

Studies of Organic and Inorganic Azides and their Decomposition Products

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An overview is presented of the thermal decomposition in the gas-phase of a series of organic azides, studied with u.v. photoelectron spectroscopy and infrared matrix isolation spectroscopy. Mechanisms are proposed for the formation and decomposition of all the products observed, based on the experimental evidence and the results of supporting electronic structure calculations. Two basic mechanisms have been identified:-

- (i) Type 1- an imine is formed after initial liberation of N₂, followed by decomposition of the imine.
- (ii) Type 2- a proton, or more generally an alkyl group, is transferred onto the “inner” N atom of the azido group from a remote site to give a cyclic transition state or intermediate, which decomposes to give N₂ and an imine. The imine then decomposes further.

Also, a series of alkali and alkaline earth metal-crown ether azide complexes have been synthesized. In most cases, single crystals were obtained which allowed X-ray crystal structures to be derived. The structures were compared with molecular structures computed by DFT calculations. This has allowed the effects of the crystal lattice on the structures and the bonding in these complexes to be investigated. The decomposition of these potential high energy density materials (HEDMs) to give N₂ and the metal-crown ether unit has been investigated by DFT and quantum chemistry calculations.

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