

# This Week's Citation Classic<sup>®</sup>

**Olah G A, Kuhn S J, Tolgyesi W S & Baker E B.** Stable carbonium ions. II. Oxocarbenium (acylium) tetrafluoroborates, hexafluorophosphates, hexafluoroantimonates and hexafluoroarsenates. Structure and chemical reactivity of acyl fluoride: Lewis acid fluoride complexes. *J. Amer. Chem. Soc.* 84:2733-40, 1962; **Olah G A, Tolgyesi W S, Kuhn S J, Moffatt M E, Bastien I J & Baker E B.** Stable carbonium ions. IV. Secondary and tertiary alkyl and aralkyl oxocarbenium hexafluoroantimonates. Formation and identification of the trimethylcarbonium ion by decarbonylation of the tert-butyl oxocarbenium ion. *J. Amer. Chem. Soc.* 85:1328-34, 1963; and, **Olah G A, Baker E B, Evans J C, Tolgyesi W S, McIntyre J S & Bastien I J.** Stable carbonium ions. V. Alkylcarbonium hexafluoroantimonates. *J. Amer. Chem. Soc.* 86:1360-73, 1964. [Exploratory Research Laboratory, Dow Chemical of Canada, Ltd., Samia, Ontario, Canada]

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*<sup>®</sup> indicates 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 oxocarbenium (acylium) tetra-fluoroborate, 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 oxocarbenium hexafluoroantimonates. In the course of this study, we observed the formation of the trimethylcarbonium ion (tert-butyl cation) by decarbonylation of the tert-butyl oxocarbenium ion (pivaloyl cation). After half a century of intensive and frustrating effort, a persistent simple alkyl cation was finally observed in  $\text{SbF}_3\text{SO}_2$  solution as the remarkably stable  $\text{SbF}_6^-$  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  $\text{SbF}_5$  diluted with  $\text{SO}_2$ . Their structure was established by  $^1\text{H}$  and  $^{13}\text{C}$  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,<sup>1</sup> 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) *carbenium* 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") carbenium 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.)