On Drago's *E-C* Equation, Pearson's HSAB Rule and the Ionic Approximation to Chemical Bonding

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An attempt is made to explain the *E-C* formalism for ionic interactions in terms of the ionic approximation to chemical bonding. Dravo's *E-C* equation is seen to be a first approximation to the bond energy equation as it is given by the ionic bonding approach. The meaning of the ratio C/E is discussed and its relation with the hardness and softness of interacting species, as these occur in Pearson's HSAB rule, shows that the electron affinity or electronegativity of elements completely determines the chemical behaviour of ionic species. This analysis illustrates the consistency of the ionic approximation to chemical bonding.

1. Introduction

The systematization of donor-acceptor or, in general, of Lewis acid-base interactions is an interesting problem in the field of general chemistry. In recent years, several rules and mechanisms for the description of such interactions have been proposed by Pearson [1], Drago [2] and Gutman [3].

In this work, Drago's *E-C* equation, as it was applied for ionic interactions [4], is examined more closely in search for a physical model, corresponding with the *E-C* parametrization procedure. The relation between hardness and softness of acids and bases (HSAB) [1] and the E and C parameters is discussed and an attempt is made to reveal the meaning, the dimensions and the absolute magnitudes of these latter. Such an attempt is now possible by making use of the results of the ionic approximation to chemical bonding recently advanced [5a].

2. Drago's E-C Equation and the Ionic Approximation to Chemical Bonding

The *E-C* equation for the enthalpy of donor-acceptor (or acid-base) interactions is [2]

$$-\Delta H_{AB} = E_A E_B + C_A C_B \qquad (1)$$

whereby each of the interacting species A and B is characterised by a set of two parameters E_A, C_A and E_B, C_B respectively.

Equation (1) yields rather impressive results: indeed, a considerable amount of experimental data is quite accurately reproduced and the predictive capacity of this equation seems reasonable.

It is significant that four parameters are needed to describe bonding between two species if the procedure is to be kept as general as possible.

Nevertheless, the deviations from the mean values of the parameters indicate that these parameters are only valid in particular situations, as to be seen for instance from the fact that ionic reactions, for which relatively large charge transfers are observed, can not be included – with a few exceptions – in the general correlation [4].

The ionic approximation to chemical bonding [5a] offers the possibility of discussing the *E-C* equation more in detail. Indeed, the following equation was proposed [5a] for the valence-electron energy of a two-centre two-electron heteronuclear bond AB, ε_{AB}:

$$\varepsilon_{AB} = I E_A + I E_B + a^2 E A_A + b^2 E A_B \qquad (2)$$

where IE_X and EA_X respectively stand for the ionization energy and the electron affinity of element X. $a^2 + b^2 = 1$ and I, the permanent polarity of the AB bond, is given by

$$I = b^2 - a^2 = (EA_B - EA_A)/(EA_A + EA_B).$$

For the enthalpy of a reaction

$$A^+ + B^- \rightarrow AB$$

one readily obtains:

$$\Delta H_{AB} = I E_A + I E_B + a^2 E A_A + b^2 E A_B - I E_B - E A_B$$
$$= I E_A - E A_A I. \qquad (3)$$

A first remark about Eq. (3) is that it is conform with rule 1 of an earlier note [5b] for explaining trends in ΔH_{AB} values in particular series of bonds. The other reaction

$$A^- + B^+ \rightarrow AB$$

similarly leads to

$$\Delta H_{AB} = I E_A + I E_B + a^2 EA_A + b^2 EA_B - I E_A - EA_A$$
$$= I E_B + EA_B I \qquad (4)$$

in agreement with rule 2 of that paper [5b].

It is now possible to rewrite Eq. (3) in a form similar to Drago's Eq. (1) reminding that the Drago relation was applied for reactions $A^+ + B^- \rightarrow AB$, where A is the acid and B the base [4]:

$$\Delta H_{AB} = \frac{EA_B}{EA_A + EA_B} \cdot (I E_A - EA_A) + \frac{1}{EA_A + EA_B} \cdot (I E_A + EA_A) EA_A . \qquad (5)$$

In this way a sum of two products is obtained, as demanded by the empirical relation (1). Moreover, since the results of McMillin and Drago [4] indicate that $E_A E_B > C_A C_B$, especially for reactions leading to alkalisalt molecules, it is tempting to make the following extension:

$$C_A = EA_A (I E_A + EA_A) , \quad C_B = (EA_A + EA_B)^{-1} , \qquad (6\,a)$$

$$E_A = I E_A - EA_A , \qquad E_B = EA_B / (EA_A + EA_B) , \qquad (6\,b)$$

the validity of which will be discussed below.

This extension is only possible by keeping in mind that A and B should be characterised by two parameters. If the present approach is valid, it automatically follows from Eqs. (5) and (6) that the *E-C* formalism is only a first approximation to our ionic bonding theory, which can only be justified under the very special conditions appearing from these equations. In this way, the Drago theory can be considered as a very rough verification of the ionic approximation to chemical bonding.

3. A Comparison of Eqs. (1) and (5)

Before a term by term comparison of Eqs. (1) and (5) is possible, it is necessary to recall the results of an earlier paper [5b], concerning the chemical inconsistency of the experimental ΔH_{AB} values, to which both Eqs. (1) and (5) should refer. The main cause for this inconsistency was ascribed to the fact that the so called experimental EA values for halogens are too low. In this way the situation becomes completely analogous to the one already discussed for E_{XX} values of halogens [5c], where it was also found that the experimental E_{XX} values do not reflect the true bonding power of halogens. These two conclusions are consistent since it was already argued that the identity $EA_X = E_{XX}$ should be valid [5a, d].

Hence, in order to be able to reproduce the experimental ΔH_{AB} values used by Drago, it is necessary to correct Eqs. (3), (5) and (6) for the divergence between EA_{Xexp} and $EA_X = E_{XX}$ deduced earlier [5c, d].

With the relation

$$EA_X = EA_{Xexp} + x_X \qquad (7)$$

where x_X is an electron affinity correction, characteristic for element X, one obtains

$$\Delta H_{AB} = I E_A + x_B - EA_A I \qquad (8)$$

instead of Equation (3).

The corresponding extension towards the E and C parameters is now less obvious and less straightforward as starting from Equation (3). Tentatively, however, one could write

$$C_A = EA_A (I E_A + x_B + EA_A) ,$$
$$C_B = (EA_A + EA_B)^{-1} , \qquad (9\,a)$$

$$E_A = I E_A + x_B - EA_A , \quad E_B = EA_B / (EA_A + EA_B) , \qquad (9\,b)$$

but the possibility that other and better definitions for these parameters may be extracted from Eq. (8) must not be excluded.

It should be remarked that calculation of experimental ΔH_{AB} values with Eq. (8) causes no problems, if the E_{XX} values collected in Table 4 of an earlier paper [5c] are used as a measure for EA_X [5a, d]. Difficulties can be expected however for reproducing McMillin and Drago's *E-C* parameters. In fact, the presence of the term x_B will cause a certain dilemma: it is obvious indeed that, by its nature, this term should be incorporated in the E_B and C_B parameters, and, not in the E_A and C_A parameters as suggested by Equations (9). This is however hard to achieve mathematically and, therefore, it is perhaps the reason why there is such large correlation between the *E-C* parameters as found by McMillin and Drago.

Since there are no computational aids at our disposal for the time being, we were not able to verify this supposition. An additional factor in favour of this conclusion however is that, as to be seen from Eq. (6), the parameters E_B and C_B are sensitive to the properties of A.

Even more striking is McMillin and Drago's remark that the *E-C* Eq. (1) fails rather systematically when charge transfers exceeding one electronic charge have to be accounted for [4]. This seems to confirm our present deductions: indeed, E_B and C_B are only (roughly) constant provided $EA_A \ll EA_B$, i. e. when the charge transfer in the AB bond is relatively small with respect to the ions $A^+ + B^-$.

If EA_A increases (in particular when $EA_A > EA_B$, the charge transfer will be larger than unity), E_B and C_B markedly deviate from the values obtained on cases where EA_A is small. For instance, a ratio $EA_B/EA_A \approx 0.1$, which is the case for several alkalihalogenides, yields in first approximation – see Eq. (5) – a value $E_B \approx 0.9$, whereas a ratio of about unity would lead to $E_B = 0.5$!. In this way, it is clearly shown how the values of the E and C parameters largely depend on the nature of the reactions used for their evaluation.

These are, however, just some general remarks and careful inspection of very case is necessary, in view of disturbing effects frequently present.

Nevertheless, these rather qualitative considerations strongly suggest that our ionic approach to the *E-C* equation may contribute to a better understanding of the E and C parameters. In first instance, their dimensions are easily revealed from Equation (5). In contrast with the statements of Drago, their absolute magnitudes are quite important. Their constitution seems satisfactory in that there seems no need for new chemical constants and indicates that, essentially, the E and C parameters are not really that complex as suggested by Drago [2].

Moreover, although four parameters are indeed needed to reproduce the experimental ΔH_{AB} values, i. e. IE_A, EA_A, x_B and EA_B, as to be seen from Eq. (8), the combination of these parameters in terms of the *E-C* formalism seems unnecessarily complicated, at least for the ionic interactions under discussion in this report. This is again illustrated by the position taken by H-bonds in the McMillin-Drago analysis: in these cases indeed, practically the same conclusion is arrived at as in our earlier work on E_{HH} [5c].

4. On the Meaning of the Ratio C/E and the Hardness and Softness of Interacting Species (HSAB Rule)

Particular interpretations of the E and C parameters lead to a classification of interacting species which – with some exceptions – roughly parallels the classification obtained on the basis of the HSAB rule.

Considering the present analysis of the E and C parameters, it is unfortunate that the HSAB concept can not be given a quantitative expression. Interesting interpretations have already been proposed [6] but, in general, the concept remains rather vague, as to be seen for instance from the Pearson-Drago polemic on this topic [7].

It has been suggested however by Klopman [6] and, confirmed by Drago [2, 8] that the ratio C/E might be used as a measure for softness and hardness in the case of neutral acids and bases. For the acids A^+ taking part in the ionic reactions considered at present, the following result is immediately obtained from Equation (6):

$$C_A/E_A \approx EA_A \qquad (10)$$

if IE_A is sufficiently large in comparison with EA_A and, even when a disturbing effect such as the term x_B is present, Eq. (9) leads to practically the same result.

Hence, for these acids, the C/E ratio simply yields the electron affinity, which we currently [5] forwarded as being the capital quantity for describing chemical bonding effects in general. Despite the fact that this C/E ratio might intuitively be brought into relation with IE_A in the first place, since A appears as the ion A^+ in the interaction, the EA_A value turns out to be guiding for the chemical behaviour of the ion A^+ too.

This is somewhat the same situation as met in our discussion of the thermo- and electrochemical series of elements [5e], where also A appears formally as the ion A^+.

Therefore, in as far as the C/E ratio is a measure for the softness or hardness of an acid, our present analysis shows that these quantities are determined in first instance by the EA value and this confirms our earlier deductions about the HSAB rule [5c], especially when looking at the relation $E_{XX} = EA_X$ [5a, d]. For bases B^- taking part in the ionic reactions considered in this report, it is readily seen that, although C_B and E_B are both dependent on the properties of A, the ratio C_B/E_B is not:

$$C_B/E_B = EA_B^{-1} \qquad (11)$$

and this is a result difficult to extract from empirical considerations. If our deductions are correct, it is an interesting result since it implies that the C/E

ratio for acids and bases does not reflect in equivalent ways the bonding behaviour of the interacting species.

5. The Ionic Approximation to Chemical Bonding as the Physical Model Underlying the *E-C* formalism

The possibility to describe the $E-C$ equation as a first approximation of the bond energy equation given by the ionic approximation to chemical bonding obviously necessitates revision of the intuitive ionic-covalent resonance model used by McMillin and Drago [4] in order to interprete their results. In fact, there is no simple correlation between the $C_A C_B$ product (6), even in its corrected form (9) and the geometrical mean rule of Pauling and Sherman [9] it was originally correlated with [4]. In contrast, the ionic approximation to chemical bonding itself is compatible with Pauling's empirical bonding equation and, as such, it can readily be reformulated in terms of an ionic-covalent resonance concept.

Basicly, the ionic approach consists in explaining chemical bonding with the aid of completely ionic structures, for each of which the explanation is elementary electrostatics [5a].

The present analysis illustrates the formal consistency of this approximation to bonding, since it is striking to see that this approach can be brought into agreement with an empirically deduced and relatively complicated $E-C$ formalism and how, again, the attention is drawn to the electron affinity of elements, which now even turn out to be representing vaguely determined properties of interacting species, such as hardness and softness. Especially when Eqs. (10) and (11) are valid, both empirical approaches, $E-C$ and HSAB, are seen to lead to the ionic approximation to chemical bonding, which hopefully might bring in some rationalization among appearently different views about bonding.

Finally, we would like to point out that, at least for ionic interactions, the *E-C* formalism seems relatively simple to understand, but difficulties can be expected when the interaction of neutral species (donor-acceptor interactions) is to be described in a similar way. We are currently investigating the possibility of extending the ionic bonding mechanism to these reactions.

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