A Comprehensive, Direct Test of Single Scale Concepts for Intermolecular Interactions

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A topic of widespread interest is the suitability of single scale rankings of acids and of bases for the purpose of predicting (*i.e.*, understanding) the preferred adduct to be formed when two bases are placed in competition for an acid, and the preferred adducts when two bases distribute between two acids [1]. Although various mathematical [2] and specific-model tests [3, 4] have cautioned against the continued use of such concepts as 'hard–soft' and 'strength' as bases for thermodynamic and kinetic results, such usage persists. The purpose of this report is to provide a less theoretical, more empirical view of the unreliability of single-scale concepts of intermolecular interactions. The results described here are both an amplification and extension of an earlier, abbreviated report [1a].

The dual parameter model originally developed by Wayland and Drago [5], and subsequently modified and extended [2], provides a unique opportunity to operationally test within a large data base the suitabilities of two single scale concepts. 'softness', defined [2, 6] as the ratio C/E, and 'strength', defined [2] as $(C^2 + E^2)^{1/2}$ from a vector algebra view of the E, C relation.

In the context of the E, C relation the enthalpy of adduct formation for acid A and base B is given by

$$A + B \rightarrow A{\cdot}B$$

$$-\Delta H = E_A E_B + C_A C_B$$

For a competitive situation involving two bases and one acid

$$A{\cdot}B_2 + B_1 \rightarrow A{\cdot}B_1 + B_2$$

$$\delta H \equiv -\Delta H_{B_1} + \Delta H_{B_2}$$

$$= E_{B_1}E_A + C_{B_1}C_A - E_{B_2}E_A - C_{B_2}C_A$$

$$= E_A(E_{B_1} - E_{B_2}) + C_A(C_{B_1} - C_{B_2})$$

>0, if B_1 forms the preferred adduct
<0, if B_2 forms the preferred adduct

TABLE I. Results for One Acid/Two Bases (percentages).

Category	Softness			Strength		
F	54.7	62.3		19.7	25.6	
MF	7.6		14.2	5.9		14.2
MP	6.6	37.7		8.3	74.4	
P	31.1			66.1		

The strategy for testing the suitability of the 'softness' and strength criteria for predicting the sign of δH is as follows: 'Softness' – selecting B_1 as the base with C/E closer to C/E for the acid should yield $\delta H > 0$, if 'softness' matching of acid and base is a viable predictor: 'strength' – selecting B_1 as the stronger base should yield $\delta H > 0$, if base 'strength' is a viable predictor.

Using the 33 acids and 48 bases of reference 2 there are 37,224 tests of each single predictor. The results of these tests were segregated according to the following four categories, with the results depicted in Table I:

(F) Fail: $\delta H \leqslant -0.5$ kcal/mol
(MF) Marginal Fail: $-0.5 < \delta H < 0.0$ kcal/mol
(MP) Marginal Pass: $0.0 < \delta H < 0.5$ kcal/mol
(P) Pass: $0.5 \leqslant \delta H$ kcal/mol

Note that only 14% of the results fall in the (MF + MP) group. Even among the 32,000 reactions which fall outside the marginal discrimination categories, the overall fail:success ratio for 'softness' is nearly 2:1, while that ratio is 0.3:1 for strength.

Eliminating from the analysis those acids and bases with tentative E, C values reduces the basis to 18.278 samples and produces less than 0.3% change in the (MP + P) category for each predictor. Eliminating all hydrogen bonding acids raises the (MP + P) percentage for strength by only 2.4 points and *lowers* that for softness by 0.4 points.

A tally of the fail:success ratios for each acid and each base class (Table II) provides no basis for the existence of a bias from any group of chemically similar acids or bases which would explain the poor results for the 'softness' predictor. Its failure is evident even for groups widely accepted as 'soft' and is rather evenly distributed among the various groups of acids and bases. The 'strength' criterion is statistically better than the 'soft' criterion, but is generally unreliable; its utility is evident only for the extremes of strength (* in Table II).

The conclusion to be drawn from Table I is straightforward: 'softness' is unreliable as a predictor of base competition for an acid; a more reliable,

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TABLE II. Acid and Base Fail: Success Ratios by Functional Group Classes.

Function	Fail:Success	
	Softness	Strength
–I (3)[a]	2.8	0.1
–NH (3)	0.7	0.3
–OH (11)	1.0	0.3
–SH (1)	0.8	0.0*
→B(2)	2.2	0.2
→Al (2)	1.4	0.3
→Ga (2)	0.8	0.6
→In (1)	0.7	0.7
→SnCl (1)	0.3	0.9
SO_2	3.4	0.0*
$Cu(hfac)_2$	3.2	0.1
$SbCl_5$	4.8	0.0*
→CH (2)	0.6	0.3
MeCo (oxime)	1.8	0.2
$[(Me_3Si)_2N]_2Zn$	2.1	0.1
–C≡N (2)	5.6	0.1
>N (3)	1.5	0.1
→N (9)	1.7	0.2
→P (2)	1.0	0.4
$>N-\overset{\vert}{C}=O$ (4)	1.4	0.2
$-O-\overset{\vert}{C}=O$ (3)	2.9	0.1
>O (7)	1.3	0.2
→N–O (4)	1.1	0.3
→P–O (3)	0.7	0.5
>S–O (2)	1.0	0.3
>S (5)	0.3	0.8
>Se (1)	0.3	0.9
Aromatic (3)	1.9	0.0*

[a]Number of compounds in class. [b]*classes of 'extreme' strengths.

but still unacceptable, statement would be that 'soft' prefers 'hard'! While strength is twice as reliable as 'softness', it too fails 25% of the time.

To explore the possibility that in dual competitions one or the other single-scale concept would become useful, we examined the double exchange reactions:

$$A_1B_2 + A_2B_1 \rightarrow A_1B_1 + A_2B_2$$

$$-\Delta H = (E_{A_1} - E_{A_2})(E_{B_1} - E_{B_2}) + (C_{A_1} - C_{A_2})(C_{B_1} - C_{B_2})$$

Matching the softer acid with the softer base and stronger acid with the stronger base produces the results in Table III (sample size = 585, 584).

TABLE III. Results for Two Acids/Two Bases (Percentages).

Category	Softness			Strength		
F		20.2	28.1		32.4	41.1
MF	20.8	7.9		20.8	8.7	
MP		12.9	71.9		12.1	58.9
P		59.0			46.8	

There is a marked improvement in the reliability of 'softness' as a predictor for dual competitions but its quality remains poor at <75% successful. The reliability of strength as a predictor of dual competitions deteriorates somewhat relative to the single competition case.

The above results provide a test based on objective data of the applicability of the single-scale predictors of 'softness' and 'strength' for the energetics of intermolecular interactions. The conclusion that these predictors fail is not new, but the simple directness, comprehensiveness and non-selectivity of the analysis provides the strongest evidence available that the difficulties with single-scale concepts are so fundamental that one is not even permitted to make predictions at the functional group level (within this present data base –SH, SO_2, $SbCl_5$ and aromatic donors may be exceptions).

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