Novel Gas Phase Ion-Molecule Reactions and Mechanisms in Atmospheric Pressure Ionization Mass Spectrometry

The interface of high pressure liquid chromatography (HPLC) to mass spectrometry (MS) has had tremendous impact on the scientific community since its inception. For trace analysis of polar analytes, HPLC-MS frequently achieves unrivaled sensitivity and selectivity over most other detection techniques. Being particularly useful to the well-funded fields of pharmaceutical, protein and biomedical analysis this has prompted tremendous advances in the quality and simplicity of commercially available instrumentation. Much of this research has been directed to the task of converting a neutral analyte under high pressure conditions to a charged molecule in a vacuum without destroying the molecule. This has been achieved by various atmospheric pressure ionization (API) techniques—particularly, electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). While mechanisms for each process have been proposed, API is still an area of active research in the field of HPLC-MS. Modifications to analyte ions may occur due to unpredicted gas-phase reactions between analytes and solvents, impurities, or matrix components. Presented in this work are previously unreported gas-phase reactions and/or mechanisms between common HPLC solvents and peroxide-based explosives or other analytes of interest. The first is the interaction of acetonitrile and specific functional groups responsible for significant suppression of ion formation. A theory based on the formation of neutral aggregates has been proposed to account for this phenomenon. As this is one of the most commonly used solvents in HPLC-MS, this work may have significant impact on the analytical community. The second is the gas-phase, nucleophilic attack of alcohols with the methylene group of hexamethylene triperoxide diamine (HMTD). This mechanism sheds some light on the reactivity of this sensitive and fragile molecule which continues to challenge chemists throughout the field.