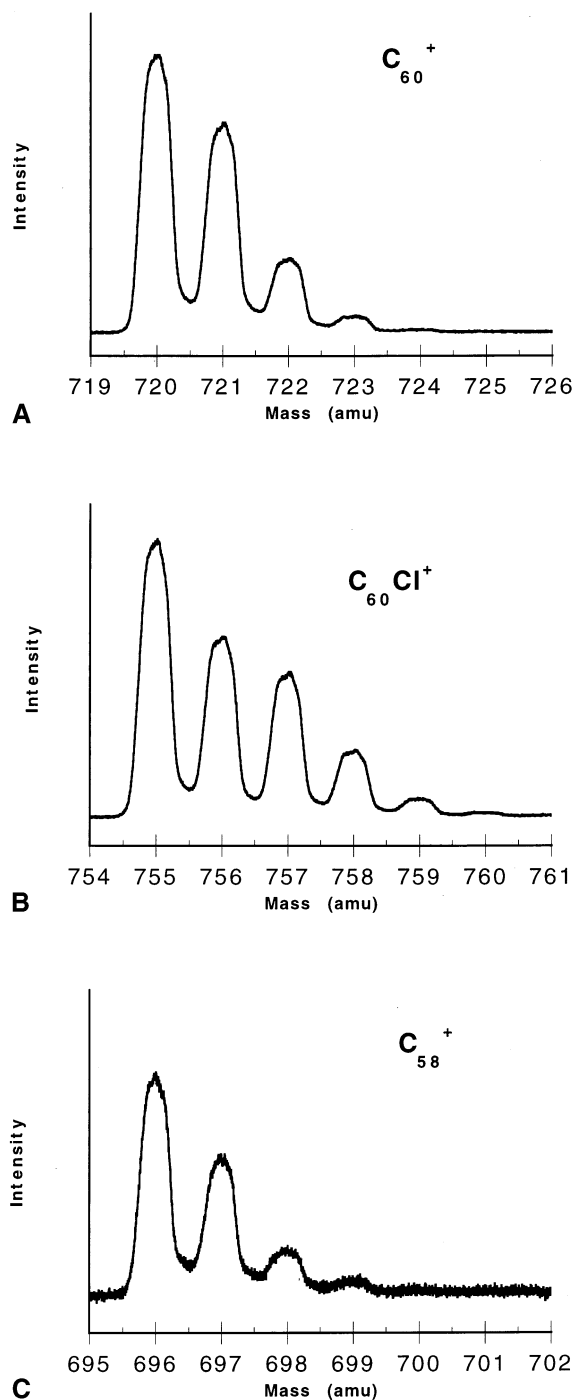


Fig. 2. High resolution spectra of the products at a pressure of 5.1 mT and a collision energy of 0.2 eV, (a)  $C_{60}^+$ , (b)  $C_{60}Cl^+$ , (c)  $C_{58}^+$ .

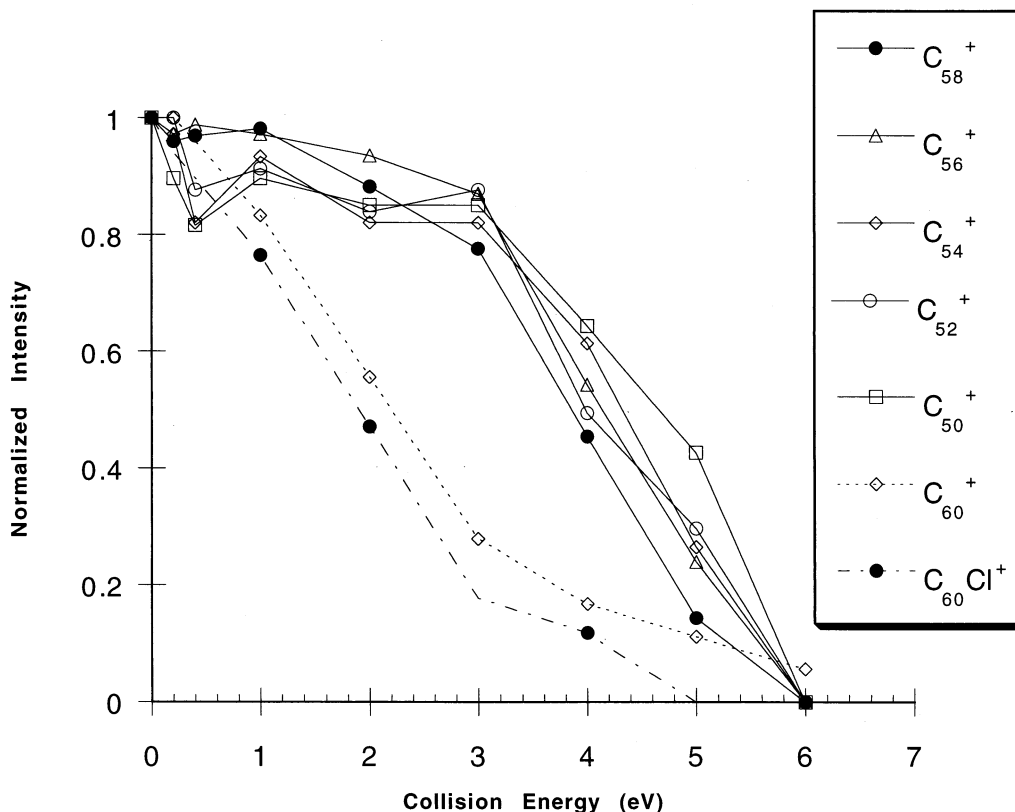


Fig. 3. Normalized collision energy dependence of the products:  $C_{60}^+$ ,  $C_{60}Cl^+$ ,  $C_{58}^+$ ,  $C_{56}^+$ ,  $C_{54}^+$ ,  $C_{52}^+$ , and  $C_{50}^+$ . The collision cell pressure was 4.5 mT of  $BCl_3$ .

each product was computed and normalized by the maximum value for each product in the range of 0–5 mTorr. The  $C_2$  loss products increase strongly with an increase in pressure and exhibit a very similar pressure dependence.

#### 4. Discussion

The reaction of  $C_{60}^{2+}$  with  $BCl_3$ ,  $BF_3$  and  $CCl_4$  will be discussed in terms of their relative ionization potentials. Table 1 shows the IP's of the species of interest.

The reaction of  $BCl_3$  with  $C_{60}^{2+}$  was predicted to occur based upon its IP < 12 eV. Using the present experimental method, species with IP's less than ~12 eV have been shown to react with  $C_{60}^{2+}$  by a charge transfer mechanism [11–13]. An extensive set of

measurements has been made by Bohme and co-workers [5,8] with the difference that their reagent ions are thermalized at room temperature. The difference in the energy of the reagent ions prepared by the two different experimental techniques accounts for the observed reactivity of  $O_2$  with an IP as high as 12.1 eV for the present experimental conditions. This is consistent with the  $C_{60}^+$  IP of 11.4 eV with the deficit being made up by energy deposited in the reagent ion during the electron impact ionization process. Studies such as [9] have indicated the ability of  $C_{60}$  to absorb internal excitation of electronic and vibrational degrees of freedom during electron impact ionization. This also is consistent with the observation of no reactivity of  $C_{60}^{2+}$  with  $BF_3$  because the  $BF_3$  IP is too high. Similarly, the extremely low IP of  $C_{60}$  accounts for the lack of reactivity of  $C_{60}^+$  in these

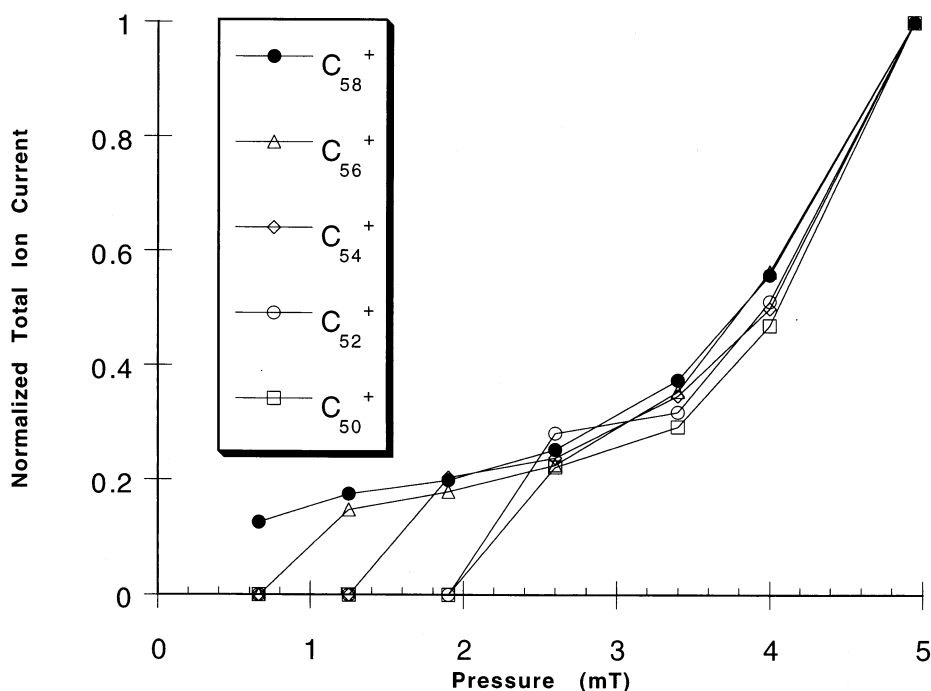


Fig. 4. Pressure dependence of the normalized total ion current of the C<sub>2</sub> loss products: C<sub>58</sub><sup>+</sup>, C<sub>56</sub><sup>+</sup>, C<sub>54</sub><sup>+</sup>, C<sub>52</sub><sup>+</sup> and C<sub>50</sub><sup>+</sup>. The collision energy was 0.2 eV.

experiments. However, CCl<sub>4</sub> was found to be unreactive with C<sub>60</sub><sup>2+</sup> and species such as O<sub>2</sub> and NH<sub>3</sub> [12,13] only react to produce loss of at most one C<sub>2</sub> unit. This indicates that the BCl<sub>3</sub> molecule reactivity is unique, possibly because the affinity of the electron deficient central B atom for the electron rich C<sub>60</sub>.

The present experimental method cannot definitively establish a reaction mechanism for the loss of multiple C<sub>2</sub> units from the fullerene cage. The colli-

sion energy dependence indicates an exothermic reaction with a very low exit barrier [14]. The pressure dependence of all of the C<sub>2</sub> loss products is practically identical. This could be caused by an initial step being rate limiting followed by an extremely rapid sequential loss of subsequent C<sub>2</sub> units. An examination of the low pressure data in Fig. 4 gives some indication that this may be the case. Note that at the lowest pressures that the appearance of each successive loss of another C<sub>2</sub> unit grows in at a higher pressure. The great difficulty in invoking such a mechanism is in understanding the energy source to drive the sequential loss. Removal of the first C<sub>2</sub> unit is a very high energy process, 36 eV and each subsequent removal requires about six more eV [9]. The majority of this energy could only come from the initial excitation during the formation of the ion by the electron impact because no other substantial energy source is available.

A second, energetically less expensive potential reaction mechanism seems to be the simultaneous removal of the entire C<sub>2n</sub> fragment from the fullerene

Table 1  
Ionization potentials

Species	Ionization potential (eV) <sup>a</sup>
C <sub>60</sub>	7.6
C <sub>60</sub> <sup>+</sup>	11.4
BCl <sub>3</sub>	11.7
BF <sub>3</sub>	15.5
CCl <sub>4</sub>	11.5
O <sub>2</sub>	12.1
NH <sub>3</sub>	10.1

<sup>a</sup> Taken from the National Institute of Standards and Technology data base.

cage. If this event were equally likely for the range of 1–8 C<sub>2</sub> units it would explain the flat product distribution instead of a rapid falloff of product intensities expected to characterize a sequential loss. Such a mechanism would also be consistent with the observed similarity of the energy dependencies of the C<sub>2</sub> loss products. It is interesting to note that even for such an extensively studied process as electron impact fragmentation of fullerene ions [9], that is has not yet been possible to distinguish between single step and sequential fragmentation mechanisms.

In conclusion, the reaction of BCl<sub>3</sub> with C<sub>60</sub><sup>2+</sup> is unique, among the hundreds of gas phase fullerene dication reactions studied, in that it produces a series of products of the form C<sub>2n</sub><sup>+</sup> where 2n = 58 – 38. Unfortunately, neither the exact reaction mechanism nor the nature of these products can be stated with certainty solely on the basis of the present experimental data. However, it seems reasonable to speculate that the products retain the fullerene cage structure.

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