Calcium Inside C_{60} and C_{70}—from Coorongite, a Precursor of Torbanite

Harry R. Rose,[a] Ian G. Dance,[a] Keith J. Fisher,*[a] Derek R. Smith,[a] Gary D. Willett[a] and M. A. Wilson[b]

[a] *School of Chemistry, University of New South Wales, PO Box 1, Kensington, New South Wales 2033, Australia*
[b] *CSIRO Division of Coal Technology, PO Box 136, North Ryde, New South Wales 2113, Australia*

Laser ablation of coorongite produced the Ca@C_{60} positive ion, which has been investigated by Fourier transform ion cyclotron resonance mass spectrometry.

Coorongite is a rubbery material that on destructive distillation affords a very large yield of highly aliphatic oil. It occurs as sheet-like deposits around the margins of lagoons, or as a residue in the dried up basins of ephemeral lakes.[1,2] It is established that the coorongite is formed from dried residues of the alga *Botryococcus braunii*.[3,4] It is believed to be a precursor to the kerogen types of oil shale known as torbanite; samples from deposits which occur in the coastal lowlands of the Coorong district of South Australia, were used in this study.

Coorongite samples were pyrolysed at 400, 450 and 500 °C in a flow of helium. One sample was treated with hydrochloric acid and then pyrolysed at 450 °C and another sample was treated with hydrochloric acid and hydrofluoric acid and then pyrolysed at 450 °C. The residues after pyrolysis were analysed by laser ablation Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Pressed powered samples were irradiated with the fundamental frequency (1064 nm) of a Nd-yttrium aluminium garnet (YAG) laser in the cell of the mass spectrometer. The procedure and mass spectrometer have been described elsewhere.[5]

Fig. 1 shows part of the positive ion spectrum obtained when the coorongite residue pyrolysed at 450 °C was irradiated with a power density of 160 kW cm^{-2}. The spectrum shows a series of fullerene ions and a series of calcium fulleride (CaC_n) ions. In addition to CaC_{60} and CaC_{70} there are calcium fulleride ions from CaC_{66} to CaC_{136} shown in the spectrum. These calcium fulleride ions have maximum intensities at CaC_{60}, CaC_{70}, CaC_{92} and CaC_{126} which do not quite match the parent fullerenes. The power density used is several orders of magnitude below that required to produce the fullerenes from graphite. Irradiation of the raw coorongite under similar conditions and at a similar power density gave no ions identified as fullerenes or metallofullerenes. Irradiation of the sample pyrolysed at 500 °C gave spectra indicating the positive ion at *m/z* 760 to be more intense than the C_{60}^+. Extraction of the pyrolysis residues with various solvents gave no evidence for the presence of C_{60} or other fullerenes. The sample initially washed with hydrochloric acid and pyrolysed at 450 °C gave a similar spectrum to that illustrated in Fig. 1, while the sample treated with hydrochloric and hydrofluoric acid and then pyrolysed at 450 °C gave a spectrum in which the ion at *m/z* 760 was considerably reduced compared to C_{60}. Analysis of the original coorongite indicated that 0.4% of calcium was present in the sample, the only other important inorganic species present was 11.6% of silicon dioxide.

Attempts were made to dissociate the *m/z* 760 positive ion with argon as collision gas. Using the conditions available in the ion cyclotron resonance cell only small amounts of dissociation products of the positive ion at *m/z* 760 were observed (see Fig. 2) and under similar conditions no dissociation products were observed for C_{60}^+. Varying the laser irradiation conditions also gave the ion corresponding to the loss of a C_2 unit from *m/z* 760 as shown in the narrow band spectrum in Fig. 3. These results suggest that like lanthanum the metal in this case calcium is inside the fullerenes.

Reactions of the positive ions of Ca@C_{60}, Ca@C_{70}, C_{60} and C_{70} were attempted with NO_2 and no reactions were observed with all these ions. The laser irradiation of the coorongite samples also gave Ca^+ ions and isolation of these ions and reaction with NO_2 gave $CaNO_2^+$. Ca^+ ions produced from the laser irradiation of calcium phosphate or calcium silicate also gave $CaNO_2^+$ on reaction with NO_2.

In a further attempt to show that calcium was present we have observed the *m/z* 760 from another similar but different source. We have shown previously that kerogen residues produce fullerenes at low power densities[6] and so experiments with mixtures of metal salts with kerogen residues have been studied to identify metallofullerenes. Thus in separate experiments mixtures of kerogen residues with calcium silicate on laser irradiation at laser powers of 50–1050 kW cm^{-2} gave similar specta to the pyrolysed coorongite samples (showing the presence of Ca@C_{60} and Ca@C_{70}). Fig. 4 shows part of the positive ion broad band spectrum of a mixture of a kerogen residue and calcium silicate. The spectrum is similar to Fig. 1 but the laser power is higher, 540 kW cm^{-2} and the calcium fulleride ions are relatively less intense than the fullerene ions. Mixtures of kerogen residues with La_2O_3 at similar laser

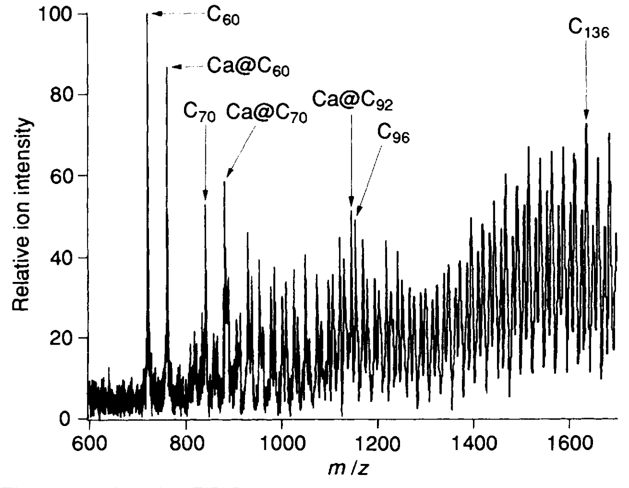

Fig. 1 A positive ion FTICR mass spectrum of the coorongite residue, after pyrolysis at 450 °C, formed by irradiation of the sample at a laser power at 160 kW cm^{-2}

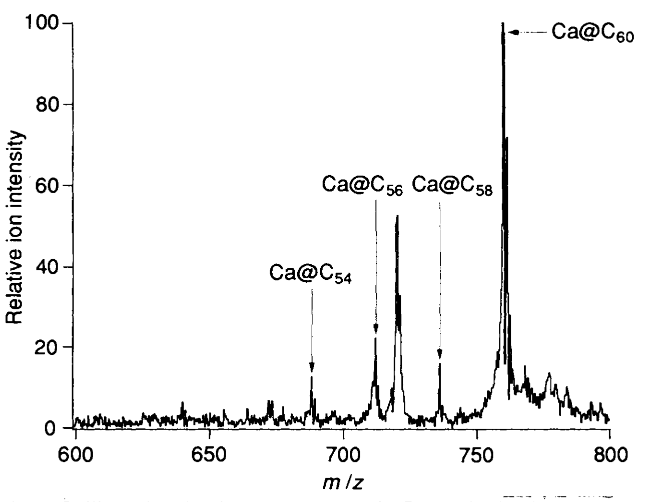

Fig. 2 Collisonal activation spectrum of Ca@C_{60}^+ indicating sequential loss of C_2 units. (C_{60}^+ present due to incomplete ejection)

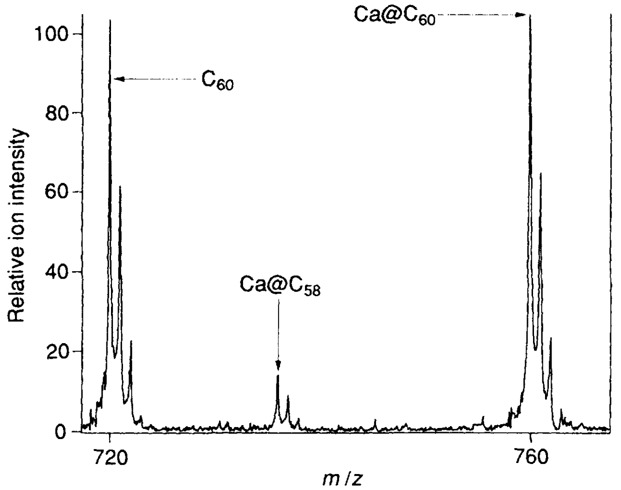

Fig. 3 Positive ion narrow band spectrum of coorongite residue irradiated at a laser power of 540 kW cm^{-2}

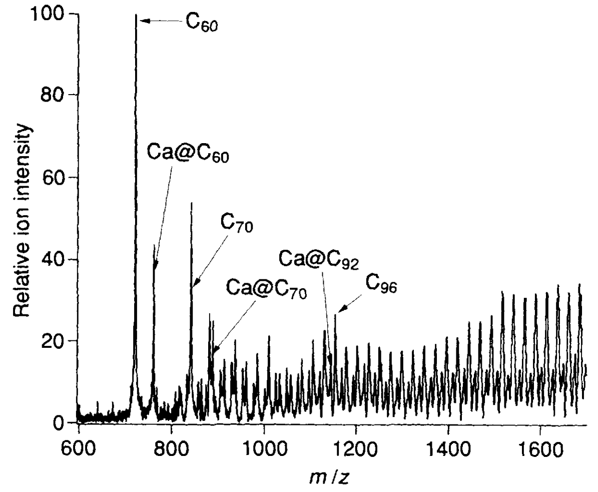

Fig. 4 Positive ion FTCIR mass spectrum of a mixed kerogen residue from pyrolysis at 450 °C and calcium silicate, formed by irradiation of the sample at 540 kW cm^{-2}

powers showed the production of the endohedral lanthanum fullerene complexes which will be reported later.

Comparing our mass spectrometric results with those for other endohedral metal fullerene compounds[7–11] leads us to believe that the positive ions observed at *m/z* 760 and 880 are the endohedral calcium compounds Ca@C$_{60}$ and Ca@C$_{70}$, respectively. As shown in Fig. 1 there are a large number of other endohedral calcium fullerene compounds. Calcium compounds of C$_{60}$ have been prepared previously but these were the intercalated calcium compounds which would be expected not to give the ions at *m/z* 760 and 880.[12,13]

This research is supported by the Australian Research Council. H. R. R. gratefully acknowledges a scholarship from the Australian International Development Assistance Bureau, and K. J. F. a National Research Fellowship. CSIRO provided financial support for M. A. W., and samples of coorongite.

Received, 22nd February 1993; Com. 3/01056B

References

1 C. Debreuil, S. Derenne, C. Largeau, C. Berkaloff and B. Rousseau, *Org. Geochem.*, 1989, **14**, 543.
2 R. F. Cane, *Geochim. Cosmochim. Acta*, 1969, **33**, 257.
3 J. R. Maxwell, A. G. Douglas, G. Eglinton and A. McCormick, *Phytochemistry*, 1968, **7**, 2157.
4 M. A. Wilson, B. D. Batts and P. G. Hatcher, *Energy Fuels*, 1988, **2**, 668.
5 P. F. Greenwood, M. G. Strachan, G. D. Willett and M. A. Wilson, *Org. Mass Spectrom.*, 1990, **25**, 353.
6 H. R. Rose, D. R. Smith, K. J. Fisher, I. G. Dance, G. D. Willett and M. A. Wilson, *Org. Mass Spectrom.*, submitted.
7 Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. K. M. Alford and R. E. Smalley, *J. Phys. Chem.*, 1991, **95**, 7564.
8 S. W. McElvany, *J. Phys. Chem.*, 1992, **96**, 4935.
9 S. W. McElvany and M. M. Ross, *J. Am. Soc. Mass Spectrom.*, 1992, **3**, 268.
10 M. M. Ross, H. H. Nelson, J. H. Callahan and S. W. McElvany, *J. Phys. Chem.*, 1992, **96**, 5231.
11 E. G. Gillan, C. Yeretzian, K. S. Min, M. M. Alvarez, R. L. Whetten and R. B. Kaner, *J. Phys. Chem.*, 1992, **96**, 6869.
12 A. R. Kortan, N. Kopylov, S. Glarum, E. M. Gyorgy, A. P. Ramirez, R. M. Fleming, F. A. Thiel and R. C. Haddon, *Nature*, 1992, **355**, 529.
13 R. C. Haddon, G. P. Kochanski, A. F. Hebard, A. T. Fiory and R. C. Morris, *Science*, 1992, **258**, 1636.