

Chemical Ionization of Saturated Hydrocarbons Using Organometallic Ion Chemistry

H.C. Michelle Byrd and Charles M. Guttman, National Institute for Standards and Technology, Polymers Division, Gaithersburg, MD 20899

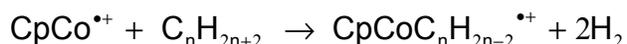
Douglas P. Ridge, University of Delaware, Dept. of Chemistry and Biochemistry, Newark, DE 19716

Saturated hydrocarbon polymers, polyethylene, polypropylene and their derivatives, are the most widely used of all synthetic polymers. Their chemical structure and composition, molecular mass, and molecular-mass distribution (MMD) are critical in determining performance properties. The potential for quick and direct measurement of chemical composition, absolute mass determination, and MMDs makes mass spectrometry (MS) especially attractive to the polymer industry. However, saturated polyolefin MS analysis requires the formation of intact macromolecular ions in the gas phase.

The difficulty in ionization of saturated polyolefins arises from the lack of a suitable ionizable site on the aliphatic chain. The present study demonstrates the feasibility of the η^5 -cyclopentadienylcobalt ion ($\text{CpCo}^{\bullet+}$) as a suitable cationization reagent for saturated hydrocarbons analysis by mass spectrometry.

In the present gas-phase study, we report preliminary results on the $\text{CpCo}^{\bullet+}$ ion reactivity toward three medium chain length n-alkanes using Fourier-transform ion cyclotron resonance mass spectrometry. C-15, C-20, and C-28 serve as lower-molecular mass models of polyethylenes. Second-order rate constants and reaction efficiencies were determined for the reactions studied.

Figure 1 shows plots of the kinetic data for the reaction of $\text{CpCo}^{\bullet+}$ ion (m/z 124) with C-15 (MM 212 amu), C-20 (MM 282 amu), and C-28 (MM 394 amu). All three alkanes were found to form an adduct ion with $\text{CpCo}^{\bullet+}$ minus two hydrogen molecules.



The $\text{CpCo}^{\bullet+}$ ion reacts predominantly by the above reaction pathway for all three alkanes ($\geq 80\%$) with no C-C bond cleavage observed. Furthermore, the dehydrogenation reaction efficiency increases with increasing chain length. These initial results suggest that the $\text{CpCo}^{\bullet+}$ ion may be a promising cationization reagent of larger saturated polyethylenes.

Figure 1. The plots of the kinetic data show that the CpCo^{+} ion of m/z 124 (■) reacts with all three alkanes by producing an adduct ion minus two hydrogen molecules (●).

