Brønsted Acidity of Neutral and Cationic Acids in Nonaqueous Solvents: Recent Developments

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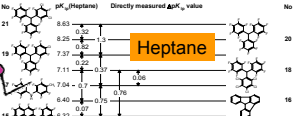
Introduction

Self-consistent acidity scales have been created in **acetonitrile (MeCN)**, **heptane** and **1,2-dichloroethane (DCE)**

Self-consistent basicity scales have been created in **acetonitrile (MeCN)** and **tetrahydrofuran (THF)**.

Heptane

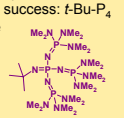
CH acids giving anions with highly delocalized charges, e.g.



were particularly useful in constructing the scales:

- no homo- or hetero-conjugation
- weak ion-ion interactions
- acidities insensitive to traces of water in the medium
- favorable spectral properties

Heptane is the least polar solvent where an acidity scale has been built [ref 7]. Key to success: *t*-Bu-P$_4$ phosphazene as the titrant:



- one of the strongest bases known
- soluble in heptane
- forms large cation with delocalized charge → weak interaction with anions

MeCN

MeCN acidity scale [ref 3]:

- 24 orders of magnitude (from pK_a 3.7 to 28.1)
- Consistency s = 0.03 pK_a units
- Practically all acid families included: alcohols, phenols, carboxylic acids, sulfonic acids, anilines, diphenylamines, disulfonimides, fluorenes, diphenylacetonitriles, phenylmalononitriles, ethyl aryl cyanoacetates, phenyl malononitriles

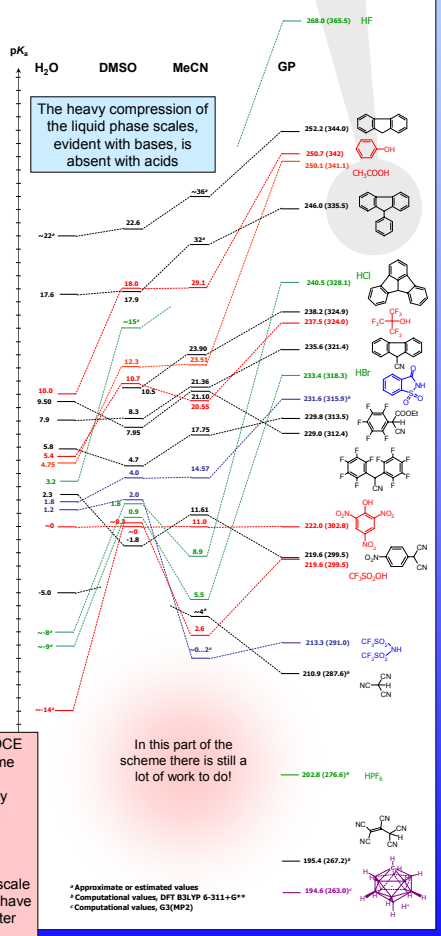
DCE

Acidity scale in DCE is about to become the strongest equilibrium acidity scale in constant medium ever composed. The strongest acids currently on the scale are estimated to have pK_a values in water around -10.

AcOH vs 9-PhFl:

- Gas phase: AcOH 4 orders weaker
- MeCN: AcOH 8 orders stronger
- H_2O: AcOH 13 orders stronger!

The heavy compression of the liquid phase scales, evident with bases, is absent with acids



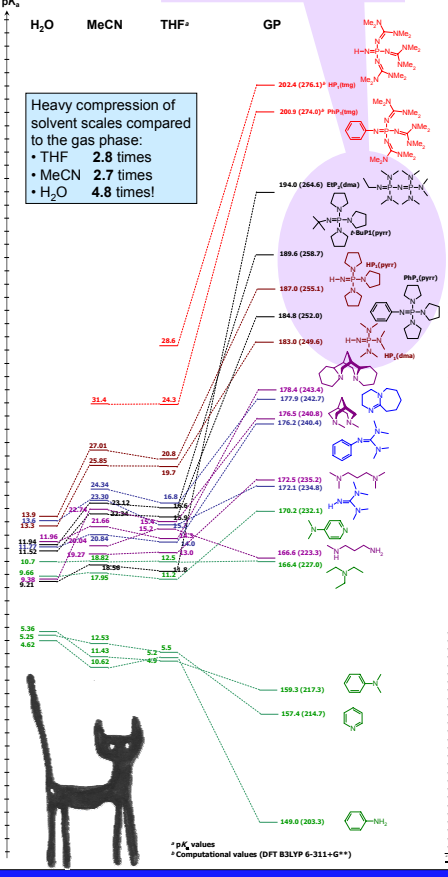
Bases

The method is based on UV-Vis spectrophotometric titration of a solution containing **simultaneously two** acids (bases) with a nonabsorbing base (acid). From the different degree of ionization of the compounds in titration points their relative acidity – the difference of their pK_a values (ΔpK_a) – is obtained.

- pK_a measurements are complemented with gas-phase basicity measurements of phosphazenes [ref 1]
- The GB scale expanded by 20 kcal/mol towards superbasic region

Heavy compression of solvent scales compared to the gas phase:

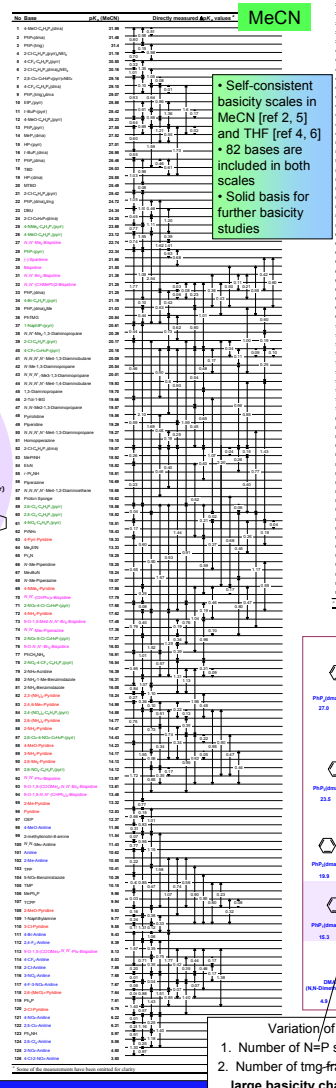
- THF **2.8** times
- MeCN **2.7** times
- H_2O **4.8** times!



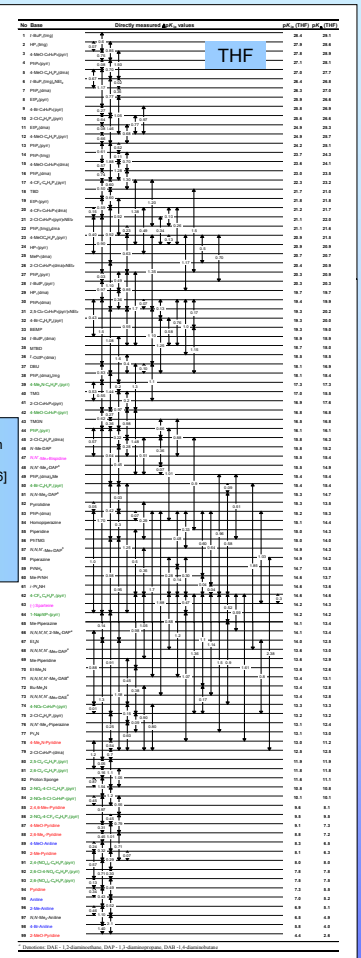
[a] pK_a values
[b] Computational values (DFT B3LYP 6-311+G**)

- Self-consistent basicity scales in MeCN [ref 2, 5] and THF [ref 4, 6]
- 82 bases are included in both scales
- Solid basis for further basicity studies

MeCN

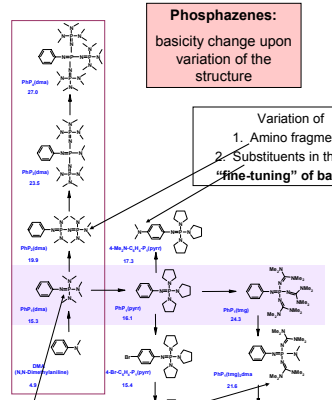


THF



Phosphazenes:

basicity change upon variation of the structure



Variation of

1. Amino fragments
2. Substituents in the ring

"fine-tuning" of basicity

Variation of

1. Number of N=P subunits
2. Number of tmg fragments

large basicity changes

(3-4 orders of magnitude)

References

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