Pearson's Hard–Soft Acid–Base Principle and the Heterolytic Dissociative Version of Pauling's Bond-energy Equation *

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A correspondence between the γ parameter recently developed, which characterises the binding site of an ion, and Klopman's frontier-orbital energy has been established to show that γ does represent the hardness of an ion. It is shown that γ can be used to describe the polarity of an A–B bond where A is an acid and B a base. Also that Pearson's hard–soft acid–base principle means that acids and bases interact selectively in an exchange reaction of the type AB + CD $\rightleftarrows$ AC + BD so as to form bonds of similar, to the extent possible, polarity between themselves.

In 1963, to explain inorganic reactivity and stabilities of metal complexes, Pearson[1] classified the donors (Lewis bases) and acceptors (Lewis acids) in inorganic reactions into three broad categories, hard, soft and borderline from polarisability considerations. A more polarisable species is softer. Earlier similar attempts were made by others.[2,3] The situation has been recently reviewed.[4] The quantitative definition of hardness (η), given by Parr and Pearson,[5] is $\eta = (E_i - E_{ea})/2$ where E_i and E_{ea} are respectively the ionisation potential and electron affinity of the chemical species in question. It was shown later[4,6] that this definition of η does not qualify the binding site(s) of a chemical species. A parameter γ has recently been introduced[4] which characterises the binding site(s) of an ion by developing a heterolytic dissociative version of Pauling's bond-energy equation[7] (1). In equation (1) $D(A^+B^-)$ is the energy required for

$$D(A^+B^-) = [D(A^+A^-) + D(B^+B^-)]/2 + 2(\gamma_{A^+} - \gamma_{B^-})^2 \quad (1)$$

the dissociation of the A–B bond into $A^+ + B^-$, and $D(A^+A^-)$ and $D(B^+B^-)$ the heterolytic dissociation energies of the A–A and B–B bonds respectively. In this paper further insight into the nature of the γ parameter is sought in an attempt to examine Pearson's hard–soft classification from a novel view point.

Results and Discussion

The Nature of the γ Parameters.—In the earlier work[4] it was speculated that the γ parameters represent the hardness of ions. Here this is shown explicitly.

While enumerating donor–acceptor interactions as charge and frontier-orbital controlled reactions in 1968 Klopman[8] devised a reactivity index for an ion from E_i and E_{ea} data which he called the 'frontier orbital energy' ($E^\ddagger$). In the gas phase for mononegative donors (m), $E^\ddagger_m$ is given by equation (2) and for monopositive acceptors (n), $E^\ddagger_n$ is given by equation (3), where

$$-E^\ddagger_m = (E_i)_0 - 0.75[(E_i)_0 - (E_{ea})_0] \quad (2)$$

$$-E^\ddagger_n = (E_i)_0 - 0.25[(E_i)_0 - (E_{ea})_0] \quad (3)$$

the subscript 0 refers to the corresponding neutral species. The factors 0.75 and 0.25 are somewhat arbitrary. Klopman has shown the parallelism between the $E^\ddagger$ values and Pearson's qualitative concept of hardness, and his work was the first attempt to quantify the idea of hardness. In terms of $E^\ddagger$, the hardness of an ionic species increases with decreasing $E^\ddagger$. I have found that for some 10 monovalent ionic bases the γ parameters correlate linearly with the $E^\ddagger_m$ values (Table 1)[9] to a very satisfactory extent (Fig. 1). The γ parameter decreases as the hardness in Klopman's concept decreases. For acceptors, however, the correspondence is not so straightforward. Good linear correlations of $E^\ddagger_n$ for monoatomic monovalent cationic acids and polyatomic monovalent cationic acids are obtained separately (Table 1, Fig. 2). The reason is not clear at present. Nevertheless the trend in the γ values is in agreement with that in Klopman's hardness of the monovalent cations.

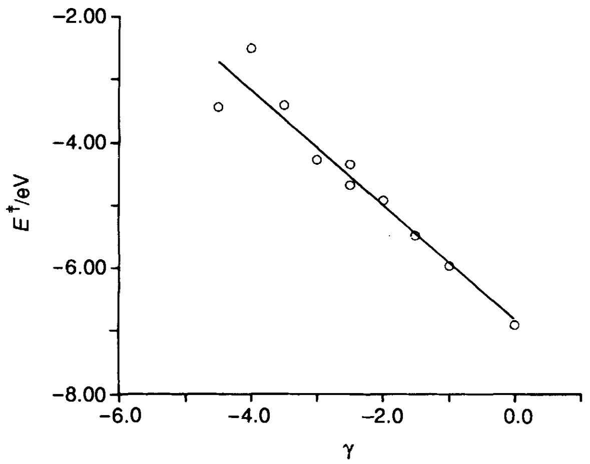

Fig. 1 Correspondence between Klopman's frontier-orbital energies $E^\ddagger$ and the γ parameters (in Datta–Singh's unit) for some monovalent anions; for data, see Table 1; H^-, not shown in the figure, is not included in the least-squares fit. Correlation coefficient = 0.964

Using Koopman's theorem, it can be shown that for a closed-shell chemical species the hardness parameter η of Parr and Pearson indicates the gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO).[9] Since in a chemical reaction, of all the orbitals on the two interacting species the HOMO and LUMO take part most actively, η can be taken as an index of reactivity. This has been appreciated by several workers.[9–12] As the hardness of a chemical species increases, its thermodynamic stability increases and consequently its reactivity decreases. (That thermodynamic stability is inversely related to kinetic stability is well known. See, for example, ref. 13.) It was stated above that the γ parameters represent some sort of reactivity

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* *Non-S.I. unit employed:* cal = 4.184 J.

Table 1 Klopman's frontier-orbital energies ($E^‡$) and γ parameters for some monovalent ionic donors and acceptors[a]

Ion	$(E_i)_0$	$(E_{ea})_0$	$-E^‡$	$-\gamma$
H^-	13.59	0.74	3.95	−1.0
F^-	17.42	3.40	6.91	0.0
Cl^-	13.01	3.62	5.97	1.0
Br^-	11.84	3.36	5.48	1.5
I^-	10.45	3.06	4.91	2.0
OH^-	13.17	1.83	4.67	2.5
SH^-	10.41	2.3	4.33	2.5
OCH_3^-	12.30[b]	1.58[b]	4.26	3.0
NH_2^-	11.40	0.74	3.41	3.5
CH_3^-	9.82	0.08	2.51	4.0
SCH_3^-	8.06	1.9	3.44	4.5
H^+	13.59	0.74	10.38	2.0
I^+	10.45	3.06	8.60	5.0
Li^+	5.39	0.62	4.20	6.0
Na^+	5.14	0.55	3.99	6.5
Cu^+	7.73	1.23	6.11	6.5
K^+	4.34	0.50	3.38	7.0
Rb^+	4.18	0.49	3.26	7.0
Cs^+	3.89	0.47	3.04	7.0
SiH_3^+	8.14	1.41	6.46	4.5
OH^+	13.17	1.83	10.33	5.0
CH_3^+	9.82	0.08	7.39	6.5
$C_2H_5^+$	8.38	−0.39	6.19	7.5
iso-$C_3H_7^+$	7.57	−0.48	5.56	8.0
tert-$C_4H_9^+$	6.93	−0.30	5.12	8.0

[a] The meanings of the symbols used are the same as in the text. The $(E_i)_0$, $(E_{ea})_0$ and $E^‡$ values are given in eV (*ca.* 1.60 × 10^{-19} J) and the γ values taken from ref. 4 are given in Datta–Singh's unit. The E_i and E_{ea} values are taken from ref. 9 unless otherwise specified. [b] From ref. 6.

Table 2 Variation of Pauling's ionic character λ in some diatomic molecules AB with $|\Delta\gamma|$[a]

Molecule AB	R[b]	μ[c]	μ_0	λ	$\lvert\Delta\gamma\rvert$
LiH	1.595[d]	5.88	7.656	0.77	7.0
HF	0.918[d]	1.82	4.406	0.41	2.0
LiF	1.564	6.33	7.507	0.84	6.0
NaF	1.926	8.16	9.245	0.88	6.5
KF	2.171	8.60	10.421	0.83	7.0
RbF	2.270	8.55	10.896	0.78	7.0
CsF	2.345	7.88	11.256	0.70	7.0
HCl	1.274[d]	1.08	6.115	0.18	1.0
LiCl	2.021	7.13	9.701	0.73	5.0
NaCl	2.361	9.00	11.333	0.79	5.5
KCl	2.667	10.27	12.802	0.80	6.0
CsCl	2.906	10.42	13.949	0.75	6.0
HBr	1.408[d]	0.82	6.758	0.12	0.5
LiBr	2.170	7.27	10.416	0.70	4.5
KBr	2.821	10.41	13.541	0.77	5.5
HI	1.608[d]	0.44	7.718	0.06	0.0
LiI	2.392	7.43	11.482	0.65	4.0

[a] The meanings of the symbols are the same as in the text. Units used: R, Å; μ and μ_0, D (*ca.* 3.33 × 10^{-30} Cm); $|\Delta\gamma|$, Datta–Singh's unit. [b] From ref. 14 unless otherwise specified. [c] From ref. 15. [d] From ref. 16.

index. Since η is also a reactivity index, we can confidently say that the γ parameters can be taken as an index of chemical hardness.

The γ Parameters and Bond Polarity.—Here we examine the nature of the A–B bond in a molecule AB, which arises out of the acid–base interaction between the cationic acid A^+ and the anionic base B^-, in terms of the γ parameters.

In valence-bond (VB) theory the total wavefunction ψ for an A–B bond can be written as in equation (4) where the contributions of the ionic structures A^+B^- and A^-B^+ compared to the fully covalent structure A–B are reflected by the coefficients b and c respectively. If the electronegativity of fragment B is greater than that of A, $b > c$. In terms of VB theory, mixing of the ionic structures gives rise to the polarity of the A–B bond. Equation (4) shows that no bond is absolutely covalent or ionic; it can only be in between these two extremes. However it is very difficult to find an experimental measure of the relative contributions of the ionic structures and the covalent one for a particular bond. The stabilisation of the covalent structure through mixing of ionic ones is known as the ionic resonance energy. Pauling's electronegativity χ is thought to be related to it. For diatomic molecules AB, Pauling suggested a rough estimate of the bond type from the dipole moment. If μ_0 is the dipole moment calculated for an AB molecule assuming a fully ionic structure, *i.e.* $\mu_0 = eR$ where e is the electronic charge and R the equilibrium internuclear distance, and μ is the experimental dipole moment, then according to Pauling the amount (λ) of ionic character of the A–B bond is equal to μ/μ_0.*[7,14] For the diatomic halides the relation between $|\chi_A - \chi_B|$ and λ is believed to be non-linear.[7] Since the γ parameter is said to characterise various ions, it is worth examining its relation with λ. Accordingly I have recalculated λ for 16 diatomic halides and

$$\psi = a\psi_{A-B} + b\psi_{A^+B^-} + c\psi_{A^-B^+} \qquad (4)$$

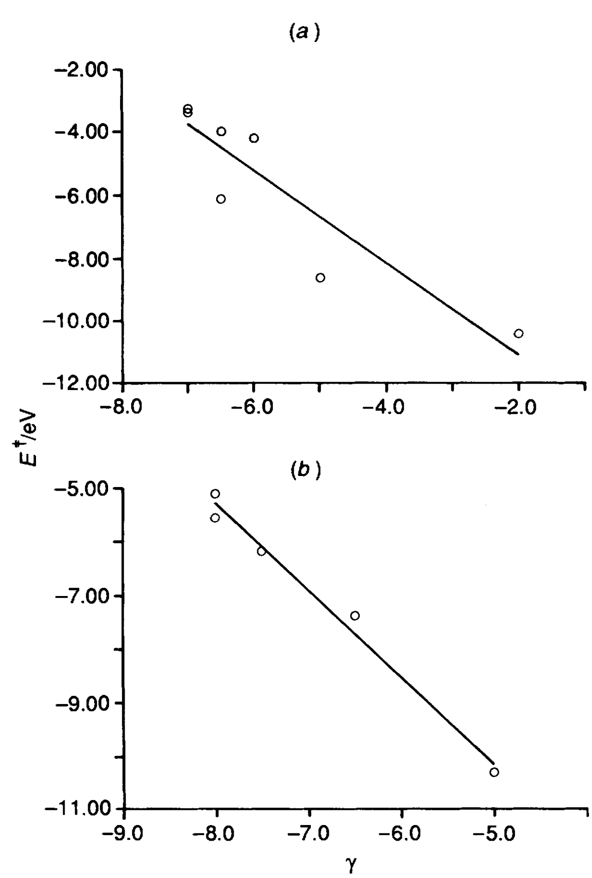

Fig. 2 Correspondence between Klopman's frontier-orbital energies $E^‡$ and the γ parameters (in Datta–Singh's unit) for (*a*) monoatomic and (*b*) polyatomic cations; for data, see Table 1; SiH_3^+, not shown in the figure, is not used for the least-squares fit in (*b*). Correlation coefficients: (*a*) 0.911 and (*b*) 0.995

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* It should be noted that even in a heteronuclear diatomic molecule the ionic bond moment is only one of the factors responsible for the molecular dipole moment. Two other important factors are the lone pairs and the difference in atomic sizes. For a comprehensive study of the various factors associated with dipole moments of heteronuclear diatomic molecules the reader is referred to the work of Brumer and Karplus[14] on 'ionic models' for alkali-metal halides.

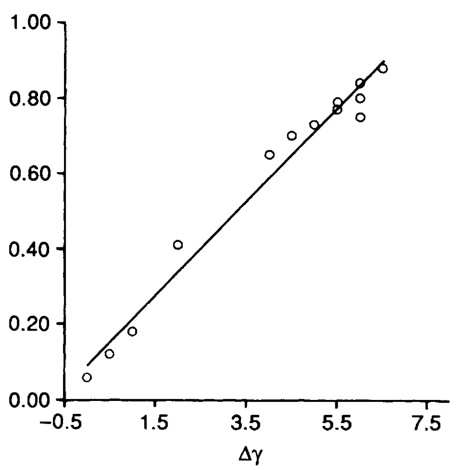

Fig. 3 Variation of Pauling's ionic character (λ) of the A–B bond in 13 diatomic molecules AB with $|\Delta\gamma|$, the difference in the γ parameter ($= |\gamma_{A^+} - \gamma_{B^-}|$) up to $|\Delta\gamma| = 6.5$ (see text); correlation coefficient = 0.990. For data see Table 1

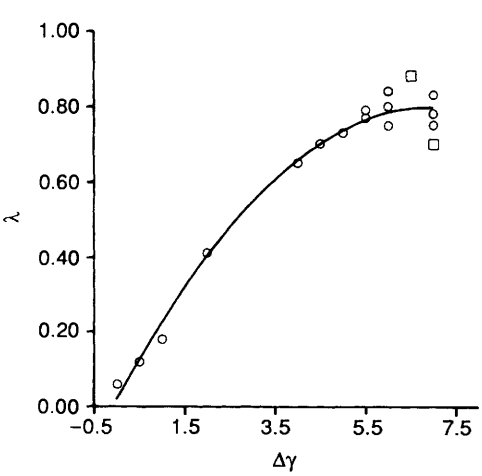

Fig. 4 Overall relation between Pauling's ionic character (λ) of the A–B bond in 17 diatomic molecules AB with $|\Delta\gamma|$; NaF and CsF, marked by □, are not used for the least squares fit. Correlation coefficient = 0.995. For data see Table 1

LiH using recent R[14,15] and μ data.[16] The results are given in Table 2. For all practical purposes up to $|\Delta\gamma| = 6.5$ the variation between λ and $|\Delta\lambda|$ is linear (Fig. 3, correlation coefficient = 0.990). However the overall relation is actually quadratic in $|\Delta\gamma|$ [equation (5); Fig. 4, correlation coefficient = 0.995]. Thus

$$\lambda = 0.020 + 0.224\,|\Delta\gamma| - 0.016\,|\Delta\gamma|^2 \qquad (5)$$

the γ parameters can be used as an index of the amount of ionic character of an A–B bond for heteronuclear diatomic molecules within the limitations of Pauling's concept.

For polyatomic molecules a similar treatment cannot be applied since the observed dipole moment is not only a resultant of various bond moments but also of contributions from other factors (see the footnote also). However the relative weight of the two ionic structures A^+B^- and A^-B^+ can be ascertained. From equation (5) it can be stated that the contribution of an ionic structure for an A–B bond increases with increasing $|\Delta\gamma|$. In the case of CH_3I, from Table 1 we find that $|\gamma_{CH_3^+} - \gamma_{I^-}| = 4.5$ and $|\gamma_{CH_3^-} - \gamma_{I^+}| = 1.0$. Consequently the inference is that the contribution of the ionic structure $CH_3^+I^-$ is more than that of the other ionic structure $CH_3^-I^+$, which is chemically true. Similarly in the CH_3–H bond the structure $CH_3^+H^-$ is of more significance than $CH_3^-H^+$ (see Table 1). This observation is supported by recent quantum-mechanical calculations of Wiberg and Breneman[17] based on Bader's approach[18] where it has been shown that in CH_4 the H atoms bear some negative charge. In the case of homonuclear diatomic molecules like H_2 and I_2, $|\Delta\gamma|$ is usually equal to 3.0 (see Table 1) which means that even for those molecules which are thought to be perfectly covalent the ionic structures are of some significance. Such a picture indeed emerges from the VB theory of H_2.[19]

Bond Polarity and Pearson's Hard–Soft Acid–Base Principle.—The main triumph of Pearson's hard–soft classification is its ability to generalise acid–base interactions which is known as Pearson's hard–soft, acid–base (HSAB) principle.[1,20] This states that a hard (h) acid prefers a hard base and a soft (s) acid a soft base. Earlier[4] the γ scale was applied to explain the HSAB principle. In terms of the γ parameters it has been observed that an exchange reaction of type (6), for which the HSAB principle

$$\mathrm{AB + CD \rightleftharpoons AC + BD} \qquad (6)$$

was originally devised, proceeds from left to right if $|\Delta\Delta\gamma|_{\text{l.h.s.}} > |\Delta\Delta\gamma|_{\text{r.h.s.}}$. The driving force seems to be the minimisation of $|\Delta\Delta\gamma|$. In view of the relation between λ and $|\Delta\gamma|$, this means that in an exchange reaction acids and bases interact selectively so as to maintain bonds of similar, to the extent possible, polarity among themselves. This is demonstrated in the examples (7)–(12) for which $\Delta H^\circ \leqslant -10$ kcal mol^{-1} in terms of λ. The

$$\mathrm{LiCl + NaF \rightleftharpoons LiF + NaCl} \qquad \Delta H^\circ = -9.5\ \mathrm{kcal\ mol^{-1}}$$
$$\lambda\ 0.73 \quad 0.88 \qquad 0.84 \quad 0.79 \qquad (7)$$

$$\mathrm{LiCl + KF \rightleftharpoons LiF + KCl} \qquad \Delta H^\circ = -10.0\ \mathrm{kcal\ mol^{-1}}$$
$$\lambda\ 0.73 \quad 0.83 \qquad 0.84 \quad 0.80 \qquad (8)$$

$$\mathrm{LiBr + KF \rightleftharpoons LiF + KBr} \qquad \Delta H^\circ = -10.5\ \mathrm{kcal\ mol^{-1}}$$
$$\lambda\ 0.70 \quad 0.83 \qquad 0.84 \quad 0.77 \qquad (9)$$

$$\mathrm{LiF + HI \rightleftharpoons LiI + HF} \qquad \Delta H^\circ = -10.6\ \mathrm{kcal\ mol^{-1}}$$
$$\lambda\ 0.84 \quad 0.05 \qquad 0.65 \quad 0.41 \qquad (10)$$

$$\mathrm{NaF + HCl \rightleftharpoons NaCl + HF} \qquad \Delta H^\circ = -16.2\ \mathrm{kcal\ mol^{-1}}$$
$$\lambda\ 0.88 \quad 0.18 \qquad 0.79 \quad 0.41 \qquad (11)$$

$$\mathrm{CsF + HCl \rightleftharpoons CsCl + HF} \qquad \Delta H^\circ = -16.7\ \mathrm{kcal\ mol^{-1}}$$
$$\lambda\ 0.70 \quad 0.18 \qquad 0.75 \quad 0.41 \qquad (12)$$

point to note is that in all these instances $|\Delta\lambda|_{\text{l.h.s.}} > |\Delta\lambda|_{\text{r.h.s.}}$, *i.e* the exchange always leads to lowering of $|\Delta\lambda|$ as expected from the principle of minimisation of $|\Delta\Delta\gamma|$ stated earlier.

Previously Williams and Hale[21] examined hard–hard and soft–soft interactions in terms of ionic and covalent interactions. Pearson also felt[6,20] that hard–hard interactions lead to ionic bonding and soft–soft ones to covalent one. The present work shows that the ionic character of the bonding between a cationic acid and an anionic base increases as the difference between their γ parameters increases.

Conclusion

A correspondence between Klopman's frontier-orbital energy $E^\ddagger$ and the previously[4] devised γ parameter for an ion has been established. Klopman[8] proposed that his $E^\ddagger$ values indicate the hardness of ionic donors or acceptors. Thus it can be stated that the γ parameter also represent the hardness of an ion. It has also been shown that the γ parameters can be used to describe the ionic/covalent character of a bond in heteronuclear diatomic molecules. For polyatomic molecules it is very difficult to construct an experimental index for the character of a bond. Nevertheless γ parameters can still help. Through several examples it has been demonstrated that an exchange reaction of type (6) always leads to products with similar bond characters. In conclusion, the present results add a new dimension to Pearson's HSAB principle.

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