

HYDRIDE AFFINITIES OF CATIONIC MAIN GROUP-ELEMENT HYDRIDES

Eva Blokker,^a Carolina Groen,^a Martijn van der Schuur,^b Auke G. Talma,^b F. Matthias Bickelhaupt^{a,c,*}

^a Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

^b Polymer Chemistry, Nouryon, Zutphenseweg 10, NL-7418 AJ Deventer, The Netherlands

^c Institute of Molecules and Materials, Radboud University, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands

* F.M.Bickelhaupt@vu.nl

The hydride ion, H⁻, is the simplest Lewis base and it plays an important role in numerous chemical and biological processes.^[1-3] The thermodynamic quantity that characterizes the stability and reactivity for these processes is the hydride affinity (HA), which is defined as the enthalpy change associated with the heterolytic dissociation of the complex between the hydride ion and the Lewis acid (here XH_{n-1}⁺):



We have systematically computed the HAs in gas phase of archetypical anionic bases across the periodic table using relativistic density functional theory (DFT) at ZORA-BP86/QZ4P [4]. We established a consistent set of values of the 298-K hydride affinities of all cationic maingroup-element hydrides (XH_{n-1}⁺) in which we have varied the central atom X along groups 14–17 and periods 2–6. The main purpose of this study is to get insight into the underlying physical features behind the periodical HA trends by using Kohn-Sham molecular orbital (MO) theory together with a quantitative bond energy decomposition analysis (EDA).^[5] The orbital interaction, or more specifically, the HOMO-LUMO energy gap, nicely determines the trend in hydride affinities across the periodic table.

REFERENCES

- [1] (a) A. Lipták, I. Jodál, P. Nánási, *Carbohydr. Res.* **1975**, *44*, 1–11; (b) J. C. Hubert, J. B. P. A. Wijnberg, W. N. Speckamp, *Tetrahedron* **1975**, *31*, 1437–1441; (c) E. Winterfeldt, *Synthesis* **1975**, *10*, 617–630.
- [2] P. Belenky, K. L. Bogan, C. Brenner, *Trends Biochem. Sci.* **2007**, *32*, 12–19.
- [3] S. R. Ovshinsky, M. A. Fetcenko, J. Ross, *Science* **1993**, *260*, 176–181.
- [4] (a) G. te Velde *et al.* *J. Comput. Chem.* **2001**, *22*, 931–967; (b) C. Fonseca Guerra *et al.* *Theor. Chem. Acc.* **1998**, *99*, 391–403.
- [5] F.M. Bickelhaupt *et al.* In: *Reviews in Computational Chemistry*; K.B Lipkowitz *et al.*; Wiley-VCH: New York, **2000**, Vol. 15, pp. 1–86.