Reactive MALDI mass spectrometry: application to high mass alkanes and polyethylene†

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A molecular solid of fullerene (C_{60}) intercalated with cobalt cyclopentadienyl dicarbonyl ($CoCp(CO)_2$) was shown to be an effective matrix for matrix-assisted laser desorption/ionization mass spectrometry (MALDI) of large alkanes (demonstrated up to $C_{94}H_{190}$) and polyethylenes that otherwise cannot be produced as intact ions in the gas phase.

The inability to produce intact, high mass alkane ions in the gas phase has been a long standing barrier to the mass spectrometric (MS) analysis of saturated hydrocarbons, thereby limiting its broader use in the petroleum and the polyolefin industries. Traditional desorption/ionization methods are either mass limited (such as field desorption/ionization[1–3] or laser desorption/ionization[4,5]) or fail to produce intact gas phase ions exclusively (such as electron impact ionization,[6] electrospray ionization,[7] or matrix assisted laser desorption/ionization (MALDI)[8–11]). Density functional calculations have shown that bare metal cationization, the typical way to ionize unsaturated hydrocarbon materials, is impossible without chain scission when applied to saturated hydrocarbons under typical desorption conditions.[12] One method to circumvent this barrier is to form salts of the saturated hydrocarbons before introduction into the mass spectrometer; however, this method requires at least one pre-existing chemically active site on the molecule (*e.g.* a terminal vinyl group) to be effective.[13–15]

Recently the use of organometallic cations has gained prominence as a way to create intact gas phase alkanes, in particular the cobalt cyclopentadienyl cation, $CoCp^+$. This trend started with the work of Jacobson and Freiser[16] on CH_4 through C_6H_{14} and was subsequently extended to $C_{15}H_{32}$, $C_{20}H_{42}$ and $C_{28}H_{58}$ by Byrd, *et al.*[17] Each study observed the loss of either one or two H_2 molecules with no C–C chain scission. Ekeberg and Uggerud,[18] working with C_2H_6, supplemented their experimental results with extended Huckel calculations and attributed the reactivity of $CoCp^+$ to its open-shell 13-electron structure. Similarly, Carpenter *et al.*[19] measured the bond energies of $CoCp^+$ complexes with H_2 and CH_4, supplementing their observations with density functional theory calculations. They verified that the Cp ligand is a strong electron-withdrawing group, which destabilizes the Co π orbitals, allowing the alkane ligands to coordinate with the remaining empty metal π orbitals. More recently, the group of Kenttämaa has used laser induced acoustic desorption to study high mass saturated hydrocarbons cationized with gas-phase $CoCp^+$, including linear alkanes up to $C_{50}H_{102}$,[20] polyethylene and polymethylene with number average molecular masses up to 655 u,[21] and petroleum distillates with both saturated and unsaturated hydrocarbon components.[22] For the case of unsaturated hydrocarbons they found either no loss of hydrogen or the loss of a single H_2 molecule depending on analyte structure.

In this manuscript organometallic cationization of high mass alkanes is applied for the first time to matrix-assisted laser desorption ionization. This has several important benefits. There are a large number of installed MALDI instruments, with a growing user base, that are routinely used for macromolecular mass spectrometry. MALDI ion sources are typically used with time of flight mass separation, which is particularly amenable to the analysis of high mass ions such as synthetic polymers and high-boiling petroleum fractions. The difficulty with the direct application of $CoCp^+$ ionization to MALDI is that the most commonly used precursor, molecular cobalt cyclopentadienyl dicarbonyl, $CoCp(CO)_2$, is highly volatile[23] and rapidly boils off into the vacuum of the mass spectrometer. To overcome this limitation a novel MALDI matrix was created that intercalates the cyclopentadienyl cobalt dicarbonyl into the fullerene (C_{60}) face centered cubic lattice. The entrainment of the organometallic in the matrix prevents it from boiling into the vacuum. Furthermore, in the experiments described here, the alkane samples are heated on the MALDI sample stage to above their melting point (*ca.* 125 °C) in order to enhance ion yield. This is possible only with a low volatility MALDI matrix[24] such as C_{60}.[25] Yet, even with heating in vacuum for periods up to several hours, the entrained cobalt cyclopentadienyl dicarbonyl is retained in the fullerene matrix.

The bimolecular fullerene organometallic matrix was created following a method similar to the one described by Crane *et al.*[26–29] for the preparation of $C_{60}\cdot 2(Cp_2Fe)$. A saturated solution of fullerene in benzene[30] was prepared by adding 450 mg of C_{60} (99.8%) to 250 mL benzene. To this was added a solution of 500 mg $CoCp(CO)_2$ in 100 mL benzene. This mixture was capped and remained undisturbed for 5 d, at which time approximately 250 mg of a deep brown precipitate was collected. The solutions were prepared under argon. The precipitate was kept refrigerated. Samples were prepared for mass spectrometry by coating the MALDI target with the bimolecular matrix from a slurry in xylene. On top of the dried matrix was deposited the analyte from a solution of *o*-xylene held at 125 °C. Deposition was performed using a nebulizer held at high temperature as described previously[25] to insure homogeneous sample coverage.

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The MALDI MS experiments were conducted on a Comstock Inc. (Oak Ridge, TN) model RTOF-260 reflectron time of flight (TOF) instrument.[31] Sample ablation was performed with the typical nitrogen gas laser (337 nm wavelength) with a spot diameter of approximately 100 µm. Atom Sciences Inc. (Oak Ridge, TN) has modified this mass spectrometer to allow resistive heating of the copper sample stage as measured by a thermocouple embedded in it. Heating the MALDI target to above the melting point of the sample under study has been shown to greatly enhance the ion yield.[25]

Fig. 1 is a typical mass spectrum of a high mass alkane produced with this method, in this case tetranonacontane ($C_{94}H_{190}$).[32] The highest mass peak at 1505 u corresponds in mass to $[Co(Cp)_2(C_{94}H_{190} - 2H_2)]^+$, that is, $C_{94}H_{190}$ minus two hydrogen molecules, cationized by cobalt and two cyclopentadienyl ligands. The figure inset also shows a peak at 1519 u, corresponding to a trace pentanoncontane impurity. The gas-phase reaction consists of oxidative addition of the alkane followed by oxidative cleavage after association *via* 3-center 2-electron M···C–H interaction to release H_2, repeated twice. Compared to the previously published studies using gas-phase preparation of the $CoCp^+$ cation that produced $[Co(Cp)(alkane - 2H_2)]^+$ or $[Co(Cp)(alkane - H_2)]^+$ ions, the results reported here produce a different structure having two Cp ligands. This can be understood by considering the variable hapticity of the cyclopentadienyl ligand, which can take on the values η^5, η^3, or η^1. While the structures seen before likely correspond to either a 17-electron configuration, *i.e.*, $[Co(\eta^5\text{-}Cp)(\eta^4\text{-}(alkane - 2H_2))]^+$, or a 15- (possibly 16-) electron configuration, *i.e.*, $[Co(\eta^5\text{-}Cp)(\eta^2\text{-}(alkane - H_2))]^+$, the new structure produced by MALDI is likely the more stable 18-electron structure, $[Co(\eta^3\text{-}Cp)_2(\eta^4\text{-}(alkane - 2H_2))]^+$.

The second highest mass peak at 909 u corresponds in mass to $[Co(\eta^5\text{-}Cp)(\eta^3\text{-}Cp)(\eta^2\text{-}C_{60})]^+$, that is C_{60} cationized by cobalt also with two cyclopentadienyl ligands, resulting in another stable 18-electron structure. Below this peak is a small peak corresponding to C_{60}^+ at 720 u. Moving lower in mass the next three peaks correspond to the cobalt cluster complexes $Co_4Cp_7^+$ (690 u), $Co_3Cp_4^+$ (437 u), and $Co_2Cp_4^+$ (378 u). Other small peaks in this region correspond to other $Co_nCp_m^+$ clusters. Even considering the variable hapticity of cyclopentadienyl, each of these clusters must have at least one 17- or 19-electron metal center, as deduced from electron counting arguments.[33] The $Co_3Cp_4^+$ cluster complex may be similar to those observed previously in solution[34–36] but lacks the requisite additional non-cyclopentadienyl ligands to form stable 18-electron structures. In the lowest mass range there resides the base peak corresponding to cobaltocenium ($CoCp_2^+$, 189 u). No peaks are observed for $CoCp(CO)_2^+$ (180 u), $CoCp(CO)^+$ (152 u), or $CoCp^+$ (124 u). The small peak at 132 u remains unassigned.

Much of what is observed can be explained through the chemistry of the laser ablation plume and through UV photolysis studies of organometallic compounds. While the first ionization potential of $CoCp(CO)_2$ is 7.35 eV[37] and the overall energy to go from $CoCp(CO)_2$ to $CoCp^+ + 2CO$ in the gas phase is 10.38 eV,[37] the well known exciton pooling nature of the MALDI ionization process[38] makes it likely that $CoCp^+$ is produced in abundance in the ablation plume. Moreover, the abundance of intermolecular collisions in the MALDI plume allows for the formation of the more stable $[Co(Cp)_2(alkane - 2H_2)]^+$ structure. In the previous gas phase work[16–18,20–22] the multiple collisions that are necessary to form this structure are infrequent so the less stable $[Co(Cp)(alkane - 2H_2)]^+$ structure was observed.

Fig. 2 shows the mass spectrum of a linear polyethylene. The peaks have a uniform spacing of 28 u and are within 1 u of the expected $[Co(Cp)_2(polyethylene - 2H_2)]^+$ structure. No polyethylene fragments were observed anywhere in the spectrum. The number of repeat units observed ranges from 36 to 97. At the extreme left of the spectrum are peaks corresponding to the cobaltocenium cationized fullerene matrix. Studies of higher mass polymers will eliminate this matrix/analyte peak interference. After subtracting the mass of the $CoCp_2$ cation and adding in the mass of the four hydrogen atoms removed in the reactive MALDI process the number-average relative molecular mass was found to be 1980 u and the mass-average relative molecular mass was 2060 u. Uncertainties were found to be ±25 u from repeat measurements. This compares well with the values of 1900 u and 2150 u as measured by the supplier using gel permeation chromatography with universal calibration, albeit with a lower

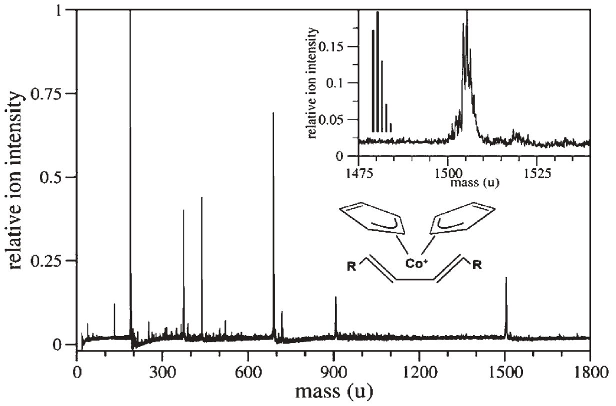

Fig. 1 MALDI mass spectrum of tetranonacontane ($C_{94}H_{190}$) using the fullerene cobalt cyclopentadienyl matrix. Insets: expanded view of tetranonacontane peak with theoretical isotope distribution shown at left. Hypothetical structure for $[Co(\eta^3\text{-}Cp)_2(\eta^4\text{-}(alkane - 2H_2))]^+$, where R represents the continuation of the alkane chain.

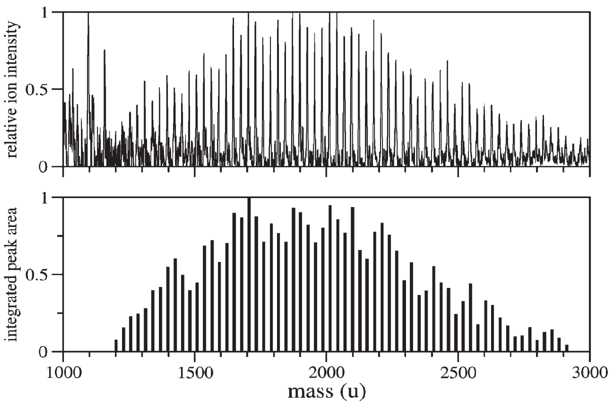

Fig. 2 Top: MALDI mass spectrum of polyethylene using the fullerene cobalt cyclopentadienyl matrix. Bottom: molecular mass distribution created by integrating the mass peaks. Note that the mass of the $CoCp_2^+$ cation (189 u) has not been subtracted.

polydispersity as often found in MALDI mass spectrometry of polymers.

Much can be understood about these results from consideration of previous UV photolysis organometallic solution work. For example, the ring slippage that occurs in these MALDI experiments has an analogous occurrence in cryogenic matrix isolation UV reactions of $CoCp(CO)_2$,[39] where $Co(\eta^5\text{-}Cp)(CO)_2$ can be converted to $Co(\eta^3\text{-}Cp)(CO)_3$ when irradiated in frozen carbon monoxide. Similarly, cyclopentadienyl ring slippage from η^5 to η^3 under UV irradiation at cryogenic temperatures has been used to explain the reaction of iridium cyclopentadienyl dicarbonyl with CH_4.[40] Ring-slipped organometallics are known to interact with alkanes, resulting in β-elimination of hydrogen.[41] In regard to the $[Co(\eta^5\text{-}Cp)(\eta^3\text{-}Cp)(\eta^2\text{-}C_{60})]^+$ peak, UV photons have been shown to create the $Co(\eta^2\text{-}C_{60})$ ligand in solutions of $Co(\eta^5\text{-}Cp)(CO)_2$ and C_{60} in tetrahydrofuran.[42]

The results presented here open up new avenues of reactive MALDI applied to analytes that are traditionally hard to produce as intact, gas phase ions. It is further envisioned that reactive MALDI may be used to selectively ionize only certain chemical species in a complex mixture, or certain chemical moieties on heterogeneous macromolecules. The joining of organometallic gas phase chemistry with the needs of the macromolecular mass spectrometry community offers a host of undiscovered possibilities.

Notes and references

1 R. P. Lattimer and H. R. Schulten, *Int. J. Mass Spectrom. Ion Phys.*, 1983, **52**, 105–116.
2 W. J. Evans, D. M. DeCoster and J. Greaves, *J. Am. Soc. Mass Spectrom.*, 1996, **7**, 1070–1074.
3 J. H. Gross, K. Vékey and A. Dallos, *J. Mass Spectrom.*, 2001, **36**, 522–528.
4 R. Chen and L. Li, *J. Am. Soc. Mass Spectrom.*, 2001, **12**, 367–375.
5 M. S. Kahr and C. L. Wilkins, *J. Am. Soc. Mass Spectrom.*, 1993, **4**, 453–460.
6 K. Ludányi, A. Dallos, Z. Kühn and K. Vékey, *J. Mass Spectrom.*, 1999, **34**, 264–267.
7 D. Zhan and J. B. Fenn, *Int. J. Mass Spectrom.*, 2000, **194**, 197–208.
8 S. Weidner, G. Kühn and J. Friedrich, *Rapid Commun. Mass Spectrom.*, 1998, **12**, 1373–1381.
9 R. Chen, T. Yalcin, W. E. Wallace, C. M. Guttman and L. Li, *J. Am. Soc. Mass Spectrom.*, 2001, **12**, 1186–1192.
10 T. Yalcin, W. E. Wallace, C. M. Guttman and L. Li, *Anal. Chem.*, 2002, **74**, 4750–4756.
11 A. J. Jaber and C. L. Wilkins, *J. Am. Soc. Mass Spectrom.*, 2005, **16**, 2009–2016.
12 A. W. Ehlers, C. G. de Koster, R. J. Meier and K. Lammertsma, *J. Phys. Chem. A*, 2001, **105**, 8691–8695.
13 B. J. Bauer, W. E. Wallace, B. M. Fanconi and C. M. Guttman, *Polymer*, 2001, **42**, 9949–9953.
14 S. Lin Gibson, L. Brunner, D. L. Vanderhart, B. J. Bauer, B. M. Fanconi, C. M. Guttman and W. E. Wallace, *Macromolecules*, 2002, **35**, 7149–7156.
15 H. Ji, N. Sato, Y. Nakamura, Y. Wan, A. Howell, Q. A. Thomas, R. F. Storey, W. K. Nonidez and J. W. Mays, *Macromolecules*, 2002, **35**, 1196–1199.
16 D. B. Jacobson and B. S. Freiser, *J. Am. Chem. Soc.*, 1985, **107**, 7399–7407.
17 H. C. M. Byrd, C. M. Guttman and D. P. Ridge, *J. Am. Soc. Mass Spectrom.*, 2003, **14**, 51–57.
18 D. Ekeberg and E. Uggerud, *Organometallics*, 1999, **18**, 40–44.
19 C. J. Carpenter, P. A. M. van Koppen, P. R. Kemper, J. E. Bushnell, P. Weis, J. K. Perry and M. T. Bowers, *Int. J. Mass Spectrom.*, 2003, **230**, 161–174.
20 J. L. Campbell, K. E. Crawford and H. I. Kenttämaa, *Anal. Chem.*, 2004, **76**, 959–963.
21 J. L. Campbell, M. N. Fiddler, K. E. Crawford, P. P. Gqamana and H. I. Kenttämaa, *Anal. Chem.*, 2005, **77**, 4020–4026.
22 K. E. Crawford, J. L. Campbell, M. N. Fiddler, P. Duan, K. Qian, M. L. Gorbaty and H. I. Kenttämaa, *Anal. Chem.*, 2005, **77**, 7916–7923.
23 B. Sztáray and T. Baer, *J. Am. Chem. Soc.*, 2000, **122**, 9219–9226.
24 W. E. Wallace, M. A. Arnould and R. Knochenmuss, *Int. J. Mass Spectrom.*, 2005, **242**, 13–22.
25 W. E. Wallace and W. R. Blair, *Int. J. Mass Spectrom.*, 2007, **263**, 82–87.
26 J. D. Crane, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1764–1765.
27 A. G. Avent, P. R. Birkett, C. Christides, J. D. Crane, A. D. Darwish, P. B. Hitchcock, H. W. Kroto, M. F. Meidine, K. Prassides, R. Taylor and D. R. M. Walton, *Pure Appl. Chem.*, 1994, **66**, 1389–1396.
28 A. G. Avent, P. R. Birkett, C. Christides, J. D. Crane, A. D. Darwish, P. B. Hitchcock, H. W. Kroto, M. F. Meidine, K. Prassides, R. Taylor and D. R. M. Walton, *J. Mol. Struct.*, 1994, **325**, 1–11.
29 M. Makha, A. Purich, C. L. Raston and A. N. Sobolev, *Eur. J. Inorg. Chem.*, 2006, 507–517.
30 R. S. Ruoff, D. S. Tse, R. Malhotra and D. C. Lorents, *J. Phys. Chem.*, 1993, **97**, 3379–3383.
31 Certain equipment, instruments or materials are identified in this paper in order to specify the experimental details adequately. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.
32 R. R. Reinhard and J. A. Dixon, *J. Org. Chem.*, 1965, **30**, 1450–1453.
33 S. M. Owen, *Polyhedron*, 1988, **7**, 253–283.
34 H. Wadepohl, T. Borchert and H. Pritzkow, *J. Chem. Soc., Chem. Commun.*, 1995, 1447–1448.
35 H. Wadepohl and S. Gebert, *Coord. Chem. Rev.*, 1995, **143**, 535–609.
36 H. Wadepohl, T. Borchert and H. Pritzkow, *Chem. Ber./Recl.*, 1997, **130**, 593–603.
37 B. Sztáray, L. Szepes and T. Baer, *J. Phys. Chem. A*, 2003, **107**, 9486–9490.
38 R. Knochenmuss, *Analyst*, 2006, **131**, 966–986.
39 O. Crichton, A. J. Rest and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1980, 167–173.
40 A. J. Rest, I. Whitwell, W. A. G. Graham, J. K. Hoyano and A. D. McMaster, *J. Chem. Soc., Chem. Commun.*, 1984, 624–626.
41 J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307–318.
42 D. M. Thompson, M. Bengough and M. C. Baird, *Organometallics*, 2002, **21**, 4762–4770.