Molecular Mass Determination of Saturated Hydrocarbons Using Organometallic Ion Chemistry

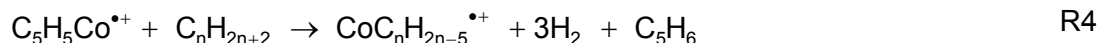H.C. Michelle Byrd,[1] Charles M. Guttman,[1] Scott Robinson,[2] and Douglas P. Ridge[2]
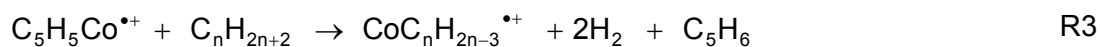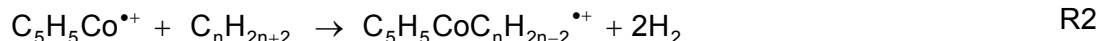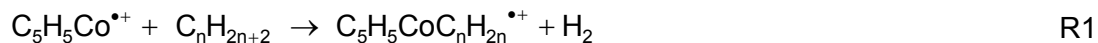
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Saturated hydrocarbon polymers, polyethylene, polypropylene and their derivatives, are the most widely used of all synthetic polymers. Their chemical structure and composition, molecular mass (MM), and molecular-mass distribution (MMD) are critical in determining performance properties. The potential for quick and direct measurement of single-chain composition and MMD makes mass spectrometry (MS) especially attractive to the polymer industry. However, using MS analysis for the determination of MMDs requires the formation of intact macromolecular ions in the gas phase, which has proven quite difficult for saturated polyolefins due to the lack of a suitable ionizable site on the aliphatic chain. The present gas-phase study demonstrates the feasibility of using η^5-cyclopentadienylcobalt ion (CpCo$^{\bullet+}$) as cationization reagent for saturated hydrocarbon analysis.

Reactivity of CpCo$^{\bullet+}$ ion towards medium n-alkanes and branched alkanes were examined using Fourier-transform mass spectrometry. C-15 through C-60 was chosen to serve as lower-molecular mass models of polyethylenes.

All alkanes studied were found to undergo the following reactions with the CpCo$^{\bullet+}$ ion.

$$C_5H_5Co^{\bullet+} + C_nH_{2n+2} \rightarrow C_5H_5CoC_nH_{2n}^{\bullet+} + H_2 \qquad \text{R1}$$

$$C_5H_5Co^{\bullet+} + C_nH_{2n+2} \rightarrow C_5H_5CoC_nH_{2n-2}^{\bullet+} + 2H_2 \qquad \text{R2}$$

$$C_5H_5Co^{\bullet+} + C_nH_{2n+2} \rightarrow CoC_nH_{2n-3}^{\bullet+} + 2H_2 + C_5H_6 \qquad \text{R3}$$

$$C_5H_5Co^{\bullet+} + C_nH_{2n+2} \rightarrow CoC_nH_{2n-5}^{\bullet+} + 3H_2 + C_5H_6 \qquad \text{R4}$$

Loss of two hydrogen molecules from the CpCo-alkane ion complex (R2) was found to dominate the reaction with all n-alkanes studied ($\geq$ 80 %) with no C-C bond cleavage observed (e.g., Figure 1a). Second order rate constants and reaction efficiencies were determined for CpCo$^{\bullet+}$ reactions with C-15, C-20, and C-28. For these alkanes, the dehydrogenation reaction efficiency increases with increasing chain length (Table 1). This trend arises in part for two reasons. First, the possible number of reactive C-C sites per molecule increases as the chain lengthens. Second, the stabilization energy increases and therefore complex lifetime increases as the alkyl chain length increases. We speculate that R2 may reach collision rate when the chain length reaches ~60 carbons. The non-dependence of chain length and reaction efficiency has important implications for future work with longer chain hydrocarbons and saturated polyolefin systems. Future plans entail determining reaction rates and efficiencies for C-36 through C-60.
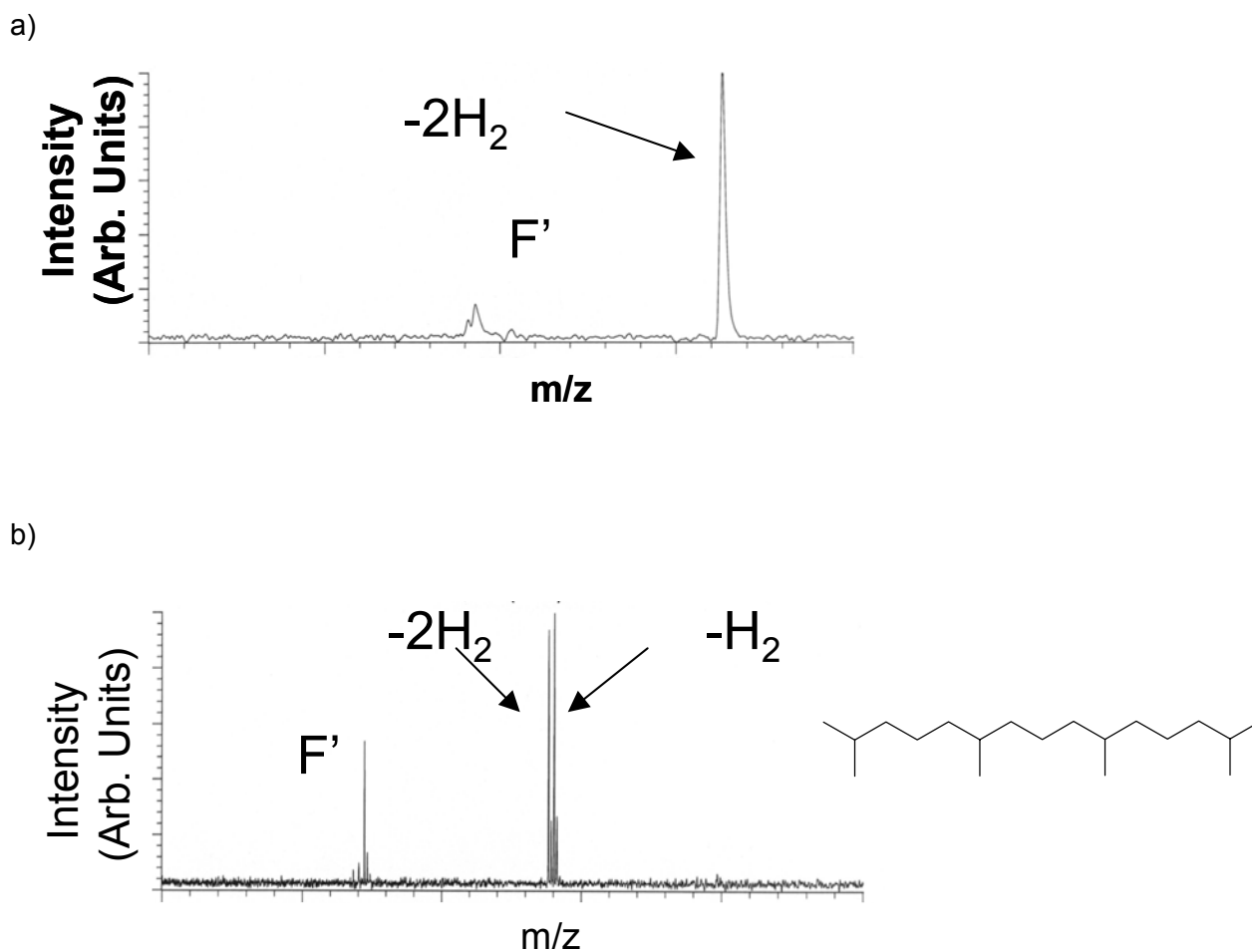
CpCo$^{\bullet+}$ ion was also reacted with low-branched alkane 2,6,10,14- tetramethylpentadecane (pristane). Unlike the n-alkanes, pristane reacts with CpCo$^{\bullet+}$ equally by single (R1) and double (R2) dehydrogenation (Figure 1a,b). Steric hindrance may contribute to enhanced efficiency for pathway R1.

Table 1. Rate Constants and Overall Reaction Efficiencies for CpCo$^{\bullet+}$ Ion Reaction with C-15, C-20, and C-28

Alkane	k_{exp}, x10^{-10} cm^3/molecule$\bullet$s	k_{coll}, x10^{-10} cm^3/molecule$\bullet$s	k_{exp}/ k_{coll}, %
C-15	2.2	14	15
C-20	4.0	15	25
C-28	7.2	17	40

The reaction rate constants and product distributions presented are within a reproducibility of $\pm$ 10 %. However, the accuracy of the reaction rate constant is within $\pm$ 50 % due to the uncertainty in the pressure measurement.

Figure 1. a) Mass spectrum of reaction between CpCo$^{\bullet+}$ and n-alkane C-60
b) Mass spectrum of reaction between CpCo$^{\bullet+}$ and pristane

a)

b)

$$F' - C_5H_6 \text{ loss from Adduct} - 2H_2$$