Chlorination of charged buckyballs: reactions of $C_{60}^{x+}$ cations ($x = 1–3$) with Cl$_2$, CCl$_4$, CDCl$_3$, CH$_2$Cl$_2$, and CH$_3$Cl

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Abstract

The chlorination of singly and multiply charged $C_{60}$ cations has been investigated with the selected-ion flow tube technique. Observations are reported for the reactions of $C_{60}^+$, $C_{60}^{2+}$ and $C_{60}^{3+}$ with Cl$_2$, CCl$_4$, CDCl$_3$, CH$_2$Cl$_2$ and CH$_3$Cl at room temperature (295 ± 2 K) in helium at a total pressure of 0.35 ± 0.02 Torr. $C_{60}^+$ and $C_{60}^{2+}$ were observed not to chlorinate, or react in any other way, with these five molecules. Chlorine also did not react with $C_{60}^{3+}$, but bimolecular chloride transfer and electron transfer reactions, reactions that result in charge reduction/charge separation, were observed to occur with CCl$_4$, CDCl$_3$, CH$_2$Cl$_2$ and CH$_3$Cl. Chloride transfer was the predominant channel seen with CCl$_4$, CDCl$_3$ and CH$_2$Cl$_2$ while electron transfer dominates the reaction with CH$_3$Cl. These results are consistent with trends in chloride affinity and ionization energy. The reluctant chlorination of the first two charge states of $C_{60}$ is attributed to the energy required to distort the carbon cage upon bond formation, while the observed chloride transfer to $C_{60}^{3+}$ is attributed to the greater electrostatic interactions with this ion. (Int J Mass Spectrom 182/183 (1999) 349–356) © 1999 Elsevier Science B.V.

Keywords: Fullerene ions; Chlorine; Chlorinated methanes; Chloride transfer; Kinetics; Charge separation; Selected-ion flow tube

1. Introduction

Ben Freiser had an early, strong interest in the formation of exohedral atomic adduct ions of $C_{60}$. For example, he was the first to demonstrate the laboratory formation of a variety of externally-bound transition-metal species $MC_{60}^+$ ($M = V, VO, Fe, Co, Ni, Cu, Rh, La$) [1,2]. The adduct ions were reported to be formed by direct attachment of $M^+$ ions generated by laser desorption to $C_{60}$ molecules at the low pressure ($\sim 1 \times 10^{-7}$ Torr) of a Fourier-transform mass spectrometer. He then went on to investigate the formation of other organometallic derivatives of $C_{60}^{3+}$ [3,4]. Our own experimental survey of the chemistry of fullerene cations showed that the second and third charge states of $C_{60}$ also may be derivatized at room temperature in helium buffer gas at $\sim 0.35$ Torr in a selected-ion flow tube (SIFT) apparatus. But we noticed that the occurrence of derivatization was very sensitive to the charge state of $C_{60}^{x+}$ [5]. Briefly, we found that monocations of $C_{60}$ under SIFT conditions bond only with strong nucleophiles such as ammonia and satu-
rated amines [6] and with molecules capable of Diels-Alder additions [7]. A reaction of \( C_{60}^+ \) with iron pentacarbonyl, first observed by Freiser et al. [8], produces derivatized \( C_{60} \text{Fe}(CO)^+ \) [9] and is the only example of a \textit{bimolecular} derivatization reaction with \( C_{60} \) that we have observed to date. Covalent bonding to \( C_{60} \) is difficult because it is necessary to distort the \( C_{60} \) carbon cage at the C site of bond formation with the substituent so as to achieve the required \( sp^3 \) hybridization. This energy barrier is more readily overcome with the higher charge states of \( C_{60} \) as the electrostatic interaction between the reactants increases [10]. For example, we have previously found \( C_{60}^{2+} \) to be very reactive toward many molecules and to exhibit a rich addition chemistry, although electron transfer becomes an important competitive reaction channel. With \( C_{60}^{3+} \), also a very reactive cation, this competition often favours electron transfer or even dissociative electron transfer, but addition is still observed [11].

Here we explore the ease of chlorination of charged buckyballs as a function of charge state in \textit{bimolecular} reactions with chlorine gas and chlorinated methanes. We have previously reported one example of a chlorination study [12]. HCl was observed not to react with \( C_{60}^+ \) or \( C_{60}^{2+} \), \( k < 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), but increasing the charge to +3 resulted in a moderately fast reaction, \( k = 3.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), leading to the two interesting charge-separation channels (1a) and (1b). (88 \( \pm \) 5\%) of the reactive collisions led to chlorination

\[
C_{60}^{1+} + \text{HCl} \rightarrow C_{60}\text{Cl}^{2+} + \text{H}^+ \quad (1a)
\]

\[
\rightarrow C_{60}\text{H}^{2+} + \text{Cl}^+ \quad (1b)
\]

Remarkably accompanied by formation of a proton, channel (1a), while (12 \( \pm \) 5\%) resulted in hydrogenation accompanied by \( \text{Cl}^+ \) formation. Both channels (1a) and (1b) involve charge separation in the products and so are constrained by energy barriers arising from coulombic repulsion [10]. No further chlorination of \( C_{60}\text{Cl}^{2+} \) was observed.

It is interesting to note that neutral \( C_{60} \) can be chlorinated only with some difficulty. Olah et al. [13] have reported that treatment of \( C_{60} \) with chlorine in chloro-organic solvents at various temperatures did not result in any detectable reaction. However, \( C_{60} \) could be chlorinated with up to 24 chlorine atoms on average at 250 °C when exposed to a slow stream of chlorine gas for several hours. At higher temperature the chlorination occurred more rapidly but complete chlorination could not be achieved. Also, the polychlorofullerenes were observed to be relatively unstable: they were observed to completely dechlorinate at 400 °C under argon and under mild ionization conditions in fast-atom bombardment (FAB) and field-ionization mass spectrometry (FIMS) experiments.

2. Experimental

The ion/molecule reactions of the fullerene cations \( C_{60}^+ \) (\( x = 1, 2, 3 \)) with the selected chlorinated molecules were achieved within the reaction region of a SIFT mass spectrometer in helium carrier gas at 0.35 \( \pm \) 0.01 Torr and 294 \( \pm \) 3 K [14,15]. The fullerene cations were produced in an ion source by electron impact ionization of the vapour of a sample of fullerene powder (~99.5 \% \( C_{60} \), SES Research): \( C_{60}^+ \) at ~50 eV, \( C_{60}^{2+} \) at ~80 eV and \( C_{60}^{3+} \) at ~100 eV. The desired \( C_{60} \) cation was selected with a quadrupole mass filter, injected into the flow tube containing He, and then allowed to thermalize by collisions with He (~4 \times 10^5 collisions) prior to entering the reaction region further downstream.

Chlorine and methyl chloride were obtained from Matheson (99.9\% and 99.5\%, respectively). Deuterated chloroform was obtained from Sigma (99.8 atom % D). Methylene chloride and chloroform were obtained from BDH (99.9\%). The vapours of the liquids were added into the flow tube as 10\% (CCl\(_4\)), 3–5\% (CDCl\(_3\)) and 25–28\% (CH\(_2\)Cl\(_2\)) mixtures in helium.

Rate coefficients were measured with pure helium buffer gas at a total pressure of 0.35 \( \pm \) 0.02 Torr in the usual manner [14,15] and have an uncertainty estimated to be less than \( \pm 30\% \).
C 60 molecules investigated, k exceed 11.2 eV. There was no evidence for Cl 2 ionization energies of the five molecules investigated. The electron-recombination energies of these molecules which span a range from 58 kcal mol -1 (for CCl 3 ) to 84 kcal mol -1 (for Cl 2 ). The Cl - and Cl affinities of C 60 are not known. The failure to observe reactions cannot be used to determine limiting values for the Cl - and Cl affinities of C 60 since these reactions are kinetically rather than thermodynamically controlled. A barrier is expected to be associated with C-Cl bond formation with C 60 as a consequence of the rehybridization from largely sp 2 to largely sp 3 required at the C atom on the C 60 surface that becomes bonded [10]. Hydride transfer also was not observed. The occurrence of H-atom transfer was difficult to rule out experimentally due to insufficient resolution of the detection quadrupole. However, available H-atom affinities [19] (see Table 2) indicate that H-atom abstraction is endothermic by at least 29 kcal mol -1 .

3.2. Reactions with C 60+ 

C 60+ was also observed not to react with any of the five molecules investigated. The electron-recombination energy of C 60+ , RE(C 60+ ) = 11.36 ± 0.05 eV [11] is comparable to the ionization energies of these molecules which span a range from 11.26 ± 0.03 eV for CH 3 Cl to 11.48 ± 0.01 eV for Cl 2 (see Table 2). However, electron transfer is not expected to occur due to the barrier arising from coulomb repulsion in the resulting charge separation [10]. Our previous measurements have demonstrated an onset for electron transfer with molecules having ionization energy (IE) = 9.51 eV [11]. There was again no evidence for Cl - transfer or Cl abstraction and, again, the Cl - and Cl affinities of C 60+ are not known. The kinetic control for Cl - transfer reactions with C 60+ will include the barrier arising from coulombic repulsion in the resulting charge separation [10]. Hydride transfer again was not observed and available H-atom affinities [19] (see Table 2) indicate that H-atom abstraction in this case is endothermic by at least 12 ± 10 kcal mol -1 .
Table 2
Helpful thermochemical data used to calculate enthalpies of reaction. Ionization energies are in eV. Atom and anion affinities are in kcal mol\(^{-1}\). The data were taken from References 17 and 18, unless indicated otherwise by references in brackets. Unless indicated otherwise, uncertainties are \(\pm \frac{1}{11} \text{kcal mol}^{-1}\). Numbers in parentheses have a higher uncertainty.

<table>
<thead>
<tr>
<th>(\text{A} )</th>
<th>(\text{IE} )</th>
<th>(\text{HA} )</th>
<th>(\text{ClA} )</th>
<th>(\text{HA} )</th>
<th>(\text{ClA} )</th>
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<td>Cl(^-)</td>
<td>11.48 ± 0.01</td>
<td>58</td>
<td>273.6</td>
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<tr>
<td>Cl(^+)</td>
<td>84</td>
<td>226</td>
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<tr>
<td>CH(_3)</td>
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<td>103</td>
<td>83</td>
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<tr>
<td>CH(_2\Cl)</td>
<td>11.26 ± 0.03</td>
<td>(283)</td>
<td></td>
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<tr>
<td>CH(_2\Cl)(^+)</td>
<td>101</td>
<td>80</td>
<td>(197)</td>
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<tr>
<td>CHCl(_2)</td>
<td>11.33 ± 0.04</td>
<td>96</td>
<td>71</td>
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<td>CHCl(_2)(^+)</td>
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<td>(268)</td>
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</tr>
<tr>
<td>CCl(_3)</td>
<td>11.37 ± 0.02</td>
<td>(264)</td>
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<tr>
<td>CCl(_4)</td>
<td>11.47 ± 0.01</td>
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<tr>
<td>C(_60)</td>
<td>7.64 ± 0.02 [18]</td>
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<tr>
<td>C(_60)(^+)</td>
<td>11.36 ± 0.05 [11]</td>
<td>67 ± 2 [19]</td>
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<tr>
<td>C(_60)(^2+)</td>
<td>15.6 ± 0.5 [11]</td>
<td>84 ± 10 [19]</td>
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<tr>
<td>C(_60)(^3+)</td>
<td>16.6 ± 1 [20]</td>
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</table>

3.3. Reactions with \(C_{60}^{3+}\)

Four of the five molecules of type XCl chosen for study reacted with \(C_{60}^{3+}\). Chlorine did not react. There was no evidence for Cl\(^-\) transfer or Cl\(^+\) abstraction. According to currently-available thermodynamic data, the reaction with chlorine is the most (thermodynamically) favourable with regard to Cl\(^-\) transfer and the least favourable to the transfer of Cl\(^2\) to \(C_{60}^{3+}\): X = Cl\(^-\) has the lowest Cl-atom affinity and X\(^+\) = Cl\(^+\) has the highest Cl\(^-\) affinity. The nonreaction with chlorine reported here supersedes our early qualitative report of a fast reaction [21].

The molecules \(\text{CH}_x\Cl_{4-x}\) with \(x = 0\text{-}3\) were observed to react with \(C_{60}^{3+}\) by bimolecular chloride transfer and electron transfer, reactions that result in charge reduction/charge separation, according to Eq. (2):

\[
C_{60}^{3+} + \text{CH}_x\Cl_{4-x} \rightarrow C_{60}\Cl^{2+} + \text{CH}_x\Cl_{3-x}^{+} \quad (2a)
\]

\[
C_{60}^{3+} + \text{CH}_x\Cl_{4-x} \rightarrow C_{60}^{2+} + \text{CH}_x\Cl_{3-x}^{+} \quad (2b)
\]

Table 2 shows that the Cl\(^-\) affinity, Cl\(^-\)A (\(\text{CH}_x\Cl_{3-x}^{+}\)), increases and IE(\(\text{CH}_x\Cl_{4-x}\)) decreases as \(x\) increases. Thus Cl\(^-\) transfer is expected to be most favourable with carbon tetrachloride and electron transfer is most favourable with methyl chloride and this is what is observed.

3.3.1. Reactions with CCl\(_4\) and DCCl\(_3\)

Plots of observed reactant and product ion signals versus neutral reactant flow for the reactions of carbon tetrachloride and chloroform with \(C_{60}^{3+}\) are shown in Figs. 1 and 2. Only Cl\(^-\) transfer was observed. There was no evidence for the occurrence of electron transfer (<1%). Also, neither of the product ions of the charge-separation reactions reacted further with CCl\(_4\), \(k < 1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\); polychlorination was not observed. Both chloride-transfer reactions are rapid and efficient. The reaction with CCl\(_4\), which is more exothermic by 8 kcal mol\(^{-1}\) than the reaction with DCCl\(_3\), is slightly faster. When compared to calculated collision rate coefficients using average-dipole orientation (ADO) theory [22], the measured rate coefficients imply reaction efficiencies of 0.76 and 0.33, respectively.
3.3.2. Reactions with CH\textsubscript{2}Cl\textsubscript{2}

The reaction of C\textsubscript{60} with methylene chloride is more than 20 times slower than the reaction with chloroform. Figure 3 shows that CH\textsubscript{2}Cl\textsubscript{2} reacts with C\textsubscript{60} primarily by Cl\textsuperscript{-} abstraction (\(\approx 91\%\)), but there is also some evidence of a minor (\(\leq 9\%\)) channel leading to electron transfer, this is evident from the product ratio analysis shown in Fig. 4 indicating what could be a finite intercept at zero flow for the % production of C\textsubscript{60}Cl\textsuperscript{2+}. Figure 4 indicates that most of the C\textsubscript{60}Cl\textsuperscript{2+} observed at higher flows is produced from C\textsubscript{60}Cl\textsuperscript{2+} in either a secondary reaction or collisional dissociation of a fraction of the C\textsubscript{60}Cl\textsuperscript{2+} produced in the primary reaction with the added methylene chloride. The former would require a relatively weak C\textsubscript{60}Cl\textsuperscript{2+}–Cl bond, whereas the latter would require internal or kinetic excitation of some of the C\textsubscript{60}Cl\textsuperscript{2+} produced in the primary reaction. Again, there was no evidence for the further chlorination of C\textsubscript{60}Cl\textsuperscript{2+} by higher-order reactions.

The observed CH\textsubscript{2}Cl\textsuperscript{+} product of the Cl\textsuperscript{-} transfer charge-separation reaction appears to react further with methylene chloride to produce CHCl\textsubscript{2}+ and C\textsubscript{2}H\textsubscript{3}Cl\textsubscript{2}+ according to reaction (3):

\[
\text{CH}_2\text{Cl}^+ + \text{CH}_2\text{Cl}_2 \rightarrow \text{CHCl}_2^+ + \text{CH}_3\text{Cl} \quad (3a)
\]

\[
\rightarrow \text{C}_2\text{H}_3\text{Cl}_2^+ + \text{HCl} \quad (3b)
\]

This chemistry was not investigated separately.

3.3.3. Reactions with CH\textsubscript{3}Cl

Methyl chloride also reacts slowly with C\textsubscript{60}+ but, unlike the reactions of the other chlorinated methanes,
electron transfer, rather than chloride transfer, is the main reaction channel. Figure 5 shows data for the occurrence of the following three reaction channels:

$$C_{60}^{3+} + CH_3Cl \rightarrow C_{60}^{2+} + CH_3Cl^+$$  \hspace{2cm} (4a)

$$\rightarrow C_{60}Cl^{2+} + CH_3^+$$  \hspace{2cm} (4b)

$$\rightarrow C_{60}CH_3^{2+} + Cl^+$$  \hspace{2cm} (4c)

The product ratio plot in Fig. 4 again indicates the same conversion of some $C_{60}Cl^{2+}$ to $C_{60}^{2+}$ at low flows of reactant observed with $CH_2Cl_2$ and presumably has the same origin. A minor fraction (11%) of the collisions of $C_{60}^{3+}$ with $CH_2Cl_2$ lead to the production of $C_{60}CH_3^{2+}$ by C–C bond formation, but electron transfer clearly predominates. The ionization energy of $CH_3Cl$ of 11.26 eV lies close to the onset for electron transfer of 11.2 eV that we have determined previously in a general study of electron-transfer reactions with $C_{60}^{3+}$. The recombination energy of $C_{60}^{3+}$ is more than 4 eV higher (see Table 2) so that electron transfer with $CH_3Cl$ is very exothermic. But electron transfer is inhibited by the barrier that arises from the coulombic repulsion between the doubly and singly charged product ions [11]. It appears that the electron transfer reaction with $CH_3Cl$, which occurs about 100 times slower than the collision rate, is close to surmounting this barrier. It should be noted that $CH_3Cl$ has the lowest ionization energy of the five molecules investigated and this accounts for our failure to observe electron transfer to $C_{60}^{3+}$ with the other four molecules. The observation of chloride transfer with $CH_3Cl$ allows the chloride affinity of $C_{60}^{3+}$ to be set at $\geq 226$ kcal mol$^{-1}$ (see Table 2).

The observed $CH_3Cl^+$ product of the $Cl^-$ transfer charge-separation reaction appears to react further with methyl chloride to produce $(CH_3)_2Cl^+$ and $C_2H_5Cl_2^+$. Separate investigations of this chemistry in which $CH_3Cl^+$ was produced from methyl chloride by electron impact in the ion source of the SIFT apparatus [23] have shown that these two ions arise from the following reaction sequence: 

$$C_{60}^{3+} + CH_3Cl \rightarrow C_{60}^{2+} + CH_3Cl^+$$  \hspace{2cm} (4a)

$$\rightarrow C_{60}Cl^{2+} + CH_3^+$$  \hspace{2cm} (4b)

$$\rightarrow C_{60}CH_3^{2+} + Cl^+$$  \hspace{2cm} (4c)

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4. Conclusions

Our measurements have shown that positively charged buckminsterfullerenes are not readily chlorinated at room temperature in reactions with chlorine and chlorinated methanes. This is certainly true of the first two charge states and, according to Olah et al. [13], is also the case with neutral C\textsubscript{60}. We suggest that these nonreactions are kinetically rather than thermodynamically controlled, viz. that kinetic barriers arise from the distortion of the C\textsubscript{60} carbon cage that is required for near-\textit{sp}\textsuperscript{3} hybridization at the C site of bond formation with Cl.

The electrostatic interaction between reagent molecules and C\textsuperscript{3+} is sufficient to promote chloride transfer to this ion in charge-reduction/charge-separation reactions with CCl\textsubscript{4}, CDCl\textsubscript{3}, and CH\textsubscript{2}Cl\textsubscript{2}. With CH\textsubscript{3}Cl chloride transfer is dominated by electron transfer but is still observed. The results are consistent with known trends in chloride affinity and ionization energy. Single or multiple chlorination with chlorine, of the type reported for neutral C\textsubscript{60} at elevated temperatures [13], does not proceed with the first three charge states of C\textsubscript{60} under SIFT conditions \textit{at room temperature}.

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References