

Fluorinated superacidic systems

George A. Olah, G.K. Surya Prakash and Alain Goeppert

Résumé

Systèmes superacides fluorés

Dans les superacides, des acidités plusieurs milliards de fois plus élevées que celle de l'acide sulfurique concentré ont été obtenues. Dans la plupart de ces superacides, le fluor très électronégatif joue un rôle essentiel. Dans les systèmes superacides, l'acidité élevée et la faible nucléophilicité des contre-ions ont rendu possible la préparation et l'observation en solution de cations stables et à longue durée de vie, en particulier des carbocations, espèces très réactives qui n'avaient été auparavant observées qu'en phase gazeuse. Les carbocations étant des intermédiaires réactionnels dans de nombreuses réactions chimiques catalysées par des acides, leur étude et leur meilleure compréhension peuvent aider à diriger une réaction dans un sens voulu afin de former les produits désirés. De nouvelles synthèses organiques, impossibles dans des acides ordinaires, incluant la synthèse d'hydrocarbures importants d'un point de vue économique, sont possibles dans les superacides. La capacité des superacides à transformer les hydrocarbures, relativement inertes, et même le méthane, a permis d'ouvrir un nouveau et fascinant domaine de la chimie.

Mots-clés

Superacide, carbocation, fluor.

Abstract

In superacids, extremely high acidities in excess of many billion times that of concentrated sulfuric acid have been obtained. In most of these superacids, electronegative fluorine is an essential element. The high acidity and extremely low nucleophilicity of the counterions in superacidic systems have made it possible to prepare in solution, stable, long-lived cations, particularly carbocations, which are very reactive species and had formerly been observed only in the gas phase. Carbocations, being intermediates in numerous acid catalyzed chemical reactions, their study and better understanding can make it possible to govern their reaction to form desired products. Novel organic syntheses that can not be achieved in ordinary acidic media are possible in superacids, including synthesis of economically important hydrocarbons. The unique ability of superacids to bring about hydrocarbon transformations, which are otherwise relatively unreactive, and even to activate methane opened a new and fascinating field in chemistry.

Keywords

Superacid, carbocation, fluorine.

Chemists for long considered Brønsted mineral acids such as sulfuric, nitric, perchloric and hydrofluoric acids to be the strongest acid systems attainable. That view changed considerably with the discovery of strong acid systems that are hundreds of millions, even many billions of times stronger than 100% sulfuric acid. Such acid systems are termed "superacids". The key element of most of these superacids is fluorine, which is truly an extraordinary element showing unique properties correlated with its higher electronegative character compared to the other elements of the periodic table.

Brønsted (protic) superacids

The name "superacid" was first suggested by James Bryant Conant in 1927 to describe acids such as perchloric and sulfuric acids in acetic acid that were stronger than conventional mineral acids and able to protonate certain weak bases such as aldehydes and ketones. This initial proposal was, however, not further followed or used in the literature. It was only in the 1960s that Ronald J. Gillespie proposed an arbitrary, but since then widely accepted definition of superacids, defining them as any acid system that is stronger than 100% sulfuric acid. This definition referring to the superacidity of Brønsted (proton donor) acids is only arbitrary. There is therefore no sharp distinction between an acidic and superacidic medium, but more of a

transition to acidic systems able to protonate increasingly weak bases. In fact, the concept of acidity can only be defined in relation to a reference base. Various physical, electrochemical and spectroscopic methods are available to measure protic (Brønsted) superacid strengths using Hammett's acidity constant measurements ($-H_0$ value, a logarithmic scale) (see *insert 1*). Sulfuric acid has an $-H_0$ of 12. Subsequently, all Brønsted acids having an $-H_0 > 12$ are considered as superacids. Anhydrous hydrogen fluoride (HF), fluorosulfonic acid (FSO₃H), trifluoromethanesulfonic acid (CF₃SO₃H) and teflic acid (TeF₅OH) are examples of fluorine containing Brønsted acids that exceed the acidity of pure sulfuric acid with $-H_0$ values ranging from 14 to 15.

Lewis superacids

Gillespie's definition of superacids relates only to Brønsted acid systems. Lewis acids (electron acceptors), on the other hand, also cover a wide range of acidities extending beyond the strength of such most frequently used systems as AlCl₃ and BF₃. In extending the concept of superacidity, Olah, Prakash and Sommer therefore suggested the use of anhydrous aluminum trichloride, the most widely used Friedel-Crafts catalyst, as the arbitrary unit to define Lewis superacids. Lewis acids stronger than anhydrous aluminum trichloride are thus categorized as Lewis superacids [1]. They include among others: BF₃, SbF₅, AsF₅, TaF₅, NbF₅,

Insert 1

Acidity measurements

A number of methods are available for estimating the Brønsted acidity of a solution. The best known and widely used is the direct measurement of hydrogen ion activity (a_{H^+}) used in defining the pH: $pH = -\log a_{H^+}$.

This can be achieved by measuring the potential of a hydrogen electrode in equilibrium in a dilute acid solution. In highly concentrated acid solutions, however, the pH concept is no longer applicable, and the acidity must be related to the degree of transformation of a weak base with its conjugated acid. This method was developed in the 1930s by Hammett and Deyrup. The bases used for these acidity measurements (nitrotoluene, nitroaniline, nitrobenzene, etc.) were consequently named Hammett bases, and lead to the Hammett acidity function H_0 :

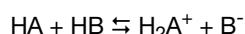
$$H_0 = pK_{BH^+} - \log \frac{BH^+}{B}$$

B is the basic form of the Hammett base and BH^+ the acid form. H_0 replaces pH and pK_{BH^+} is the dissociation constant representative of the base used. The ionization ratio BH^+/B is generally measured by spectroscopic means (UV, NMR, etc.). The Hammett acidity function is a logarithmic scale on which 100% sulfuric acid has an $-H_0$ of 12.

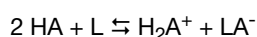
$B(OSO_2CF_3)_3$ and $Sb(OTeF_5)_5$. Measuring the exact strength of these Lewis acids remains, however, a difficult task. Some effort toward this direction is being made [2].

Conjugated Brønsted-Lewis superacids

To reach acidities beyond the limit of simple Brønsted superacids ($-H_0 \approx 15$), a strong acid has to be added to an even stronger acid in order to increase the ionization. This can be achieved by dissolving a strong Brønsted acid, HB, capable of ionizing in the medium:



or by adding a strong Lewis acid (L) which will shift the autoprotonation equilibrium by forming a more delocalized counterion of the strong acid:



Conjugated Brønsted-Lewis superacids include polysulfuric acids (oleums) which are SO_3 containing sulfuric acid. With 50 mol% SO_3 in H_2SO_4 , an $-H_0$ value of 14.5 is reached. Much higher acidities can be obtained by the addition of Lewis acid fluorides such as SbF_5 , NbF_5 or AsF_5 to HF, HSO_3F and CF_3SO_3H (see figure 1). Two superacid systems used very frequently are HSO_3F-SbF_5 , also called Magic Acid (see insert 2), and HF- SbF_5 . By addition of SbF_5 to HF and HSO_3F , the acidity of the medium increases dramatically, reaching several million times that of sulfuric acid. The acidity, $-H_0$, of HSO_3F increases from 15.1 to 21.0 on addition of 25 mol% of SbF_5 , multiplying the acidity by about a million times. HF- SbF_5 mixtures are even stronger. As shown in figure 2, with 5 mol% SbF_5 , the $-H_0$ is already close to 21.0, a thousand times stronger than the value obtained with HSO_3F-SbF_5 with the same SbF_5 concentration. The acidity increases further with higher SbF_5 concentrations. Such high acidities, however, are difficult to exactly measure. Values in excess of $-H_0 = 26$ have been estimated for 1:1 HF- SbF_5 solutions.

If we take as an example HF- SbF_5 solutions, the very high acidity can be explained by the extraordinary affinity of

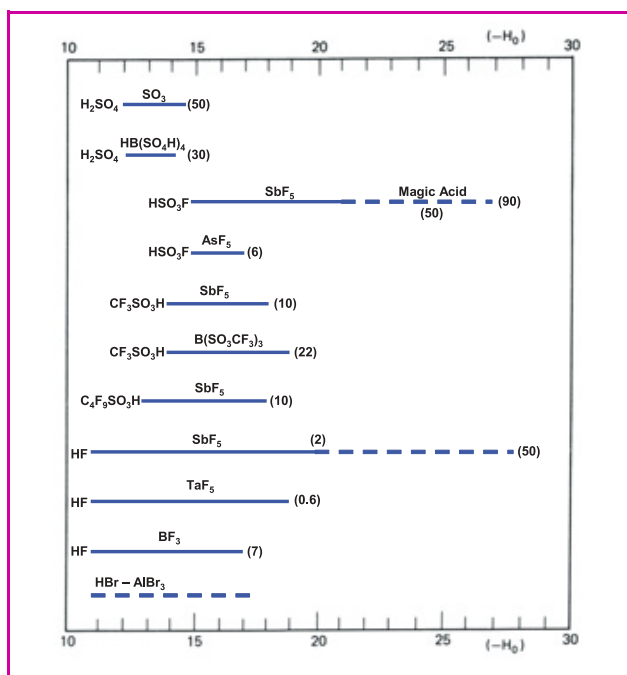


Figure 1 - Acidity ranges for the most common superacids. The broken bar are estimated values, in () mol% Lewis acid [1].

Insert 2

Origin of the "Magic Acid"

The name "Magic Acid" of HSO_3F-SbF_5 originated in George A. Olah's laboratory at Case Western Reserve University in the winter of 1966. The HSO_3F-SbF_5 superacid was extensively used in this group to generate stable carbocations. One day, his postdoctoral student, Joe Lukas, put a small piece of Christmas candle left over from the lab party into the acid system and found that it dissolved readily. He then ran a proton NMR measurement of the solution and to the amazement of everybody, obtained a sharp spectrum of the *t*-butyl cation. The long-chain paraffin, of which the candle is made, had undergone extensive cleavage and isomerization to form the more stable tertiary cation. It impressed researchers in the lab so much that they began to nickname the acid system Magic Acid. The name stuck and soon other started to use it too. It is now a registered trade name and has found its way into the chemical literature.

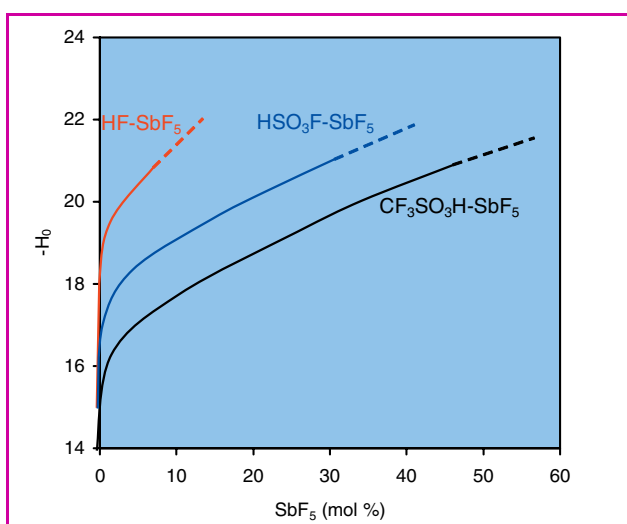


Figure 2 - $-H_0$ measurement of different superacids as a function of SbF_5 concentration (adapted from [3]).

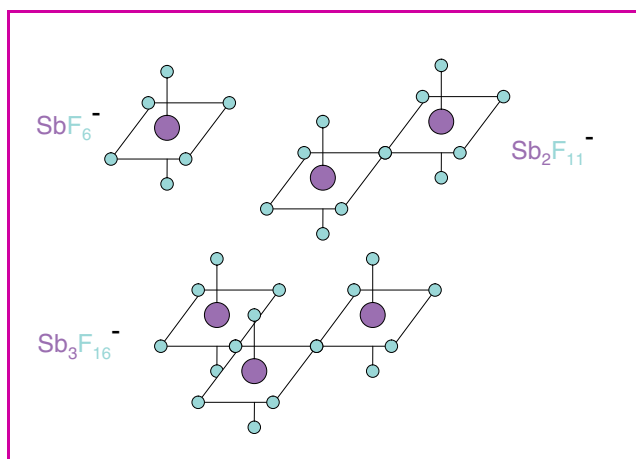
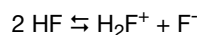
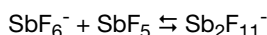
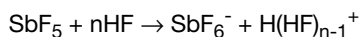


Figure 3 - Examples of anions present in HF-SbF₅ superacid systems.

antimony pentafluoride (SbF₅) for the fluorine anions F⁻ formed in the autoprotection reaction of HF:



The reaction equilibrium is shifted to the right, producing more protic species and increasing the acidity. The addition of SbF₅ to HF leads first to the formation of the monomeric anion, SbF₆⁻. With increasing concentrations of SbF₅ in the media, and consequently increasing acidities, larger anions are formed: Sb₂F₁₁⁻, Sb₃F₁₆⁻ and Sb₄F₂₁⁻. The structures of these anions are presented in figure 3. In these complex and bulky fluoro-anions, the negative charge is highly dispersed. They are consequently very weak nucleophiles and show low reactivity. The formation of these large counter-ions with very low basicity and nucleophilicity is essential to the superacid character of the media:



HF plays both the role of acid and solvent. The protons formed by reaction with SbF₅ are solvated by unionized HF and form hydrogen bonded chain-like species. The structures of the formed cations depend on the concentration of SbF₅. At lower concentrations, enough unionized HF is present to form long chains: H₇F₆⁺, H₈F₇⁺ or longer. However, at higher SbF₅ concentrations, where less unionized HF is present, the less solvated species, H₃F₂⁺ and H₂F⁺ are present in increasing concentrations (figure 4) [4].

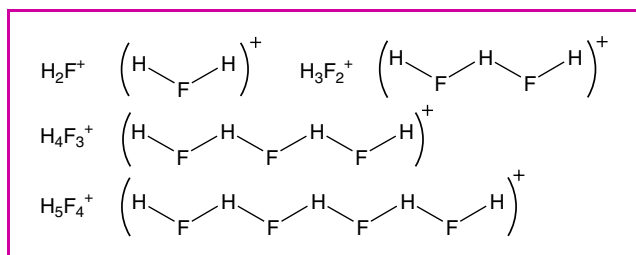


Figure 4 - Examples of cationic species present in HF-SbF₅ superacid systems.

Related superacid systems in which SbF₅ is replaced by AsF₅, TaF₅, NbF₅ or BF₃ are lower in acidity than Magic and fluoroantimonic acids. Systems combining SbF₅ with triflic acid and higher perfluoroalkanesulfonic acids (C_nF_{2n+1}SO₃H) have also been studied. Other stable anions including AuF₆⁻, Sb(OTeF₅)₆⁻, CB₁₁F₆H₆⁻ have been utilized, but their parent acids have not been studied in any detail [5-6].

Solid superacids

As chemical applications of superacids became important, efforts were made to attach them to solid supports. The main advantage compared with liquid acid catalysts is the ease of separation from the reaction mixture, which allows continuous operation as well as regeneration and reutilization of the catalyst. Because of their extreme chemical reactivity, SbF₅, HF-SbF₅ and HSO₃F-SbF₅ can be immobilized only to a limited numbers of supports including fluorinated alumina, fluorinated resins, graphite and fluorinated graphite. On such carriers, at temperature as low as 70°C, HF-SbF₅ and HSO₃F-SbF₅ readily isomerize straight-chain alkanes such as n-hexane and n-heptane. However, relatively fast deactivation as well as leaching problems limited the applicability of these catalysts. Solid polymeric perfluorinated sulfonic acids, especially DuPont's Nafion-H[®] ionic resin have also been extensively studied as solid superacid catalysts. Many transition metal oxides and sulfates as well as zeolites and other silicoaluminates containing Brønsted (proton donor, often OH groups) sites, Lewis type (electron acceptor) sites or both have also shown superacid character, although generally only at higher temperatures. Zeolites are for example widely used in large quantities in the petrochemical industry for the cracking of heavy petroleum fractions.

Applications of superacids

The high acidity and extremely low nucleophilicity of the counter ions of superacidic systems is especially useful for the preparation of stable, electron deficient cations, including carbocations. Many of these cations, which were formerly suggested only as fleeting metastable intermediates in many organic reactions and were detectable only in the gas phase in mass spectrometric studies, can be conveniently studied in superacid solution. New chemical transformations and synthesis that are not possible using conventional acids can also be achieved with superacids. These include transformation and syntheses of many industrially important hydrocarbons. The unique ability of superacids to bring about hydrocarbon transformations, even to activate methane (the principal component of natural gas) for electrophilic reactions, has opened up a fascinating new field in chemistry.

Superacids such as Magic Acid or fluoroantimonic acid have made it possible to prepare stable, long-lived carbocations, which are too reactive to exist as stable species in less acidic media. To understand carbocations is essential to understand chemistry. By knowing what carbocations look like and how they react, it is possible to govern their reactions to form products we require. Stable superacidic solutions of a large variety of carbocations have been obtained. Many of structurally diverse carbocations as well as related acyl cations and acidic carboxonium ions and other heteroatom stabilized carbocations have been prepared in superacidic solutions, even isolated as stable

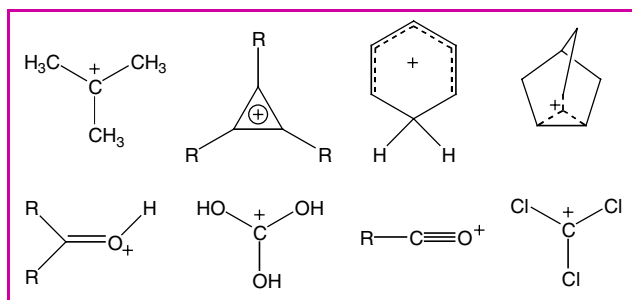


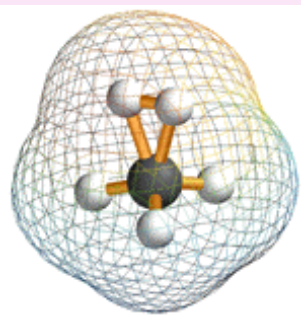
Figure 5 - Examples of stable cations that have been prepared in superacidic solutions.

salts and characterized by X-ray crystallography [1]. Some of the examples are shown in *figure 5*. Many noble gas cations have also been investigated with interesting counteranions (XeOTeF_5^+ can for example be combined with $\text{Sb}(\text{OTeF}_5)_6^-$) [7].

The astonishing acidity of Magic Acid and related superacids allows protonation of exceedingly weak bases. Not only all conceivable π -electron (such as olefins, acetylenes and aromatics) and n -donors (such as ethers, amines and sulfides) but also weak σ -electron donors such as saturated hydrocarbons including the parent alkane methane are protonated. The ability of superacids to protonate saturated hydrocarbons (alkanes) rests on the ability of the two-electron two-center covalent bond to share its bonded electron pair with empty orbitals (π - or σ -) of a strongly electron deficient reagent such as a protic acid. The so-called carbonium ions formed are pentacoordinated species in which two electrons are delocalized over three centers (see *insert 3*). These are, however, very unstable and react further to form species with a trivalent center: carbenium ions (*figure 6*).

Insert 3

The methonium cation



Due to their unstable nature, carbonium ions are extremely short-lived and therefore difficult to observe and characterize. The smallest of them is the protonated form of methane: methonium ion CH_5^+ . The methonium ion was first discovered by mass spectrometry in the 1950s and has also been reported in superacid solutions. Its actual structure remained, however,

elusive. Elucidating the nature of CH_5^+ and similar carbocations is important because they are highly reactive intermediates in the transformations of hydrocarbons catalyzed by strong acids. Numerous experimental and theoretical studies trying to understand the fundamental nature of CH_5^+ have been conducted over the years. It is, however, only last year that the first low resolution broad-frequency infrared spectrum of CH_5^+ has been observed, giving experimental indication to the intimate structure of this species. Despite highly unstable and fluxional nature of CH_5^+ , which seems to have a constantly fluctuating structure, this experimental study found that this species can be considered as a CH_3^+ cation to which a H_2 molecule has been linked by a three center two electron bond.

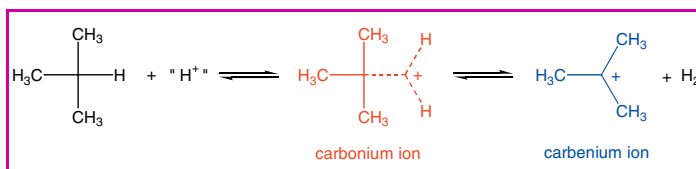


Figure 6 - Formation of carbonium and carbenium ions in superacids: example of isobutane.

Superacids are suitable catalysts for a number of chemical transformations, particularly of hydrocarbons. Straight chain alkanes with five to eight carbon atoms, as found in petroleum, have considerably lower octane numbers than their branched isomers and are thus not suited for use in internal combustion engines running on gasoline. To provide the world with the large amounts of high octane gasoline needed to sustain our modern transportation system, there is therefore a need for higher octane branched isomers. Isomerization of straight chain alkanes, which can be catalyzed by superacids is one possibility. Isomerizations are generally carried out under thermodynamically controlled conditions and lead to equilibria. The ionic equilibria in superacid systems generally favor increasing amounts of higher octane branched isomers at lower temperatures. An other process to obtain high octane gasoline which can also be easily carried out under superacidic conditions is alkylation, which is the combination of an alkene with an alkane to form a longer, branched alkane (*figure 7*).

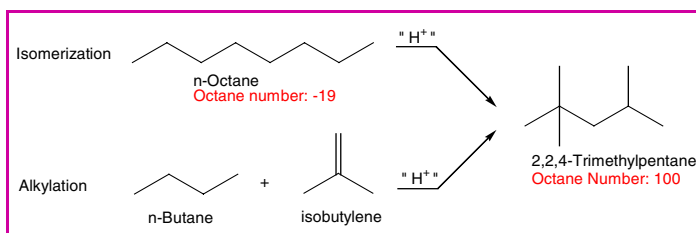


Figure 7 - Example of products obtained in isomerization and alkylation reactions of hydrocarbons

In fact, mixtures of branched alkanes are obtained in both reactions.

Even polymerization of saturated hydrocarbons including methane to gasoline range hydrocarbons have been effected under superacid treatment [8]. Many important organic transformations such as alkylation, ionic hydrogenation, carbonylation, halogenation, nitration, hydroxylation, amination, etc. of aromatics as well as alkanes can be conveniently carried out under superacidic catalysis [1]. In many such reactions, superelectrophilic activation of the electrophile occurs leading to enhanced reactivity. Many inorganic sulfur, selenium, tellurium and halogen cations can also be generated in superacid medium.

References

- [1] Olah G.A., Prakash G.K.S., Sommer J., *Superacids*, Wiley Interscience, New York, 1985.
- [2] Christie K.O., Dixon D.A., McLemore D., Wilson W.W., Sheehy J.A., Boatz J.A., On a quantitative scale for Lewis acidity and recent progress in polynitrogen chemistry, *J. Fluorine Chem.*, 2000, 101, p. 151.
- [3] Jost R., Sommer J., Tracking the limits of superacidity, *Rev. Chem. Intern.*, 1988, 9, p. 171.
- [4] Culmann J.-C., Fauconet M., Jost R., Sommer J., Fluoroanions and cations in the HF-SbF_5 superacid system. A ^{19}F and ^1H NMR study, *New J. Chem.*, 1999, 23, p. 863.

- [5] Lehmann J.F., Schrobilgen G.J., Structural and vibrational characterization of $[\text{KrF}][\text{AuF}_6]$ and $\alpha\text{-}[\text{O}_2][\text{AuF}_6]$ using single crystal X-ray diffraction, Raman spectroscopy and electron structure calculations, *J. Fluorine Chem.*, **2003**, 119, p. 109.
- [6] Mercier H.P.A., Moran M.D., Sanders J.C.P., Schrobilgen G.J., Suontamo R.J., Synthesis, structural characterization, and computational study of the strong oxidant salt $[\text{XeOTeF}_5][\text{Sb}(\text{OTeF}_5)_6]\cdot\text{SO}_2\text{ClF}$, *Inorg. Chem.*, **2005**, 44, p. 49.
- [7] Mercier H.P.A., Moran M.D., Schrobilgen G.J., Steinberg C., Suontamo R.J., The syntheses of carbocations by use of the noble-gas oxidant, $[\text{XeOTeF}_5][\text{Sb}(\text{OTeF}_5)_6]$: the syntheses and characterization of the CX_3^+ ($\text{X} = \text{Cl}, \text{Br}, \text{OTeF}_5$) and $\text{CBr}(\text{OTeF}_5)_2^+$ cations and theoretical studies of CX_3^+ and BX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OTeF}_5$), *J. Am. Chem. Soc.*, **2004**, 126, p. 5533.
- [8] Olah G.A., Prakash G.K.S., Sommer J., Superacids, *Science*, **1979**, 206, p. 13.



G.A. Olah



G.K.S. Prakash



A. Goeppert

George A. Olah, Nobel Prize in Chemistry (1994), and **G.K. Surya Prakash** are Professors, **Dr. Alain Goeppert** is a scientist at Loker Hydrocarbon Research Institute, Los Angeles*.

* Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, CA 90089-1661 (USA).

DuPont Plunkett Awards 2007

L'innovation avec les fluoropolymères



DuPont lance un appel à candidatures pour l'édition 2007 de son concours Plunkett Awards – ainsi nommé en hommage à Roy J. Plunkett, le scientifique de DuPont qui découvrit le polytétrafluoréthylène en 1938.

Ce concours a pour objet de distinguer les innovations ou améliorations apportées par des transformateurs ou des utilisateurs à des produits usinés commercialisés depuis le 1^{er} juillet 2001, dans lesquels un ou plusieurs fluoropolymères de DuPont constitue un composant essentiel (DuPont™ Teflon®, DuPont™ Tefzel® et DuPont™ Zonyl®, proposés sous la forme de films, fibres, traitements de finition, revêtements, résines et additifs fluorés).

Inscription jusqu'au 31 décembre 2006

• <http://www.plunkett.teflon.com>