

Determination and Gas-phase Stability Evaluation of Organometallic Complexes by Nanoelectrospray Ionization and Collision-induced Dissociation Tandem Mass Spectrometry

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Abstract

Rationale: The structures of organometallic complexes determine their stable functioning in product performance. Electrospray ionization-mass spectrometry (ESI-MS) is used in studying metal complexes, but it exhibits limitations in analyzing labile organometallics. Therefore, identifying a method of detecting unstable organometallics and evaluating their stabilities is necessary, providing a theoretical basis for material selection and performance evaluation. **Methods:** The standard complexes Zn(BTZ)₂, Fe(acac)₃, and Sn(Oct)₂ were analyzed using nanoelectrospray ionization-quadrupole orbitrap MS (nanoESI-MS) and compared with ESI-MS. Alkylamine-Ag⁺ complexes were analyzed using nanoESI and collision-induced dissociation MS/MS (CID-MS/MS). Breakdown plots of the ion relative abundances against collision energies expressed in terms of the center-of-mass were constructed according to the obtained product ion spectra. Quantum chemical calculations based on density functional theory were performed to calculate the binding energies between the alkylamines and Ag⁺. **Results:** The molecular ions of the three standard complexes were only detected using nanoESI-MS, which confirmed the suitability of soft nanoESI for use in detecting unstable organometallics. The gas-phase stabilities of the amine-Ag⁺ complexes, as estimated using the breakdown plots constructed by plotting the data obtained via nanoESI and CID-MS/MS, were consistent with the established theories, previous studies, and binding energies calculated using computational methods. **Conclusions:** NanoESI-MS is suitable for detecting labile organometallics and enables the structural analyses of unknown organometallic additives. A novel approach based on nanoESI and CID-MS/MS was developed to determine the gas-phase stabilities of organometallics, enabling their quantification and comparison and providing a technical basis for product improvement, which is essential in developing industrial materials.

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