Chloronium cations, R-Cl'-R, in condensed phases: Formation, thermal stability, and reactivity

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Halonium ions (R$_1$Hal$^+$) are reactive intermediates in electrophilic chemistry and are effective methylating and protonating agents for a variety of compounds. Chloronium cations are most reactive and they were obtained as stable carborane salts, (R$_1$-Cl$^+$-R$_2$)(CHB$_{11}$Cl$_{11}$-') with R$_1$/R$_2$ = CH$_3$, CH$_2$Cl, C$_2$H$_5$, and C$_3$H$_7$, at ambient conditions. We have studied: The thermal stability of the salts of chloronium ions at room and elevated temperature (up to 150°C), interaction of the R$_1$-Cl$^+$-R$_2$ cations (R$_1$/R$_2$ = CH$_3$ or CH$_2$Cl) of the solid salts with vapors of CH$_2$Cl$_2$ and CHCl$_3$ and chloronium salts in dichloromethane solutions with accompanying reactions. The asymmetric cations are mostly unstable, for example, the CICH$_2$-Cl$^+$-CH$_3$, when kept at room temperature in one day it disproportionated into symmetric cations, (CH$_3$)$_2$Cl$^+$ and (CH$_2$Cl)$_2$Cl$^+$. At 100°C, disproportionation was completed within 5 minutes. The molecular fragment ClCH$_2$-(X) of the compounds with X = CHB$_{11}$Cl$_{11}$-, -Cl+-CH$_2$Cl, or -Cl+-CH$_3$, is involved in exchange reactions with CH$_2$Cl$_2$ and CHCl$_3$, converting to CH$_3$-(X) with formation of chloroform and CCl$_4$, respectively. Chloronium cations can also decompose with the removal of the bridging Cl-atom as HCl, to form different carbocations. Hence, they can be a useful in many applications in the conventional chemical practice for special tasks.

Biography

Evgenii S Stoyanov has received his PhD degree from Vernadsky Institute of Geochemistry and Analytical Chemistry (Academy of Sciences of USSR), Moscow, Russia, and the Doctor of Science degree in Chemistry in 1991 from Mendeleev University of Chemical Technology, Russia. Presently, he is a Leading Researcher at the Institute of Organic Chemistry (Siberian Branch of Russian Academy of Sciences), Novosibirsk, Russia, and leading the study of carbocations by using the solid super-acids. He has published 139 papers in reputed journals.

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