Theoretical limits of basicity in condensed state and in gas phase

A.V. Kulsha
Lyceum of Belarusian State University, Minsk, Belarus,
e-mail: *Andrey_601@tut.by*

Brønsted superbases have wide applications in organic chemistry because of their capability to activate C—H bonds [1]. The strongest known neutral Brønsted bases are substituted aminophosphazenes developed in late 1980's by Reinhard Schwesinger [2], their gas-phase basicity surpasses 1200 kJ/mol. Since that time many researchers have been designing even stronger bases, but none of them have been produced experimentally.

In this work, the reasons of instability of very basic compounds are investigated by means of high-level quantum-chemical calculations. Hexamethylphosphoramide is proposed as a reliable ionizing solvent for superbases covering 60 units of pH, while cyclopentane is proposed as a non-ionizing solvent with extremely low acidity. Three novel stable neutral superbases are designed and studied along with metastable and anionic structures possessing record-breaking basicities.

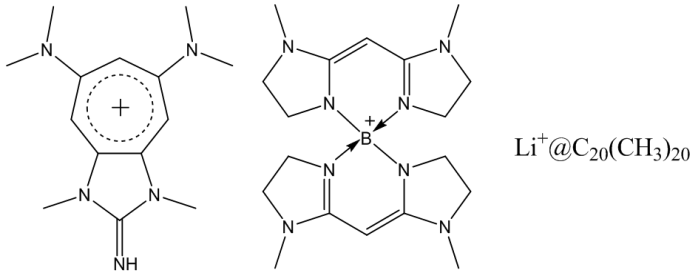

Fig. Protonated forms of proposed bases and their predicted pK_a values in HMPA

It is found that the base $Li@C_{20}(CH_3)_{19}CH_2$ appears to be close to basicity limit in the solution. Gas phase basicity limit for neutral molecules is probably reached by K_3N (1400 kJ/mol) in terms of Brønsted equilibrium; neutral structures that are metastable against self-deprotonation easily surpass gas-phase basicity of 1700 kJ/mol. Anionic species like $K_2F_5^{3-}$ could reach values beyond 2000 kJ/mol, while structures that decompose upon protonation could have no basicity limit at all.

References

[1] Superbases for Organic Synthesis / Ed. T. Ishikawa. Wiley, 2009. 336 pp.
[2] R. Schwesinger et al. Liebigs Ann. (1996) 1996:1055