

On an Ionic Approximation to Donor-Acceptor and Ion-Molecule Bonding, with Reference to Solvation Effects

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An ionic, i. e. essentially electrostatic, approximation to donor-acceptor bonding between neutral species, ion-molecule interactions and corresponding solvation effects is forwarded. Drago's E-C equation for donor-acceptor reactions and the elimination of solvation procedure (ESP), presented by Drago et al., can consistently be incorporated in the general scheme. The theory yields further correct values for bulk ion-solvation enthalpies of cations H^+ , Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ in water with the aid of ionization energies and electron affinities only. The formulae deduced for these types of chemical bonding represent the equivalent of the electronegativity-based theory for the description of ordinary chemical bonding between atoms, introduced earlier.

1. Introduction

In a recent paper¹, Drago's E-C equation for ionic interactions² was shown to be a first approximation of the general bond energy equation obtained from an ionic bonding theory. Originally, the E-C equation was proposed to account for donor-acceptor interactions between neutral molecules³, and it is for these interactions that the E-C equation was most successfully applied⁴.

Contrary to the ionic interactions studied before^{1,2}, which are free from disturbing solvent interactions, donor-acceptor (D-A) interactions are most commonly studied in solutions, where obviously self-interactions and solvent interactions are potentially disturbing effects and as such will contribute to the observed enthalpy of formation of a given D-A complex. Solvent effects are difficult to evaluate, but a systematic study of ion-molecule reactions reveals a great deal about trends in solvation phenomena.

In this report, general enthalpy equations deduced from the ionic bonding theory⁵ are given for donor-acceptor interactions between neutral species and between ions and molecules. An attempt is also made to incorporate at least part of solvent effects in the general scheme. Donor-acceptor bonding is of special interest for our previously introduced ionic approximation to chemical bonding, since this type of bonding allows us to extend this theory – under not too severe conditions – to polyatomic molecules as well and to reactions between relatively complicated species.

2. Donor-Acceptor Interactions

2.1. The Enthalpy of Donor-Acceptor Interactions

2.1.1. Theory

For an ideal gas phase donor-acceptor reaction



where A is the acceptor (acid) and D the donor (base), the results of our ionic bonding theory^{1,5} for diatomic molecules can directly be applied under the conditions that

- (i) the resulting AD bond is a simple two-electron two-centre bond of the same nature as the bonds in homo- and heteronuclear diatomic molecules studied previously;
- (ii) this bond is the only interaction between A and D; and
- (iii) intramolecular rearrangements in A and/or D after AD is formed have not to be accounted for.

Whereas the former two conditions are not too drastic, the last one is only rarely fulfilled.

For a two-electron two-centre bond AB, A and B being atoms, the following valence electron energy ϵ_{AB} was deduced⁵

$$\epsilon_{AB} = IE_A + IE_B + a^2 EA_A + b^2 EA_B, \quad (2)$$

where all symbols have their usual meaning: IE_X and EA_X are respectively the valence electron energy and the electron affinity of element X. $a^2 + b^2 = 1$ and the polarity I of the bond AB is given by $I = b^2 - a^2$.



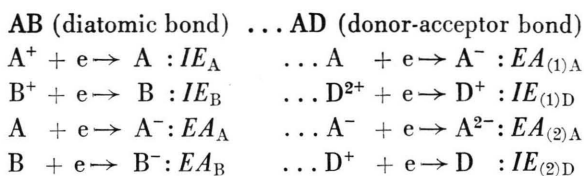
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An extension to donor-acceptor bonds AD is easily made under the conditions (i) – (iii) by considering the following corresponding orbital characteristics:



The valence electron energy ε_{AD} of a donor-acceptor bond AD may then be written as

$$\varepsilon_{AD} = IE_{(1)D} + EA_{(1)A} + a^2 EA_{(2)A} + b^2 IE_{(2)D} \quad (3)$$

and the bond polarity can be expressed as

$$I_{AD} = (IE_{(2)D} - EA_{(2)A}) / (IE_{(2)D} + EA_{(2)A}) \quad (4)$$

leading to the occupation numbers $(1+I)$ for D and $(1-I)$ for A in the donor-acceptor bond AD. This gives the charges $(1-I)^+$ on D and $(1-I)^-$ on A. Since in general $IE_{(2)D} \gg EA_{(2)A}$, these fractional charges will be rather small.

For the enthalpy ΔH_{AD} of the gas phase reaction one (1) readily follows

$$\Delta H_{AD} = \varepsilon_{AD} - (IE_{(1)D} + IE_{(2)D}) \quad (5)$$

$$= EA_{(1)A} - EA_{(2)A} \cdot I_{AD} \quad (6)$$

in complete analogy with the enthalpy for ionic interactions¹. Illustrating I -values are

$$\begin{aligned} I &= -1, \text{A}^{2-}\text{D}^{2+} \text{ bond if } IE_{(2)D} = 0, \\ I &= 0, \text{A}^-\text{D}^+ \text{ bond if } IE_{(2)D} = EA_{(2)A}, \\ I &= +1, \text{AD bond (no bond) if } EA_{(2)A} = 0, \end{aligned}$$

and in the latter case no complex will be formed. ΔH_{AD} can finally be written as

$$\begin{aligned} \Delta H_{AD} &= EA_{(1)A} - EA_{(2)A} \\ &\times (IE_{(2)D} - EA_{(2)A}) / (IE_{(2)D} + EA_{(2)A}). \end{aligned} \quad (7)$$

2.1.2. Discussion

Equation (7) indicates that in a given series of donor-acceptor interactions with constant acceptor A, the enthalpy decreases with increasing $IE_{(2)D}$, which seems to be the trend generally observed⁶. More generally, this observation strengthens our idea that the $\Delta H_{AB}(1)$ values for similar ionic interactions $\text{A}^+ + \text{B}^- \rightarrow \text{AB}$, considered previously⁷, are indeed not reproducing the expected general trend.

Since obviously the “donor” properties of D decrease with increasing $IE_{(2)D}$ values, Eq. (7) correctly reproduces intuitive ideas about donor-acceptor interactions in general.

Moreover, it can reasonably be assumed that both $EA_{(1)A}$ and $EA_{(2)A}$ are relatively small in comparison with the IE_D values, hence $I_{AD} \approx 1$ and ΔH_{AD} will be relatively small also. This agrees with observation for most donor-acceptor interactions between neutral molecules, but, although these enthalpies usually are much smaller than those characterising ordinary atomic or ionic interactions, the bonding mechanism is essentially the same.

Unfortunately, quantitative deductions are hard to give, not only because of condition (iii) given in Sect. 2.1.1. in particular, but also because little is known with certainty (if known at all) about $EA_{(1)A}$ and $EA_{(2)A}$ values.

Nevertheless, this qualitative discussion also reveals that ΔH_{AD} values will give an idea about the acceptor properties of A. Indeed, if we assume that $|EA_{(1)A}| > |EA_{(2)A}|$, gas phase enthalpies will be “grouped” around the $EA_{(1)A}$ values of the different neutral acceptors considered. Several of the ΔH_{AD} values tabulated in the work of Drago et al.⁴ seem to justify this approximation.

In contrast with ordinary AB bonds (A and B being neutral atoms), where the ionic structures A^+B^- and A^-B^+ were considered for explaining the stability of the AB bond, it is necessary for a consistent explanation of donor-acceptor AD bonds to consider the structures $\text{A}^{2-}\text{D}^{2+}$ and A D (no bond). After all, this is just a more detailed but modified version of the usually invoked “bond-no bond” resonance formalism, introduced by Mulliken⁸.

2.2. Length of Donor-Acceptor Bonds

It is of interest to obtain information about the equilibrium internuclear separation in the donor-acceptor bond. Usually, it is assumed that a first estimate for the length of a donor-acceptor bond can be obtained just by taking, exactly as in the case of diatomic AB bonds, the sum of the covalent radii of the elements carrying the active sites in the donor and the acceptor molecule.

However, one may apply the same criterion for donor-acceptor bonds as the one used for ordinary atomic interactions⁹.

For a donor-acceptor bond AD one thus obtains:

$$4 a^2 e^2 / r_{AD} = a^2 IE_{(1)D} + b^2 EA_{(1)A} \quad (8)$$

which leads to

$$4e^2/r_{AD} = IE_{(1)D} + IE_{(2)D} EA_{(1)A}/EA_{(2)A} \quad (9)$$

wherefrom the bond length is directly available through the orbital characteristics of A and D. Indeed, the total Coulomb energy available in a donor-acceptor bond AD is only $4a^2e^2/r_{AD}$, if, as previously⁹, Born-type repulsions are neglected.

It seems unrealistic, however, for this kind of interactions not to account for enhancing contributions (such as polarization in the first place), especially in the neighborhood of the equilibrium distance. Representing such effects by x_A and x_D for the structures A^2-D^{2+} and A D respectively, one could write:

$$4a^2(1+x_A)e^2/r_{AD} + x_D b^2e^2/r_{AD} = a^2 IE_{(1)D} + b^2 EA_{(1)A} \quad (10)$$

instead of Equation (8).

Reminding that $x \ll 1$ and that $b^2 \gg a^2$, the following simplification results:

$$(4e^2/r_{AD}) [1 - b^2(1 - x_D/4)] = IE_{(1)D} [1 - b^2(1 - EA_{(1)A}/IE_{(1)D})] \quad (11)$$

whence one deduces:

$$r_{AD} \approx 4e^2/IE_{(1)D} \quad (12)$$

since always $IE_{(1)D} \gg EA_{(1)A}$ also.

Even the rough approximation (12) seems not unreasonable since it predicts bond lengths of a few Å for most donor-acceptor bonds. Quantitatively however, closer examination is of course necessary, but experimental data are rarely available.

3. Ion-molecule Interactions

A specific class of donor-acceptor interactions can be considered, i.e. those between cations and donors and between anions and acceptors, wherein both the donor and acceptor molecule are neutral species. These ion-molecule reactions are of basic interest since, through the Ion Cyclotron Resonance technique for instance, these reactions can readily be followed. There is the added advantage that these reactions are usually studied in the gas phase and thus reveal the process of ion-solvation in its finer details.

3.1. Enthalpy of Ion-molecule Reactions

In analogy with the scheme given in Sect. 2.1.1, we will characterise the valence orbital energies of

the cation A^+ by IE_A and EA_A and those of the donor molecule M by $IE_{(1)M}$ and $IE_{(2)M}$.

The enthalpy of the cation-molecule reaction



is then given by

$$\Delta H_{A^+M} = IE_A - EA_A (IE_{(2)M} - EA_A) / (IE_{(2)M} + EA_A) \quad (14)$$

Similarly, the enthalpy of an anion-molecule reaction



may be written as

$$\Delta H_{B^-M} = EA_{(1)M} - EA_{(2)M} (EA_B - EA_{(2)M}) / (EA_B + EA_{(2)M}) \quad (16)$$

These reactions, of obvious interest for ion-solvation effects, will be applied below to several individual cases.

3.2. Length of Ion-molecule Bonds

Applying the same criterion as in Sect. 2.2, the following relation between bond length and orbital characteristics is readily deduced for the A^+M bond

$$2e^2/r_{A^+M} = IE_{(1)M} + IE_{(2)M} \cdot IE_A / EA_A \quad (17)$$

and a similar inclusion of x-terms in this case leads to a rough estimate for r_{A^+M} as

$$r_{A^+M} \approx 2e^2/IE_{(1)M} \quad (18)$$

In the case of the bond H^+He for instance, the bond length predicted by Eq. (18) is about 0.5 Å, whereas in the case of the bond H^+H_2O , about 1 Å is obtained.

For anion-molecule reactions, a similar equation may easily be written down.

It should be noticed that frequently intermolecular rearrangements in the species B^-M and A^+M occur, of which several cases will be discussed below.

4. Solvent Interactions

It is well known that there are a number of disturbing effects to be accounted for when studying donor-acceptor interactions. For example the explicit consideration of effect (iii) mentioned in Sect. 2.1.1 would necessitate an extension of the ionic bonding approximation to polyvalent atoms, which has not yet been attempted. For instance, this

effect will be operative when the acid BF_3 is involved in donor-acceptor bonds, since the intermolecular donor-acceptor bond in the BF_3 molecule itself, or part of it, will have to be broken on complex formation with an external donor.

Unfortunately, other effects might come into play as well: there is the possibility that experimentally determined $EA_{(2)A}$ values (if available) show systematic discrepancies, similar to those encountered for the EA_X values of halogens, reported earlier^{1, 7}. Moreover, there is the questionable procedure to evaluate enthalpy values for donor-acceptor interactions between neutral species through empirical relations, based on spectroscopic observations.

Finally, there remains the question about solvent effects and their impact on enthalpy values as soon as complex formation is studied in solution, although the above review of disturbing effects is far from complete.

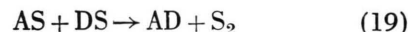
With the earlier work of Kébarle¹⁰ on ion-solvation, much has been revealed about solvation effects in general. Although recent quantummechanical approaches to solvation^{11, 12} seem to overshadow the classical approximations^{10, 13, 14}, it seems useful to attempt to incorporate at least part of the solvent effects consistently in the present scheme.

In order to do so, it should be reminded that solvent-solvent interactions are by definition interactions between neutral species, just as for instance atom-atom interactions. Since we have shown in Sect. 2 that the neutral molecule-molecule interactions, if they can be classified as donor-acceptor interactions, indeed proceed essentially through the same mechanism as atom-atom interactions (the same ϵ_{AB} may be written down), it is tempting to conclude that a considerable number of solvent-solvent interactions are primordially governed by interactions between donor and acceptor functions present in the neutral solvent molecules. A typical self-explanatory example is offered by the water-molecule. The limitations of this approach are evident: since only bifunctional solvent interactions can be considered, chain formation of the solvent molecule is accepted as a guide for bulk solvent behaviour. However, since tridimensional ordering occurs basically in solid species only, one has a chance of arriving at reasonable results, especially if we restrict ourselves to the study of closely related systems.

Theory

Characterising the acceptor-function of a solvent molecule S by $EA_{(1)S}$ and $EA_{(2)S}$ and its donor-function by $IE_{(1)S}$ and $IE_{(2)S}$, it is readily verified that, when dealing with an amphoteric solvent in which both functions are present, results can be obtained for donor-acceptor interactions in solution, consistent with the ionic approximation to chemical bonding.

Thus, the reaction



considers complex formation AD in the solvent S starting from dilute solutions of A and D in S , while the initially broken chain of solvent molecules is restored (S_2), in agreement with the preliminaries outlined above.

Solvation of the complex AD can occur for instance if $A(D)$ also carries a donor-function (acceptor-function) which does not interfere with its acceptor-function (donor-function). This can be visualized as



The enthalpy for both reactions (19) and (20) will invariantly be given by

$$\begin{aligned} \Delta H_{AD} = & EA_{(1)A} - EA_{(2)A} I_{AD} + EA_{(1)S} - EA_{(2)S} I_{SS} \\ & - EA_{(1)A} + EA_{(2)A} I_{AS} - EA_{(1)S} + EA_{(2)S} I_{DS}. \end{aligned} \quad (21)$$

After rearrangement one obtains

$$\begin{aligned} \Delta H_{AD} = & 2 EA_{(2)A} (IE_{(2)S} - IE_{(2)D}) / (IE_{(2)S} + EA_{(2)A}) \\ & \cdot (EA_{(2)A} + IE_{(2)D}) - 2 EA_{(2)S} (IE_{(2)S} \\ & - IE_{(2)D}) / (IE_{(2)S} + EA_{(2)S}) (IE_{(2)D} + EA_{(2)S}). \end{aligned} \quad (22)$$

If for instance the acceptor function of A is much stronger than that of S , i.e. if $EA_{(2)A} \gg EA_{(2)S}$, which is the case for strong acceptors in rather poorly acidic solvents, one obtains the following simplified result

$$\begin{aligned} \Delta H_{AD} \approx & 2 EA_{(2)A} (IE_S - IE_D) / (IE_S + EA_A) \\ & \cdot (IE_B + EA_A), \end{aligned} \quad (23)$$

where for the sake of simplicity all subscripts (2) have been omitted.

It should be remarked that Eq. (23), for instance, is completely different from Eq. (7) giving the gas phase enthalpy for the same complex.

Hence, from this analysis, it follows that the characteristics of the solvent can play a decisive role for the enthalpy of complex formation in solution.

This will be illustrated further on for a particular case, known in the literature as the Elimination of Solvation Procedure (ESP)¹⁵.

5. Applications

5.1. Drago's E-C Equation for Gas Phase Donor-Acceptor Interactions

Drago's E-C equation^{3, 4} for reproducing enthalpies of donor-acceptor interactions is

$$-\Delta H_{AD} = E_A E_D + C_A C_D \quad (24)$$

where E_X and C_X are both positive numbers characteristic for the acceptor and the donor.

Exactly as in the case of ionic interactions¹, Eq. (7) may now be rewritten as:

$$\Delta H_{AD} = [IE_{(2)D} / (IE_{(2)D} + EA_{(2)A})] (EA_{(1)A} - EA_{(2)A}) + EA_{(2)A} \cdot (EA_{(1)A} + EA_{(2)A}) / (IE_{(2)D} + EA_{(2)A}) \quad (25)$$

and a similar procedure may tentatively be applied to reveal the nature of the E and C parameters:

$$E_A = EA_{(1)A} - EA_{(2)A}, \quad E_D = IE_{(2)D} / (IE_{(2)D} + EA_{(2)A}), \quad (26 a)$$

$$C_A = EA_{(2)A} (EA_{(1)A} + EA_{(2)A}), \quad C_D = (IE_{(2)D} + EA_{(2)A})^{-1}$$

since it is readily concluded from Drago's analysis for strong acids that $E_A E_D < C_A C_D$.

However, this procedure is only valid for true gas phase interactions, as pointed out above, whereas in the study of Drago et al.⁴ other systems were included also. This should be kept in mind throughout the discussion to follow.

Since in general $EA_{(2)A} \ll IE_{(2)D}$, a limiting value for E_D of about unity can be expected from Eq. (26 a), whereas correspondingly $C_D \approx IE_{(2)D}^{-1}$. It is striking to see that about 75% of the donors listed by Drago⁴ have $E_D = 1 \pm 0.35$. Hence in order that for a considerable number of acids $E_A E_D$ corresponds with the quantity in (25) one should conclude $-E_A \approx EA_{(1)A} - EA_{(2)A}$. In fact, this interpretation of E_A seems to be in agreement with our expectation since the strongest acids, such as R_3Al for instance, have the larger E_A and since also their absolute magnitude (of the order of kcal/Mole) seems plausible. Another formal consequence of this analysis is that, E_D being always a positive quantity, $EA_{(1)A} - EA_{(2)A} < 0$, or, as expected,

$$|EA_{(1)A}| > |EA_{(2)A}|.$$

A similar argument may be given for the C -parameters, although, exactly as in our discussion about ionic interactions¹, C_D is affected by the nature of the acceptor molecules used in the compilation. For those donors where E_D is about unity, we may conclude (see above) that the C_D values collected by Drago are several orders of magnitude too large, whereas the opposite will be true for the C_A values. For instance, the mean C_D value reported by Drago is about 5.1, whereas the mean C_A is about 0.73. Using a mean value for $IE_{(2)D}$ of 10 eV, one obtains a mean value for the product $C_A C_D$ of about 3.5 kcal/mole or, on the average, a product $EA_{(2)A} (EA_{(1)A} + EA_{(2)A}) \approx 1.5$ (eV)², which should be considered as an average for the absolute C_A given by Equation (26 b). Moreover, it seems in agreement with the absolute value of the E_A parameter.

Moreover, sign-analysis of the $C_A C_D$ product leads to $EA_{(2)A} \cdot (EA_{(1)A} + EA_{(2)A}) > 0$, or $EA_{(2)A}$, the enthalpy of the process $A^- + e \rightarrow A^{2-}$, always negative, unless $|EA_{(2)A}| > |EA_{(1)A}|$, which would be in contradiction with our analysis of the E -parameters given above.

It must therefore be concluded that, if the Drago analysis of the gas phase enthalpies is consistent with our theory, the process



should always be exothermic!

This is a rather singular result, which is a consequence of our interpretation of the E - C values listed by Drago. The fact that these enthalpies can indeed be split up in the way suggested by Drago seems to be in favour of this conclusion, but it should be anticipated that this is difficult to verify experimentally.

From this analysis it also follows that hydrogen bonded complexes are stable on account of negative $EA_{(1)A}$ and $EA_{(2)A}$ values. It is clear however that these values will depend on the polarity of the hydrogen-bond in the non-bonded acceptor molecule. Within the constraints of the ionic approximation to chemical bonding, this polarity will determine the probability with which the hydrogen in this bond will behave as if it were the ion H^+ .

Finally, we would like to point out that even systematic errors in the determination of the enthalpy will not alter the present conclusions. If indeed there is a systematic error of $\pm x$ in the gas

phase enthalpy, this error will be absorbed in the $EA_{(1)A}$ value of Eq. (7), leading to

$$\Delta H_{AD} = EA'_{(1)A} - EA_{(2)A} I_{AD} \quad (28)$$

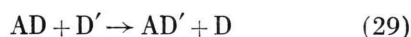
with $EA'_{(1)A} = EA_{(1)A} \mp x$ and with $x < EA_{(1)A}$.

Given the fact that numerous enthalpy values have been obtained through empirical relations with spectroscopic data, this might have had a considerable impact on the E - C parameters obtained by Drago. Nevertheless, we believe that the main causes for divergences between this theoretical approach and Drago's will be due to condition (iii) of Sect. 2.1.1 and to solvent effects.

5.2. Drago's Elimination of Solvation Procedure (ESP)¹⁵

In Sect. 4 we advanced a tentative procedure to incorporate solvent effects consistently into the present scheme. The interesting case-study carried out by Drago and his collaborators¹⁵ revealed that in a series of displacement reactions involving the acid mF-phenol the enthalpy was independent on the solvent.

For a gas phase displacement reaction



where the same acid is used, the enthalpy is readily obtained from Eq. (7) as:

$$\Delta H = 2 EA_{(2)A}^2 (IE_{(2)D} - IE_{(2)D'}) / (IE_{(2)D} + EA_{(2)A}) \times (IE_{(2)D'} + EA_{(2)A}) \quad (30)$$

indicating that reaction (29) in the gas phase is exothermic only when $|IE_{(2)D}| > |IE_{(2)D'}|$, or if D' is a better donor than D . In the following equations, the subscript (2) will be omitted, since it is a characteristic of displacement reaction of this kind that enthalpies formerly denoted by the subscript (1) always cancel.

If $D = S$, and if D' is solvated by S as in reaction (19), the enthalpy (22) is obtained.

Hence, carrying out a complexation of A with D' in a series of different solvents $S, S', S'' \dots$ one will obtain a difference in enthalpy Δ given in first instance by

$$\Delta = (\Delta H_{AD'})_S - \Delta H_{AD'}_{S'}, \quad \Delta \approx 2 EA_A^2 (IE_S - IE_{S'}) / (IE_S + EA_A) (IE_{S'} + EA_A) \quad (31)$$

corrected by a very small difference between a similar term in EA_S^2 and $EA_{S'}^2$, which, on the condition

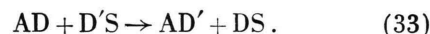
that EA_A is much larger than either EA_S and $EA_{S'}$ (otherwise the complex AD' would not be observed), can readily be neglected.

The enthalpy difference given by (31) is *not dependent on the donor*, whence for a given series of interactions $AD, AD' \dots$ the difference (31) will always be reproduced, as observed by Drago (see the results presented in Table IV in Reference¹⁵).

Similarly, if an exchange reaction such as (29) is carried out in a solvent S , the enthalpy will be given by:

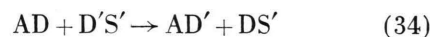
$$\Delta H = 2 EA_A^2 (IE_D - IE_{D'}) / (IE_D + EA_A) (IE_{D'} + EA_A) - 2 EA_S^2 (IE_D - IE_{D'}) / (IE_D + EA_S) (IE_{D'} + EA_S) \quad (32)$$

for the reaction is then:



The enthalpy (32) is equal to the gas phase enthalpy (30) minus a small correction term, depending on the acidity of the solvent molecule.

Correspondingly, the enthalpy of the reaction between A, D and D' in a different solvent S'



will differ from enthalpy (32) by an even smaller negligible amount Δ' , given by

$$\Delta' = 2 EA_{S'}^2 (IE_D - IE_{D'}) / (IE_D + EA_{S'}) (IE_{D'} + EA_{S'}) - 2 EA_S^2 (IE_D - IE_{D'}) / (IE_D + EA_S) (IE_{D'} + EA_S) [\approx 0]. \quad (35)$$

This is exactly what is observed by the investigation of Drago¹⁵. Moreover, we may extract the conclusion that, on the condition that $EA_A \gg EA_S$, the enthalpies of displacement reactions observed in a given solvent, poorly acidic, are of comparable magnitude as those observed in the gas phase, and hence, are automatically not solvent dependent. The enthalpies of the displacement reactions studied by Drago are indeed simply related to the sequence of IE_D values: they gradually increase with increasing difference $IE_D - IE_{D'}$, in agreement with the present expectations, i. e. Equation (32).

Nevertheless, more experimental material is needed before definite conclusions can be reached about cancellation of solvent effects on the basis of our present solvation theory.

A major shortcoming of this approach indeed is that solvent effects, not operating through the donor-acceptor interaction mechanism, are left out of con-

sideration. Although cancellation of such terms can also occur in the displacement reactions considered in this section, their effects will be most pronounced in reactions such as (19).

5.3. Gutman's Donor Numbers (DN)¹⁶

It has been suggested by Gutman¹⁶ that donors might be classified according to their Donor Number (DN), defined as the negative of the enthalpy of the reaction



in 1,2-dichloroethane.

Similar DN numbers for the same donors can be obtained from reactions with other acids, but the whole procedure has seriously been questioned by Drago^{4, 17}.

Applying our solvation theory to the Gutman procedure leads to an enthalpy (21) if both the donor and SbCl_5 are solvated by a donor-acceptor interaction with 1,2-dichloroethane. However, considering the large number of donors, used by Gutman, occasional failures of this equation can be expected. Of these, a particular one may be, on the condition that the acid SbCl_5 is always interacting with the same solvent S as $\text{SbCl}_5 \cdot \text{S}$, that a given donor dissolves "ideally" in S. One then can obtain reactions such as:



leading to an enthalpy:

$$\Delta H = 2 EA_{(2)A}^2 (IE_{(2)S} - IE_{(2)D}) / (IE_{(2)S} + EA_{(2)}) \\ (IE_{(2)D} + EA_{(2)A}) + x_S \quad (38)$$

wherein

$$x_S = EA_{(1)S} - EA_{(2)} I_{SS}. \quad (39)$$

Depending on the properties of D, a shift in ΔH_{AD} is not impossible, which, by this procedure, is ascribed to D. Similarly, other than donor-acceptor solvent effects, can either enlarge or reduce such shifts. In this way, even reversal of donor orders could occur.

A consequence of these effects is that several different enthalpy relations, such as (21) and (38), will have to be used in order to fit the experimentally obtained plot DN vs. $IE_{(2)D}$. In this way, our analysis supports the idea that a considerable part of the controversy about donor and acceptor powers of species comes from specific solvent interactions or violation of condition (iii) in Section 2.1.1.

5.4. On the C/E Ratio of Donors and Acceptors and its Relation with Hardness and Softness

The C/E ratio of donors and acceptors has been brought into relation with their softness^{4, 14}, a concept introduced by Pearson¹⁸. Although an important solvent effect on hardness and softness has been demonstrated¹⁴, it is of interest to apply the same evaluation of the C/E ratio as in our discussion of ionic interactions¹.

For acids and bases one respectively obtains for the gas phase C/E ratio, reminding Eq. (26):

$$C_A/E_A \approx EA_{(2)A}, \quad C_D/E_D \approx 1/IE_{(2)D} \quad (40)$$

if, especially for A, disturbing effects as discussed in Sect. 5.1 are absent.

With this restriction in mind, result (40) adds to the confusion concerning the hardness and softness of acids and bases. We agree with Blint, McMahon and Beauchamp¹⁹ that any scale of acidity (basicity) depends on the reference abase (acid). Absolute scales can only be considered when ideal acids and bases are used. Thus classifying acids according to their interaction with an ideal donor, to be characterised by $IE_D = 0$, corresponding with free electrons, leads to a classification in function of the orbital energy values of the isolated acid, i. e. IE_A and EA_A for atoms and ions and $EA_{(1)A}$ and $EA_{(2)A}$ for neutral molecular acceptors. Classifying donors according to their interaction with an ideal acid, to be characterised by a zero effective nuclear charge in the valence orbital also, leads to an (absolute) scale of donors in function of the orbital characteristics of the isolated donor, i. e. IE_D and EA_D for atoms and ions and $IE_{(1)D}$ and $IE_{(2)D}$ for neutral molecular donors. On the condition that solvent effects can be incorporated according to the scheme forwarded in Sect. 4, the relative position of acids and bases will be unaffected by solvent effects. This point is discussed more in detail in the next section.

5.5. Ion-solvation as an Example of Ion-molecule Interactions

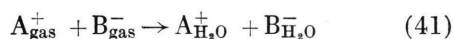
One of the interesting problems in solution chemistry is the evaluation of ion-solvation but these phenomena are of considerable importance also for biochemistry and for the chemistry of the troposphere. Experimental results on the gas phase ion-water interactions, obtained by ICR technique¹⁰, revealed the enthalpy changes accompanying addition of individual water molecules to the originally

free ion. If the number of water molecules clustered around the ion is large enough, the total enthalpy approaches the enthalpy obtained from measurements in solution. These results indicate that part of the electron accepting power of a cation for instance is still being saturated when a second water molecule is interacting with the species $M^+ \cdot H_2O$.

Recent quantummechanical approaches to this problem^{11, 12} yield encouraging results, also for the finer details of ion-solvent interaction, but it might be of interest to apply our solvation theory to these kinds of interactions too.

The classical electrostatic approximation¹³ has long been used to account for solvation effects. Since after all, our present formalism is also an electrostatic approach (ionic approximation to chemical bonding), its predictions can be considered as the necessary link between the classical and bonding-like approaches to solvent interaction.

It has long been recognised²⁰ that the enthalpies of reactions



are such as to reveal a specific and constant enthalpy for each ion-water interaction, which can be evaluated after a suited reference has been introduced²⁰.

Application of our theory to reaction (41) leads to

$$S_2 \rightarrow S + S \quad \Delta H_{SS} = -EA_{(1)S} + EA_{(2)S} I_{SS}, \quad (42a)$$

$$A^+ + S \rightarrow A^+S \quad \Delta H_{A^+S} = IE_A - EA_A I_{A^+S}, \quad (42b)$$

$$B^- + S \rightarrow B^-S \quad \Delta H_{B^-S} = EA_{(1)S} - EA_{(2)S} I_{B^-S} \quad (42c)$$

where process (42a) indicates that first of all solvent-solvent interactions have to be broken. Although the total enthalpy

$$\Delta H = \Delta H_{SS} + \Delta H_{A^+S} + \Delta H_{B^-S} \quad (43)$$

indeed reveals the specificity of ion-solvent interactions, it is difficult to split it up in only two contributions in view of the presence of the (always constant) enthalpy (42a).

However, if the enthalpy (42b) for cation-solvation is calculated for H^+ and the alkali-ions, the results, collected in Table 1, are obtained. The "experimental" estimates²⁰ are also shown.

Although the agreement is in part fortuitous, it is tempting to conclude that our very simple equations reasonably account for (bulk) solvent effects. Indeed, the calculated enthalpies for cation-solvation represent upper limits for the individual enthalpies

Table 1. Experimental and calculated cation-solvation enthalpies.

Ion A^+	$-\Delta H_{A^+} (H_2O)_{\text{calc. a, b}}$	$-\Delta H_{A^+} (H_2O)_{\text{calc. a, c}}$
H^+	264	258 - 283
Li^+	105	118 - 140
Na^+	103	94.5 - 116.5
K^+	89	75 - 97
Rb^+	85	69 - 90.5
Cs^+	80	62 - 83.5

a all values in kcal/mole. b EA_A assumed equal to E_{AA} ²¹.

c Taken from Ref.²⁰, the actual value depends on the standard used in the calculation.

measured in the gas phase, indicating that for instance in simple species such as $A^+ \cdot H_2O$ relatively strong repulsion (destabilizing) can be operative.

As to the solvation enthalpy of anions, the situations is more complicated. In fact, bulk solvation enthalpy for a pair of ions can only be evaluated quantitatively if the electron affinity of B is accurately known²⁰. A revision of these values⁷ would necessitate revision of the enthalpy values (43) used in the evaluation of specific ion-solvation enthalpies. Moreover, it seems that anion-solvation enthalpies, as evaluated in the classical way, have built in contributions from solvent-solvent interactions, i.e. process (42a). Finally, it is not certain whether or not rearrangements actually do take place in solvated species. For example, anion-solvation $B^-(H_2O)$ could lead to hydroxyl-solvation $OH^-(HB, H_2O)$ and in view of the difficulties reported for the evaluation of E_{HB} values²², these anion-solvation enthalpies will lead to similar difficulties.

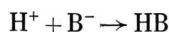
Nevertheless, cation-solvation seems reasonably accounted for by the present mechanism, at least if we restrict ourselves to bulk solvation effects. Hence, our theory cannot account for the enthalpy of singly solvated species but trends can well be reproduced, whence, in the following section, trends in gas phase basicities (proton affinities) will be discussed.

5.6. Gas Phase Proton Affinities (Basicities) of Anions and Neutral Species

An intriguing aspect of the present study consists in explaining gas phase proton affinities of neutral molecules, which, in recent years, have become available through ICR measurements. According to our theory, the proton affinity (PA) of an anion B^- is given by

$$\Delta H_{AB} = -PA(B^-) = IE_H - EA_H I_{HB} \quad (44)$$

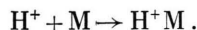
for an ionic reaction



whereas the proton affinity of a neutral molecule M, $PA(\text{M})$ is deduced as:

$$\Delta H_{\text{H}^+\text{M}} = -PA(\text{M}) = IE_{\text{H}} - EA_{\text{H}} I_{\text{H}^+\text{M}} \quad (45)$$

characterising the process



The interest for our ionic approximation to chemical bonding of experimentally observed trends in $PA(\text{M})$ values is obvious, since such trends should reveal the absolute magnitude of the electron affinity of hydrogen. Indeed, for the ionic approach to chemical bonding to be valid, the relation

$$EA_{\text{X}} = E_{\text{XX}} \quad (46)$$

should be valid^{5, 21}.

The only stumbling block thus far met for applying the ionic bonding approximation to homonuclear bonding⁵ was the large divergence between the E_{HH} value of about 4.5 eV and the Hylleraas-Pekeris EA_{H} value, calculated quantummechanically, of about 0.75 eV²³.

Although it is difficult to obtain consistent absolute enthalpies for singly solvated species (see foregoing section) we believe the wide divergence in $PA(\text{M})$ values, obtained from ICR techniques, are in favour of an electron affinity for hydrogen of the same order of magnitude as the hydrogen homonuclear bond energy. This is what should be concluded from the recent compilation of proton affinities given by Dunbar²⁴.

Indeed, the difference in $PA(\text{M})$ of two molecules with $IE_{(2)\text{M}}$ of 10 eV and 9 eV should amount to 4.75 kcal/mole with EA_{H} equal to 4.5 eV, whereas with the EA_{H} value of 0.75 eV only 0.23 kcal/mole is obtained.

Possible rearrangements in singly solvated protons can also be accounted for qualitatively. Consider for instance the PA of alkali hydroxides MOH, calculated by Kebabian et al.²⁵. Herein the rearrangement $\text{H}^+ \cdot \text{MOH} \rightarrow \text{M}^+ \cdot \text{H}_2\text{O}$ is largely exothermic because $EA_{(\text{OH})} \ll IE_{(2)\text{MOH}}$ and because $EA_{\text{H}} \gg EA_{\text{M}}$, in agreement with the large EA_{H} suggested above.

Nevertheless, the fact that large discrepancies remain between the gas phase basicities and those

calculated by the present scheme (those obtained are smaller than the lowest PA value of $IE_{\text{H}} - EA_{\text{H}} \approx 9.1$ eV predicted by our theory), indicate that large repulsive effects are operative in single species like for instance $\text{H}^+ \cdot \text{H}_2\text{O}$. In this respect, it might be useful to recall the parallel criterion to be fulfilled in order that the interacting species are stable by the amount represented in the different enthalpy equations given above, i.e. the criterion that the bond length in these bonds be given as in Section 3.2. As soon as for instance this bond length can not be obtained, destabilization will occur, just as the one observed in a number of homonuclear bonds⁵. Since the predicted bond length is smaller the larger the ionization energy $IE_{(2)\text{M}}$ of the donor molecule, large deviations may be expected for the proton affinities of noble gases in the first place, in particular H^+He .

Unless rather spectacular trends can be revealed for these repulsion forces, we conclude that the electron affinity of hydrogen is larger than the calculated one, especially for the low occupancy numbers obtained for proton-molecule reactions.

6. Conclusion

Although the ionic approximation to chemical bonding provides us with a very simple formulation of bonding parameters, which can consistently be applied to atom-atom, ion-ion, molecule-molecule and ion-molecule interactions and which allows one to incorporate a significant part of solvent effects consistently in the general scheme, it raises numerous questions of which several are left unanswered. Further investigations on these points might contribute to evaluate finally the validity and the significance of this theory.

Nevertheless, the rather unusual procedure to evaluate solvent effects without any explicit reference to the classical approximations, seems to illustrate that the importance of the electron-pair in chemistry, as early recognised by Lewis, can not be underestimated.

We are investigating further possibilities of applying this very simple physical model to various problems of chemical interest, since in most cases it remains in agreement with intuitive ideas about bonding problems.

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