Atmopsheric Chemistry Tracers of Diesel Exhaust Emissions

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Project Description

The project will involve using the Proton Transfer Reaction Mass Spectrometer (PTR-MS) instrument to determine if it can be used to measure the concentration of long chain alkane compounds (C_{10}-C_{25}) emitted into urban atmospheres from diesel exhaust. It has been hypothesized that these compounds rapidly oxidize in the atmosphere to form low volatility products that condense on existing fine airborne particles, significantly increasing the amount of organic particulate mass in urban atmospheres. Particulate matter (PM) mass concentrations are regulated by the EPA so there is a need to better understand PM sources from both a regulator stand point and from an atmospheric chemistry perspective. To test this hypothesis, direct measurement of long chain alkanes in air is necessary but this is a difficult problem owing to their low concentrations (less than ng / m^3) and the large number of compounds involved (thousand of isomers). The measurement approach in this project is to use chemical ionization mass spectrometry to determine the total mass of such compounds in air rather than trying to measuring each organic component as has been done in the past.

The PTR-MS instrument measures organics in real time by a proton transfer reaction to make an ion that is detected by a quadrupole mass spectrometer. H_3O^+ is used in a gas phase reaction with an organic R.

$$H_3O^+ + R \rightarrow RH^+ + H_2O$$

This reaction is usually non-dissociative (RH^+ doesn't fall apart into smaller ions) and so compounds are identified by their molecular weight. For example benzene with molecular weight = 78 amu would be measured at mass 79. This technique is used to measure pollutants in urban air, hydrocarbon emissions from trees, and compounds in your breath!

What we want to test in this project is whether alkanes will undergo dissociative proton transfer reactions and fall apart into a common set of ion fragments.

$$RH^+ \rightarrow R_1^+ + R_2$$

If the thousand of alkanes emitted from diesel exhaust form a few common ion fragments, which I think they will, then this would allow the PTR-MS to quantify their total concentration in air, something that hasn't been done before. We will test this measurement approach in a Department of Energy field experiment in Sacramento, CA next summer.