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Absolute Hardness: Companion Parameter to Absolute Electronegativity

Robert G. Parr*† **and Ralph G. Pearson**‡

Contribution from the Institute for Theoretical Physics and the Department of Chemistry, University of California, Santa Barbara, California 93106, and the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received May 4, 1983*

Abstract: For neutral and charged species, atomic and molecular, a property called absolute hardness η is defined. Let $E(N)$ be a ground-state electronic energy as a function of the number of electrons N. As is well-known, the derivative of $E(N)$ with respect to N, keeping nuclear charges Z fixed, is the chemical potential μ or the negative of the absolute electronegativity χ: $\mu = (\partial E/\partial N)_Z = -\chi$. The corresponding second derivative is hardness: $2\eta = (\partial\mu/\partial N)_Z = -(\partial\chi/\partial N)_Z = (\partial^2 E/\partial N^2)_Z$. Operational definitions of χ and η are provided by the finite difference formulas (the first due to Mulliken) $\chi = {}^1/_2(I + A)$, $\eta = {}^1/_2(I - A)$, where I and A are the ionization potential and electron affinity of the species in question. Softness is the opposite of hardness: a low value of η means high softness. The principle of hard and soft acids and bases is derived theoretically by making use of the hypothesis that extra stability attends bonding of A to B when the ionization potentials of A and B in the molecule (after charge transfer) are the same. For bases B, hardness is identified as the hardness of the species B^+. Tables of absolute hardness are given for a number of free atoms, Lewis acids, and Lewis bases, and the values are found to agree well with chemical facts.

I. Introduction

The intrinsic properties of distinct isolated chemical species (atoms, ions, molecules) are significant input for the determination of the properties of combined systems (molecules, molecular ions), though they are in no simple sense completely sufficient.

One atomic parameter has long been known to be of great use in chemistry, the average of the ionization potential and electron affinity: the electronegativity of Pauling and Mulliken. More generally, for a species S, with ionization potential I_S and electron affinity A_S, the quantity

$$\chi_S = \tfrac{1}{2}(I_S + A_S) = -\mu_S \qquad (1)$$

measures the escaping tendency of electrons from S. Here χ is the *absolute electronegativity*.[1] Its negative, μ, is the *chemical potential* of the electrons; it has much the same significance as the chemical potential in the classical thermodynamics of macroscopic systems.[2]

The original rationalization of eq 1 by Mulliken is as follows.[1] Let X and Y be two systems of interest. The condition that they have equal electronegativities is that the energy changes for the two disproportionation reactions,

$$X + Y \rightarrow X^+ + Y^- \qquad (2a)$$

and

$$X + Y \rightarrow X^- + Y^+ \qquad (2b)$$

be equal. The first is $I_X - A_Y$, the second is $I_Y - A_X$; they are equal if $I_X + A_X = I_Y + A_Y$.

Another interpretation of the meaning of χ has been developed at length in the literature[3] and is important for establishing the equivalence of $-\chi$ and μ. If the total electronic energy of an atom or molecule, S, is plotted as a function of N, the total number of electrons, a result similar to that shown in Figure 1 will be obtained. The first ionization potential for the species will be much larger than the electron affinity and much smaller than the second ionization potential.

The first electron affinity of neutral S will be small and positive, or zero. A zero value means that the electron will not add, but will be more stable at infinity. Except for very rare cases, the second electron affinity will be zero. The curve then flattens out at a constant value of the energy, independent of further increase in N. For third and fourth ionization potentials, the curve rises very sharply (as N decreases). From a chemical point of view, values of N such that $Z - N$ is more than +3 rarely need to be considered. (Here Z is the total number of nuclear charges in the atom or molecule.)

Experimentally we only know points on the curve in Figure 1 for integral values of N. However, it is convenient to consider that a smooth curve connects the various points. In a molecule it is natural to think of the individual atoms having electron populations which are not necessarily integral. Assuming a differentiable curve, the electronegativity may be defined as[2]

$$\chi_S = -(\partial E/\partial N)_Z \qquad (3)$$

Since the slope, $(\partial E/\partial N)_Z$, is equal rigorously to the chemical potential μ of the density functional theory,[2] we have recovered part of eq 1. The remainder results from taking the finite difference approximation to the negative slope of the E vs. N curve.

Equation 1 may be considered as operationally defining absolute electronegativity, independent of the form of the function $E(N)$. It is also valid even for cases where such a smooth function does not exist.[4]

II. Absolute Hardness

Given the demonstrated importance of the first derivative of the $E(N)$ curve, or the finite difference approximation to it, what property of the curve should be next in importance? Clearly, it is the second derivative, or the finite difference approximation to it! We define this as *absolute hardness*, the quantity

$$\eta_S = \tfrac{1}{2}(\partial^2 E/\partial N^2)_Z \qquad (4)$$

The corresponding operational definition is the corresponding finite difference formula

$$\eta_S = \tfrac{1}{2}(I_S - A_S) \qquad (5)$$

We note from eq 3 and 4 that hardness is related to electronegativity or chemical potential through the identity

$$2\eta_S = (\partial\mu_S/\partial N)_Z = -(\partial\chi_S/\partial N)_Z \qquad (6)$$

The nonchemical meaning of the word "hardness" is resistance to deformation or change. Equation 6 shows that chemical hardness is resistance of the chemical potential to change in the number of electrons.

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* Address correspondence to this author at the University of North Carolina.

† Institute for Theoretical Physics and University of North Carolina.

‡ Department of Chemistry, University of California.

(1) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782–93 (1934).

(2) R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, *J. Chem. Phys.*, **68**, 3801–7 (1978).

(3) For example, H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc. London, Ser. A*, **235**, 136–43 (1956); R. P. Iczkowski and J. L. Margrave, *J. Am. Chem. Soc.*, **83**, 3547–51 (1961).

(4) J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., *Phys. Rev. Lett.*, **49**, 1691–94 (1982).

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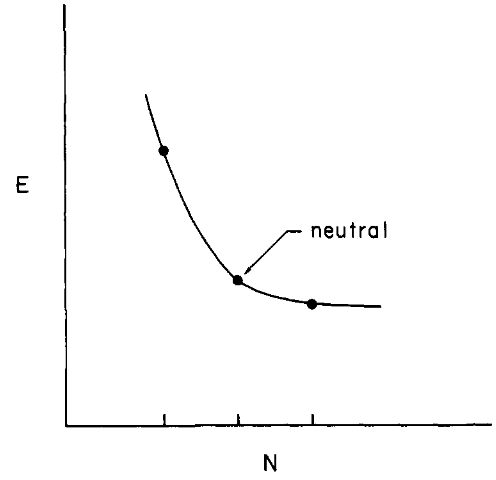

Figure 1.

Hardness is identically one-half of the energy change for the disproportionation reaction

$$S + S \rightarrow S^+ + S^- \tag{7}$$

Since always[5]

$$I_S \geq A_S \tag{8}$$

the minimum value of hardness is zero. Zero hardness constitutes maximum softness. Maximum softness means (as it should) no energy change associated with the disproportionation reaction of eq 7. A bulk metal has $I = A$, $\eta = 0$, and maximum softness.

III. Hard and Soft Acids and Bases

The concept of chemical hardness and softness was introduced[6] in connection with the behavior of Lewis acids and bases:

$$A + {:}B \rightarrow A{:}B \tag{9}$$

Depending on the stability of the complex, A:B, formed with certain reference bases, Lewis acids were divided into two categories. Similarly Lewis bases were divided into two categories, depending on the characteristics of the donor atom. These two categories of base were called hard and soft, respectively, with the following characteristics: *soft base*, the donor atom is of high polarizability and low electronegativity and is easily oxidized and associated with empty, low-lying orbitals; *hard base*, the donor atom is of low polarizability and high electronegativity, is hard to oxidize, and is associated with empty orbitals of high energy and is hence inaccessible. The two categories of acid were also called hard and soft, with the following properties: *soft acids*, the acceptor atom is of low positive charge and large size and has several easily excited outer electrons; *hard acids*, the acceptor atom is of high positive charge and small size and does not have easily excited outer electrons. This classification was an operational one, designed to accord with the following rule: hard acids prefer to coordinate to hard bases and soft acids to soft bases. This is the principle of hard and soft acids and bases, which has found wide utility.[7]

A major defect of the HSAB principle is that it has been difficult to quantify. Also acids and bases were simply put into a few categories without any attempt to rank-order them. While many scales of hardness and softness have been proposed, none of them seems to have wide applicability.[7,8]

A wealth of experimental data is available for reaction 9 in terms of bond energies, equilibrium constants, and rate constants. These data cannot be explained by any one intrinsic property of the reactants, even if extrinsic factors such as solvation are excluded. At least one more intrinsic factor (and probably several) must be of importance.

One such factor is easily recognized. For want of a better name this has been called the intrinsic "strength". The meaning of this term is simply that we expect OH^- always to be a stronger base than H_2O, even though both are hard bases. Similarly Mg^{2+} will be a stronger Lewis acid than Na^+, though both are hard. Classical electrostatic factors of charge, size, and charge distribution may be used to estimate intrinsic strength. Because of the great difference in strength, it has been difficult to say whether H_2O is harder than OH^-, or even is there are any significant chemical effects due to such a difference.

We believe that the concept of absolute hardness as defined in the present paper, eq 4 or eq 5, is essentially equivalent to the hardness concept as developed for chemical reactions. We proceed now to show this, first by deducing the HSAB principle from our definition of hardness and then by presenting and examining hardness values.

IV. Theoretical Deduction of the HSAB Principle

Following is a proof of the HSAB principle from a simple model, utilizing the concept of absolute hardness.

Formation of A:B from A and B: may be regarded as comprising two components: shift of some charge from B to A and formation of the actual chemical bond. We focus initially on the first effect.

We suppose that we may write for A in the molecule

$$E_A = E_{A^0} + \mu_{A^0}(N_A - N_{A^0}) + \eta_A(N_A - N_{A^0})^2 \tag{10a}$$

where superscript zero refers to the original reactants, and similarly

$$E_B = E_{B^0} + \mu_{B^0}(N_B - N_{B^0}) + \eta_B(N_B - N_{B^0})^2 \tag{10b}$$

The electron numbers $N_A = N_{A^0} + \Delta N$ and $N_B = N_{B^0} - \Delta N$ are to be determined (as has already been discussed and illustrated)[9] so that the chemical potentials of A and B are equal in the molecule. Thus ΔN is such that $\mu_A = \mu_{A^0} + 2\eta_A\Delta N = \mu_B = \mu_{B^0} - 2\eta_B\Delta N = \mu_{AB'}$ or

$$\Delta N = (\mu_{B^0} - \mu_{A^0})/2(\eta_A + \eta_B) = (\chi_{A^0} - \chi_{B^0})/2(\eta_A + \eta_B) \tag{11}$$

With this ΔN, call it ΔN^*, values of E_A and E_B are defined from eq 10.

We can next calculate the energy change due to charge transfer

$$\Delta E = (E_A - E_{A^0}) + (E_B - E_{B^0}) = -\tfrac{1}{2}(\mu_{B^0} - \mu_{A^0})\Delta N = -\tfrac{1}{4}(\chi_{A^0} - \chi_{B^0})^2/(\eta_A + \eta_B) \tag{12}$$

As expected, an energy lowering results from electron transfer. Furthermore, we see that differences in electronegativity drive the electron transfer, and the sum of the absolute hardness parameters inhibits electron transfer.

If both acid and base are soft, $\eta_A + \eta_B$ is a small number, and for a reasonable difference in electronegativities, ΔE is substantial and stabilizing. This explains the HSAB principle, in part: soft prefers soft. But if both acid and base are hard, there is little electron transfer and energy stabilization from electron transfer, for a given difference in electronegativities. This result seems paradoxical.

To resolve the paradox we must consider the second effect, the formation of the chemical bond. After electron transfer the chemical potentials of A and B have been equalized

$$I_{A^*} + A_{A^*} = I_{B^*} + A_{B^*} \tag{13}$$

and we also find

$$I_{B^*} - I_{A^*} = \eta_B - \eta_A \tag{14}$$

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[5] R. F. Nalewajski and J. F. Capitani, *J. Chem. Phys.*, **77**, 2514–26 (1982).

[6] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533–3539 (1963); *Science*, **151**, 172–77 (1966).

[7] R. G. Pearson, "Hard and Soft Acids and Bases", Dowden, Hutchinson and Ross, Stroudenburg, Pa., 1973; T. L. Ho, "Hard and Soft Acids and Bases in Organic Chemistry", Academic Press, New York, 1977; W. B. Jensen, "The Lewis Acid–Base Concept", Wiley-Interscience, New York, 1980, Chapter 8.

[8] R. G. Pearson and R. J. Mawby, in "Halogen Chemistry", V. Gutmann, Ed., Vol. III, Academic Press, New York, 1967, Chapter II.

[9] (a) H. K. Ray, L. Samuels, and R. G. Parr, *J. Chem. Phys.*, **70**, 3680–84 (1979); (b) R. G. Parr and L. J. Bartolotti, *J. Am. Chem. Soc.*, **104**, 3801–3 (1982).

Table I. Experimental Hardness Parameters η for Atoms (eV)

atom	I^a	A^b	χ^c	η^d
H	13.59	0.75	7.17	6.42
Li	5.39	0.62	3.00	2.38
B	8.30	0.28	4.29	4.01
C	11.26	1.27	6.27	5.00
N	14.53	0.0	7.27	7.27
O	13.61	1.46	7.53	6.08
F	17.42	3.40	10.41	7.01
Na	5.14	0.55	2.85	2.30
Al	5.98	0.44	3.21	2.77
Si	8.15	1.38	4.76	3.38
P	10.48	0.75	5.62	4.86
S	10.36	2.08	6.22	4.12
Cl	13.01	3.62	7.31	4.70
K	4.34	0.50	2.41	1.92
V	6.74	0.53	3.64	3.11
Cr	6.76	0.67	3.76	3.05
Fe	7.90	0.16	4.03	3.87
Co	7.86	0.66	4.26	3.60
Ni	7.63	1.16	4.44	3.24
Cu	7.72	1.23	4.48	3.25
Se	9.75	2.02	5.89	3.86
Br	11.84	3.36	7.60	4.24
Rb	4.18	0.49	2.34	1.85
Zr	6.84	0.43	3.63	3.21
Nb	6.88	0.89	3.88	2.99
Mo	7.10	0.75	3.92	3.17
Rh	7.46	1.14	4.30	3.16
Pd	8.33	0.56	4.44	3.88
Ag	7.57	1.30	4.44	3.14
Sn	7.34	1.25	4.30	3.05
Sb	8.64	1.05	4.84	3.79
Te	9.01	1.97	5.49	3.52
I	10.45	3.06	6.76	3.70
Ba	5.21	0.0^e	2.6	2.6
Pt	9.01	2.1	5.6	3.5
Au	9.22	2.3	5.8	3.5

[a] All values from C. E. Moore, "Atomic Energy Levels", Natl. Bur. Stand. (U.S.) Circ. No. 467, Vol. I, 1949; Vol. II, 1952; Vol. III, 1958. [b] Sources given in ref 9b, except as indicated. [c] $\chi = \frac{1}{2}(I + A)$, as in eq 1 of text. [d] $\eta = \frac{1}{2}(I - A)$, as in eq 5 of text. [e] H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, 4, 539 (1975).

Table II. Hardness Parameters for Some Bases (eV)[a]

base	I_{B^+}	A_{B^+}	$\eta_B{}^b$
F^-	17.42	3.40	7.0
Cl^-	13.01	3.62	4.7
Br^-	11.84	3.36	4.2
I^-	10.45	3.06	3.7
H^-	13.59	0.75	6.8
CH_3^-	9.82	1.8	4.0
N_3^-	11.6	1.8	4.9
NH_2^-	11.3	0.74	5.3
OH^-	13.0	1.83	5.6
NO_2^-	12.9	3.99	4.5
CN^-	14.2	3.6	5.3
SH^-	10.4	2.3	4.1
ClO^-	11.1	2.2	4.5
CO	26	14.0	6.0
H_2O	26.6^c	12.6	7.0
H_2S	21^c	10.5	5.3
NH_3	24^d	10.2	6.9
PH_3	20^d	10.0	5.0

[a] All data from H. M. Rosenstock et al., *J. Phys. Chem. Ref. Data*, 6, Suppl. No. 1 (1977), except as noted. [b] $\eta_B = \frac{1}{2}(I_{B^+} - A_{B^+})$, as in eq 15 of text. [c] J. H. Beynon et al., *Org. Mass Spectrom.*, 16, 454 (1981). [d] Estimated from photoelectron spectra of PH_3 and NH_3. D. W. Turner et al., "Molecular Photoelectron Spectroscopy", John Wiley and Sons, New York, 1970, p 360.

Table III. Hardness Parameters, η_A, for Some Lewis Acids (eV)[a]

acid	I_A	A_A	χ_A	$\eta_A{}^b$
H^+	∞	13.59	∞	∞
Li^+	75.6	5.39	40.5	35.1
Na^+	47.3	5.14	26.2	21.1
Rb^+	27.5	4.18	15.8	11.7
Cu^+	20.3	7.72	14.0	6.3
Ag^+	21.5	7.57	14.6	6.9
Au^+	20.5	9.22	14.9	5.7
Tl^+	20.4	6.11	13.3	7.2
Mg^{2+}	80.1	15.03	47.6	32.5
Ca^{2+}	51.2	11.87	31.6	19.7
Ti^{2+}	27.5	13.57	20.6	7.0
Mn^{2+}	33.7	15.14	24.4	9.3
Fe^{2+}	30.6	16.18	23.4	7.3
Ni^{2+}	35.2	18.15	26.7	8.5
Cu^{2+}	36.8	20.29	28.6	8.3
Zn^{2+}	39.7	17.96	28.8	10.8
Cd^{2+}	37.5	16.90	27.2	10.3
Hg^{2+}	34.2	18.75	26.5	7.7
Pb^{2+}	31.9	15.03	23.5	8.5
Ba^{2+}	35.5	10.00	22.8	12.8
Pd^{2+}	32.9	19.42	26.2	6.8
Al^{3+}	120.0	28.4	74.2	45.8
Al^{3+}	120.0	28.4	74.2	45.8
Sc^{3+}	73.9	24.8	49.3	24.6
Fe^{3+}	56.8	30.6	43.7	13.1
La^{3+}	50.0	19.2	34.6	15.4
Tl^{3+}	50.7	29.8	40.3	10.5
I^+	19.1	10.5	14.8	4.3
Br^+	21.6	11.8	16.7	4.9
I_2	9.3	2.6	6.0	3.4
Cl_2	11.4	2.4	6.9	4.5
CO_2	13.8	0.0	6.9	6.9
SO_2	12.3	1.1	6.7	5.6
$AlCl_3$	12.8	~1	6.9	5.9

[a] Data are from C. E. Moore, as in Table I, and from H. M. Rosenstock, et al., as in Table II. [b] $\eta_A = \frac{1}{2}(I_A - A_A)$, as in eq 16 of text.

Thus, if both η_A and η_B are small, and/or if they are equal, the ionization potentials in A and B have been equalized in the molecule AB.

In orbital language this means that the one-electron energies of atomic orbitals on A and B have been made equal, or nearly so. In both MO theory and VB theory, equal orbital energies favor strong covalent bonding, if orbital sizes are not too disparate.

In soft acid–soft base combinations, the two electrons of the bond have comparable probabilities of being on A or B. This, together with the favorable effect of eq 14, shows that covalent bonding is dominant in soft–soft combinations and that good bonding will result.

For hard acid–hard base combinations eq 13 is still valid, and if both η_A and η_B are large, they might cancel each other. But this does not necessarily produce strong covalent bonding. Since there is little electron transfer from B to A, the bonding electrons must, on the average, remain on B. Ionic bonding, however, will usually be favorable. The characteristics of a hard acid, high positive charge and small size, favor electrostatic interaction with B, which retains most of its negative charge, and which presents a favorable dipole interaction with a lone pair of electrons pointing at A.

For a hard–soft combination, on the other hand, stability is enhanced neither by charge transfer (eq 12) nor by the condition favoring covalent bonding, $I_{B^*} - I_{A^*}$ small (eq 14).

This completes our theoretical derivation of the HSAB principle. The conclusion that soft–soft interactions are largely covalent, and that hard–hard interactions are largely ionic, is not novel. This has been realized from the beginning and discussed in various ways by several authors. (Klopman, in particular, has given a lucid description of the bonding in these terms.[10])

V. Tables of Absolute Hardness

By taking appropriate experimental values for ionization potentials and electron affinities from the literature, values of absolute

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(10) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223–234 (1968).

hardness have been calculated for a number of simple chemical species. These are displayed in Tables I–III. Some values of the absolute electronegativity also are included.

Table I gives data for a number of atoms of the elements. The formulas used are eq 1 for electronegativity and eq 5 for hardness, where I and A are for the neutral species. An atom, in principle, can act as a Lewis acid or a Lewis base. Actually the chemistry of single atoms is rarely discussed in terms of acid–base interactions. Their behavior is much more closely related to free radical chemistry. Atoms of the nonmetallic elements do show some Lewis acid character. Atoms of the metals sometimes behave as Lewis acids, and sometimes as bases. Table I is still useful in showing how χ and η can vary from element to element, all in a common reference state.

Table II gives data for a number of typical Lewis bases. A problem arises because many bases are anions. This puts them at the foot of the curve shown in Figure 1. That is, they are in a region where both the slope and curvature are close to zero. For fluoride ion, for example, use of eq 5 would give $\eta = {}^1/_2(3.40 + 0) = 1.7$, a number that is not very informative. The special character of F^-, in fact, is contained in the value of 17.42 eV for the ionization potential of the fluorine atom (Table I). The question becomes one of where the curvature in Figure 1 should be selected. If eq 10 were really valid over a wide range, η would be constant. But it clearly is not, as has been discussed elsewhere.[9b] Since a base donates electrons, the curvature becomes larger as the base performs its chemical function. We have chosen to evaluate η for a base at the point where $\Delta N = 1$, or half-transfer of a pair of electrons. This choice means that for F^-, η is the same as η in Table I, and so on. Our working definition of the hardness of a base B is then

$$\eta_B = \eta(\text{species } B^+) = {}^1\!/\!_2(I_{B^+} - A_{B^+}) \qquad (15)$$

Table III contains data for a group of Lewis acids A, hardness for them being defined by

$$\eta_A = \eta(\text{species A}) = {}^1\!/\!_2(I_A - A_A) \qquad 16)$$

One might argue that to be consistent with the treatment of bases, one should use $\eta_A = \eta(\text{species } A^-)$. However, note that in eq 14 the hardness of B refers to a species going (in ionization) from a charge ΔN to a charge $\Delta N + 1$, while the hardness of A refers to a species going from a charge $-\Delta N$ to a charge $-\Delta N + 1$. If ΔN were 0.5, the average charge on B would be +1 (ionizing from $B^{+0.5}$ to $B^{+1.5}$). The average charge on A would be zero (from $A^{-0.5}$ to $A^{+0.5}$). This value of ΔN seems more reasonable than $\Delta N = 1$.

VI. Discussion of the Hardness Values

The values of absolute hardness shown in the tables are highly satisfactory when compared with the known chemical behavior of the selected systems. The chief exception is hydrogen, which is out of line in all three tables, and must be considered as a special case. Excluding H^-, the bases in Table II are put in a very reasonable order. The hard bases, F^- and OH^-, have large values of η_B, and the soft bases, SH^- and CH_3^-, have small values. Even the neutral bases seem to be in about the right places vis ã vis the anionic ones. It will be of interest to add more bases to the list, as more data on electron affinities and ionization potentials become available.

The Lewis acids in Table III are also well ordered. The hard acids, such as Na^+, Mg^{2+}, and Al^{3+}, have large η_A values, and the soft acids, such as Br^+, Ag^+, and Pd^{2+}, have small values. The metal ions which are considered as borderline, such as Mn^{2+} to Zn^{2+}, have intermediate values. The expected increased softness in going down a column in the periodic table, e.g., Mg^{2+} to Ba^{2+}, or Ni^{2+} to Pd^{2+}, shows up well. Unfortunately Pt^{2+} cannot be included since the third IP is not known. The expected increased hardness with increased oxidation state can be seen by comparing Fe^0 (in Table I) with Fe^{2+} and Fe^{3+}.

There are some discrepancies. For example, Tl^+ has $\eta_A = 7.2$ and Tl^{3+} has $\eta_A = 10.5$, even though the latter is chemically softer. Still a comparison of Tl^{3+} with the other trivalent ions of Table III shows the expected soft character.

A number of neutral Lewis acids are also listed in Table III. These all have small η_A values, and a comparison with the ionic acids must be made with caution. With the possible exception of $AlCl_3$, the neutrals seem to fall into the right order, CO_2 being a harder acid than SO_2, and so on.

The neutral atoms of Table I also have small value of η, in general. This agrees with their limited acid–base behavior. The non-metallic atoms behave as soft Lewis acids.[6] The metallic atoms, as noted for Fe(0), are soft Lewis acids. It should be noted that when transition-metal atoms act as Lewis acids, it is usually in an excited, or valence, state. Iron atoms are $(3d)^8$ and not $(3d)^6(4s)^2$ when acting as acids. Correcting for this effect will lower the η values in Table I.

$AlCl_3$ is included in Table III, even though the electron affinity is not known, to illustrate an important and complicating feature. Comparing with Al^{3+}, we see that the effect of adding three chloride ions is to lower the hardness considerably. This is a very reasonable result. We would expect any Lewis base to lower the η_A value of an ionic acid. Soft bases would be particularly effective, because of electron transfer. In fact, AlH_3, like BH_3, would be a soft Lewis acid.

The complication occurs because we rarely deal with the chemistry of isolated ions. The coordination chemistry of Al^{3+} in aqueous solution does not involve the bare ion, but species such as $Al(H_2O)_n^{3+}$. The ionization potentials of such moieties are not known at present, and η_A cannot be calculated. But we can be sure that it will be less than the value of 45.8 given for Al^{3+} in the table.

We conclude that the very large value given for Al^{3+} in the table must be considered as a hypothetical upper limit, in discussing the real chemistry of aluminum ion. The same remark applies to the other cations of Table III. For bases the situation is simpler, since normally a base coordinates only to a single Lewis acid. Examples of bases bridging two metal ions are known, however. We would expect such bases to be hardened.

VII. Conclusion

Many complications are present in particular chemical circumstances. Nevertheless, it seems useful to tabulate the simple state-independent, environment-independent hardness parameters, as we have done. And many more factors would have to be considered before one could hope to compute bond energies or equilibrium constants.

As has recently been discussed in some detail,[4,11] the definition of continuous $E(N)$ curves is a matter of some difficulty, although each particular physical situation in fact defines such a curve [statistical mechanics sometimes needs to be invoked]. Indeed, the derivatives $\mu = (\partial E/\partial N)_Z$ and $\eta = {}^1/_2(\partial^2 E/\partial N^2)_Z$ may differ from situation to situation for a particular species. This mandates regarding the formulas $\mu = {}^1/_2(I + A)$ and $\eta = {}^1/_2(I - A)$ as defining the "absolute" μ and η; these formulas define μ and η for a species independent of any assumptions about $E(N)$.

One could extend the HSAB postulate to the more detailed one implied by eq 14: An acid A with hardness η_A prefers to bind to a base B with precisely the same hardness, $\eta_B = \eta_A$. This would be purely speculation at present, however. The difficulties discussed at the end of section V would have to be surmounted before this extended hypothesis could be tested. Note in this connection that a perfect theory of this effect would require that the numerical values of hardnesses for acids should span the same range as do the values of hardnesses for bases, a condition which the values in Table II and III do not satisfy. This underlines the tentativeness of eq 15 and 16.

The quantities $I - A$ defining η are not new in the theory of electronic structure; indeed, they are quite old. For a radical, naively, $(I - A) = (ss/ss)$, where (ss/ss) is a self-repulsion integral; this is just the Pariser formula for self repulsion[12] which is so

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(11) R. G. Parr and L. J. Bartolotti, *J. Phys. Chem.*, in press.

(12) R. Pariser, *J. Chem. Phys.*, **21**, 568–69 (1953).

important in the Pariser–Parr[13] and subsequent derivative semiempirical theories of electronic structure of molecules.[14] It also is the basic parameter in the Hubbard model of solids;[15] for an insulator it is just the band gap. Our whole discussion has been, however, completely independent of a particular theory of electronic structure.

The hardness of a chemical species, then, is half the derivative of its chemical potential with respect to the number of electrons: $2\eta = (\partial\mu/\partial N)_Z$. There seem to be no other acceptable definitions.[16]

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[13] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466–471; 767–76 (1953).

[14] This includes all theories of CNDO, NNDO, and MINDO types.

[15] J. Hubbard, *Proc. R. soc. London, Ser. A*, **276**, 238–57 (1963).

[16] The factor of 2 is arbitrary, to create a symmetry between $(I + A)/2$ and $(I - A)/2$.

EPR Study of the Electronic Structure and Dynamic Jahn–Teller Effect in Nickelocenium Cation

M. V. Rajasekharan,[1a] R. Bucher,[1b] E. Deiss,[1c] L. Zoller,[1d] A. K. Salzer,[1d] E. Moser,[1d] J. Weber,[1e] and J. H. Ammeter*[1d]

Contribution from the Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland, the Swiss Federal Institute of Technology, 8092 Zürich, Switzerland, and the Section de Chimie, Université de Genève, 1211 Genève 4, Switzerland. *Received June 9, 1983*

Abstract: The nickelocenium cation doped with the magnetic isotope ^{61}Ni has been diluted into several diamagnetic host lattices and studied by EPR spectroscopy at low temperatures in polycrystalline samples. From the analysis of the ^{61}Ni hyperfine tensor, supplemented by EHMO and MS-Xα calculations, a quantitative comparison of the covalency and the dynamic Jahn–Teller effects with the related d^7 system cobaltocene has been possible. From line-width studies as a function of temperature we conclude that the line shape at low temperatures (4 K) is mainly due to inhomogeneous broadening effects; the spin–lattice relaxation increasing rapidly at higher temperatures cannot be explained solely by an Orbach mechanism via a closeby upper Kramers doublet in a satisfactory way.

EPR studies of low-spin d^5 and d^7 sandwich compounds give information on the nature of the degenerate or almost degenerate electronic ground state, i.e., on the covalency of the metal–ligand bonds (via spin-density distributions from magnetic hyperfine coupling constants) and on dynamic Jahn–Teller effects (via so called Ham-type reduction factors multiplying orbital angular momentum contributions to the *g* values).[2] So far the following metallocenes, bisbenzene complexes, and mixed sandwich complexes with varying degrees of substitution of the C_nH_n aromatic rings with either d^5 δ^3 ($^2\Delta$) or d^7 π^1 ($^2\Pi$) type ground states[2] have been studied by EPR:[3] Fe(Cp)$_2^+$,[4] Mn(Cp)$_2$,[5] Ru(Cp)$_2^+$[6] (d^5), Co(Cp)$_2$,[7] Ni(Cp)$_2^+$,[8] Fe(Cp)(Bz),[9] Co(Cp)(Bz)$^+$,[10] Fe(Bz)$_2^+$,[9] and Co(Bz)$_2^{2+}$[10] (d^7, Cp = cyclopentadienyl, Bz = benzene). In all cases a pronounced dependence of the EPR parameters (*g* tensor, metal hyperfine tensor) upon the crystalline host lattice or glassy solvent has been observed. Most of the variation could be attributed to changes in the relative weights of the two close lying pseudodegenerate electronic states caused by changes in the low-symmetry components of the solvent fields, but also—to a lesser degree—to variations in the amplitudes of dynamic Jahn–Teller distortions.[11] In this paper we discuss the EPR spectra of the nickelocenium cation.

The nickelocenium cation is isoelectronic with cobaltocene. Magnetic susceptibility measurements yielded similar moments for cobaltocene and nickelocenium salts.[12] EPR measurements[8] further confirmed a d^7 electronic configuration for nickel in this ion. The resulting $^2E_{1g}$ ground state (using D_{5d} notation) or $^2\Pi$ ground state (using $C_{\infty v}$ notation) is Jahn–Teller active. The emphasis in the earlier EPR work[8] was on evaluating the vibronic coupling parameters from an analysis of the *g* tensor data alone. Absence of any nuclear hyperfine coupling data made necessary

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[1] (a) University of Zürich. Present address: Central University Hyderabad, School of Chemistry, Hyderabad-500134, India. (b) Swiss Federal Institute of Technology. Present address: Dr. W. Ingold AG, 8902 Urdorf. (c) University of Zürich. Present address: EIR, 5303 Würenlingen, Switzerland. (d) University of Zürich, Institute of Inorganic Chemistry. (e) Université de Genève, Section de Chimie, 1211 Genève, Switzerland.

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