



Chemical Education

A CHIMIA Column

A reflection about the use of superlatives when teaching general chemistry

Superlatives in Teaching General Chemistry

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Abstract: What is the strongest Brønsted acid, the strongest base, the strongest oxidizing agent? If not understood in an absolute, once-and-for-ever sense, the answers to such questions may help at extending and reinforcing the meaning of simple concepts in first-year chemistry courses. Moreover, they serve the purpose of introducing research aspects and linking them to general chemistry.

Keywords: Acidity functions · Brønsted acids and bases · Oxidizing agents · Superacids · Superbases

Superlatives are a common category used in all types of discourse. It is easy and often tempting to think in terms of the greatest, largest, or strongest, whenever we quantify, classify, or simply describe objects and their qualities and even people. However, one needs to be careful and to realize that it is mostly necessary to imbedding a superlative into the right context. So is the Mont Blanc the highest mountain? Yes, if one specifies “in Europe”. Is it pedagogically appropriate and wise to do the same when teaching for instance acid-base and redox chemistry in a general chemistry course, *i.e.* to speak about the strongest acid or oxidant and taking the risk of making much too absolute statements? I personally argue in favour of doing this for one specific reason, *i.e.* the opportunity of broadening simple concepts by linking the often dry aspects of general chemistry to current research. This Column is aimed at illustrating some examples.

Superacidic media^[1] are by definition more acidic than pure H_2SO_4 and are able, as Brønsted acids, to protonate extremely weak bases, including, for example, methane.^[2] Such media are obtained by adding a strong Lewis acid, typically SbF_5 , to HF or HSO_3F and their acidity is commonly described by the Hammett acidity function H_0 .^[3] Thus, so-called magic acid, $\text{HSO}_3\text{F}/\text{SbF}_5$, reaches values of H_0 below *ca.* -22 – -23 for mixtures containing up to 90 mol% of SbF_5 ($H_0 = -12$ for pure H_2SO_4). Similar acidities can be reached by liquid mixtures of HF and SbF_5 and these two systems are considered the most acidic. However, their composition is quite complex and it is difficult to pinpoint a single discrete molecular species as *the* strongest acid, despite the fact that the adducts of SbF_5 and AsF_5 with HF, *i.e.* HSbF_6 ^[4] and HAsF_6 ,^[5] respectively, have been structurally characterized recently. Yet, species fulfilling the somewhat arbitrary criterion of being a well-defined molecular species isolable in form of a pure substance and deserving the attribute *strongest acid* do exist. As reported by Reed and coworkers^[6] less than two decades ago, polyhaloge-

nated carborane anions of the type $[\text{CB}_{11}\text{H}_{12-n}\text{X}_n]^-$ are extremely weak, non-coordinating bases, whose neutral conjugate acids can be isolated and even purified by sublimation. Among these, the compound $\text{H}[\text{CHB}_{11}\text{Cl}_{11}]$ has been described as *the* strongest acid – stronger than more common pure Brønsted superacids, such as HSO_3F ($H_0 = -15.1$) or $\text{CF}_3\text{SO}_3\text{H}$ ($H_0 = -14.1$) by an estimated 2 to 5 H_0 units. Its structure is illustrated in Fig. 1.^[7] By its non-oxidizing nature, this compound has been used to protonate *e.g.* C_{60} and benzene and to isolate the cations HC_{60}^+ and C_6H_7^+ , respectively, as the corresponding salts.

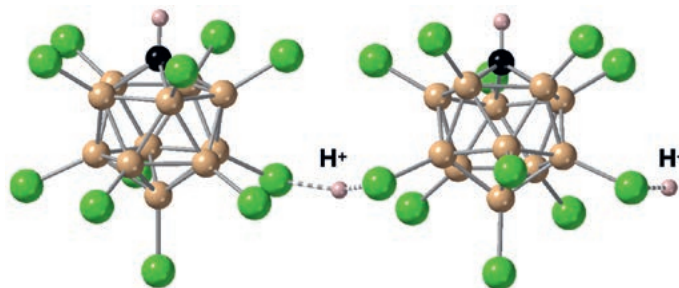


Fig. 1. Solid-state structure of $\text{H}[\text{CHB}_{11}\text{Cl}_{11}]$ (CCDC 606170). Note that H^+ ‘sits’ between chlorine atoms of two adjacent $\text{CHB}_{11}\text{Cl}_{11}$ anions.

When it comes to very strong bases, it is clear that “beating” alkyl lithium compounds is no easy endeavor. The conjugate acid of BuLi, for instance, is *n*-butane, an extremely weak Brønsted acid with an estimated $\text{p}K_a$ in DMSO of 55 (!). However, BuLi and other organo alkali metal complexes form various oligomers both in the solid state and in solution depending on the solvent,^[8] such that the acting base is not just the alkyl anion alone. Thus, one could again apply the same criterion as with acids and look for discrete, neutral, and metal-free molecular species displaying extreme basicities.^[9] Phosphazenes, also called Schwesinger bases, are here very prominent and can be used to deprotonate a variety of lowest-acidity functional groups in a variety of organic non-protic solvents. Fig. 2 shows the structure of the protonated form (HB^+ isolated as PF_6^- salt) of such a phosphazene base.^[10] The corresponding conjugate acid displays a $\text{p}K_a(\text{HB}^+)$ of *ca.* 47 in acetonitrile and of 34–35 in DMSO.

Many resonance structures can be drawn for a phosphazeni-um cation. It is thus an excellent example illustrating the general idea according to which factors increasing the stability of the conjugate acid will account for enhanced basicity.

Recent work by Sundermeyer and coworkers has shown that the same principles can be adopted for the design of neutral carbodiphosphorane superbases having a carbon atom as the site that gets protonated. The conjugate acid of the compound shown in Fig. 3 has a $\text{p}K_a(\text{HB}^+)$ of 35.8 in THF.^[11]

Another area of general chemistry in which it is easy to succumb to the use of superlatives is redox chemistry. When clas-

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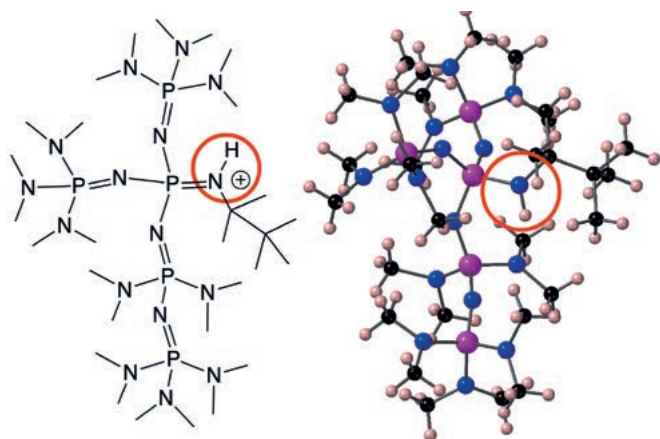


Fig. 2. Structure of the protonated form of a P₅ Schwesinger base (unique site of protonation circled, PF₆⁻ counterion omitted for clarity, CCDC 1231563).

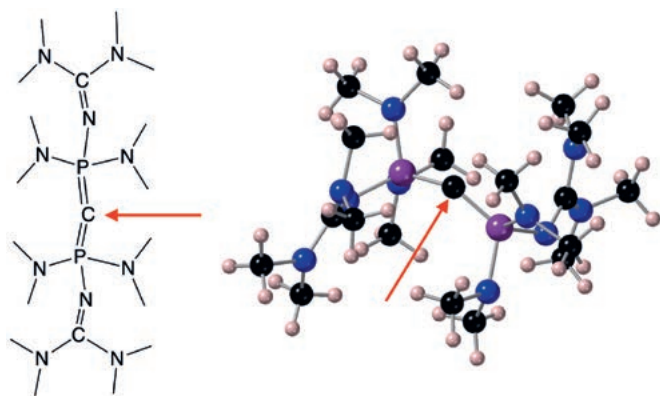
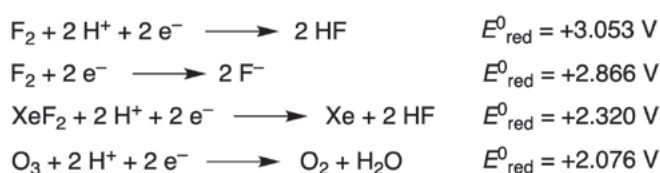


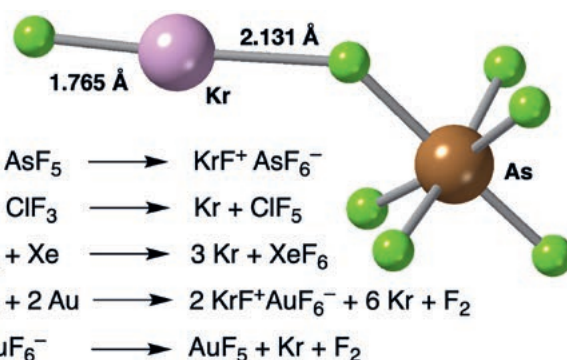
Fig. 3. Structure of a carbodiphosphorane suberbbase (site of unique protonation indicated by arrow, CCDC 1903840).

sifying oxidants, one usually shows a table with half-reactions and their corresponding standard reduction potentials. Many text books arrange E^0 values in descending order, such that the couple F₂/F⁻ is invariably at the top, thereby implying that elemental fluorine is (by far) *the strongest* oxidant (Scheme 1). Is this true? Some lanthanides and actinides in the formal oxidation state +IV display E^0 values for the couple M⁴⁺/M³⁺ higher than 3 V, thus representing oxidants stronger than fluorine.^[12]

Scheme 1 shows that one of the first molecular compounds of the noble gases, XeF₂, is also quite a potent oxidant. It is intuitively understandable that corresponding krypton derivatives^[13] should be even stronger. Scheme 2 shows some of the chemistry displayed by KrF₂.



Scheme 1. Some typical strong oxidants, their reduction half-reaction and standard reduction potentials.



Scheme 2. Some reactions of KrF₂ as fluorinating oxidant and the structure of KrF⁺AsF₆⁻ (CCDC 1720742).

In particular, the adduct of KrF₂ with AsF₅, a crystalline compound,^[14] is a discrete molecular species containing the KrF⁺ cation. The latter is able to take Xe directly to XeF₆, ClF₃ to ClF₅, and, even more impressively, Au to AuF₅. No other known oxidant is able to do this! Is KrF⁺ therefore *the strongest* known oxidant, despite the fact that there are no E^0 values available?

In conclusion, showing the chase for superlative molecular properties may help towards a better understanding of fundamental concepts in general chemistry. Have fun with chemical records!

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