Dialkyl halonium ions, $R_2X^+$ (X=F, Cl): Stability and chemical properties

Halonium ions ($R_2Hal^+$) are reactive intermediates in electrophilic chemistry and are effective methylating and protonating agents for a variety of compounds. Chloronium cations (Figure 1) in their salts ($C_{n}H_{2n+1})_{2}Cl^+(CHB_{11}Cl_{11}^-)$, at $n=1$ to 3 and with exceptionally stable carborane anions, are stable at ambient and elevated temperatures. Their temperature of decomposition decreases with the $n$ increasing from 1 (ca. 150°C) to 3 (ca. 80°C) because of increasing ionicity of C-Cl bonds in the C-Cl^-C bridge. At room temperature, the salts of cations at $n \geq 4$ are unstable and decompose. It was shown indirectly that the unstable salt of fluoronium ions ($CH_3^+_{2}F^+(CHB_{11}F_{11}^-)$ must exist at low temperatures. The proposed ($CH_3^+_{2}F^+$) cation is much more reactive than the corresponding chloronium, showing at room temperature the chemical properties expected of chloronium at elevated temperatures. ($CH_3^+_{2}F^+$ and $CH^+_4F^+\cdot CH_4$ are decomposed yielding cations $C_4H^+_4$ or $C_3H^+_3$, respectively. Interaction of chloronium cations with chloroalkanes was studied here; for example, interaction of ($CH_3^+_{2}Cl^+$ with $CH_3Cl$ at 160°C results in formation of the tert-Bu^+ cation. Interactions of the salts of chloronium ions, $R^-Cl^+-R$ ($R=CH_3$ or $CH_4$), with gaseous and liquid di-chloromethane have been studied. In liquid $CH_2Cl_2$, they act as catalysts converting $CH_2Cl_2$ to $CHCl_3/CCl_4$ (chlorination) or to $CH_3Cl/CH_4$ (dechlorination). The mechanism of the catalytic processes was determined.

Biography

Evgenii S Stoyanov completed his graduation at Moscow State University in 1971; PhD in 1974 and began scientific career at Institute of Inorganic Chemistry of the Academy of Science of the USSR as Researcher. From 1983, he headed a Laboratory for Spectroscopy Methods of Investigation. He completed his Doctor of Science in Chemistry in 1991 and became a Lead Researcher at Institute of Catalysis of the Russian Academy of Science and Full Professor, Head of the Department of Chemistry at Novosibirsk State Pedagogical University. From 2004, he worked as invited Professor and Professional Researcher at University of California, Riverside, USA. From 2015, he headed the scientific direction for the study of carbocations using solid super acids at Institute of Organic Chemistry (Russian Academy of Sciences, Novosibirsk), as Leading Researcher.

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