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Chloronium cations, R-Cl$^+$-R, in condenced phases: Formation, thermal stability, and reactivity

Evgenii S Stoyanov
Novosibirsk State University, Russia

Halonium ions (R_2Hal^+) 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_2Cl, C_2H_5 and C_3H_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_2Cl) of the solid salts with vapors of CH_2Cl_2 and $CHCl_3$ and chloronium salts in dichloromethane solutions with accompanying reactions. The asymmetric cations are mostly unstable, for example, the $ClCH_2$-Cl$^+$-CH_3 when kept at room temperature in one day it disproportionated into symmetric cations, $(CH_3)_2Cl^+$ and $(CH_2Cl)_2Cl^+$. 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_2Cl, or -Cl$^+$-CH_3, is involved in exchange reactions with CH_2Cl_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 Mendeleyev 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.

evgenii@nioch.nsc.ru

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