

Explosives on Surfaces: A Sticky Problem

Explosive compounds need to be detected on a variety of surfaces - clothing, suitcases, shoes, etc. Every surface will interact with the compounds and the degree of adhesion will vary, surface to surface. By and large, detection of these compounds relies on getting the molecules off the surface and into the gas phase. While there have been significant advances in instrumentation for both laboratory and in-the-field application, a device to be used for airport security will require certification by federal authorities. Certification will depend upon a sound understanding of device performance and thus, the knowledge of the energetic effects of surfaces, ubiquitous in all measurement scenarios, must be part of the certification process. A NIST-led research team works to provide such data.

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The most fundamental measure of the interaction strength with a surface is the enthalpy, ΔH . On solids, this describes an adsorption process (ΔH_{ADS}), while on polymers and liquids, an absorption process (ΔH_{SOL}). The vapor-phase concentration of explosive compounds is dependent on the enthalpies associated with the surface upon which the explosive residues have sorbed. Surprisingly, there has been very little attention given to this important parameter, primarily due to the experimental difficulties associated with its determination. In earlier work on sorption, we developed a technique to use capillary gas chromatography to measure the surface energetics of organics on soil surrogates. We have extended this work to energetic materials and measured the enthalpy of trinitrobenzene (TNB), trinitrotoluene (TNT), and hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine (HMX) sorbed on a polydimethyl siloxane surface. In addition to these high explosives, we have measured their taggants: 2-nitrotoluene, 3-nitrotoluene, and 4-nitrotoluene. The surface substrate is used as a gas chromatographic stationary phase, and it also is used as a lubricant, release agent, coating, and principal component in silicone rubbers. The ΔH_{SOL} for TNB, TNT, RDX, and HMX were measured to be $(57.85 \pm 0.2, 59.48 \pm 0.2, \text{ and } 62.36 \pm 0.2, 72.10 \pm 0.02)$ kJ/mole, respectively. For the taggants, we measured enthalpy values for 2-nitrotoluene, 3-nitrotoluene and 4-nitrotoluene of $(49.8, 50.7, 51.0)$ kJ/mole, respectively, with similar uncertainties as obtained for the high explo-

With heightened awareness of homeland security issues the detection of explosive or energetic materials at high sensitivity and with a low error rate has become a pressing priority.

sives. We also determined (by measurement of Kováts retention indices) that the energy required to desorb an explosive is similar to that required for C_{14} to C_{16} n-alkanes suggesting perhaps a surrogate for instrument calibration. Moreover, we noted that the enthalpy of vaporization for pure TNT and TNB are higher (by ≈ 20 kJ/mole) than the ΔH_{SOL} values. This means that it takes less energy to “desorb” an explosive molecule from PDMS or “PDMS-like” material than it would to volatilize (for example, by heating) a molecule from a solid particle of the pure explosive. One potential application, suggested by this discovery, would be the development of enhanced polymeric release surfaces for wipe testing.

In addition to the vapor-phase measurements, we have made similar measurements in the liquid (water) phase. Here, we have used a clay surface as a soil surrogate. These measurements are significant in that residual energetic materials in the environment are a serious threat, especially in live-fire military training venues. Here, for example, we measured ΔH_{ADS} for RDX = (24.7 ± 0.7) kJ/mole, while that for benzene was measured as (18.9 ± 1.3) kJ/mole. These data indicate that while the enthalpies are not especially high, one can expect RDX to persist in the environment longer than benzene.

Below is a retention plot showing the capacity factor of benzene and RDX plotted against temperature, in water as the mobile phase. This illustrates the environmental persistence of energetic materials such as RDX.

