Christopher A. Latendresse

University of Rhode Island, Chemistry Department

TNT Reactivity with Amines – Clarification of Mechanisms for Detection Applications

Abstract:

Trinitrotoluene (TNT) is a common explosive analyte that is of interest due to its toxicity and possible use in terroristic activity. Although contact-mode sensors are of importance for TNT determination after a threat has been perceived, stand-off trace detection is needed to detect threats before they are in close proximity. This requires the utilization of TNT vapors, which is challenging given the low vapor pressure (8.02×10^{-6} mmHg at 25°C) of TNT[1]. Recent literature proposes a class of solid-vapor phase TNT sensors that rely on TNT reactivity with amines, with products that have absorbance bands in the visible range. Commonly, these absorbance features are used in a resonance energy transfer (RET) pairing of the TNT product with a fluorescent reporter molecule, by which energy transfer alters the observed fluorescence intensity. These proposals invoke several different mechanisms (such as charge-transfer complex formation[2], Brönsted-Lowry Acid/Base reaction[3], sigma adduct/Meisenheimer complex formation[4]) to justify similar absorbance spectroscopy, which serves to confuse what the true reaction products may be. While these proposed mechanisms rely on similar reactivity of TNT with alkoxides, the current literature has focused on applications of this chemistry instead of a mechanistic understanding. To our knowledge, there has not been a thorough investigation into the reaction(s) that the sensor proposals are constructed upon, especially on a meaningful timescale for sensing. Our investigation proposes to clarify what products are observed in solvents of differing polarity, their relative kinetics and thermodynamic stability, molar absorptivity, and to propose the likelihood of these products existing in the aforementioned solid-vapor phase sensors.

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