



Superacids

George A. Olah
G. K. Surya Prakash

University of Southern California

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GLOSSARY

Brönsted superacids Proton donor acids stronger than 100% sulfuric acid.

Carbenium ions Compounds containing a trivalent, tricoordinate carbon bearing a positive charge. Also called “classical cations.”

Carbocations Compounds containing carbon bearing a positive charge which encompass both carbenium and carbonium ions.

Carbonium ions Compounds containing high coordinate carbon bearing a positive charge with multicenter bonding. Also called “nonclassical” cations.

Conjugate Brönsted–Lewis superacids Superacidic proton donor acids comprised of a combination of Brönsted and Lewis acids.

Hammett’s acidity constant, H_0 A logarithmic thermodynamic scale used to relate acidity of proton donor acids.

Immobilized superacids Superacids (both Brönsted and Lewis types) bound to inert supports such as graphite, fluorinated graphite, etc.

Lewis superacids Electron acceptor acids stronger than aluminum trichloride.

Solid superacids Solid materials possessing superacid

sites. May be of the Brönsted or the Lewis superacid type.

Superacids Acid systems that encompass both Brönsted and Lewis superacids as well as their conjugate combinations.

Superelectrophiles Electrophiles that are further activated by Brönsted or Lewis superacid complexation.

CHEMISTS long considered mineral acids such as sulfuric and nitric acids to be the strongest protic acids to exist. More recently this view has changed considerably with the discovery of extremely strong acid systems that are hundreds of millions, even billions, of times stronger than 100% sulfuric acid. Such acid systems are termed “superacids.” The term “superacids” was first suggested by Conant and Hull in 1927 to describe acids such as perchloric acid in glacial acetic acid that were capable of protonating certain weak bases such as aldehydes and ketones.

Superacids encompass both Brönsted (proton donor) and Lewis (electron acceptor) acids as well as their conjugate pairs. The concept of acidity and acid strength can be defined only in relation to a reference base. According to an arbitrary but widely accepted suggestion

by Gillespie, all Brønsted (protic) acids stronger than 100% sulfuric acid are classified as superacids. Various methods are available to measure protic superacid strengths (*vide infra*). Lewis acids also cover a wide range of acidities extending beyond the strength of the most frequently used systems such as AlCl_3 and BF_3 . Olah *et al.* (1985) 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 considered Lewis superacids. There remain, however, many difficulties in measuring the strength of Lewis acid (*vide infra*).

The high acidity and the extremely low nucleophilicity of the counterions of superacidic systems are 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 and were detectable only in the gas phase in mass spectrometric studies, can be conveniently studied in superacid solutions. New chemical transformations and syntheses that are not possible using conventional acids can also be achieved with superacids. These include transformations 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.

I. ACID STRENGTH AND ACIDITY SCALE

The chemical species that plays the key role in Brønsted acids is the hydrogen ion, that is, the proton: H^+ . Since the proton is the hydrogen nucleus with no electron in its $1s$ orbital, it is not prone to electronic repulsion. The proton consequently exercises a powerful polarizing effect. Due to its extreme electron affinity, proton cannot be found as a free “naked” species in the condensed state. It is always associated with one or more molecules of acid or the solvent (or any other nucleophile present). The strength of protic acid thus depends on the degree of association of the proton in the condensed state. Free protons can exist only in the gas phase and represent the ultimate acidity. Due to the very small size of a proton (10^5 times smaller than any other cation) and the fact that only $1s$ orbital is used in bonding by hydrogen, proton transfer is a very facile reaction, reaching diffusion-controlled rates, and does not necessitate important reorganization of the electronic valence shells. Understanding the nature of the proton is important when generalizing quantitative relationships in acidity measurements.

A number of methods are available for estimating acidity of protic acids in solution. The best known is the direct measurement of the hydrogen ion activity used in defining pH [Eq. (1)].

$$\text{pH} = \log a_{\text{H}^+}. \quad (1)$$

This can be achieved by measuring the potential of a hydrogen electrode in equilibrium with a dilute acid solution. In highly concentrated acid solutions, however, the pH concept is no longer applicable, and the acidity must be related very closely to the degree of transformation of a base with its conjugate acid, keeping in mind that this will depend on the base itself and on medium effects. The advantage of this method was shown in the 1930s by Hammett and Deyrup, who investigated the proton donor ability of the H_2O – H_2SO_4 system over the whole concentration range by measuring the extent to which a series of nitroanilines were protonated. This was the first application of the very useful Hammett acidity function [Eq. (2)].

$$H_0 = \text{p}K_{\text{BH}^+} - \log \frac{\text{BH}^+}{\text{B}}. \quad (2)$$

The $\text{p}K_{\text{BH}^+}$ is the dissociation constant of the conjugate acid (BH^+) and BH^+/B is the ionization ratio, which is generally measured by spectroscopic means [ultraviolet, nuclear magnetic resonance (NMR), and dynamic NMR]. Hammett’s “ H_0 ” scale is a logarithmic scale on which 100% sulfuric acid has an H_0 value of -12.0 .

Various other techniques are also available for acidity measurements of protic acids. These include electrochemical methods, kinetic rate measurements, and heats of protonation of weak bases. Even with all these techniques it is still difficult to measure the acidity of extremely acidic superacids, because of the unavailability of suitable weak reference bases.

In contrast to protic (Brønsted) acids, a common quantitative method to determine the strength of Lewis acids does not exist. Whereas the Brønsted acid–base interaction always involves a common denominator—the proton (H^+) transfer, which allows direct comparison—no such common relationship exists in the Lewis acid–base interaction. The result is that the definition of “strength” has no real meaning with Lewis acids.

The “strength” or “coordinating power” of different Lewis acids can vary widely against different Lewis bases. Despite the apparent difficulties, a number of qualitative relationships have been developed to characterize Lewis acids. Schwarzenbach and Chatt classified Lewis acids into two types: *class a* and *class b*. *Class a* Lewis acids form their most stable complexes with the donors in the first row of the periodic table—N, O, and F. *Class b* acids, on the other hand, complex best with donors in the second or subsequent row—Cl, Br, I, P, S, etc. Guttmann has

introduced a series of donor numbers (DN) and acceptor numbers (AN) for various solvents in an attempt to quantify complexing tendencies of Lewis acids. Based on a similar premise, Drago came up with parameter E , which measures the covalent bonding potential of each series of Lewis acids as well as bases.

Pearson has proposed a qualitative scheme in which a Lewis acid and base are characterized by two parameters, one of which is referred to as strength and the other as softness. Thus, the equilibrium constant for a simple Lewis acid–base reaction would be a function of four parameters, two for each partner. Subsequently, Pearson introduced the hard and soft acids and bases (HSAB) principle to rationalize behavior and reactivity in a qualitative way. Hard acids correspond roughly in their behavior to Schwarzenbach and Chatt's class a acids. They are characterized by small acceptor atoms that have outer electrons that are not easily excited and that bear a considerable positive charge. Soft acids, which correspond to class b acids, have acceptor atoms of a lower positive charge and a large size, with easily excited outer electrons. Hard and soft bases are defined accordingly. Pearson's HSAB principle states that hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. The principle has proved useful in rationalizing and classifying a large number of chemical reactions involving acid–base interactions in a qualitative manner, but it gives no basis for quantitative treatment.

Many attempts have been made in the literature to rate qualitatively the activity of Lewis acid catalysts in Friedel–Crafts-type reactions. However, such ratings depend largely on the nature of the reaction for which the Lewis acid catalyst is employed.

Thus, the classification of Lewis superacids as those stronger than anhydrous aluminum trichloride is only arbitrary. Just as in the case of Gillespie's classification of Brønsted superacids, it is important to recognize that acids stronger than conventional Lewis acid halides exist, with increasingly unique properties.

Another area of difficulty is measuring the acid strength of solid superacids. Since solid superacid catalysts are used extensively in the chemical industry, particularly in the petroleum field, a reliable method for measuring the acidity of solids would be extremely useful. The main difficulty to start with is that the activity coefficients for solid species are unknown and thus no thermodynamic acidity function can be properly defined. On the other hand, because the solid by definition is heterogeneous, acidic and basic sites can coexist with variable strength. The surface area available for colorimetric determinations may have acidic properties widely different from those of the bulk material; this is especially true for well-structured solids such as zeolites.

The complete description of the acidic properties of a solid requires the determination of the acid strengths as well as the number of acid sites. The methods that have been used to answer these questions are basically the same as those used for the liquid acids. Three methods are generally quoted: (1) rate measurement to relate the catalytic activity to the acidity, (2) the spectrophotometric method to estimate the acidity from the color change of adequate indicators, and (3) titration by a strong enough base for the measurement of the amount of acid. The above experimental techniques vary somewhat, but all the results obtained should be interpreted with caution because of the complexity of the solid acid catalysts. The presence of various sites of different activity on the same solid acid, the change in activity with temperature, and the difficulty of knowing the precise structure of the catalyst are some of the major handicaps in the determination of the strength of solid superacids.

II. SUPERACID SYSTEMS

Following Conant's early work, the field of superacids, which had been dormant till the late 1950s, started to undergo rapid development in the early 1960s, involving the discovery of new systems and an understanding of their nature as well as their chemistry. As mentioned, superacids encompass both Brønsted and Lewis types and their conjugate combinations.

A. Brønsted Superacids

Using Gillespie's arbitrary definition, Brønsted superacids are those with an acidity exceeding that of 100% sulfuric acid (H_0 , -12). These include perchloric acid (HClO_4), fluorosulfuric acid (FSO_3H), trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$), and higher perfluoroalkanesulfonic acid ($\text{C}_n\text{F}_{n+2}\text{SO}_3\text{H}$). Physical properties of some of the most commonly used superacids are listed in [Table I](#).

Studies by Gillespie have shown that truly anhydrous hydrogen fluoride (HF), which is extremely difficult to obtain in the pure form, has a Hammett acidity constant (H_0) of -15.1 rather than the -11.0 found for the usual anhydrous acid. However, traces of water impurity drop the acidity to the generally observed value. Thus for practical purposes, hydrogen fluoride, which always contains some water impurity, is not discussed here, as its acidity of $H_0 = -11.0$ is lower than that of H_2SO_4 .

Teflic acid (TeF_5OH) has been suggested to have an acidity comparable to that of fluorosulfuric acid. However, no concrete acidity measurements are available to support such a claim. A number of carbocationic salts bearing carborane anions [$\text{CB}_{11}\text{H}_6\text{Cl}_6^-$, etc.] have been studied. However, their parent Brønsted acids,