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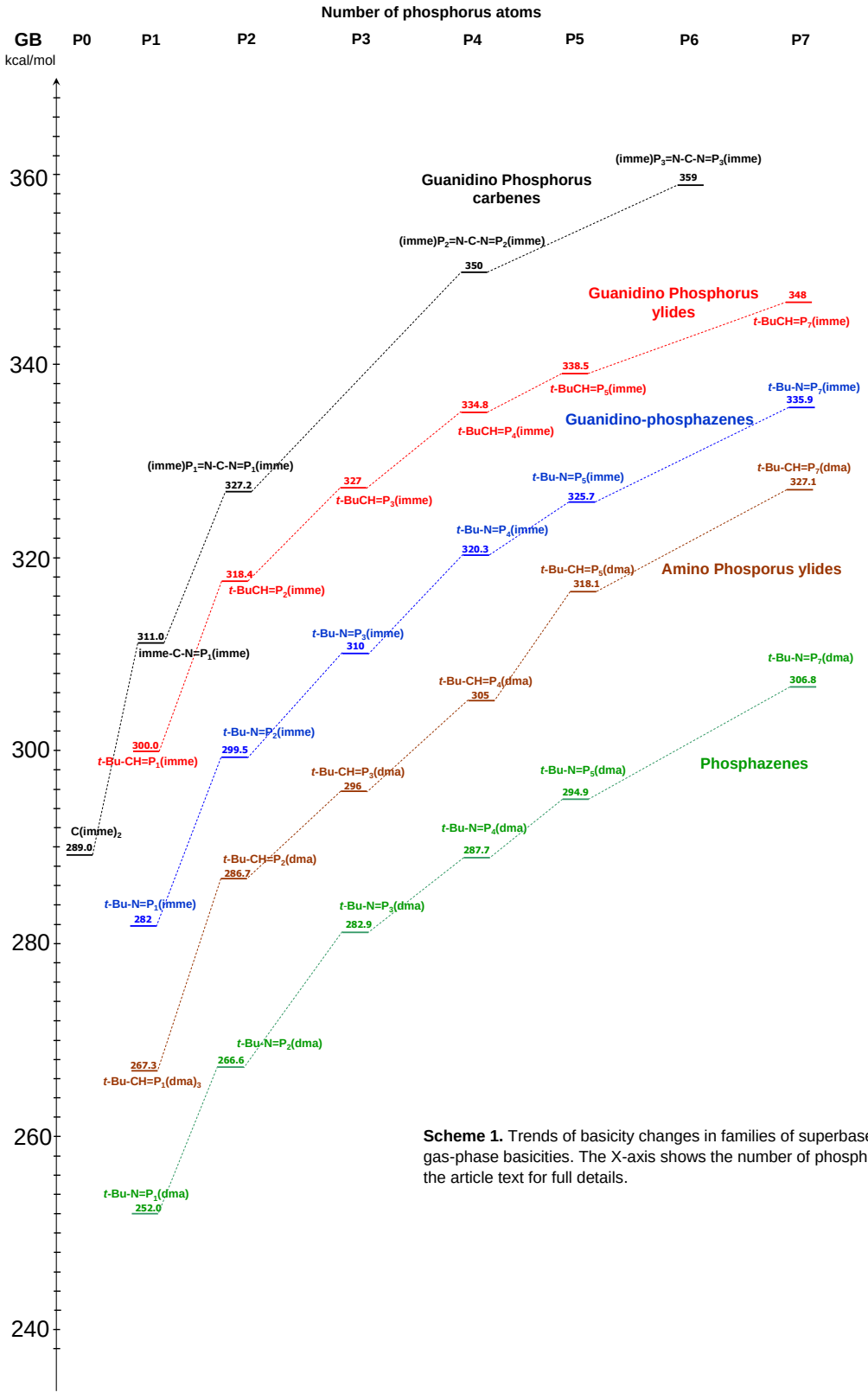
Basicity Limits of Neutral Organic Superbases. Ivo Leito,* Ilmar A. Koppel,* Ivar Koppel, Karl Kaupmees, Sofja Tshepelevitsh, and Jaan Saame.



Scheme 1. Trends of basicity changes in families of superbases. The Y-axis shows computational gas-phase basicities. The X-axis shows the number of phosphorus atoms in molecular scaffolds. See the article text for full details.

Table 1. Results of model validation and superbase basicity limit predictions with eq 1.[a]

Base series	***a***	***k*** [b]		
Gas phase			GB_{max}	**RMSD**[c]
Validation			kcal mol^{-1}	kcal mol^{-1}
HN=P$_n$(H)	0.32	1.78	268	1.6
HN=P$_n$(Me)	0.27	1.29	307	1.8
(*i*Pr)$_2$C=P$_n$(H)	0.18	1.43	290	1.8
H$_2$C=P$_n$(Me)	0.26	1.34	325	1.9
R-NH$_2$	0.05	1.61	214	0.5
R^{1}R^{2}R^{3}N	0.15	1.40	231	0.6
Prediction				
*t*Bu-N=P$_n$(dma)	0.28	1.30	320	1.6
*t*Bu-CH=P$_n$(dma)	0.29	1.25	348	1.8
*t*Bu-N=P$_n$(imme)	0.25	1.33	347	0.7
*t*Bu-CH=P$_n$(imme)	0.21	1.38	355	0.9
(imme)P$_n$=N-C-N=P$_m$(imme)	0.22	1.37	372	0.8
Solution			pK_{a_max}	**RMSD**
Prediction			–	–
Ph-N=P$_n$(dma) in THF	0.79	1.45	32	0.4
*t*Bu-N=P$_n$(dma) in MeCN	0.67	1.29	56	0.1

[a] See the article text and SI for full details. [b] $k \equiv e^b$, see above. [c] Root mean square deviation of the computed/experimental GB values from those predicted by eq 1.

Basicity changes in compound families are modelled with the following equation:

$$GB = GB_{\max}(1 - a\mathrm{e}^{-bn}) \quad (1)$$

where *n* is the number of phosphorus atoms, *GB* is the gas-phase basicity, GB_{max} is the maximum GB obtainable with the particular series and *a* and *b* are coefficients. In the case of pK_a predictions in acetonitrile or tetrahydrofuran *GB* and GB_{max} are substituted by pK_a and pK_{a_max}.