This Week's Citation Classic


These papers disclosed the first use of the Lewis acid antimony pentafluoride in preparing stable carbonium ions. They also established the structures of a series of stable alkylcarbonium fluoroantimonates and the study of stable, long-lived carbocations. [The SCI® indicator that these papers have been cited in more than 170, 120, and 210 publications, respectively]

Stable Carbocations

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In 1962, with my colleagues S.J. Kuhn, W.S. Tolgyesi, and E.B. Baker, I reported the preparation and study of a series of stable primary oxocarbonium (acylium) tetrafluoroborate, hexafluorophosphate, hexafluoroantimonate, and hexafluoroarsenate complexes. It was in this paper that the use of the powerful Lewis acid antimony pentafluoride was first disclosed in preparing stable carbonium ions. The next year, in continuation of our work, we reported the study of secondary and tertiary alkyl and aralkyl oxocarbonium hexafluoroantimonates. In the course of this study, we observed the formation of the trimethylcarbonium ion ( tert-butyl cation) by decarbonylation of the tert-butyl oxocarbonium ion (pivaloyl cation). After half a century of intensive and frustrating effort, a persistent simple alkyl cation was finally observed in SbF₅/ SO₂ solution as the remarkably stable SbF₆ salt and was characterized by NMR spectroscopy. The work was then followed up by our 1964 paper. In this paper, we reported the preparation of a series of stable alkylcarbonium fluoroantimonates from the corresponding alkyl fluorides in excess SbF₅ diluted with SO₂. Their structure was established by ¹H and ¹³C NMR, as well as IR spectroscopy (no small achievement at the time when FT methods were not yet developed and we were dealing by necessity with relatively dilute solutions of the ions). The chemical reactivity of the prepared alkyl cation salts was also investigated. This paper established the study of stable, long-lived carbocations as a general method and opened up a worldwide study of this most significant class of reactive reaction intermediates.

In 1972, I was able, based on an extensive body of published work, to develop a general concept for the positive ions of carbon compounds. I suggested in this paper the generic name "carbocations" for all the cations of carbon compounds, in accordance with the "carbanion" naming of the negative ions. Within organic cations (i.e., carbocations), trivalent (classical) carbonium ions can be differentiated (by fundamental spectroscopic differences) from five (or higher) coordinate (nonclassical) carbonium ions. It is rewarding that the IUPAC later adapted this naming system, and it is now generally used.

Our superacidic stable carbocation studies reported in these early papers not only resulted in extensive subsequent structural studies (including conclusion of the long-standing "nonclassical norbornyl ion" controversy), but also opened up the electrophilic chemistry of C-H and C-C bonds. New areas of preparative and even industrial chemistry were developed, including the electrophilic conversion of saturated hydrocarbons (even methane) to useful derivatives.

1. Olah G A. The general concept and structure of carbocations based on differentiation of trivalent ("classical") carbonium ions from three-center bound penta- or tetracoordinated ("nonclassical") carbonium ions. The role of carbocations in electrophilic reactions. J. Amer. Chem. Soc. 94:808-20, 1972. (Cited 220 times.)

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