doi:10.1246/cl.2011.478

Published on the web April 16, 2011

Formation Mechanism of C_2^+ in a Gas Chromatography Coupled to Time-of-flight Mass Spectrometry

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The presence of several inorganic compounds induced the degradation of poly(tetrafluoroethylene) into C_2^+ in different abundances in a gas chromatography coupled to time-of-flight mass spectrometry. A probable formation mechanism of C_2^+ was proposed. The finding is significant and useful for generating molecular C_2 ions in laboratory conditions.

Unlike N_2, O_2, and F_2 molecules, a C_2 molecule and its associated ions such as C_2^+, C_2^-, and C_2^{2+} ions are quite rare,[1,2] owing to their low bonding stability and high reactivity.[3] So far, there is little data describing the variability in relative abundances (RA, %) of these species. This may be because most of them have only been found in interstellar space or under extreme laboratory conditions such as production by laser ablation of graphite.[4–7] In this case, it would be very interesting and useful to obtain the molecular C_2 ions in laboratory conditions for theoretical considerations, especially for practical applications.

In this work, C_2^+ was observed under vacuum of a gas chromatography coupled to time-of-flight mass spectrometry (GC-TOF-MS). It was found that the presence of three inorganic compounds: ammonium molybdate tetrahydrate (AMT), NH_4Cl, and MoO_3, changed the degradation pattern of poly(tetrafluoroethylene) (PTFE) and induced C_2^+ in different RA values. The preparation method and heating program of the adducts of PTFE with the compounds in GC-TOF-MS measurement were based on reported work.[8,9] A proposed mechanism describing the degradation process of PTFE is also illustrated to explain the difference in RA values between PTFE and its adducts.

Figure 1 illustrates the total ion current (TIC) curves of PTFE and its adducts. Free PTFE did not decompose until 32.25 min (the first step), and then underwent a rapid thermal decomposition at 35.82 min (the second step).

The comparison of the TIC profiles of PTFE and its adducts provided clear evidence of different effects of the inorganic compounds on the thermal degradation of PTFE in vacuum. For example, the presence of NH_4Cl greatly promoted the first step degradation of PTFE at 31.94 min. A similar effect, but lower in intensity, was also discovered in the case of the existence of AMT. Moreover, no noticeable release signals concerning the decomposition of NH_4Cl or AMT itself were seen. Contrarily, the addition of free MoO_3 resulted in a decrease in the level of the first step degradation of PTFE.

Figure 2 depicted mass spectra of free PTFE and its adducts with AMT and NH_4Cl at the first degradation step. The PTFE only showed two main peaks at m/z 43.990 (CO_2^+) and 84.971 (SiF_3^+). In our opinion, the appearance of the two fragments was a result of the onset of etching of the activated species derived from the degradation of PTFE on the quartz injection chamber, as described in eq 1.[10,11] Interestingly, no observable peaks appeared in the mass spectrum of PTFE–MoO_3, suggesting the etching did not happen in this case.

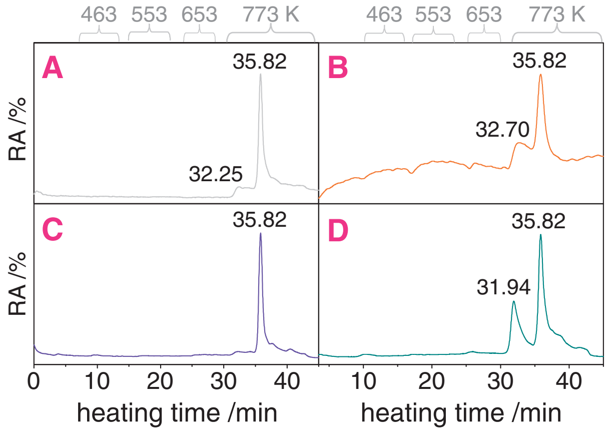

Figure 1. TIC curves of PTFE (A) and its adducts with AMT (B), MoO_3 (C), and NH_4Cl (D).

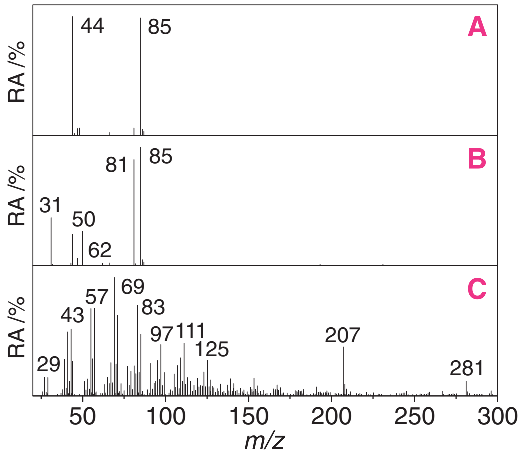

Figure 2. Mass spectra of PTFE (A) and its adducts with AMT (B), NH_4Cl (C) at the first degradation step.

$$\mathrm{PTFE} + \mathrm{SiO_2} \xrightarrow{\Delta} \mathrm{SiF_3}\uparrow + \mathrm{CO_2}\uparrow \qquad (1)$$

Besides the two strong peaks due to CO_2^+ and SiF_3^+, several new peaks such as m/z 30.999 (CF^+), 49.997 (CF_2^+), and 80.994 ($C_2F_3^+$) appeared in Figure 2B. This means that the degradation of the PTFE was promoted by the presence of AMT.

Surprisingly, numerous peaks appeared in the mass spectrum of PTFE–NH_4Cl. And many of them are hydrocarbon ions such as m/z 29.038 ($C_2H_5^+$), 43.055 ($C_3H_7^+$), 57.071 ($C_4H_9^+$), 69.071 ($C_5H_9^+$), 83.086 ($C_6H_{11}^+$), 97.102 ($C_7H_{13}^+$), 111.118

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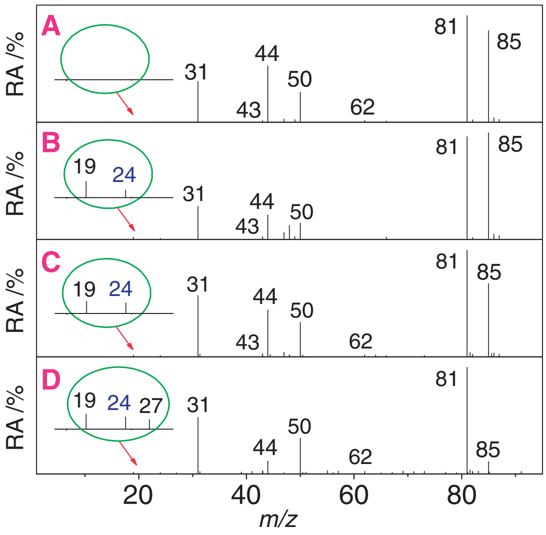

Figure 3. Mass spectra of PTFE (A) and its adducts with AMT (B), MoO_3 (C), and NH_4Cl (D) at 35.82 min. The insets are the enlargement of the graphs in the range of m/z between 15 and 30, with a magnification of 20 times relative to the primary vertical axis.

($C_8H_{15}^+$), and $C_aH_bF_c^+$ (a, b, and c are integer) ions such as 73.047 ($C_4H_6F^+$), 107.065 ($C_5H_9F_2^+$), 133.016 ($C_3H_2F_5^+$), and 207.034 ($C_{10}H_{13}Cl_2^+$). This phenomenon strongly implies that there is interaction between HCl(g) and PTFE in the system.

Figure 3 shows the mass spectra of PTFE and its adducts at the second degradation step (main degradation process). As shown in Figures 3B–3D, the maximum degradation time of PTFE in the presence of the inorganic compounds did not change at all (at 35.82 min). And all major peaks, such as CF^+, CF_2^+, $C_2F_3^+$, and SiF_3^+ in the mass spectrum of PTFE (Figure 3A) also occurred in the cases of the adducts (Figures 3B–3D). These suggested that the main degradation process of PTFE was not fundamentally affected by the addition of the inorganic compounds. However, there was some interesting difference between PTFE and its adducts.

From Figure 3A and its inset, no signals of C_2^+ at m/z 24.000 were detected in the mass spectrum, but C_2^+ with a RA value of 1.12% (Figure 3B and its inset) was observable in the case of PTFE–AMT. Similar situations also arose in PTFE–NH_4Cl (1.36%) and PTFE–MoO_3 (1.14%). This led us to consider that the generation of C_2^+ originated from the effect of the inorganic components on the degradation mechanism of PTFE. On the basis of the signals shown in Figures 2 and 3, a proposed process with respect to the thermal depolymerization of PTFE was plotted in Figure 4.

Initially, a small amount of PTFE interacted with SiO_2 at 773 K. Subsequently, the fluorocarbon chain of PTFE began to degrade into small fragments such as $C_2F_2^+$, (61.998) and $C_2F_3^+$. And then, the small fragments continued to decompose into smaller fragments such as CF^+, C_2F^+, and CF_2^+, as shown in Figure 4.

It is worth noting that the two fragments: $C_2F_2^+$ and C_2F^+ may play an important role in the formation of C_2^+. Several proposed chemical reactions describing the decomposition process of the $C_2F_2^+$ are given in eqs 2–4.

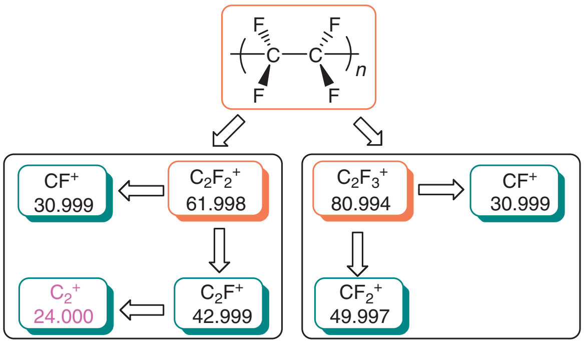

Figure 4. A proposed depolymerization mechanism of PTFE.

$$C_2F_2^+ \rightarrow 2CF^+ + e^- \qquad (2)$$

$$C_2F_2^+ \xrightarrow{a} C_2F^+ + F \xrightarrow{b} C_2^+ + F \qquad (3)$$

$$C_2F_2^+ \cancel{\rightarrow} C_2^+ + F_2 \qquad (4)$$

According to the mass spectra in Figure 3, we inferred that the inorganic compounds might have an influence on the decomposition performance of $C_2F_2^+$ and C_2F^+. On the one hand, as seen in Figure 3, the RA of CF^+ was much higher than that of $C_2F_2^+$ or C_2F^+, suggesting that during the degradation of PTFE, eq 2 was the major decomposition reaction of $C_2F_2^+$, and eq 3a was very difficult, since the RA values of both C_2F^+ (m/z, 42.999) and F^+ (m/z, 19.000) were rather low especially in Figure 3A. On the other hand, the RA value of C_2F^+ increased while the C_2^+ signal appeared in the mass spectra of the adducts when compared to that of free PTFE. All of these provide an important indication that the inorganic components did not have much influence on eq 2, but greatly promoted the formation of C_2^+ by eq 3, rather than by eq 4 because F_2^+ was not found in these cases. That is why C_2^+ was present in the mass spectra of the adducts but not in the mass spectrum of free PTFE. Since the presence of the inorganic components caused such a specific phenomenon, it should be reasonable that there may be some other components which could enhance the release of C_2^+ more easily and effectively.

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