PREPARATIVE PROSPECTS OF "HIGH TEMPERATURE" SPECIES

Thomas D. Coyle, F. E. Brinckman, J. J. Ritter
National Bureau of Standards
Washington, D. C. 20234

and

Gerald F. Kokoszka
State University of New York
Plattsburgh, New York 12901

Much of the emphasis of traditional high temperature chemistry in the past two decades has been placed on the elaboration of thermodynamic, kinetic, and structural features of chemical systems. Less attention, perhaps, has been given until quite recently to the implications of the results of high-temperature investigations for the synthetically oriented chemist. It has become increasingly evident, however, that the variety of unconventional and intrinsically interesting species accessible in significant concentrations under energetic regimes are potentially valuable reagents, and that these reactive intermediates can provide the means for syntheses of novel systems not yet achieved by more usual routes.

From the synthetic viewpoint, the availability of potential intermediates under energetic conditions is of primary importance, and the nature of the excitation employed is perhaps secondary. Accordingly, "high temperature" techniques in the literal sense are but one facet of a more general synthetic rationale, which also embraces alternate modes of excitation such as electric or microwave discharge procedures and photochemical syntheses. Even more generally, one may extend this synthetic viewpoint to the rational utilization of stable compounds, themselves formed by energetic routes, which provide sources of preformed

submolecular entities not otherwise available for synthetic exploitation. Thus, the energetic synthesis may provide the starting point for a derivative chemistry that might not be accessible by exclusively high energy procedures.

In this paper, we describe some recent activities in the authors' laboratories utilizing this somewhat permissive view of "high temperature" processes as a synthetic tool.

The preparation of catenated systems involving elements other than carbon is an area in which synthesis has traditionally relied heavily on the "energetic chemistry" approach. While conventional condensation reactions are applicable under some conditions, much of the synthetic progress in the area of catenated hydrides and halides of the representative elements, for example, has relied either on hydrolytic procedures using derivatives in which the catenation is "preformed" by high temperature preparative routes, or on thermal or discharge excitation. Thus, synthesis of catenated halides has been frequently achieved by discharge routes involving chlorides or compounds of the heavier halogens. Procedures involving fluorides have been generally unsuccessful, and it is frequently assumed that the reactive species in fluoride discharges are incompatible with retention of homoelemental bonding. In the course of investigations of the discharge reactions of covalent fluorides of elements such as boron, silicon, germanium, and phosphorus, we have demonstrated, mass spectrometrically and in bulk, the occurrence of catenation in fluoride-based systems. In more complex systems involving silicon, halogen redistribution and catenation to mixed halopolysilanes has been observed.

Some of these compounds have subsequently been prepared by alternate routes and investigated in detail by NMR double resonance techniques.

Of more general occurrence in microwave-excited fluoride plasmas is reaction with oxides or oxygen itself to produce oxyhalide species such as OBF and $OSiF_2$ which appear to undergo a series of secondary reactions to produce an array of simple and polymeric oxyfluorides. Progress made to date toward the elucidation of products and of principal reaction pathways suggests that relatively straightforward four-center addition reactions of the principal oxyfluoride intermediates are involved.

The well-known discharge synthesis of the boron subhalides provides a ready source of these compounds, which exemplify a class of reagents, accessible by energetic routes, for which an extensive derivative chemistry can be developed. A number of hitherto unreported organo derivatives have now been prepared. Reactions with a number of organic and organometallic reagents have been observed in which these compounds function as a formal source of BX groups. A comparison is suggested with the high-temperature boron-halogen chemistry investigated by others, including the possibility that the nominally stable subhalides may function under some conditions as low temperature sources of high temperature species.

Photochemical excitation is a particularly attractive source of a more selective energy input in systems, such as organometallics, that are potentially degradable by more rigorous high-temperature procedures. New synthetic results in organoboron photochemistry include the synthesis of an ethynyl derivative of three-coordinate boron. The relationship of photochemical and other energetic processes has been probed in studies of free radical chemistry of phosphorus. The radicals PCl_2 and PCl_4 have been characterized and their chemical consequences investigated.