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Analysis of Saturated Hydrocarbons by Using Chemical Ionization Combined with Laser-Induced Acoustic Desorption/Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Laser-induced acoustic desorption (LIAD), combined with chemical ionization by the cyclopentadienyl cobalt radical cation (CpCo•+), is demonstrated to facilitate the analysis of saturated hydrocarbons by Fourier transform ion cyclotron resonance mass spectrometry. The LIAD/CpCo•+ method produces unique pseudomolecular ions for alkanes from $C_{24}H_{50}$ to $C_{50}H_{102}$. These alkanes were tested individually and in artificial mixtures of up to seven components. Only one product ion, $[R + CpCo - 2H_2]^{•+}$, was detected for each alkane (R). The product ions' relative abundances correspond to the relative molar concentration of each alkane in mixtures. These findings provide a solid groundwork for the future application of this method for hydrocarbon polymer analyses.

Mass spectrometry is a powerful tool that can afford fast, accurate, and sensitive analyses of polymers.[1,2] However, the success of these analyses depends on two factors: (1) the stability of the polymer chain under desorption and ionization conditions and (2) the presence of ionizable functional groups. Nonpolar saturated hydrocarbon polymers, such as polyethylene (PE), are known to fragment upon heating in mass spectrometry experiments (e.g., thermal desorption during field ionization experiments).[3] In addition, these polymers contain no easily ionizable functional groups. Hence, they have proven difficult to analyze by using conventional mass spectrometry methods.[2]

Field desorption mass spectrometry (FD-MS) analysis of low molecular weight PE yields mainly molecular ions $(M^{•+})$ of the polymer molecules, but the technique suffers from both low- and high-mass discrimination.[4,5] In addition to FD-MS, laser desorption/ionization (LDI) methods using transition metal ion attachment have been examined for the characterization of various PE samples.[6–10] Unfortunately, the desorption process is believed to discriminate against higher mass molecules, while low-mass hydrocarbons undergo skeletal fragmentation upon cation attachment. Methods that rely upon chemical derivatization of PE samples to add ionizable functional groups have also shown promise.[11,12] However, the derivatization step results in spectra that represent only the vinyl-terminated PE molecules, not the bulk, saturated polymer.

Ideally, a mass spectrometric method for hydrocarbon polymer analysis should involve desorption of intact hydrocarbons into the gas phase, and ionization of these hydrocarbons without fragmentation, to yield product ions that are representative of the neutral hydrocarbon's molecular weight (MW). Additionally, uniform efficiency for both desorption and ionization of all molecules in the polymer sample, and the ability to independently optimize desorption and ionization, are desirable.
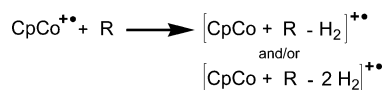
Laser-induced acoustic desorption[13–18] (LIAD) is a relatively new desorption method that has shown promise for introduction of nonvolatile, thermally labile species into the gas-phase environment of a mass spectrometer. By using a simple LIAD probe developed in our laboratory, a wide variety of molecules have been desorbed as intact neutral species into a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR).[17,18] These experiments allow for the independent optimization of the desorption and ionization steps—a benefit not applicable to MALDI or other LDI methods.[20,21] Therefore, the choice of ionization

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(1) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527−570.
(2) *Mass Spectrometry of Polymers*; Mountado, G., Lattimer, R. P., Eds.; CRC Press: Boca Raton, FL, 2002.
(3) Schulten, H.-R.; Simmleit, N.; Müller, R. *Anal. Chem.* **1987**, *59*, 2903−2908.
(4) Evans, W. J.; DeCoster, D. M.; Greaves, J. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 1070−1074.
(5) Gross, J. H.; Weidner, S. M. I. *Eur. J. Mass Spectrom.* **2000**, *6*, 11−17.
(6) Kühn, G.; Weidner, St.; Just, U.; Hohner, G. *J. Chromatogr., A* **1996**, *732*, 111−117.

(7) Chen, R.; Yalcin, T.; Wallace, W. E.; Guttman, C. M.; Li, L. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 1186−1192.
(8) Chen, R.; Li, L. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 367−375.
(9) Dutta, T. K.; Harayama, S. *Anal. Chem.* **2001**, *73*, 864−869.
(10) Yalcin, T.; Wallace, W. E.; Guttman, C. M.; Li, L. *Anal. Chem.* **2002**, *74*, 4750−4756.
(11) Bauer, B. J.; Wallace, W. E.; Fanconi, B. M.; Guttman, C. M. *Polymer* **2001**, *42*, 9949−9953.
(12) Lin-Gibson, S.; Brunner, L.; Vanderhart, D. L.; Bauer, B. J.; Fanconi, B. M.; Guttman, C. M.; Wallace, W. E. *Macromolecules* **2002**, *35*, 7149−7156.
(13) Lindner, B.; Seydel, U. *Anal. Chem.* **1985**, *57*, 895−899.
(14) Lindner, B. *Int. J. Mass Spectrom. Ion Processes* **1991**, *103*, 203-218.
(15) Golovlev, V. V.; Allman, S. L.; Garrett, W. R.; Chen, C. H. *Appl. Phys. Lett.* **1997**, *71*, 852−854.
(16) Golovlev, V. V.; Allman, S. L.; Garrett, W. R.; Taranenko, N. I.; Chen, C. H. *Int. J. Mass Spectrom. Ion Processes* **1997**, *169/170*, 69−78.
(17) Pérez, J.; Ramírez-Arizmendi, L. E.; Petzold, C. J.; Guler, L. P.; Nelson, E. D., Kenttämaa, H. I. *Int. J. Mass Spectrom.* **2000**, *198*, 173−188.
(18) Petzold, C. J.; Ramiréz-Arizmendi, L. E.; Heidbrink, J. L.; Pérez, J.; Kenttämaa, H. I. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 192−194.
(19) Dreisewerd, K. *Chem. Rev.* **2003**, *103*, 395−425.
(20) Knochenmuss, R.; Zenobi, R. *Chem. Rev.* **2003**, *103*, 441−452.

Scheme 1

$$CpCo^{+\bullet} + R \longrightarrow \left[CpCo + R - H_2 \right]^{+\bullet}$$
$$\text{and/or}$$
$$\left[CpCo + R - 2\,H_2 \right]^{+\bullet}$$

Scheme 2

m/z 189   *m/z* 124

method is not dictated by the desorption method, and reactions other than protonation or deprotonation can be employed for ionization of the analyte (e.g., electron ionization, ion–molecule reactions).

A chemical ionization (CI) method that affords MW information for saturated hydrocarbon molecules involves the use of the η^5-cyclopentadienyl cobalt radical cation (CpCo$^{\bullet+}$). Investigations into the gas-phase reactivity of CpCo$^{\bullet+}$ by Jacobson and Freiser,[21] and later by Ekeberg and co-workers,[22] revealed that reactions of this ion with small linear and cyclic alkanes predominantly produce adduct ions with concomitant loss of one or two molecules of hydrogen (Scheme 1). Little to no fragmentation of the ionized alkanes was observed. More recently, Byrd and co-workers[23] successfully demonstrated the utility of CpCo$^{\bullet+}$ as a CI reagent ion for the determination of molecular weights of linear alkanes up to octacosane ($C_{28}H_{58}$). Their results indicate that the efficiencies for alkane–CpCo$^{\bullet+}$ reactions are high (>40% for octacosane).[23]

However, the aforementioned experiments employed thermal desorption for the introduction of the hydrocarbons into the mass spectrometer. Another approach must be utilized for desorption of larger hydrocarbons since the rate of thermal decomposition becomes competitive with the rate of vaporization for larger species.[24] In this article, we describe the results of preliminary experiments that employ LIAD/FT-ICR and the CpCo$^{\bullet+}$ reagent ion for the analysis of saturated hydrocarbons.

EXPERIMENTAL SECTION

Chemicals. Individual alkanes were purchased from Sigma-Aldrich and used without purification. Bis(cyclopentadienyl)cobalt, employed in the synthesis of the CpCo$^{\bullet+}$ reagent ion (vide infra), was purchased from Sigma-Aldrich (St. Louis, MO) and used without purification.

Reagent Ion Generation. The CpCo$^{\bullet+}$ reagent ion was generated by using a two-step process. Bis(cyclopentadienyl)cobalt was introduced through a Varian leak valve into one side of the FT-ICR dual cell and subjected to electron ionization to form cobaltocenium ion (*m/z* 189). Transfer of this ion into the "clean" side of the dual cell, followed by sustained off-resonance collision-activated dissociation (SORI-CAD),[27] resulted in the formation of the CpCo$^{\bullet+}$ reagent ion (*m/z* 124) with concomitant loss of cyclopentadienyl radical. After allowing the CpCo$^{\bullet+}$ ions to cool for 1 s radiatively and collisionally (with Ar at ∼10^{-5} Torr), stored waveform inverse Fourier transform[28a,b] excitation pulses were
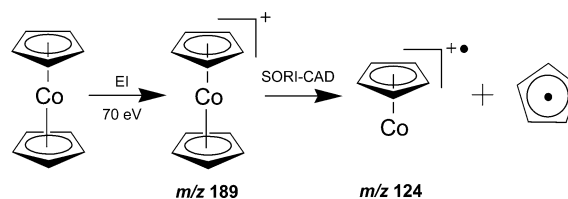
employed to isolate the reagent ion in the cell. The hydrocarbon samples were then desorbed by LIAD into the same cell for reactions with the CpCo$^{\bullet+}$ ions.

Instrumentation. All experiments were performed using a Nicolet model FTMS-2000 Fourier transform ion cyclotron resonance mass spectrometer equipped with a differentially pumped dual cell in a 3-T magnetic field. Two Edwards Diffstak 160 diffusion pumps (700 L/s), each backed by an Alcatel 2010 (3.2 L/s) dual rotary-vane pump, maintained a nominal baseline pressure inside the vacuum chamber of the FT-ICR of <10^{-9} Torr as measured by Bayard–Alpert ionization gauges located on each side of the dual cell. Samples may be introduced into either side of the instrument via one of several means: thermal solids probe, LIAD probe,[17] Varian leak valves, batch inlets that employ Andonian leak valves, or pulsed valves.[25]

The fundamental and practical aspects of the LIAD probe utilized in these experiments were documented earlier.[26] Sample preparation consisted of depositing 500 μL of a 1 mg/mL hydrocarbon solution in CS$_2$ (vide infra) onto one side of a 12.7-μm titanium foil. Once the sample had dried, the foil was mounted onto the LIAD probe. Fifty laser shots ($\lambda = 532$ nm, laser power density ∼10^9 W/cm^2) were fired in a circular pattern on the backside of the foil (opposite to the deposited sample) from a Nd:YAG laser (Minilite II, Continuum, Santa Clara, CA). Approximately 5% of the foil's total surface area was irradiated with laser shots. These pulses generate ultrasonic acoustic waves that propagate though the foil, resulting in desorption of neutral molecules from the opposite side of the foil. The desorbed neutral molecules, which have a residence time in the cell of ∼1 ms,[17] can then react with a reagent ion of choice that has been isolated and trapped in the cell of the FT-ICR.

Sample Preparation. Saturated hydrocarbon samples were dissolved in CS$_2$ at a concentration of ∼1 mg/mL. Each solution was heated to boiling (46 °C) in order to dissolve all of the
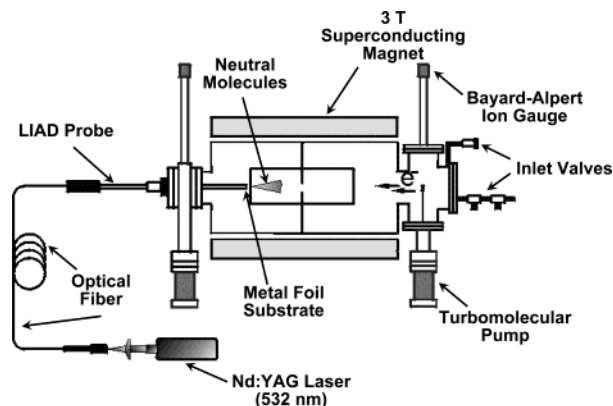
(21) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 7399–7407.
(22) Ekeberg, D.; Uggerud, E.; Lin, H.-Y.; Sohlberg, K.; Chen, H.; Ridge, D. P. *Organometallics* **1999**, *18*, 40–44.
(23) Byrd, H. C. M.; Guttman, C. M.; Ridge, D. P. *J. Am. Soc. Mass Spectrom.* **2003**, *14*, 51–57.
(24) Daves, G. D., Jr. *Acc. Chem. Res.* **1979**, *12*, 359–365.
(25) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96–101.
(26) Pérez, J.; Petzold, C. J.; Watkins, M. A.; Vaughn, W. E.; Kenttämaa, H. I. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 1105–1110.
(27) Gauthier, J. W.; Trautman, T. R.; Jacobson, D. B. *Anal. Chim. Acta* **1991**, *246*, 211–225.
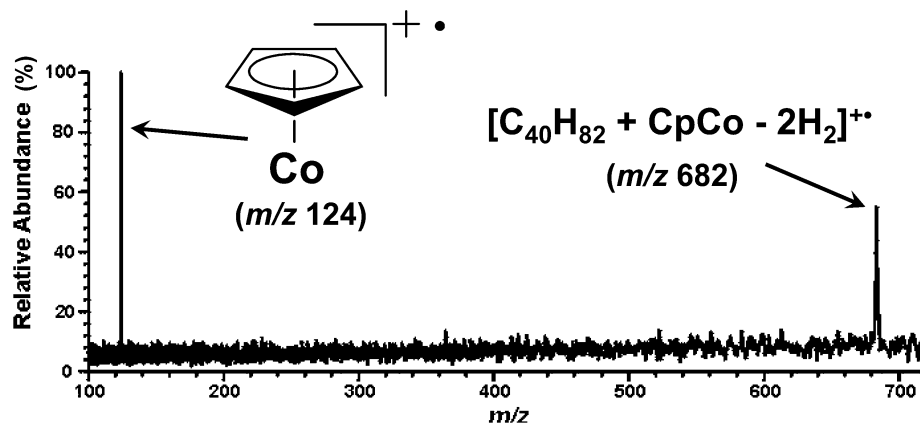
Figure 1. Schematic diagram of the FT-ICR instrument, including the LIAD probe.

Figure 2. Mass spectrum of LIAD-desorbed tetracontane ($C_{40}H_{82}$) after reaction with CpCo$^{\bullet+}$ ions to form the [$C_{40}H_{82}$ + CpCo − 2H$_2$]$^{\bullet+}$ ion.

Table 1. Comparison of the Results Observed by Jacobson and Freiser[21] and Gqamana et al.[29] (This Laboratory) for Reactions between the CpCo$^{\bullet+}$ Ion and Small Cyclic Hydrocarbons

| hydrocarbon | product | branching ratio (%) | |
		Jacobson and Freiser[21]	Gqamana et al.[29]
cyclopentane	adduct − H$_2$	0	10
	adduct − 2H$_2$	100	90
cyclopentene	adduct − 2H$_2$ − H$^{\bullet}$	100	100
cyclohexane	adduct − H$_2$	70	75
	adduct − 2H$_2$	30	25

Table 2. Saturated Hydrocarbons Studied Here, Including Their Molecular Weights and the Major Product Ions of Reactions with CpCo$^{\bullet+}$

hydrocarbon	molecular formula	MW	product ion (m/z)
tetracosane	$C_{24}H_{50}$	338	458
hexacosane	$C_{26}H_{54}$	366	486
octacosane	$C_{28}H_{58}$	394	514
nonacosane	$C_{29}H_{60}$	408	528
triacontane	$C_{30}H_{62}$	422	542
hentriacontane	$C_{31}H_{64}$	436	556
dotriacontane	$C_{32}H_{66}$	450	570
tritriacontane	$C_{33}H_{68}$	464	584
tetratriacontane	$C_{34}H_{70}$	478	598
hexatriacontane	$C_{36}H_{74}$	506	626
tetracontane	$C_{40}H_{82}$	562	682
tetratetracontane	$C_{44}H_{90}$	618	738
pentacontane	$C_{50}H_{102}$	702	822

hydrocarbon. Approximately 500 μL of this CS$_2$ solution was applied to a 12.7-μm Ti foil and the solvent was evaporated, either at ambient or at a slightly elevated temperature. The foil was then mounted onto the LIAD probe and inserted into the FT-ICR.

RESULTS AND DISCUSSION

Generation of the CpCo$^{\bullet+}$ Reagent Ion. In previous studies, the CpCo$^{\bullet+}$ ion was generated by two different methods. Jacobson and Freiser[21] allowed laser-ablated cobalt cations to react with cyclopentadiene in an FT-ICR. Ekeberg and co-workers,[22] as well as Byrd and co-workers,[23] utilized electron ionization-induced fragmentation of cyclopentadienylcobalt dicarbonyl to produce CpCo$^{\bullet+}$. The present study employed a third method: electron ionization of bis(cyclopentadienyl)cobalt followed by SORI-CAD of the molecular ion to form the CpCo$^{\bullet+}$ ion (vide supra, Scheme 2). Further SORI-CAD of this ion produced only one fragment—cobalt ion of m/z 59—in agreement with the work of Jacobson and Freiser.[21] In addition, the CpCo$^{\bullet+}$ ion generated via the SORI-CAD method was found to react with small cyclic hydrocarbons to yield products with branching ratios similar to those documented by Jacobson and Freiser,[29] confirming that the CpCo$^{\bullet+}$ ion exhibited the same reactivity toward alkanes. These results are displayed in Table 1.

Reactions of CpCo$^{\bullet+}$ with Individual Alkanes. Linear alkanes ranging from tetracosane ($C_{24}H_{50}$) to pentacontane ($C_{50}H_{102}$) were subjected to LIAD/CpCo$^{\bullet+}$ in an FT-ICR and their reaction

products detected. For example, tetracontane ($C_{40}H_{82}$) molecules were desorbed into the gas phase by using LIAD (Figure 1) and allowed to react with CpCo$^{\bullet+}$ reagent ions in the FT-ICR cell. The only product ion peak observed in the mass spectrum, m/z 682, corresponds to the expected reaction product, [R + CpCo − 2H$_2$]$^{\bullet+}$ (R = $C_{40}H_{82}$) (Figure 2). Similar experiments were performed with several other linear alkanes (Table 1), and in each case, the expected ion, [R + CpCo − 2H$_2$]$^{\bullet+}$, was the only product.

Another interesting characteristic of these CpCo$^{\bullet+}$-alkane reactions is their high efficiency, often approaching 100%. Given that the residence time of a LIAD-desorbed neutral molecule in the cell is only on the order of 1 ms,[17] the detection of high abundances of [R + CpCo − 2H$_2$]$^{\bullet+}$ product ions demonstrates the speed of this reaction. This reaction's high efficiency, combined with the fact that each product ion has a m/z value 120 mass units higher than the MW of the neutral alkane, demonstrates that the LIAD/CpCo$^{\bullet+}$ method can be used to quickly and easily determine the MW of alkanes in a mass spectrometer.

Reactions of CpCo$^{\bullet+}$ with Mixtures of Alkanes. In an effort to experimentally model PE samples, artificial mixtures containing three, four, and seven (Figure 3a and b) linear alkanes were examined by using the LIAD/CpCo$^{\bullet+}$ method. The mass spectra, which are the sum of four 50-shot experiments, showed the expected product ion ([R + CpCo − 2H$_2$]$^{\bullet+}$) for all of the hydrocarbons present in each mixture (see Table 2); no other product ions were observed. As indicated in the mass spectra in Figure 3, the relative abundances of the product ions correlate

(28) (a) Marshall, A. G.; Wang, T.-C. L.; Ricca, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 7893−7897. (b) Chen, L.; Wang, T.-C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1987**, *59*, 449−454

(29) Gqamana, P. P.; Campbell, J. L.; Williams, K. P.; Nash, J. J.; Kenttämaa, H. I. In preparation.

(a) $C_{28}H_{58}$, $C_{29}H_{60}$, $C_{30}H_{62}$, $C_{31}H_{64}$, $C_{32}H_{66}$, $C_{33}H_{68}$, $C_{34}H_{70}$

Molar Ratio	1.00	1.10	0.89	1.13	0.72	0.80	1.28
Ion Signal Ratio	1.00	1.10	0.74	1.12	0.69	0.73	1.11
m/z	514	528	542	556	570	584	598

(b) $C_{24}H_{50}$, $C_{26}H_{54}$, $C_{28}H_{58}$, $C_{30}H_{62}$, $C_{32}H_{66}$, $C_{34}H_{70}$, $C_{36}H_{74}$

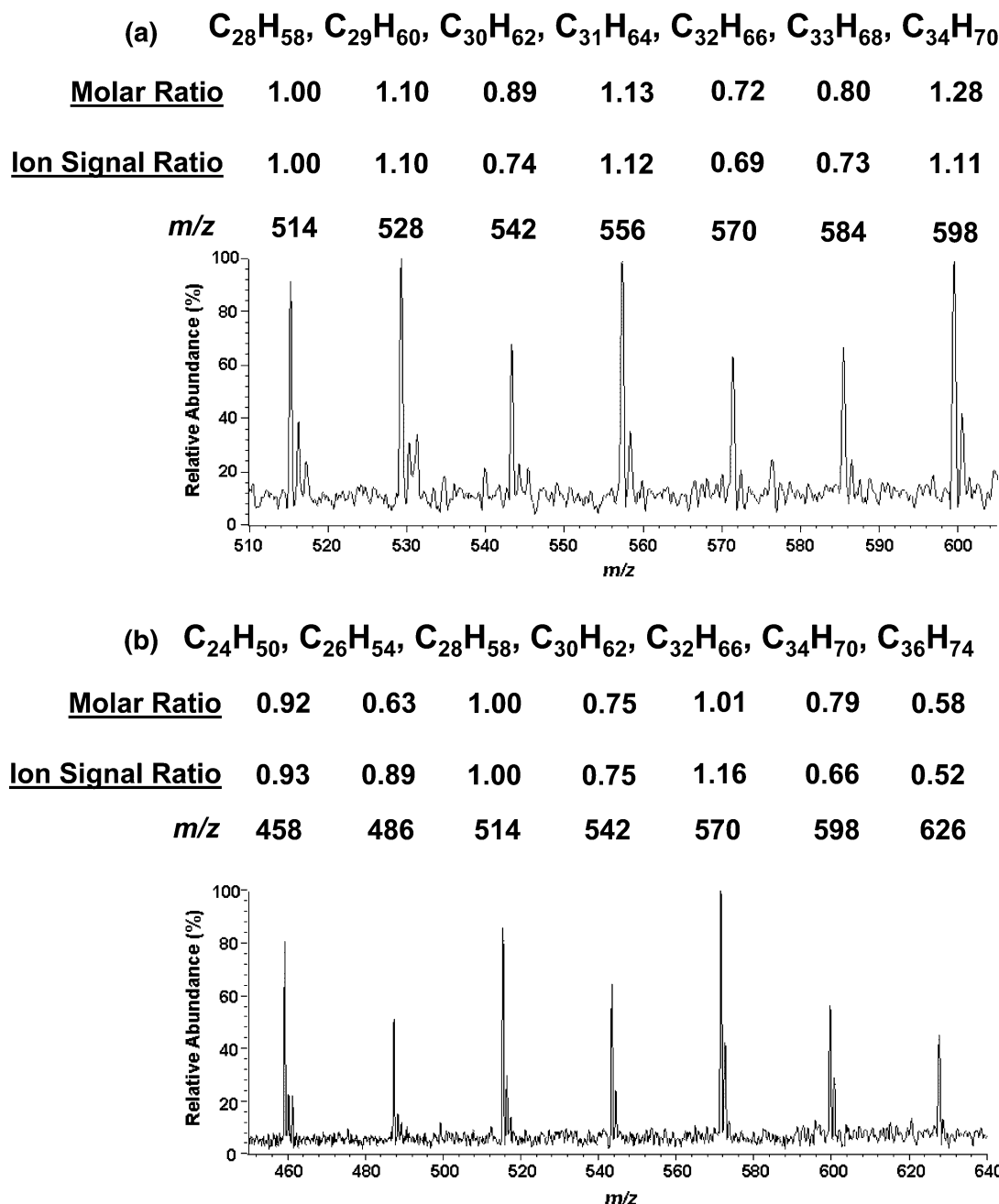| Molar Ratio	0.92	0.63	1.00	0.75	1.01	0.79	0.58
Ion Signal Ratio	0.93	0.89	1.00	0.75	1.16	0.66	0.52
m/z	458	486	514	542	570	598	626

Figure 3. (a) Mass spectrum of a seven-component mixture of saturated linear hydrocarbons ($C_{28}H_{58}$–$C_{34}H_{70}$, inclusive), desorbed by LIAD (sum of four 50-shot experiments), and allowed to react with the CpCo$^{•+}$ ion. A comparison of the relative ion signal and the molar ratio of each of the hydrocarbons in solution is also given. (b) Mass spectrum of a seven-component mixture of saturated linear hydrocarbons (alkanes containing an even number of carbons between $C_{24}H_{50}$ and $C_{36}H_{70}$, inclusive), desorbed by LIAD (sum of four 50-shot experiments), and allowed to react with the CpCo$^{•+}$ ion. A comparison of the relative ion signal and the solution molar ratio for each of the hydrocarbons is also given. Both the molar ratio and the ion signal ratio are normalized to the molar concentration and signal abundance for octacosane ($C_{28}H_{58}$). The only product ion observed for each alkane was the [R + CpCo − 2H$_2$]$^{•+}$ ion and the corresponding one ^{13}C-isotope-containing ion.

well with the relative molar concentrations of the corresponding saturated hydrocarbons in the CS$_2$ solution. This result suggests that each of the alkanes in the mixture was subject to an overall equally efficient desorption/ionization process.

CONCLUSIONS

The combination of LIAD and CpCo$^{•+}$ chemical ionization mass spectrometry shows promise as a new technique for analyses of saturated hydrocarbons. This method avoids cumbersome and time-consuming derivatizations and yields mass spectra that are free of complicating fragment ion peaks. The only ion produced for each alkane, [R + CpCo − 2H$_2$]$^{•+}$, is representative of the MW of the alkane, which results in relatively simple-to-interpret mass spectra. Mass spectra indicate no bias against either the lower or higher mass alkanes. The preliminary results detailed here suggest that mixtures of low-MW alkanes can be readily analyzed to yield MW and composition information by using the LIAD/CpCo$^{•+}$ method. Future research will focus on implementa-

tion of the LIAD/CpCo$^{\bullet+}$ method in the analysis of higher MW saturated hydrocarbons and saturated hydrocarbon polymers, such as PE.