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CHLORONIUM CATIONS AND CARBOCATIONS IN CONDENSED PHASES: STABILIZATION AND PROPERTIES

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The simple chloronium salts with exceptionally stable carborane anion, R_2Cl^+ ($CHB^{11}Cl_{11}^-$), with $R=CH_3$ (see Figure), C_2H_5 and $(CH_3)_2CH$ are stable at room temperature and serve as intermediates in obtaining different carbocations. Some chemical properties of chloronium ions in dichloroethane solutions and in the solid salts at room and elevated temperatures (up to 150°C) are reported. Decomposition of chloronium salts resulted in the formation of the high purity carbocation salts. Their detailed IR spectra showed a strong discrepancy with the generally accepted theory of hyperconjugative stabilization of saturated carbocations, based on the modern ab initio calculations. We proposed a refined theory that allowed us to interpret the IR spectra of all carbocations having sp^2 carbon atom in gaseous, liquid, and solid phases. It was proved that CH_3/CH_2 groups of carbocations, which are involved in hyperconjugation, show the stretch and band vibration typical for those of corresponding groups of the neutral alkanes (that is retain their isoelectronic nature) in IR spectra. Hyperconjugation and polarization are equally important and closely linked in stabilization of carbocations: the strengthening of one effect weakens the second and vice versa. We obtained the salts of unsaturated chloronium cations and unsaturated carbocations with conjugated multiple CC bonds, which are stable at ambient conditions for the first time.

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