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Carbocations in condensed phases: Stabilization via hyperconjugation, polarization, and hydrogen bonding

A unified concept of the carbocations stabilization in gas, liquid, and solid phases is proposed. For the *tert*-butyl cation (*t*-Bu⁺), which is an iconic example of carbocations, the empirical gas-phase infrared (IR) spectrum shares only a deceptive similarity with the spectrum predicted by theory (for optimized *t*-Bu⁺ structure). They have important but so far unnoticed differences. At the same time, the IR spectra of *t*-Bu⁺ show a strong similarity to gas and condensed phases, thereby confirming that the nature of intramolecular stabilization of carbocations does not depend on the phase state. The IR spectroscopic analysis of the hydrogen bonding of *t*-Bu⁺ with the environment, together with X-ray crystallographic data, reveals that one CH₃ group of *t*-Bu⁺ differs from the two others. It is presumably polarized and less involved in hyperconjugation in comparison with the other CH₃ groups, which are strongly hyperconjugated. The pattern of changes in the IR spectra of carbocations in their salts with the least basic anion (fluorinated carborane CHB₁₁F₁₁⁻) in the series CH₃⁺, C₂H₅⁺, *i*-C₃H₇⁺, cyclo-C₄H₇⁺, cyclo-C₅H₉⁺, methylcyclopentyl⁺, *tert*-butyl⁺, 2-methylbutyl⁺ and 2,3-dimethylbutyl⁺, together with the available X-ray crystallographic data, shows that the current understanding of the intramolecular stabilization of carbocations, which is based on the modern *ab initio* computations contradicts a number of empirical facts. In the report, these contradictions are discussed and an explanation for all the empirical data is offered. Nonetheless, this explanation does not resolve the existing discrepancies with the calculations.

Biography

Evgenii S Stoyanov received a PhD degree from Vernadsky Institute of Geochemistry & 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. He has published 139 papers in reputable journals.

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