CONTRIBUTION FROM THE WILLIAM A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

A Quantitative Evaluation of the HSAB Concept

BY RUSSELL S. DRAGO* AND ROBERT A. KABLER

Received March 20, 1972

Over the years there have been many attempts to find empirical parameters which predict rates and equilibrium constants for reactions.[1-4] These studies invariably employ free energy data in polar solvents to arrive at empirical constants. With contributions to the data employed, from enthalpies and entropies of reactions and solvation of all of the species involved, there is little wonder that relatively little insight into the molecular interpretation of intermolecular interactions has resulted. The parameters contain contributions from all of these effects. The essential solvent-free ΔE of the reaction which is the quantity to be interpreted quantum mechanically cannot be factored out of the parameters. Accordingly, we should not be very surprised to find that many of our qualitative concepts of chemical reactivity are completely incorrect when trends in reactions in polar solvents form the basis for the explanations. Our approach[5,6] has involved the parameterization of solvation-minimized or solvent-free enthalpies and in this article we shall use these data to test a recent, very highly publicized, qualitative model for intermolecular interactions: the hard-soft acid-base model, HSAB.

Recently we reported[5] a nonlinear least-squares fit of 280 enthalpies of adduct formation to the equation

$$-\Delta H = C_A C_B + E_A E_B \qquad (1)$$

The subscripts A and B refer to donors (B) and acceptors (A) of which there are 74 leading to 144 unknowns. The products $E_A E_B$ and $C_A C_B$ were roughly related[6] to trends in the electrostatic and covalent contributions to the enthalpy. In certain systems, other effects are incorporated into these quantities. We also reported[6] a matrix formulation for acid-base interactions which enables one to transform the reported parameters into another set of parameters which could correspond to some new model one wished to impose on the system.

The HSAB model has been used and accepted mainly as a qualitative model. However, if data became available we certainly should demand that our qualitative explanations be capable of withstanding a quantitative test at least to the approximate degree of accuracy that one would employ in qualitative usage. If it fails this test, it should be rejected particularly if the approach can be replaced by a better model that can also be applied qualitatively with almost equal facility.

First, we shall examine the possibility that our E and C parameters are directly related to hardness which Pearson relates to electrostatic bonding and softness which is related to covalency, etc. As can be seen by the data in Table I, such a direct translation cannot be made. If the C number of our present fit is softness and the E number hardness, m-$CF_3C_6H_4OH$ would be both harder and softer than phenol. Clearly, this is impossible by the definition of the words hard and soft and by Pearson's definition of hard and soft acids and bases which imply that these quantities are related with one being the opposite property of the other. Although difficulties with interpreting the behavior of the proton relative to some other acids have been attributed[7] to the strength of interaction, the idea that some substances are just stronger acids or bases than others with regard to both covalent and electrostatic interaction invariably is ignored in HSAB. For example, one never finds the same substance being listed as both hard and soft. Furthermore, in the lists[7] of soft acids, for example, one finds substances as widely varying in their strength of interaction as chloranil, I_2, BH_3, and Pt^{2+}. Trimethylaluminum is a hard acid, but due to the weakness of the acid I_2, the soft sulfur donor tetrahydrothiophene, $(CH_2)_4S$, will react more strongly with the hard acid aluminum trimethyl than with the soft acid I_2. This occurs in violation of the principal tenant of HSAB theory that "soft prefers soft and hard prefers hard" but is predicted by the E and C model because both the E and C numbers for aluminum trimethyl are larger than those of iodine. Many other breakdowns can be predicted by referring to Table I and finding acids or bases whose E and C numbers are both larger than those of another. Other difficulties that one can encounter even in the qualitative use of HSAB have been described.[5]

TABLE I

AN ORDERED SET OF ACIDS AND BASES IN WHICH E AND C BOTH INCREASE

Acids	C_A	E_A	Bases	C_A	E_A
$CHCl_3$	0.150	3.31	C_6H_6	0.707	0.486
C_6H_5OH	0.442	4.33	CH_3CN	1.34	0.886
m-$CF_3C_6H_4OH$	0.530	4.48	$(CH_3)_2CO$	2.33	0.987
$B(CH_3)_3$	1.70	6.14	$(CH_3)_2SO$	2.85	1.34
			NH_3	3.46	1.36

As both Klopman[8] and Pearson[7b] have pointed out, hardness and softness are related to the C/E ratio. However, all predictive value about the magnitude of the interaction is lost in the ratio as can be seen from the fact that 1.49/16.9 for trimethylaluminum is about the same ratio as 0.509/5.56 for hexafluoroisopropyl alcohol.

It can be shown with difficulty than no transformation matrix exists which converts our parameters for the acids and bases into numbers that are consistent with a hard-soft interpretation. That this is so and the extent to which the HSAB concept fails as a quantitative model can be shown by converting the HSAB concept as qualitatively applied to a quantitative equation and attempting to fit enthalpy data to it. If a transformation matrix exists, our least-squares

---

[1] See C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964), for a review of the very extensive organic literature on this subject.

[2] S. Ahrland, *Struct. Bonding (Berlin)*, **5**, 118 (1968), and references therein.

[3] M. Misono, *et al.*, *J. Inorg. Nucl. Chem.*, **29**, 2685 (1967).

[4] F. Lohman, *Chem. Phys. Lett.*, **2**, 659 (1968).

[5] R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, **93**, 6014 (1971).

[6] R. S. Drago and B. B. Wayland, *ibid.*, **87**, 3571 (1965).

[7] (a) R. G. Pearson, *ibid.*, **85**, 3533 (1963); (b) *Science*, **151**, 172 (1966); (c) *Chem. Brit.*, **3**, 103 (1967); (d) *J. Chem. Educ.*, **45**, 581 (1968); (e) *ibid.*, **45**, 643 (1968); (f) R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

[8] G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

program will find it and fit the data as well as our E and C equation does.

A literal translation of the HSAB concept would be given by

$$-\Delta H = (K - H_A)(K' - H_B) + H_AH_B \qquad (2)$$

where H_A is the hardness of the acid and K is the same constant for all acids which converts hardness into the opposite quantity softness. K' and H_B are similar quantities for bases. We selected representative enthalpy data from our earlier article and used a nonlinear least-squares program[5] to obtain the parameters K, K', H_A, and H_B which best fit the data. The minimum number of parameters needed to obtain a unique solution were fixed in each case and are indicated in Table II.

TABLE II

A COMPARISON OF THE DATA FIT FOR EQ 1–4

		$-\Delta H$, kcal/mol				
Acid	Base	Measd	E and C	HSAB[b]	Eq 3[c]	Eq 4[c]
I_2	C_5H_5N	7.8	7.9	7.9	7.7	7.9
	NH_3	4.8	4.8	6.1	6.2	6.1
	$(CH_3)_3N$	12.1	12.3	9.9	9.4	9.7
	$(CH_2)_4S$	8.3	3.2	5.1	5.1	5.1
	$(C_2H_5)_2O$	4.2	4.2	5.3	5.4	5.2
C_6H_5OH	C_5H_5N	8.0	7.9	8.6	8.0	8.1
	NH_3	7.8	7.4	6.2	6.4	6.3
	$(CH_3)_3N$	8.8	8.6	10.0	9.8	10.0
	$(CH_2)_4S$	4.9	5.0	5.2	5.3	5.3
	$(C_2H_5)_2O$	6.0	5.6	5.4	5.6	5.5
SO_2	C_5H_5N	6.0	6.2	6.3	6.2	6.3
	NH_3	*a*	4.0	4.7	5.1	4.7
	$(CH_3)_3N$	10.3	10.1	9.9	7.6	7.8
$Al(CH_3)_3$	C_5H_5N	26.7	28.9	26.6	27.4	26.7
	NH_3	27.6	28.0	21.9	21.9	21.8
	$(CH_3)_3N$	30.0	30.2	31.6	33.9	31.9
	$(CH_2)_4S$	17.0	17.1	19.3	17.8	19.2
	$(C_2H_5)_2O$	20.2	20.9	19.7	19.0	19.5
$HCCl_3$	C_5H_5N	4.9	4.9	4.2	4.1	4.3
	$(CH_3)_3N$	4.8	4.9	5.5	5.0	5.6
	$(CH_2)_4S$	2.4	2.3	2.3	2.9	2.2
$(CH_3)_2CHOH$	C_5H_5N	9.8	9.7	9.4	9.3	9.4
	$(CH_3)_3N$	11.5	11.0	11.5	11.5	11.4
	$(CH_2)_3S$	5.8	5.9	6.2	6.1	6.3
	$(C_2H_5)_2O$	7.2	7.0	6.4	6.5	6.4

[a] The enthalpy has not been measured, but the covariance–variance analysis on the E and C fit indicates that this number can be predicted to at least 5%. [b] The parameter H_A was fixed for I_2 and C_6H_5OH and H_B for C_5H_5N. [c] The parameter H_A was fixed for I_2.

In view of the very poor fit of the data to this model, we decided to try a model involving a nonliteral translation of hard and soft in which the parameters are reciprocal quantities

$$-\Delta H = H_AH_B + \frac{1}{H_A}\frac{1}{H_B} \qquad (3)$$

where H_A and H_B have the same meaning as above. We were also interested in trying to fit the equation

$$-\Delta H = H_AH_B + \frac{k}{H_AH_B} \qquad (4)$$

where k is a best fit scaling factor determined by the program. The results of all these attempted fits are reported in Table II along with the results calculated by our E and C equation using parameters previously reported[5] and the experimental numbers. (An even better fit of these data has been obtained using our E and C equation on this limited set of data.)

As illustrated by the data in Table II, we can conclude that the HSAB concept as it is most commonly employed is fundamentally incorrect. A hardness–softness strength equation could be written as

$$-\Delta H = S_A(C_A/E_A)S_B(C_B/E_B) + K_A(E_A/C_A)K_B(E_B/C_B)$$

where S is the strength of softness and K the strength of hardness. However, $C_A = S_A(C_A/E_A)$ and $E_A = K_A(E_A/C_A)$, so this is a simple rewrite of eq 1 with no obvious advantages for this additional complication since "strength of hardness" and "strength of softness" would have to change in a way contrary to the accepted definition of the words.

One could counter the above conclusion by saying that the hard–soft model is very valuable to the synthetic chemist and should be retained for that reason. In this connection, we should hasten to point out that a miss by 1.4 kcal mol^{-1} in the enthalpy corresponds to about an order of magnitude miss in the equilibrium constant. A product may not be obtained when K is 90 but can usually be isolated when K is 900. Thus, we can see from Table II that many incorrect qualitative predictions are also expected from HSAB. We suggest that a qualitative approach employ the terms "large C property" or "frontier controlled" for soft and "large E property" or "charge controlled" for hard. Substances can then be considered to have both a large C and a large E relative to some other substance. Large size, low ionization energy, and other properties leading to softness[7] often contribute to a large C, while small size and high charge, etc., contribute to a large E. Listings of acids and bases according to large E's and large C's could very well contain the same substance in both tables. The exact meaning of the term large C or large E as applied to molecular interactions is not very precise, but even if the HSAB model were correct, the same criticism can be leveled against the words hard and soft. A compromise for those who prefer something more catchy could involve referring to acids and bases as soft and charged. Now an opposite relation is not implied by the words and a substance that is very soft may also be charged.[9]

Acknowledgment.—The authors acknowledge the generous support of the National Science Foundation through Grant USNSF GP 31431X and the Paint Research Institute.

---

(9) NOTE ADDED IN PROOF.—We wish to comment briefly on the reply to our paper by Pearson which immediately follows. We do not claim that Pearson did not recognize the existence of strength, but that almost invariably in the explanation of chemical reactivity, only hardness and softness are employed. This disregard of strength is evidenced by the absence in the very extensive published literature on this concept of tables of strength. The arbitrary decision (in Pearson's third from the last paragraph) to use two independent parameters to describe acid–base interactions was not ours, but Pearson's, when he selected and almost invariably employed the two properties, hardness and softness, in describing chemical reactivity. If just hard and soft work so well and so often for him, why do so many of our systems in Table II not work? By appropriately selecting four parameters, we have solved for and obtained parameters on other systems which agree with the qualitative and semiquantitative assessments of the importance of covalent and electrostatic binding in adducts. This agreement and testing of the model is *not biased* by our parameter selection. Obviously, our parameters are not good measures of the incomplete concept of hardness and softness. Footnote 5 is incorrect. The two papers do not treat the same sets of data and they use different standards. The minimum is very shallow and we place many constraints on our solution. Jolly, *et al.*, make no attempt to interpret their parameters.