Endohedral Barium and Strontium Fullerenes

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Mixtures of barium (or strontium) salts and kerogen residues, after pyrolysis at 450 °C, produce endohedral metallofullerene ions on laser irradiation at low laser powers.

Various endohedral metallofullerene compounds have recently been synthesized and identified mass spectrometrically. The metals inside the fullerenes are the electropositive lanthanoid elements.[1] These elements have similar ionic radii (M^{3+} 103–118 pm) and first ionization potentials (5.47–6.14 eV) to the alkaline earth elements (M^{2+} 99–134 pm, 5.21–6.1 eV). Our studies of the laser ablation of Coorongite[2] have revealed the existence of endohedral calcium fullerene compounds $Ca@C_{60}$ and $Ca@C_{70}$. The similarity between the lanthanoids and the alkaline earth elements suggested that strontium and barium might also form endohedral fullerene compounds.

We have previously shown that kerogen residues formed by heating demineralized shale in a flow of helium at 400–500 °C produce fullerene ions on laser irradiation (using 1064 nm) at low laser power densities.[3] Kerogen is the organic material present in oil source rocks from which petroleum is formed. On pyrolysis, either naturally in geochemical systems, or artificially in the laboratory, it yields significant quantities of oil. The residues, however, have quite different structures depending on the temperature of pyrolysis. Elemental analysis of the raw kerogen and the pyrolysed residues showed a decrease in the H/C ratio from 1.8 in the raw kerogen to 0.6 in the residue after pyrolysis at 500 °C. The solid state ^{13}C NMR spectra showed an increase in the proportion of aromatic carbons to aliphatic carbons. Expressed as a ratio C_{ar}/C_{aliph} the value for raw kerogen was 0.2 rising to 0.9 for the kerogen residue after pyrolysis at 500 °C. The increase in aromatic character was also accompanied by a decrease in the relative mass of the residue.

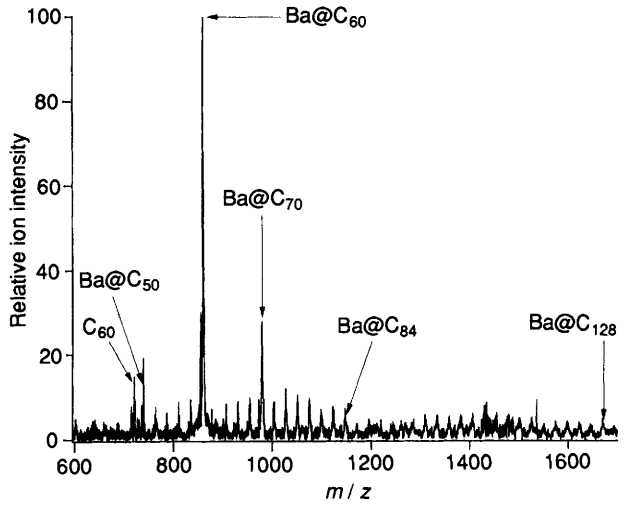

Fig. 1 A positive ion FT ICR mass spectrum of a mixture of barium sulfate and raw kerogen pyrolysed together at 450 °C and then irradiated at a laser power of 170 kW cm^{-2}

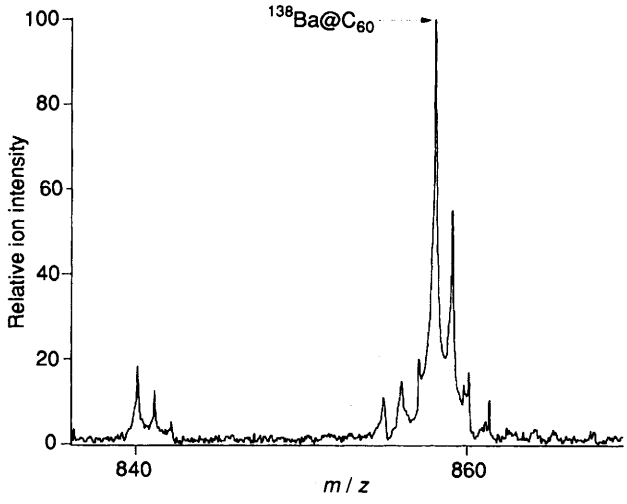

Fig. 2 Positive ion narrow band spectrum of $Ba@C_{60}$ showing the isotopic pattern of barium

Laser ablation of mixtures of calcium silicate with kerogen residues also produced metallofullerene ions, $Ca@C_{60}$ and $Ca@C_{70}$ ions.[2] Mixing suitable barium or strontium salts with kerogen residues and laser irradiation of the mixtures seemed an ideal method to attempt to observe endohedral barium or strontium fullerene ions.

In our initial studies of mixtures of calcium salts with the kerogens, the observation of the endohedral calcium compound seemed to be related to the observation of Ca^+ from the calcium salt at approximately similar laser powers as the observation of fullerenes from the kerogen residue. Cognisant of this empirical observation we examined several strontium and barium salts by laser ablation Fourier transform ion cyclotron mass spectrometry. Barium carbonate and strontium oxalate were shown to give the required naked metal monocations on ablation with the fundamental frequency of the Nd-YAG laser at laser powers of approximately 150–600 kW cm^{-2}. These compounds were mixed with a kerogen residue, obtained by pyrolysis at 450 °C, and on laser irradiation at laser powers of approximately 500 kW cm^{-2} gave positive ion spectra indicating the presence of the metallofullerenes of C_{60} and C_{70}. Barium sulfate mixed with the raw kerogen and then pyrolysed at 450 °C, also gave positive ion spectra containing the metallofullerenes. At present the $Ba@C_{60}$ and $Ba@C_{70}$ ions have been shown to have high intensity and thus are more easy to study; this communication will concentrate on barium.

Fig. 1 shows the positive ion spectrum obtained by pyrolysing barium sulfate with raw kerogen at 450 °C and laser irradiation at 170 kW cm^{-2}. This spectrum shows that almost all the ions are barium fullerides and the diminishing intensity of the ions still allows assignment of the barium fullerides up to $Ba@C_{128}$; note the low intensity of C_{60} and the absence of the other fullerene ions. Extraction (using toluene) of the barium sulfate kerogen sample after pyrolysis showed no evidence for the presence of the fullerenes and so the ions observed must be formed by the laser irradiation. Similar results were obtained when the kerogen residue obtained by pyrolysis at 450 °C was mixed with barium carbonate and laser irradiated.

Whereas calcium has one major isotope, there are several isotopes of barium with high enough isotopic abundance to observe the isotope pattern of $Ba@C_{60}$. Fig. 2 shows the positive ion narrow band spectrum of $Ba@C_{60}$ (produced from the mixture of barium carbonate and kerogen pyrolysed at 450 °C); the distribution of the major isotopes of barium is ^{135}Ba 6.6%, ^{136}Ba 7.8%, ^{137}Ba 11.3% and ^{138}Ba 71.7%, resulting in the major ion of $^{138}Ba@C_{60}$ being at *m/z* 858 and the ions at lower mass being the lighter isotopes of barium with C_{60}. Fig. 2 also shows the ion C_{70} at *m/z* 840.

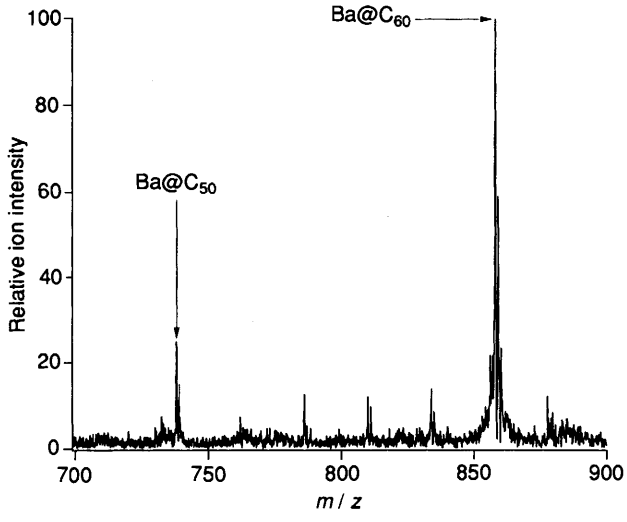

Fig. 3 Collisional activation spectrum of $Ba@C_{60}^+$ indicating sequential loss of C_2 units and $Ba@C_{50}^+$ being the major product ion

To prove that the barium was inside C_{60}, collisional activation and ion–molecule reaction studies were undertaken. Fig. 3 shows the results of collisional dissociation studies of $Ba@C_{60}^+$ with argon as collision gas. The ions dissociated with loss of C_2 units and $Ba@C_{50}$ was observed to be the major product ion; under similar conditions C_{60}^+ was stable. No C_{60}^+ or Ba^+ was observed during the collisional activation studies. There was no reaction of NO_2 or N_2O with $Ba@C_{60}^+$. NO_2 did react with Ba^+ produced during the ablation of the barium carbonate–kerogen pyrolysis residue mixture and NO_2 also reacted with Ba^+ formed from irradiation of $BaCO_3$. The products of the reaction of Ba^+, produced during the ablation of kerogen mixture, with NO_2 were $BaOH^+$, BaO_2^+ and $BaNO_2^+$, indicating the presence of water formed during laser irradiation of the kerogen–barium carbonate mixture. $BaNO_2^+$ was formed in the reaction of Ba^+ (obtained from $BaCO_3$) with NO_2.

Similar studies are being carried out with strontium salts and kerogen residues. Fig. 4 shows part of the broad band spectrum of strontium oxalate mixed with a kerogen residue obtained by pyrolysis at 450 °C, produced by laser irradiation

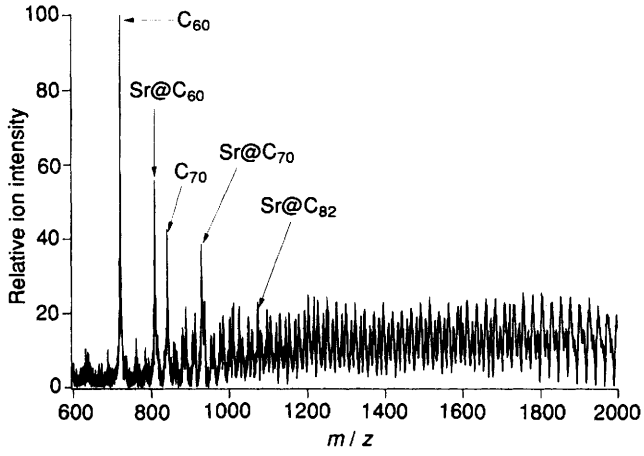

Fig. 4 Positive ion FT ICR mass spectrum of a mixture of strontium oxalate and a kerogen residue (produced by pyrolysis at 450 °C) formed by irradiation of the sample at 240 kW cm^{-2}

at 240 kW cm^{-2}. Isolation of the ion at *m/z* 808 and attempted reactions with NO_2 and N_2O gave no products indicating the *m/z* 808 ion was $Sr@C_{60}^+$.

The strontium mixtures form an extensive set of metallofullerene ions; the fullerene ions are also abundant in the strontium systems in contrast to the barium systems. There are similarities in that with both the barium and strontium systems the $M@C_{60}$ and $M@C_{70}$ ions have much higher intensity than the other $M@C_n$ ions and the $M@C_{82}$ ion is not as prominent as with the endohedral lanthanoid metal ions.[1]

Although strontium[4] and barium[5,6] fulleride compounds have been previously prepared, these compounds were the intercalation compounds (salts) formed by the reactions of the metals with C_{60}. These compounds would not be expected to give ions with the properties described in this communciation.

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