Research in the chemical effects of the nuclear transformations during the past 50 years is reviewed.

Introduction

Hot-atom chemistry (HAC) is the study of the chemical reactions that occur between high-energy atoms and ions and (usually) thermal-energy atoms, molecules, ions, and radicals. Studies involve atoms and ions that are produced photochemically, by velocity selection as in atomic-beam studies, as well as by nuclear processes. This review of a half-century of hot-atom chemistry is concerned only with the last means of production and a more appropriate title would be the Chemical Effects of Nuclear Transformations (CENT). In fact, the two phrases, HAC and CENT are often used interchangeably in describing the chemical processes that occur when hot atoms and ions are produced by nuclear means.

SZILARD and CHALMERS in 1934 were the first to report a study of CENT. They showed that when ethyl iodine was irradiated with neutrons, much of the $^{128}$I produced in the $^{127}$I(n, $\gamma$) $^{128}$I nuclear reaction could be extracted by water, indicating that the $^{128}$I ruptured from its parent compound as a result of the nuclear process. Very few studies were reported during the next 10-15 years, primarily because of the lack of availability of neutron sources. As research nuclear reactors with high neutron fluxes became available in the late 1940's and early 1950's, interest in CENT studies increased markedly and attracted the interest of researchers worldwide. Over two thousand articles have been published dealing with all aspects of CENT and this review of a half-century of hot atom chemistry provides only a sampling of the work in this field.

A large amount of energy is released in a nuclear transformation and a fraction of this energy can be imparted as recoil energy to the atom (isotope) undergoing the nuclear transformation, causing the activated isotope to dissociate from the molecule.
to which it was bonded. Typical energies are about 200 eV in the \( (n, \gamma) \) activation process, 192,000 eV for the \( ^3\text{T} \) in the \( ^3\text{He}(n, p)^3\text{T} \) activation, and even larger energies in the production of isotopes by nuclear fission. A 2.0 MeV beta decay can result in a recoil energy of up to about 20 eV. And even the relatively weak isomeric transition (IT) process can result indirectly in a recoil energy of a few eV since IT is often accompanied by the release of a large number of Auger electrons resulting in a distribution of positive charge on the molecule with subsequent Coulombic repulsion and dissociation of the IT-activated isotope.

Bond energies are typically less than about 4 eV so that bond rupture is almost always assured for the more energetic activation processes. The hot atom usually cannot form a stable bond in the first few collisions with room-temperature (0.025 eV) molecules. Only after sufficient collisions which involve the loss of much of the excess energy is the hot atom able to react to form a stable product. Complicating the picture is the fact that many if not most of the hot atoms are really not atoms when they are formed but more likely are ions in varying ionic excitation states. And, even though translational kinetic energy can be lost in sequential collisions, the ionic and excitation state of the "slowed down" hot atom may not be known.

Although atomic and molecular beam studies allow investigating individual chemical interactions at selected energies, hot atom chemical studies only allow observing the overall chemical processes. However, the judicious use of additives that can moderate the reaction by absorbing excess kinetic energy of the hot atoms (inert gases for instance) and/or neutralize charged species (additives with ionization potentials than are lower than that of the hot atom), has made it possible to sort out and describe some of the hot-atom chemical mechanisms.

Most of the early studies were concerned with the hot atom chemistry of \( (n, \gamma) \)- and IT-activated halogen isotopes and \( ^3\text{T} \) activated by the \( ^3\text{He} (n, p)^3\text{T} \) process, in all three phases: solid, liquid, and gas. In later years interest expanded to include, among others, studies of the HAC of metal-organic and inorganic solid compounds, other methods of production such as beta decay, and the use of HAC to study nuclear fission.

Hot atom studies have relevance to many other chemical studies. Upper atmosphere chemistry where high-energy atoms are produced is just one example. Another is ion-implantation. Labeling of chemical compounds and radiopharmaceuticals is yet another example.

A number of reviews and symposia on hot atom chemistry have appeared in recent years and detail the progress in this field.