Reactivity, Equilibrium and Electronegativity

G. Van Hooydonk

Centrale Bibliotheek, Rijksuniversiteit te Gent, Belgium

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The enthalpy ΔH of general displacement reactions

$$AB + CD \rightarrow AD + CB$$

is derived with the aid of the ionic approximation to chemical bonding. This enthalpy compares favourably well with Pauling's corresponding equation $\Delta H = -46\ (\chi_B - \chi_D)(\chi_A - \chi_C)$. These expressions are used as a basis to discuss various aspects of chemical reactivity: reversals in reactivity, ambident reactivity, the Hammett relation, the McDaniel-Yingst equation, the Drago E–C equation, the resolution of acid strength, the proton affinities of negative and neutral species and the hard and soft acid-base (HSAB) rule. Qualitatively, and in some cases even quantitatively, reasonable results are obtained, demonstrating the great flexibility of an electronegativity-based theory of chemical reactivity.

1. Introduction

During the last decade a significant progress has been made towards an understanding of chemical reactivity on a very sophisticated basis, both qualitatively (the Woodward-Hoffmann rules [1]) and quantitatively (Klopman's GP approach [2] with special emphasis on the HSAB principle [3]). Nevertheless, much remainis to be done, especially in the field of solvent interactions. Well-known examples of empirical approaches to reactivity are the linear free energy relationships in various forms [4] which seem to bring some order into the vast amount of experimental data about chemical reactivity.

The present study is devoted to an ionic approximation to chemical reactivity and equilibrium: in fact, and surprisingly enough, ionic reaction mechanisms are most widely used in organic chemistry. We also tried to introduce an explanation for reactions where the simple Pauling bond energy equation [5] does not apply. Since this equation can for instance not be used to account for solvent effects, we have applied our recently introduced scheme for incorporating such effects completely consistent with the scheme proposed earlier for atom-atom, ion-molecule, ion-ion and donor-acceptor interactions [6]. Indeed, Pauling's bond energy equation

$$D_{AB} = (1/2)\,(D_{AA} + D_{BB}) + 23\,(\chi_B - \chi_A)^2 \quad (1)$$

does not apply to two electron transfer reactions such as

$$H^+ + H_2O \rightarrow \rightarrow H^+ \cdot H_2O\,, \quad (2\,a)$$

$$BF_3 + Et_2O \rightarrow BF_3 \cdot Et_2O \quad (2\,b)$$

which are key-reactions in any discussion about chemical reactivity. Apart from accounting for an equation such as (1), the ionic bonding approximation yields consistent expressions for the enthalpies of reactions (2).

These relations will allow us to account systematically for a number of peculiarities observed on chemical reactions such as ambidency, reversal of the sign of the reaction constant ϱ in the Hammett-relation, reversals of nucleophilic orders etc.

2. Theory

Displacement reactions such as

$$AB + CD \rightarrow AD + CB \quad (3)$$

represent the larger part of the material the experimental chemist is confronted with. Its enthalpy can be calculated if a suited expression for the valence electron energy ε_{AB} is available. According to the ionic approximation to chemical bonding [6], ε_{AB} for a two-centre two-electron bond AB is

$$\varepsilon_{AB} = I\,E_A + I\,E_B + a^2\,EA_A + b^2\,EA_B \quad (4\,a)$$

$$= a^2\,(I\,E_A + EA_A) + b^2\,(I\,E_B + EA_B) + e^2/r_{AB} \quad (4\,b)$$

$$= I\,E_A + I\,E_B + E_{AB} \quad (4\,c)$$

where E_{AB} $(= -D_{AB})$ is the bond energy, $I\,E_X$ and EA_X respectively represent the energy of the valence electron and the electron affinity of element X and r_{AB} is the equilibrium bond length. a^2 and b^2 measure the relative contributions of the ionic structures A^-B^+ and A^+B^- respectively to the ground state of the diatomic molecule AB and obey the

Reprint requests to Dr. G. Van Hooydonk, Centrale Bibliotheek, Rijksuniversiteit te Gent, Rozier 9, *B-9000 Gent/Belgium.*

relationships $a^2+b^2=1$ and $b^2-a^2=I_{AB}$. This latter quantity, the polarity of the AB bond, is given by

$$I_{AB}=(EA_B-EA_A)/(EA_A+EA_B) \qquad (5)$$

which fixes the values of a^2 and b^2.

The enthalpy ΔH_{ABCD} of reaction (3) is then given by

$$\Delta H_{ABCD}=2(EA_B-EA_D)(EA_A-EA_C)K_{ABCD} \qquad (6\,a)$$

wherein

$$K_{ABCD}=\frac{(EA_A+EA_C)EA_B\,EA_D+(EA_B+EA_D)EA_A\,EA_C}{(EA_A+EA_B)(EA_C+EA_D)(EA_A+EA_D)(EA_C+EA_B)}<0\,. \qquad (6\,b)$$

It is directly seen that Eq. (6 a) is completely consistent with Pauling's equation

$$\Delta H_{ABCD}=-46(\chi_B-\chi_D)(\chi_A-\chi_C) \qquad (7)$$

provided we put $K_{ABCD}\approx -1$ and $\chi_X=-EA_X/23$. The basic results of the discussion to follow applies qualitatively as well to the Pauling Eq. (7) as to Equation (6 a).

By making the usual approximation $-RT\ln K=\Delta G_{ABCD}\approx\Delta H_{ABCD}$, Eq. (6) is the starting point for our discussion of chemical equilibrium.

Before proceeding as such, a brief description of how solvent effects will be accounted for has to be given. The crude assumption is made[6] that the larger part of solvent-solvent interactions may be characterized as donor-acceptor bonds between donor and acceptor functions present in the individual solvent molecules S, respectively represented as S_D and S_A.

For the total energy ε_{SS} of such a bond one obtains, in analogy with Equation (4):

$$\varepsilon_{SS}=IE_{S_A}+IE_{S_D}+a^2\,EA_{S_A}+b^2\,EA_{S_D} \qquad (8)$$

and a bond energy

$$E_{S_AS_A}=IE_{S_A}-EA_{S_A}(EA_{S_D}-EA_{S_A})/(EA_{S_A}+EA_{S_D}) \qquad (9)$$

where IE_{S_D} and EA_{S_D} refer to the donor function S_D of the solventmolecule S, and IE_{S_A} and EA_{S_A} to its acceptor function S_A. In particular, these last two quantities are the enthalpies of the reactions

$$S_A+e\rightarrow S_A^-,\qquad S_A^-+e\rightarrow S_A^{--}. \qquad (10\,a,b)$$

Representing a solvation or ionic dissociation process as

$$AB+S_2\rightarrow A^+S_D+B^-S_A \qquad (11)$$

the enthalpy

$$\Delta H_{ABS_2}=2(EA_B-EA_{S_D})(EA_A-EA_{S_A})K_{ABS_2} \qquad (12)$$

is obtained, conform with the general Equation (6).

This simple example illustrates the wide applicability of this attack of solvent effects. Indeed, if AB in reaction (11) is a donor-acceptor bond, a completely similar enthalpy may directly be written down.

3. Results and Discussion

3.1. General Trends in Reactivity of Chemical Species

As a guide for the rather qualitative discussion of reactivity in this section, the simplified Pauling-like Eqs. (6 a) and (7) will be used. The latter equation is well known in the literature since it has been applied for obtaining group-electronegativities[7], and it has been used by Pearson[8] as an argument in favour of the HSAB rule[8] and as a criticism of Pauling's approach. This latter point is of course of importance in the present context.

On the working condition that in Eq. (6 a) $K\approx -1$, ΔH_{ABCD} of reactions (3) may be represented as in Fig. 1, if as reference reagents C and D are kept constant and given an electronegativity of -2 and -3 eV respectively. Using the explicit value of K, as given in Eq. (6 b), would simply cause a systematic distortion in the sense that all straight lines drawn in Fig. 1 should be replaced by slightly curved lines.

A glance at Fig. 1 reveals that there are four regions of interest:

$$\left.\begin{array}{lll} 1. & |A|<|C|;\ |B|<|D| & \text{exothermic}\\ 2. & |A|<|C|;\ |B|>|D| & \text{endothermic}\\ 3. & |A|>|C|;\ |B|<|D| & \text{endothermic}\\ 4. & |A|>|C|;\ |B|>|D| & \text{exothermic} \end{array}\right\}\text{if } |X|=|EA_X|\,.$$

Thus, the reaction

$$CsI+LiF\rightarrow LiI+CsF \qquad (13)$$

with $|A|<|C|$ and $|B|<|D|$ is predicted to be exothermic, although experimentally it is found to be

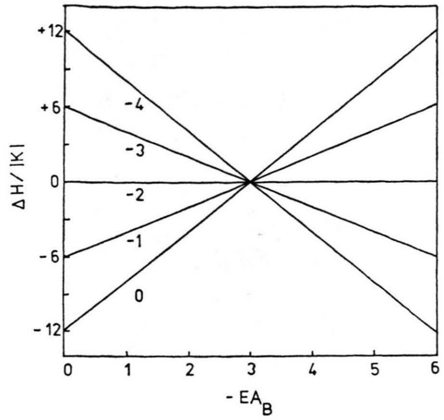

Fig. 1. Plot of $\Delta H/|K|$ versus EA_B for several values of EA_A. Numbers near straight lines are corresponding EA_A values.

endothermic with an enthalpy of about $+10$ kcal/mole! Reactions of this kind might therefore illustrate the HSAB principle[8], since the hard-hard (LiF) and soft-soft (CsI) combinations are preferred and it seems that everything goes wrong with a Pauling-like approach. In fact, Eqs. (6 a) and (7) predict, in accordance with Pauling's view about chemical bonding, that the formation of CsF, the "hard-soft" combination, is always the more exothermic one.

This would be a dramatic situation if it were not so that out of the 12 possible reactions of CsI with other alkalihalogenides only 2 are endothermic (just two involving Li!), the remainder 10 being exothermic in agreement with Eqs. (6 a) and (7)! (See Table 1.)

Table 1. Enthalpies of reaction[a] for $CsI + AB \rightarrow CsB + AI$.

AB	ΔH	AB	ΔH	AB	ΔH	AB	ΔH
LiF	+6.4	NaF	−4.7	KF	−5.2	RbF	−4.0
LiCl	+1.3	NaCl	−1.2	KCl	−1.5	RbCl	−1.0
LiBr	−0.4	NaBr	−2.0	KBr	−1.9	RbBr	−3.0

[a] Enthalpies are given in kcal/mole and are taken from a compilation by B. Fieselmann and R. Ferreira, An. Acad. brasil. Cienc. **44**, 217 [1972].

It may thus be asked whether the HSAB rule for these gas-phase reactions is not the rule for the exceptions rather than the rule. We will return to this problem later on.

These qualitative considerations about Fig. 1 can also be extended to the problem of reversals in reactivity, which are on the basis of what is now known as the HSAB rule. Assume there is a shift Δx in $\Delta G = \Delta H \pm \Delta x$, which may be due to an extra entropy term, a solvent effect not operating through the donor-acceptor mechanism, a rearrangement in one of the reagentia, steric hindrance appearing in one of the species, a specific lone electron pair repulsion effect in a molecule... Figure 2 represents such a situation, where we have assumed $\Delta x < 0$ as an example. Thereby A and D are now kept constant and given an EA_X value of respectively -2 and -3 eV.

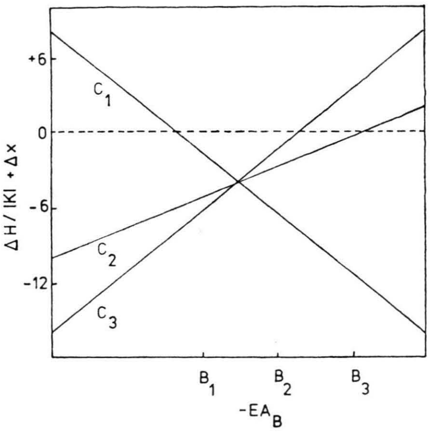

Fig. 2. Plot of $\Delta H/|K| + \Delta x$ versus EA_B for several different EA_C values C_1, C_2 and C_3.

It is directly verified that, if the bases $B_1, B_2, \ldots, B_n$ under these circumstances react in the order $B_1 < B_2 < \ldots < B_n$ (as for instance expected from their electronegativity) towards a given acid C_1, these very same bases will react in completely reversed order, i. e. $B_n < \ldots < B_2 < B_1$ towards another acid C_2. This is a phenomenon well known to inorganic chemists (see introduction to Klopman's paper[2] and also his book[9]) but also to organic chemists, since it is known that, as an example, the nucleophilic order may be reversed upon varying the nature of the acid.

This situation is best illustrated in the following way: assume ΔH proportional with the quantity $\log k/k_0$ and the sequence of B's roughly parallelling Hammetts's substituent constants σ[4a], then Fig. 2 is simply a plot of Hammett relations the slope of the straight lines in the figure being related to the reaction constant ϱ (for a detailed discussion, see following section).

Therefore, one should conclude that the elementary Eqs. (6 a) and (7) are sufficiently flexible to express various experimental data consistently.

Finally, consider the question of ambident reactivity, which can occur when at least one of the reacting molecules is a polyatomic one, containing n active sites (atoms) $C_1, C_2, \ldots, C_n$. Figure 2 also reveals that a particular nucleophile, say B_1, will preferentially react with an active site C_3, whereas another one, B_2, will most probably react with a different site C_1 of the same molecule, in agreement with Equation (6). Numerous cases have indeed found where such situation occurs[9] and it would be of interest to see whether the present theory is quantitatively in agreement with such behaviour or not.

In the following sections, more specific results will therefore be discussed although our major aim was to demonstrate that Eq. (6) is indeed useful as a framework to discuss chemical reactivity in its relation with electronegativity.

3.2. Hammett's Relation [4a]

As pointed out above, Pauling's equation (7) cannot be applied to various reactions of basic interest: as a specific example, we mention the dissociation of an acid HX in a solvent S, being the refence material for the widely used Hammett relation. This example was already worked out in Sect. 2 as an illustration of our approach to solvent effects, therefore Hammett's relation can directly be rewritten in terms of the quantities appearing in Equation (6).

Thus the reaction

$$AB + S_2 \rightarrow A^+S_D + B^-S_A \qquad (14)$$

may be compared with a standard

$$A_0B_0 + S_2 \rightarrow A_0^-S_D + B_0^-S_A \qquad (15)$$

which upon combination leads to competition between

$$AB + A_0^+S_D + B_0^-S_A \rightarrow A_0B_0 + A^+S_D + B^-S_A\,.$$

If $A = A_0 = H$ (dissociation of acids), one obtains

$$HB + B_0^-S_A \rightarrow HB_0 + B^-S_A \qquad (16)$$

for which the enthalpy is

$$\Delta H_{HBB_0^-S_A} = 2\,(EA_B - EA_{B_0})\,(EA_H - EA_{S_A})\,K_{HBB_0^-S_A}\,. \qquad (17)$$

If entropy-differences cancel, Eq. (17) compares well with Hammett's relation for equilibria

$$\log K/K_0\,(\propto \Delta H_0 - \Delta H) = \sigma\,\varrho\,. \qquad (18)$$

Indeed, when the nucleophiles B and B_0 are for instance a substituted benzoic acid and benzoic acid, one recognizes a Hammett substituent constant σ related to $(EA_B - EA_{B_0})$ and a Hammett reaction constant ϱ related to the remainder of the factors in Equation (17).

Moreover, the influence of the medium (the solvent) is represented by EA_{S_A}, the electron accepting power of the solvent molecule, whence ϱ will be a function of EA_{S_A} as found experimentally[4a]. Another factor influencing the value of ϱ as it is found in the literature is the scaling procedure used to construct the Hammett σ-series. In fact, the effect of an X-group in para position to the acid function will be larger for $-COOH$ than for $-CH_2COOH$: for example, the ϱ-values for the ionization of the acids phenol, benzoic acid, phenylacetic acid and -propionic acid are respectively: $+2.008$, 1.000, 0.471 and 0.212[4a].

Once the sequence in σ-values has been fixed by a given reference, one should in principle be able to account for the reactivity constant ϱ both in magnitude and in sign, which is a very difficult question[4a]. Reminding that in practice ϱ-values are mainly determined by the detailed reaction mechanism (the rate-determining step) and that the present formalism applies to equilibria in the first place, we will only tentatively give some applications of our theory to this rather complicated question.

First of all, all ionization processes mentioned above should of course have the same positive ϱ-values and all these were obtained on equilibrium data. Now consider consecutively reactions (19 a, b and c) for which the ϱ-values given in parentheses were derived from rates:

a) the alkaline hydrolysis of ethylbenzoates in acetone[4a] ($\varrho_a = +2.373$)

$$R_aEt + NaOH \rightarrow R_aNa + EtOH; \qquad (19\,a)$$

b) benzylchlorides with iodide ($\varrho_b = +0.783$)

$$R_bCl + NaI \rightarrow R_bI + NaCl; \qquad (19\,b)$$

c) phenolate with ethyliodide ($\varrho_c = -0.991$)

$$R_cNa + EtI \rightarrow R_cEt + NaI\,. \qquad (19\,c)$$

Denoting the unsubstituted products by R_0 we have the following competitive reactions

$$\text{a)}\quad R_aEt + R_{0_a}Na \rightarrow R_{0_a}Et + R_aNa\,, \qquad (20\,a)$$

$$\text{b)}\quad R_bCl + R_{0_b}I \rightarrow R_{0_b}Cl + R_bI\,, \qquad (20\,b)$$

$$\text{c)}\quad R_cNa + R_{0_c}Et \rightarrow R_{0_c}Na + R_cEt\,. \qquad (20\,c)$$

The enthalpies of these reaction are in the same order

$$\Delta H_a = 2\,(EA_{R_a} - EA_{R_{0_a}})\,(EA_{Et} - EA_{Na})\,K_a\,, \qquad (21\,a)$$

$$\Delta H_b = 2\,(EA_{R_b} - EA_{R_{0_b}})\,(EA_{Cl} - EA_{I})\,K_b\,, \qquad (21\,b)$$

$$\Delta H_c = 2\,(EA_{R_c} - EA_{R_{0_c}})\,(EA_{Na} - EA_{Et})\,K_c\,, \qquad (21\,c)$$

and it is easily concluded that the sign of ϱ_c must be opposite to that of ϱ_a and ϱ_b since in fact $|EA_{Et}| > |EA_{Na}|$; $|EA_{Cl}| > |EA_I|$ and $|EA_{Na}| < |EA_{Et}|$.

This might possibly explain various alterations in sign of the reaction constant ϱ, although conclusive evidence can of course not be given on account of the difficulties mentioned above.

A final remark in this section concerns a specific solvent effect, which is usually explained in terms of classical solvation theories. Considering again Eq. (17), it is readily deduced that altering the solvent will alter EA_{SA}. Hence, in general, ionization processes of acids, such as (14), will be less endothermic when the solvent's EA_{SA} value becomes more negative, but the same effect is also produced when the ionization potential of the solvent molecule is reduced. However, for displacement reactions like (16) only the effect of altering EA_{SA} remains. This latter effect is well known to analytical chemists as resulting in the resolution of acid strength upon altering the solvent[10, 11]. This point will be discussed more fully in Section 3.5.

3.3. The McDaniel-Yingst Equation[12]

The equation proposed by McDaniel and Yingst[12] for an acid HL reads

$$1.364\,pK_a - 23.06\,E^0 = D_{HL} - (1/2)(D_{HH} + D_{LL}) = \Delta \qquad (22)$$

wherein Δ is given by the Pauling relation (1) as

$$\Delta = D_{HL} - (1/2)\,(D_{HH} + D_{LL}) = 23\,(\chi_L - \chi_H)^2\,. \qquad (23)$$

In this way chemical reactivity, as determined by pK_a and E^0, the standard oxydation potential, is related to electronegativity χ_X in a very elegant way. Therefore Eq. (22) is of special interest for the present topic, although the equation itself was not originally proposed for a discussion of chemical reactivity in the first place.

Pauling's bond energy Eq. (1) shows many drawbacks, one of these appearing directly from Eq. (22), i. e. the occurence of negative values for the so-called "extra" ionic resonance energy Δ, defined as in (23). Such negative Δ-values were already found earlier for alkalihydrides and have not yet been explained satisfactorily. The McDaniel-Yingst equation however is well founded and the presence of negative Δ-values therein makes Pauling's bond energy equation rather suspicious.

Equation (22) was indeed derived by equating the following enthalpies of reaction (for the complete cycles see Ref. [12]):

$$H^+ \cdot H_2O + L^- \cdot H_2O \xrightarrow{\Delta H_5} HL(H_2O)\,. \qquad (24\,a)$$

$$H^+ \cdot H_2O + L^- \cdot H_2O \xrightarrow{\Delta H_{10}} (1/2)\,H_2(H_2O) + (1/2)\,L_2(H_2O) \qquad (24\,b)$$

$$H(g) + L(g) \xrightarrow{\Delta H_3} HL(g) \qquad (25\,a)$$

$$H(g) + L(g) \xrightarrow{\Delta H_8} (1/2)\,H_2(g) + (1/2)\,L_2(g) \qquad (25\,b)$$

$$\Delta H_5 - \Delta H_{10} = \Delta H_3 - \Delta H_8\,. \qquad (26)$$

From (26), Eq. (22) may be derived directly. The result is that more cases are found with negative Δ, which are not accessible from thermochemical data through Equation (23).

Applying our general bonding equation to the processes (24 a) and (24 b) directly leads to the value

$$\Delta H_5 - \Delta H_{10} = (1/2)\,(EA_L - EA_H)^2 / (EA_H + EA_L) \qquad (27)$$

which was introduced earlier in the electronegativity-equalization theory[13] as the expression for the extra ionic resonance energy, defined as

$$E_{HL} - (1/2)\,(E_{HH} + E_{LL})\,.$$

This latter quantity also equals the right hand side of Eq. (26); thus our treatment consistently reproduces the McDaniel-Yingst equation.

However, in process (24 b) a significant contribution to the enthalpy ΔH_{10} comes – especially in the case of halogens – from the appearance of lone-electron-pair (LEP) repulsions. Consider for instance the F^- ion which on oxidative coupling transforms into F_2. The $E_{FF} = -37$ kcal/mole is much lower than the value expected from the bonding power of fluorine towards elements carrying no LEP's in their valence shell, such as the alkali's [14]. Reminding that the EA_X values in (27) are estimated ones [14], one can introduce LEP repulsion or any other disturbing effect specific to the homonuclear bond by a characteristic x_X, defined as

$$x_X = EA_{exp} - EA_X \approx D_{XX} - D_{XX(exp)} \, . \qquad (28)$$

In this way, Eq. (27) transforms into

$$\Delta H_5 - \Delta H_{10} = (1/2)\,(EA_L - EA_H)^2/\,(EA_H + EA_L) - (1/2)\,(x_H + x_L) \qquad (29)$$

leading directly to

$$\Delta H_5 - \Delta H_{10} = (1/2)\,(D_{LL(exp)} + D_{HH(exp)}) - D_{HL(exp)} \qquad (30)$$

if the results of an earlier paper [14] are introduced, i. e.

$$D_{HL(exp)} = (1/2)\,(D_{HH} + D_{LL})\,(1 + I^2) \qquad (31)$$

where I is the polarity of the HL bond, defined as in Eq. (5) and where the "estimated" D_{XX} are strictly proportional to the original Pauling electronegativity-values χ_X [14].

Since Eq. (30) also stands for the difference $\Delta H_3 - \Delta H_8$, we correspondingly deduce for heteronuclear HL bonds

$$1.364\, pK_a - 23.06\, E^0 = (1/2)\,(D_{LL} - D_{HH})^2/(D_{HH} + D_{LL}) - 18.0 + (1/2)x_L \qquad (32)$$

since x_H was approximately deduced as -36 kcal/mole [14]. The result is shown in Fig. 3, which may be used to compute unknown D_{XX} values which will still be proportional to χ_X. These findings therefore support the idea that Δ-values, defined by (23) should always be positive. Very often however, this essential feature is masked by very large disturbing effects, such as LEP repulsion. In this way, Pauling χ_X-values are shown to have built-in contributions from LEP repulsions in the first place.

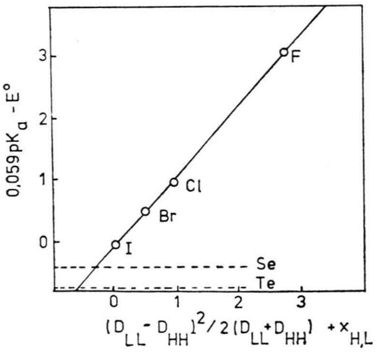

Fig. 3. Plot of 0.059 $pK_a - E^0$ versus $(D_{LL} - D_{HH})^2/2\,(D_{HH} + D_{LL}) + x_{H,L}$ with $x_{H,L} = (1/2)\,(x_H + x_L)$. Values for Δ the extra ionic resonance energy for Se and Te may be obtained by the extrapolation, indicated in the figure.

Hence, negative Δ-values will experimentally be found when $D_{LL} \approx D_{HH}$ and when simultaneously x_L tends to zero, which is indeed the trend observed as to be seen from the values of Δ for iodine and tellurium.

3.4. Drago's E and C Parameters

We have recently fully discussed Drago's $E - C$ equation [4e] (which is a modified linear energy relationship as the Swain-Edwards equation [4c, d]) for ionic and donor-acceptor reactions [6, 15]. It was found that under appropriate conditions an equation resembling the $E - C$ equation of Drago can be regenerated from our ionic bonding theory.

As ionic and donor-acceptor interactions involve two-electron transfers, one readily obtains from Eq. (4 a) the following enthalpy for such processes:

$$\Delta H_{AB} = E_{AB} = \varepsilon_{AB} - (I\,E_B + EA_B) \qquad (33)$$

$$= I\,E_A - a^2\,(EA_B - EA_A) \, . \qquad (34)$$

In order to obtain an $E - C$ equation of the form [4e]

$$-\Delta H_{AB} = E_A\,E_B + C_A\,C_B \qquad (35)$$

one could rewrite Eq. (34) as

$$\Delta H_{AB} = EA_B\,(EA_A + EA_B)^{-1}\,(I\,E_A - EA_A) + EA_A\,(I\,E_A + EA_A)\,(EA_A + EA_B)^{-1} \qquad (36)$$

in which the $E - C$ parameters can be recognized, but which also clearly shows that for instance E_B and C_B are functions of the properties of A.

Now, a recent justification of the $E - C$ equation by Marks and Drago [16] indeed shows that some of the parameters of one bonding partner depend on the properties of the other. A similar conclusion was obtained from the ionic bonding approximation [15].

However, let us write down the enthalpy of reaction (3) as given by Drago's $E - C$ equation:

$$\Delta H_{ABCD} = (E_B - E_D)\,(E_A - E_C) + (C_B - C_D)\,(C_A - C_C) \, . \qquad (37)$$

This equation ressembles the general Eq. (6) and even Pauling's Eq. (7) but it is difficult to assess the exo- and endothermic boundaries for a given series of reactions: only in one case the predictions of both approaches will be the same, i. e. when the differences $E_X - E_Y$ run parallel (also in sign) with the differences $C_X - C_Y$.

Since it is assumed by Drago that a four parameter equation is needed to account for a process such as

$$A^+ + B^- \rightarrow AB \tag{38}$$

with an enthalpy

$$\Delta H = I\,E_A - EA_B + E_{AB} \tag{39}$$

two out of the four $E-C$ parameters should simply be related to $I\,E_A$ and EA_B which are completely independent quantities. Therefore, the conclusion that E_{AB} be expressible as a function of two independent parameters only, one characterizing A, the other B, which is our working hypothesis [see for instance Eq. (31)], is directly deduced from Drago's hypothesis. In a reaction such as (3) all terms $I\,E_X$ and EA_X of course cancel, leaving only four independent parameters to describe its enthalpy. Equation (37) contains no less than 8 parameters which at least looks like an over-parametrization. However, if Eq. (37) would yield correct enthalpies, the procedure could still be acceptable. The fact that Eq. (37) for instance gives the correct enthalpy of the reaction

$$CsI + LiF \rightarrow LiI + CsF \tag{13}$$

is taken by Drago as being in favour of his approach[4e]. If, as a generalization, all 12 reactions

$$CsI + AX \rightarrow CsX + AI \tag{40}$$

are considered, for which the enthalpy reads

$$\Delta H_{CsIAX} = (E_X - E_I)(E_A - E_{Cs}) + (C_X - C_I)(C_A - C_{Cs}) \tag{41}$$

it is seen that they are all predicted to be "endothermic", although the major part is exothermic (vide supra), since Eq. (41) contains nothing but positive (or zero) factors! Therefore, the $E-C$ equation, in spite of the four parameters occuring in it, can not account for the finer details of the chemical behaviour. Moreover, comparison of Drago's $E-C$ equation with Hammett's rule suggests the number of $E-C$ parameters be reduced[4e]. In fact, Hammett's relation is a simple two parameter relation, to be compared with Eq. (37), and there is no difficulty whatsoever in making it compatible with the present approach.

Finally, we shall further illustrate the difficulties inherent to the $E-C$ procedure, by considering the results of the recent justification of the $E-C$ equation by Marks and Drago[16]. Their analysis resulted in the rather familiar expression

$$-\Delta H_{AB} = [(B-A)^2 + 4\,a\,b]^{1/2} \tag{42}$$

likely to be obtained from any quantumchemical procedure, by solving the secular equation and putting overlap integrals equal to zero. Klopman's contribution[17] shows for instance how well E_{AB} values and hence ΔH_{ABCD} values can be calculated with the use of such formulas.

However, squaring each individual ΔH_{AB} value as given by (42) and adding as $\Delta H^2_{AD} + \Delta H^2_{CB} - \Delta H^2_{AB} - \Delta H^2_{CD}$ leads to a quantity X equal to

$$X = 2(B-D)(A-C) + 4(b-d)(c-a) \tag{43}$$

very similar to the Drago expression (37), but where the relation between X and ΔH_{ABCD} is not simple.

3.5. *Study of Acids and Bases in Different Solvents and the Resolution of Acid Strength*

The influence of the solvent in acid-base chemistry has long been recognized as a very important question for the analytical chemist. We already mentioned in section 3.2. the resolution of the acid strength as a function of the properties of the solvent molecules.

Recapitulating the process of dissociation of an acid HX in a solvent S as

$$HX + S_2 \rightarrow H^+ \cdot S_D + X^- \cdot S_A \tag{44}$$

gives the enthalpy

$$\Delta H_{HXS_2} = 2(EA_X - EA_{S_D})(EA_H - EA_{S_A})\,K_{HXS_2}\,. \tag{45}$$

Although the extension to pK_a is not straightforward at all, one can conclude that a relatively important term in determining pK_a will be this enthalpy, hence

$$pK_a \propto (EA_X - EA_{S_D})(EA_H - EA_{S_A})\,K_{HXS_2}\,. \tag{46}$$

A reduction of the ionization potential $-EA_{S_D}$ of the solvent molecule will reduce pK_a, as is very well known by the effect of substituting NH_3 for H_2O as a solvent for the study of very weak acids, being characterized by a relatively small EA_X. Indeed, the ionization potentials of the ammonia and water molecules are respectively 10.15 and 12.6 eV.

However, as remarked in Sect. 3.2, alterations in EA_{S_D} will in general be accompanied by alterations in EA_{S_A} whence the situation may not always be as clear as one could expect from Equation (46).

There is, nevertheless, a very simple way of extracting the influence of EA_{S_A} alone by considering the well known displacement reaction of the kind

$$HX + X_0^-S_A \rightarrow HX_0 + X^-S_A \qquad (47)$$

a classical example[18], for which the enthalpy reads

$$\Delta H_{HXX_0^-S_A} = 2(EA_X - EA_{X_0})(EA_H - EA_{S_A}) K_{HXX_0^-S_A} \qquad (48)$$

independent of the EA_{S_D} of the solvent molecule.

The resolution of acid strengths can be given a Hammett-like expression such as

$$(pK_{aHX} - pK_{aHX_0})_{S_1} = R(pK_{aHX} - pK_{aHX_0})_{S_2} \qquad (49)$$

wherein S_1 and S_2 are different solvents and R, the resolution of acid strength, is defined as the ratio of differences in dissociation constants for the same pair of acids. This resolution *R* has been the subject of several papers and the qualitative explanations for it remarkebly parallel the ones dictated by our approach. In fact, it has been found that, if S_2 is water and S_1 an aprotic solvent, such as DMSO, *R* for non-orthosubstituted benzoic acids is 2.4[11]. The main cause is ascribed to considerable solvation of the anions in water in comparison with aprotic solvents, which, according to Eq. (48) is mainly due to the relatively large EA_{S_A} of water, as demonstrated in its ability to form hydrogegn bonds, or to accept electrons. Therefore, the ionic bonding approximation even seems to give a rationale to discuss the resolution of acid strength for closely related systems.

3.6. *Ion-molecule Reactions*

By all means the most powerful method to obtain quantitative and detailed information about solvent effects is the study of solvation of ions in the gas phase by means of ICR techniques[19, 20]. We already accounted for the bulk hydration enthalpies of several cations[6], although we were not able to resolve the finer details of ion solvation. Anyhow, a summation of the enthalpies of the separate solvating steps leads to a set of enthalpy-values completely consistent with those measured in solution[21]. After all, it should be reminded that solvation processes – and practically all of the displacement reactions studied above – are reactions between relatively complicated polyatomic molecules, for which the ionic bonding approximation has not yet been adapted.

Under these restrictions, it is, nevertheless, possible to write down the valence electron energy of a (diatomic) ion-molecule bond, such as H^+M, where M is a neutral, carrying a LEP:

$$\varepsilon_{H^+M} = I\,E_H + I\,E_M + a^2\,EA_H + b^2\,EA_M \qquad (50)$$

wherein EA_M now represents the negative of the ionization potential of M^6, i.e. $EA_M = -$I.P.

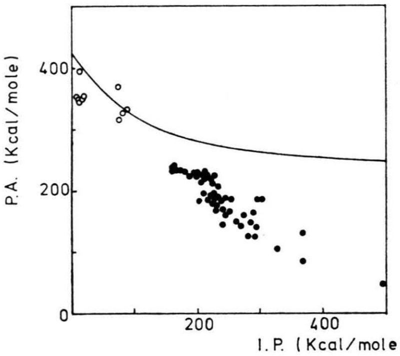

Fig. 4. Plot of experimental proton affinities PA(M) versus experimental ionization potentials I.P. of M whereby theoretical curve has been drawn (○: negative M; ●: neutral M).

Gas-phase basicities PA(M), the proton affinities of neutral species M are thus readily obtained for the reaction

$$H^+ + M \rightarrow H^+M \qquad (51)$$

$$-\mathrm{PA(M)} = \Delta H_{H^+M} = I\,E_H - EA_H(EA_M - EA_H)/(EA_H + EA_M)\,. \qquad (52)$$

The curve representing PA(M) as a function of $-EA_M$ is given in Fig. 4, where also various experimental values are indicated, calculated with $EA_H = E_{HH} = 104.5$ kcal/mole[30].

Although the observed trend is correctly reproduced for the whole range of neutral M and anions X^-, i.e. PA(M) in general decreases with increasing ionization potential of M, large discrepancies are found quantitatively in that $\mathrm{PA(M)}_{calc} > \mathrm{PA(M)}_{exp}$, the difference increasing as $-EA_M$ increases.
At least, the theory predicts too large PA(M) values, indicating that relatively large disturbing effects might be present in the singly solvated species, in agreement with the remarks given above. Moreover, it should be reminded that the bulk hydration enthalpy of cations is very much larger than that of the singly solvated species $A^+ \cdot H_2O$, so that subsequent introduction of solvent molecules is still a

relatively large exothermic process. This inherent possibility of repulsion terms, together with the fact that solvated species are polyatomic ones, will be the major cause for the divergences found for the absolute PA(M) values.

Nevertheless, the general trend of PA(M) to decrease with increasing ionization potential of M, as predicted by Eq. (52) seems no longer obeyed by the anions, especially the halogens. Indeed, these experimental values largely depend on the electron affinity of the halogen, the PA values for HF, HCl, HBr and HI being respectively 370, 333, 324 and 314 kcal/mole[22]. This drastically violates the general trend and would indicate a possible revision of the EA_X values, as remarked previously[23].

As no activation energy is present for gaseous displacement reactions such as

$$H^+M_0 + M \rightarrow H^+ \cdot M + M_0 \qquad (53)$$

our general enthalpy Eq. (52) may directly be applied to yield

$$\Delta H_{H^+M_0M} = 2\, EA_H^2 (EA_{M_0} - EA_M) / (EA_H + EA_{M_0})(EA_H - EA_M) \qquad (54)$$

indicating that reaction (53) is exotherm when $|EA_{M_0}| > |EA_M|$ or when M is a better donor than M_0.

In order to verify Eq. (54) we have selected a series of PA(M) for which the disturbing term $PA(M)_{calc} - PA(M)_{exp}$ for each M is as small as possible. Table 2 represents the results for the amine-series, which has by far the largest PA(M) value.

Although still discrepancies remain, it is surprising that this very simple approach to ion-chemistry yields results comparable with experimental data. It should also be remarked that PA(M) values reported in the literature may vary according to the authors. For instance, PA(M) values for Me_2NH and Me_3N of respectively 224.9 and 229.1 kcal/mole have been reported by Aue et alii[25].

It might be useful to recall in this context the impact of solvent effects going from the liquid to the gaseous phase. In fact, the reaction in solution

$$HB + B_0^-S_A \rightarrow HB_0 + B^-S_A \qquad (55)$$

where it is assumed that only "singly" solvated species occur, has an enthalpy

$$\Delta H_{HBB_0^-S_A} = 2(EA_B - EA_{B_0}) \times (EA_H - EA_{S_A})\, K_{HBB_0^-S_A}\,. \qquad (56)$$

In the limit $EA_{S_A} \rightarrow 0$, one obtains the gas-phase enthalpy

$$\Delta H_{HBB_0^-} = 2\, EA_H^2 (EA_B - EA_{B_0}) / (EA_H + EA_B) \times (EA_H + EA_{B_0}) \qquad (57)$$

or, gas-phase displacement enthalpies represent upper limits to the liquid phase enthalpies, the diminishing factor being the acidity or the electron accepting power of the solvent molecules. Therefore, if only singly solvated species occur, reversals in proton affinities when going from the gaseous to the liquid phase should not occur. The fact that in some cases like the alcohols reversals are observed[26] is a well-known anomaly and suggests a breakdown of the diatomic bond approach in these cases, as represent in reaction (55). Nevertheless, other important results on solvation effects can be accounted for by our approach (vide supra), such as for instance the ESP (elimination of solvent procedure[27]).

It is also readily verified that any gas-phase cation solvation process

$$A^+ + M \rightarrow A^+M \qquad (58)$$

should give the same order of cation affinity for a given series of M as obtained for PA(M), since for the corresponding enthalpy of displacement one obtains

$$\Delta H_{A^+M_0M} = 2\, EA_A^2 (EA_{M_0} - EA_M) / (EA_{M_0} + EA_A) \times (EA_M + EA_A)\,. \qquad (59)$$

Such a situation is actually found for the methyl cation affinity series, showing again a decrease in cation affinity with increasing ionization potential of M[28]. Some reversals however are found, which

Table 2. Experimental and calculated enthalpies of displacement reactions $H^+ \cdot NH_3 + R_nNH_{3-n} \rightarrow H^+ \cdot R_nNH_{3-n} + NH_3$ [a].

R_nNH_{3-n}	$-\Delta H_{exp}$	$-\Delta H_{calc}$	$-EA_M$ [b]	$PA(M)_{exp}$ [b]	$PA(M)_{calc} - PA(M)_{exp}$
NH_3	0	0	235	207	66
$MeNH_2$	9.3	5.8	206.8	216.3	63
Me_2NH	15.4	9.8	190.0	222.3	61
Me_3N	19.6	12.4	180.3	226.6	59

[a] All values in kcal/mole. [b] Taken from Ref. 24.

will be due to the relatively complex nature of the species involved (polyatomic molecules). Loss of planarity of the CH_3^+ species is also important in these reactions in comparison with H^+-reactions.

3.7. The Hard and Soft Acid Base (HSAB) Principle and the Classification of Chemical Species

The fact that our very simple analysis thus far seemed qualitatively in agreement with a variety of experimental data (of which those supporting the Hammett-rule for instance are not the least) calls for a comparison with another scheme introduced for a qualitative description of chemical reactions: the HSAB rule[3]. This is an intriguing question since, as we indicated in Sect. 3.1, the HSAB rule and the present, electronegativity-based, approach very often represent two extremes: Pearson's rule states that always the hard-hard and soft-soft combinations are preferred over the hard-soft ones, whereas the present theory, with Pauling, leads to the opposite result. The HSAB rule is however closely connected with reactions in solution. As pointed out above, it fails for several gas-phase reactions indeed, and it was even shown by Klopman explicitly[2] that the HSAB rule makes no sense if systems are considered in the gaseous phase. For instance, neglecting all solvation terms in Klopman's quantitative measure for hardness and softness[2] yields basically a classification of species just in function of IE_X and EA_X quantities, obviously related to orbital electronegativity, for which the hard-soft rule should accordingly be applied. If the HSAB rule makes no sense in the gaseous phase but only when solvents come into play, its position becomes even more precarious as we see that a considerable part of solvent effects can be treated in a Pauling-like way, i.e. with preference of the hard-soft combination throughout. This may be further illustrated by the following argument: the solvation enthalpy of any cation is given by

$$A^+ + H_2O \rightarrow A^+ \cdot H_2O\,, \qquad (60)$$

$$\Delta H_{A^+H_2O} = IE_A - EA_A(EA_{H_2O_D} - EA_A)/(EA_{H_2O_D} + EA_A)\,. \qquad (61)$$

This enthalpy should compare well with the desolvation-energy calculated by Klopman[2] as the important terms to determine the relative hard- and softness of species. For cations with a charge larger than unity, it is readily conluded that the solvation enthalpy (61) will roughly parallel IE_A values, especially when the EA_A values are comparable with the corresponding value for H_2O, i.e. -12.6 eV. On the other hand, for very low EA_A values, IE_A will also be a good measure for the enthalpy of solvation.

Correspondingly, we have plotted the solvation energies, calculated by Klopman[2], versus IE_A values of cations. The result is shown in Figure 5.

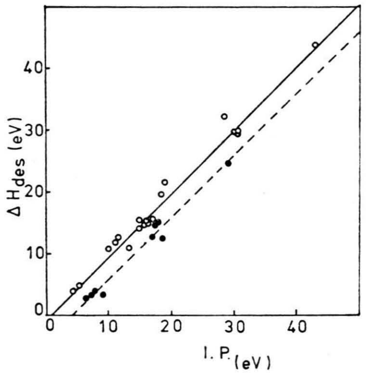

Fig. 5. Plot of desolvation enthalpies ΔH_{des} of different cations, calculated by Klopman[2], versus their ionization potential. Least squares fit shown for ○: hard and borderline acids, and for ●: soft acids.

It is remarkable to see that all so-called hard and "borderline" acids obey the simplified Eq. (61), the situation for the so-called soft acids being such as to reveal an "anomalous" shift to low solvation. This is illustrated by the characteristics of the straight lines, calculated by a least squares fit:

a) all acids: intercept 3.16; slope 0.90; fit $r^2 = 0.94$;

b) hard and borderline acids: intercept 1.07; slope 0.95; fit $r^2 = 0.97$;

c) soft acids: intercept 4.14; slope 1.01; fit $r^2 = 0.96$.

These results first of all support our approach to solvent effects but indicate once more that Pearson's HSAB rule seems to be the rule for the exceptions rather than the rule.

Therefore, according to the results reported above, the "ideal" chemical species should be characterized by its electronegativity alone (which roughly parallels a simplfied hard-soft scale) and the rule regarding their relative reactivity is that the species with the larger electronegativity (hard) prefers bonding with the one having lower electronegativity (soft).

4. Conclusion

In the absence of activation energy contributions and of specific rate-determining steps, a general conclusion from this report is that a Pauling-like formulation of chemical reactivity provides an unexpectedly consistent but still qualitative framework to discuss chemical reactivity, even in some of its finer details. For instance, reversals in reactivity, ambidency, . . . are qualitatively accounted for. Unexpectedly, experimental results from various fields of chemistry (inorganic, organic, analytical and physical, including donor-acceptor bonding and to some extent ion-molecule bonding) can consistently be interpreted. Moreover, the complete theory should also provide estimates for bond lengths and dipole moments[29], but further work on these lines is still needed. The rather unusual treatment of solvent effects turns out to be completely consistent with more classical approaches.

Detailed reaction mechanisms have not yet been discussed although the theory could – if disturbing effects are absent – probably indicate which are the rate-determining steps in a given reaction. In fact, the first step in any ordinary displacement reaction (3) is always some kind of dissociation of bonds in the reacting molecules, a basically endothermic process, giving rise to an "activation energy" in the first place.

An essential point in favour of our approach is the relative ease with which the occurence of ions in chemical reactions is allowed for: ionic reaction mechanisms are most frequently used in organic chemistry, where on account of the relatively small electronegativity differences between organic species in general, this is rather strange. Organic chemists for instance early realized that even energetically very unfavorable ions are responsible for several common reactions: as an example, we cite the halogenation of aromatics as being an electrophilic substitution. It may be useful in this context to remind the pi-electron benzene formula dictated by the ionic approximation to chemical bonding[30], i. e.

which could be the basis for an alternative rationale to discuss aromatic reactivity. Recent VB calculations on benzene[31] indeed confirmed the importance of ionic structures such as those given above.

The most interesting conclusion however is that the present theory is most supported by Hammett's rule, and, in fact, the existence of this rule forced us to reconsider the possibility of a two parameter approach to chemical bonding, which, as is now realized, finds its simpliest expression in a purely ionic approximation to chemical bonding, where a quantity, such as electronegativity, has great physical significance.

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