to pure ethylene polymerizing under hypothetical homogeneous conditions. The calculation also assumes that k_d is independent of pressure. The rate constants of unimolecular decomposition often decrease somewhat with pressure,[6] but the pressure coefficient of k_d for DTBP varies with the solvent,[22] and it seems hazardous to assume a particular correction factor valid for the present case. Experiments in which it was attempted to measure rates of initiation with diphenyl picryl hydrazyl gave unsharp induction periods but suggested that the initiation rate decreased by less than 30 per cent. as the pressure was increased over the interval considered in Table I. We conclude that the values of $R_p[M]^{-1}\{K_d[I]\}^{-1/2}$ listed provide a good approximation to the value of $k_p(\epsilon/k_t)^{1/2}$ and its pressure coefficient. Assuming the efficiency factor ϵ to be of the order of unity, it is of interest to compare the values of Table I with those obtained at lower pressures. Values of $k_p/k_t^{1/2}$ reported for low pressure systems at 130° vary from 0.03 to 0.3 l.$^{1/2}$ mole$^{-1/2}$ sec.$^{-1/2}$,[23] whereas an intermediate pressure system (less than 100 atm.) at 83° gave a value of 0.015[24] which, assuming $E_p - E_t/2$ (the activation energies for propagation and termination) to equal 7 kcal. would give 0.05 at 130°. Clearly, these values are on the average lower, but within about an order of magnitude of those reported here, and the difference is probably accounted for by the large pressure gap existing between them. Laita[24] has measured k_p and k_t separately and attributed the reason for the surprisingly low value of $k_p/k_t^{1/2}$ for ethylene, both, to the high termination constant of 10^9 and a rather low propagation constant.

Acknowledgments.—John J. Kurpen has helped with part of the experimental work and A. W. Wotring has given advice on equipment design. We are also indebted to Professor John S. Rowlinson and to the referee for pertinent comments.

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Thermodynamic Properties of Donor–Acceptor Complexes

BY WILLIS B. PERSON[1]

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The empirically observed linear relations between ΔS and ΔH for series of different donors with a standard acceptor are examined. Investigation of the various terms contributing to ΔH and ΔS suggests that the linear relations are due to a linear relation between ΔS_v and ΔE_0^0. The latter relation can occur if the logarithms of the new force constants in the complex are linearly proportional to ΔE_0^0. Empirical examination of this relation suggests it is probably reasonable for a series of chemically related donors with a standard acceptor.

Introduction

One of the characteristics of the thermodynamic properties of electron donor–acceptor complexes is that the entropies of formation of a set of complexes depend linearly on the enthalpy changes when these properties are compared for a series of related donors with a standard acceptor molecule. Such linear relations have been noted particularly for hydrogen bonded complexes[2] and for complexes in which iodine is the acceptor.[3–6] A qualitative explanation for this relationship is that the decrease in entropy on forming the complex becomes greater due to the more restricted configuration of the atoms as the complex becomes more stable (ΔH becomes a larger negative quantity). However, it is not obvious that the relationship between ΔS and ΔH should be *linear*, nor is it clear just which of the various contributions to ΔS and ΔH should be most important in determining the relationship between them. In order to gain some insight into these questions, let us briefly review the calculation of ΔH and ΔS for a typical donor–acceptor reaction.

Calculation of ΔH and ΔS

Consider the gas-phase reaction

$$NH_3 + I_2 = NH_3 \cdot I_2$$

The procedure for calculating ΔH and ΔS for such a reaction is very well known. Shepp and Bauer,[7] for example, give details of such calculations for similar reactions. The calculations for the ammonia–iodine reaction are summarized in Table I. We see there that ΔS is the resultant sum of a large negative term, ΔS_{tr+r}, due mostly to the loss of five translational and rotational degrees of freedom by the system, and a smaller positive terms, ΔS_v, due to the five new vibrational degrees of freedom of the complex.

In Table I, we see that the value of ΔS_{tr+r} is essentially independent of the donor. Varying the donor will change slightly the values of the mass ratio and the ratio of moments of inertia, but the dominant term in ΔS_{tr+r} is the term containing the

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(2) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

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TABLE I

SUMMARY OF THE CONTRIBUTIONS TO THE STANDARD ENTROPY AND ENTHALPY CHANGES[a] (AT 25°) FOR THE GAS-PHASE REACTION

$$NH_3(D) + I_2(A) = NH_3{\cdot}I_2(DA$$

$$\Delta S = \Delta S_{tr+r} + \Delta S_v$$

$$\Delta S_{tr+r} = R\left[-7/2\ln T + 3/2\ln(M_{DA}/M_DM_A) + 1/2\ln\frac{(I_x'I_y'I_z)_{DA}}{(I_x'I_y'I_z')_D(I_A')^2} - \ln\frac{\sigma_{DA}}{\sigma_D\sigma_A}\right] + 3.095$$

$$\Delta S_v{}^b = (\Delta S_v)_D + (\Delta S_v)_A + (\Delta S_v)_{5\text{new vibns.}}$$

$$\begin{aligned}
\Delta S_{tr+r}\ -7/2R\ln T &= -39.7\ \text{e.u.}\\
+3/2R\ln\frac{M_{DA}}{M_DM_A} &= -8.2\\
+1/2R\ln\frac{\Pi(I_i')_{DA}}{[\Pi(I_i')_D](I_A')^2} &= +3.1\\
-R\ln\frac{\sigma_{DA}}{\sigma_D\sigma_A} &= +1.4\\
+3.1 &= +3.1\\
\text{Total }\Delta S_{tr+r} &= -40.3\ \text{e.u}
\end{aligned}$$

ΔS_v (1) Assume $\nu_{NI} = 200$, $\nu_{\delta NI_2} = 50$ and $\nu_{NH_3rock} = 600$ cm.$^{-1}$. Then $\Delta S_v = +12.7$ e.u.

(2) Assume $\nu_{NI} = 50$, $\nu_{\delta NI_2} = 12.5$, and $\nu_{NH_3rock} = 150$ cm.$^{-1}$. Then $\Delta S_v = +25.3$ e.u.

$$\Delta S = -40.3 + 12.7 = -27.6\ \text{e.u.}$$

or

$$\Delta S = -40.3 + 25.3 = -15.0\ \text{e.u.}$$

In solution, $\Delta S_{soln.} = \Delta S + \Delta S_{solv.} = \Delta S + 6.4$

$\Delta S_{soln.} = -21$ or -9 e.u. ($\Delta S_{soln.}$ (exp.)$^c = -8$ e.u.)

$$\begin{aligned}
\Delta H &= \Delta E_0{}^0 + \Delta H^0{}_{tr+r} + \Delta H_v = \Delta H_{soln}\\
\Delta H_{tr+r} &= -(7/2)RT = -2.08\ \text{kcal. mole}^{-1}\\
\Delta H_v{}^b &= (\Delta H_v)_D + (\Delta H_v)_A + (\Delta H_v)_{5\text{ new vibns.}}
\end{aligned}$$

ΔH_v: (1) $\nu_{NI} = 200$, $\nu_{\delta NI_2} = 50$, $\nu_{NH_3rock} = 600$ cm.$^{-1}$

$\Delta H_v = 1.59$ kcal. mole^{-1}

(2) $\nu_{NI} = 50$; $\nu_{\delta NI_2} = 12.5$, $\nu_{NH_3rock} = 150$ cm.$^{-1}$

$\Delta H_v = 2.48$ kcal. mole^{-1}

$$\Delta H = \Delta E_0{}^0 - 0.5 \text{ or } \Delta E_0{}^0 + 0.4$$

[a] For a definition of terms see ref. 7, or K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953. [b] We assume that the contribution to ΔS_v and ΔH_v due to the change in frequencies of the donor molecule, $(\Delta S_v)_D$, or the acceptor molecule, $(\Delta S_v)_A$, due to complex formation is zero. For NH_3, which acts as a lone-pair donor, the bonding in the complex should be essentially the same as in the uncomplexed molecule. Thus its vibration frequencies should remain constant. For the I_2 molecule, which acts as a σ-acceptor with a resultant weakening of the I–I bond, the frequency might be expected to decrease from 200 to, perhaps, 150 cm.$^{-1}$. This will result in a contribution of about +0.5 e.u. to the total ΔS_v. [c] From ref. 6.

temperature, which is obviously constant for all donors. On the other hand, ΔS_v will be sensitive to the donor. For very weak complexes, the new vibrational degrees of freedom will not be much different from the translational and rotational degrees of freedom whence they came, so $\Delta S_v \approx +40$ e.u. For very strong complexes, $\Delta S_v \approx 0$, since there will be no contribution to the entropy if the vibrational degrees of freedom are too restricted. Thus, ΔS_v might be expected to vary between 0 and +40 from strong to weak complexes.

For the $NH_3{\cdot}I_2$ complex (C_{3v} symmetry) we expect one N–I stretching frequency, one doubly-degenerate N–I_2 bending frequency and one doubly-degenerate NH_3 rocking frequency to account for the five degrees of freedom in the complex. A reasonable upper limit to the vibration frequencies for ammonia complexes can be estimated from a knowledge of the spectra of the fairly strong metal-ammine complexes.[8] These values give the lower limit for ΔS_v in Table I. Another calculation using lower frequencies is included to show how ΔS_v varies.

In order to compare the calculated gas-phase entropy change in Table I to the experimental measurements made with dilute *n*-heptane solutions,[6] we must estimate the change in the entropy of solution between reactants and products. We cannot do this with much certainty, but if we assume that the solutions are ideal (or that the nonideality cancels) then the entropy of solution is given mainly by the change in standard states and is +6.4 e.u. for our example.[9] Thus, from the calculations in Table I, the entropy change in solution for the formation of the $NH_3{\cdot}I_2$ complex should vary from −22 to +6.4 e.u. depending on the strength of the interaction, as measured by the magnitude of the new vibrational frequencies. The experimental value is −8 e.u.[6] Thus, it

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(8) See, for example, E. P. Bertin, I. Nakagawa, S. Mizushima, J. L. Lane and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 525 (1958).

(9) See ref. 2, p. 348, for a detailed discussion of this conversion.

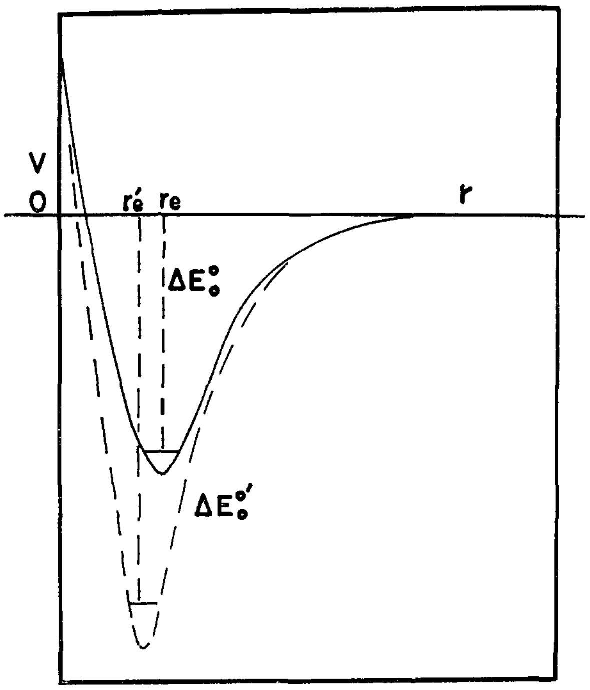

Fig. 1.—Hypothetical Morse curves for two chemically similar D–A bonds. Note the much higher curvature at the minimum for the curve associated with the stronger bond.

seems likely that it would be possible to calculate ΔS with reasonable values of the unknown frequencies.

A similar calculation for ΔH is also summarized in Table I. If we assume ideal solutions, we see that ΔH is essentially equal to ΔE_0^0. As complexes with different donors are examined, the variation in ΔH will be determined by the change in ΔE_0^0.

The Linear Relation Between ΔS and ΔH_0[10]

From the calculations summarized in Table I, we see that the variation in ΔS for a series of complexes (ignoring steric effects) is primarily due to the change in ΔS_v, while the variation in ΔH is due to the change in ΔE_0^0. Thus, the empirical linear relation between ΔS and ΔH implies that ΔS_v is related linearly to ΔE_0^0. Now let us consider the further implications of this argument and try to find some justification for such a relationship.

Shepp and Bauer have shown[7] that ΔS_v for weak[11] complexes (such as $NH_3 \cdot I_2$) is given by

$$\frac{\Delta S_v}{R} \simeq \text{const.} - \frac{1}{2} \ln \prod_{i=1}^{5} k_i + 5/2 \ln <\mu> + 1/24 \frac{h}{2\pi kT} \sum_{i=1}^{5} \frac{k_i}{<\mu>} \quad (1)$$

Here the five k_i's are the force constants for the five new vibrations of the complex, and $\langle\mu\rangle$ is a "properly averaged reduced mass."[7] For our example,

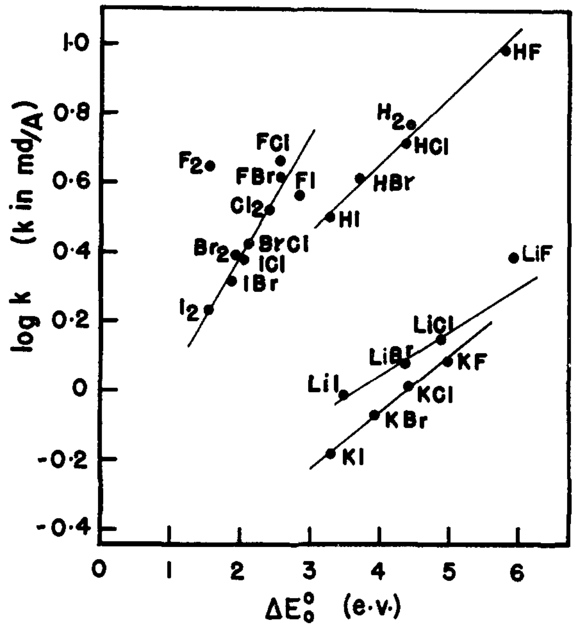

Fig. 2.—Plot of the logarithm of the stretching force constant against the dissociation energy for a few typical types of compounds. The data are from ref. 13, except for the lithium halides, which are taken from W. Klemperer, W. G. Norris and A. Büchler, *J. Chem. Phys.*, **33**, 1534 (1960).

and for most molecular complexes, $\langle\mu\rangle$ will be a fairly large number (approximately M_D) so the last term in equation 1 is probably negligible. If we find empirically that the linear relation between ΔS and ΔH exists independently of the mass of the donor, as is apparently true, then we must conclude that the linear relation results from a linear relationship between $\Sigma \log k_i$ and ΔE_0^0.[12]

In order to investigate whether such a relationship is reasonable, let us consider just the N–I stretching vibration, since this is the easiest one to understand. The arguments for the rocking motions of the NH_3 group will be more complicated, but essentially similar. First of all, we can easily see that there should be *some* relationship between k_{NI} and ΔE^0_0. The potential energy associated with stretching the N–I bond will be given approximately by a Morse potential curve such as that shown in Fig. 1. For a stronger complex, the dissociation energy, ΔE_0^0 will be greater, r_e will be smaller and the curvature at the minimum, $(\partial^2 V/\partial r^2)_{r=r_e} = k_{N-I}$ will therefore also be greater. These relations are shown in Fig. 1. In fact k, r_e and ΔE_0^0 are related approximately by $kr_e/\Delta E_0^0 \simeq$ constant.[13] However, it is not easy to see the relation between any two of these three parameters.

In order to determine whether or not log k might be expected to be *linearly* proportional to ΔE_0^0, we have examined the force constants for a number of diatomic molecules empirically. We have plotted

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[10] The argument given here assumes that the entropy and enthalpy changes on solution do not vary with the donor. Partial justification for this assumption of ideal solutions is provided by the fact that K_f for I_2 complexes does not usually vary markedly as the solvent is changed. No positive experimental test is known to this author, however.

[11] This equation is a classical expression valid only for low frequencies. Pitzer [K. S. Pitzer, *J. Am. Chem. Soc.*, **79**, 1804 (1957)] indicates that such formulae are accurate for $\nu < 1.1\ T$.

[12] Ignoring the variation of ΔS_V with ln $<\mu>$ seems to introduce a flaw in the argument at this point. However, this term probably helps to cancel the terms containing the mass and moment of inertia ratios in ΔS_{tr+r}, so that *total* entropy change, ΔS, is essentially independent of the mass of the donor.

[13] See, for example, G. R. Somayajulu, *J. Chem. Phys.*, **33**, 1541 (1960).

log *k vs.* ΔE_0^0 for over 50 diatomic molecules for which data were available. Some typical results are shown in Fig. 2. For each series of chemically related molecules a linear relation is indeed found. For example log *k* is linearly proportional to ΔE_0^0 for the halogens (except for F_2); data for the hydrogen halides fall on another line, and so forth. Deviations do occur, and one must use different straight lines for different types of compounds, but Fig. 2 illustrates that a linear relation between the logarithm of the stretching force constant and the dissociation energy probably exists for a series of chemically similar bonds in stable diatomic molecules.

We suggest, therefore, that the linear relation between log k_{DA} and ΔE_0^0 for the weak donor–acceptor complexes, which is required by the empirical observation that ΔS and ΔH are linearly related, is not at all unlikely. Extension of the results shown in Fig. 2 to the weak donor–acceptor complexes requires quite an extrapolation. (If $\nu_{N-I} = 50$ cm.$^{-1}$, as in Table I, then $k_{NI} \simeq 0.02$ *md/A* for the $NH_3 \cdot I_2$ complex. Values of *k* this small are not shown at all in Fig. 2.) However, there does not seem to be any reason to question that log *k* would not be linearly related to ΔE_0^0 for weak complexes as well as for molecules.

We might wonder why such a relationship would hold between log *k* and ΔE_0^0. The answer is probably just that the use of the logarithmic function of *k* compresses the scale so that a linear relation holds over the rather limited range of *k* values which occur in a series of chemically related compounds. The value of ΔE_0^0 does not change widely for a series of related donor-acceptor complexes (ΔH goes from -4 to -12 kcal. for the amine complexes[6]). On the other hand *k* undergoes a much larger proportionate change (possibly k_{NI} changes by a factor of 20–50 from the weak $NH_3 \cdot I_2$ complex to the stronger complexes). The use of log *k* decreases the extent of this variation so that a linear relation may well be found.

By the same reasoning we can justify a linear relation between log *k* and ΔE_0^0 for the bending force constants as well. The magnitudes of these constants will certainly be dependent on ΔE_0^0, and the use of the logarithm ought to result in linear relations for these force constants as well. Thus, the linear relation between ΔS_v and ΔE_0^0 demanded by the empirical linear relation between ΔS_v and ΔE_0^0 seems to be due to the following combination of circumstances. (1) The new vibrational frequencies are low ($\nu < 1.1\ T$), so that the use of the classical equation 1 for ΔS_v is justified. (2) In this equation ΔS_v is linearly dependent on log *k*, since the higher terms in the expansion are negligible. (3) The use of the logarithm function slows the variation so that log *k* is proportional to ΔE_0^0. (4) The mass terms essentially cancel in computing ΔS, and the other terms (except log *k*'s and ΔE_0^0's) contributing to ΔH and ΔS are essentially constant for a series of related complexes.

It is certainly not difficult to understand why the empirical correlations of ΔS with ΔH give lines with different slope for donors of different chemical types.[5] Furthermore, the deviations observed for the tertiary amines[6] are easy to understand in terms of an additional steric contribution to the entropy due to the restriction in configuration of the alkyl groups when the complex forms.

Let us now test the ideas presented here by attempting to predict the slope of the lines relating ΔS to ΔH. *If* the linear relation between log *k* and ΔE_0^0 for the *weak* complexes is similar to those shown in Fig. 2, we see from that figure that the slopes $\Delta(\log k)/\Delta(\Delta E_0^0, \text{e.v.})$ are expected to vary from 0.2 to 1. For simplicity take this slope to be 1.0 and assume that this slope applies for all five force constants for the new vibrations of the complex. From equation 1 and the argument presented above, we see that the slope of the line relating ΔS to ΔH will be given by

$$\Delta(\Delta S)/\Delta(\Delta H, \text{kcal.}) = R \cdot 5/2 \cdot \frac{2.303}{23}\,[\Delta(\log k)/\Delta(\Delta E_0^0, \text{e.v.}) \qquad (2)$$

Here *R* is the gas constant in cal. deg.$^{-1}$ mole^{-1}, 2.303 is the conversion from log to $\ln_e$, and 23 is the conversion form e.v. to kcal. mole^{-1}. From equation 2, we find that the slope predicted for $\Delta(\Delta S)/\Delta(\Delta H)$ is 0.5. The reported value for the amine complexes is about 2.0.[6]

The discrepancy between these two values for the slope suggests that the slope, $\Delta(\log k)\Delta(\Delta E_0^0, \text{e.v.})$, should be much larger for weak complexes than for the stronger bonds shown in Fig. 2. If this slope were about 4.0 instead of 1.0, the predicted slope would agree with the reported experimental value.

Support for this higher value of the slope comes from the following consideration. We have seen above (Table I) that the frequencies in the stronger complexes must be increased by about a factor of four in order to obtain agreement with the observed entropies. The force constant will then increase at least by a factor of 16. Thus, $\Delta(\log k)$ will be about 1.2 over the range of amine complexes. The change in energy of formation $\Delta(\Delta E_0^0)$ is about 8 kcal./mole,[6] or 0.3 e.v. Thus. $\Delta(\log k)/(\Delta(\Delta E_0^0)$ is about 4.0 from this argument.[14]

We may further note qualitatively that a greater dependence of *k* on ΔE_0^0 may be expected for weak complexes than for stronger ones, since *k* should change very rapidly as the potential energy curve begins to form a minimum.

Conclusion

In the examination we have made of the linear relationships which are found empirically between ΔS and ΔH for donor–acceptor complexes, we have shown that this empirical relation implies that there is a linear relation between Σ log k_i and ΔE_0^0. For complexes of the type we have considered here ($NR_3 \cdot I_2$, C_{3v} symmetry) the only other explanation for the linear relationship appears to be the possibility that the entropy and enthalpy of *solvation* are more important than the other contributions to ΔS and ΔH which we have considered and that $\Delta S_{solv.}$ depends linearly on ΔE_0^0. Since this possibility does not seem reasonable,[10] we accept the implication that log *k* is linearly related to ΔE_0^0. To test this suggestion, we examined in Fig. 2 some data for a number of stable diatomic molecules, where the linear relation appears to be reason-

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[14] The exact agreement here is fortuitous, obviously.

able for stretching vibrations. Further argument suggests that this relationship probably holds also for the bending force constants.

Finally, we should like to point out the general applicability of these arguments to a wide number of phenomena. Linear relations between ΔH and ΔS are very important in organic chemistry. Taft has pointed out[15] that this condition is necessary if the Hammett sigma relations are to hold. The empirical success of these relations may well be due to the same set of curious circumstances which leads to the observed linear relation between ΔS and ΔH for iodine complexes.

Acknowledgments.—Partial financial support from the National Science Foundation is gratefully acknowledged. It is a pleasure to acknowledge helpful discussions with Professors G. C. Pimentel and R. S. Mulliken.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

Electronegativity. I. Orbital Electronegativity of Neutral Atoms

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Electronegativity is discussed on the basis of Mulliken's definition ($\chi = E_v + I_v$), which leads to the conclusion, that it is not a property of atoms in their ground state, but of atoms in the same conditions in which they are found in molecules, the valence state. Valence state promotion energies are calculated and reported for a large variety of states of the atoms and ions of the first and second period. Combining these promotion energies with ionization potentials and electron affinities yields the electronegativities of a number of valence states. It is found that electronegativity can be defined in this way only for bonding orbitals, and the term "orbital electronegativity" is suggested for the values listed. The calculated orbital electronegativities for σ orbitals are found to be higher in every case than for π orbitals, and to be linearly related to the amount of s character in the hybrid orbitals. As expected, the electronegativity increases with increasing s character of the orbital considered.

Electronegativity is a measure of the power of a chemically bonded atom to attract electrons to itself. This concept, first introduced by Pauling,[1] was rapidly accepted and many applications have been found in all fields of chemistry. Pauling set up a scale of electronegativities of the elements, by comparing the energy of the heteronuclear bond A–B with the average, arithmetic[2] or geometric,[3] of the homonuclear bond energies of the molecules A–A and B–B. With this method, no absolute values can be obtained, and because of the inherent uncertainties in thermochemical data this relative scale is somewhat indefinite. Despite these inadequacies, a wide variety of chemical phenomena have been reasonably explained by use of electronegativities.

The degree of electron transfer in the bond A–B toward the negative atom may be regarded as good measure of electronegativity difference. Unfortunately, such electron transfer is not directly observable and calculations of electron distribution for any molecule is an involved problem in itself, even for simple molecules, and not a suitable method to use as a base for an electronegativity scale. Since such exact results are not available, several alternate scales of electronegativity have been proposed, based on various observable properties of molecules which are related to the electron distribution. Such properties are dipole moments,[4] force constants[5] and nuclear quadrupole resonance frequencies.[6] The accomplishments in this field have been carefully reviewed by Pritchard and Skinner.[7]

The best theoretical definition of electronegativity is given by Mulliken,[8] based on the concept that the energy expended in going from the covalent molecule A–B to the ionic states A^+B^- and A^-B^+ is equal if A and B have the same electronegativity. Thence, he concludes[9] that the electronegativity of A is proportional to

$$\chi^A = I_v^A + E_v^A \qquad (1)$$

where I_v^A and E_v^A are the appropriate valence state ionization potential and electron affinity, respectively. Electronegativities obtained from equation 1 are, to a good approximation, proportional to Pauling's values.[10]

Pauling[1] defined electronegativity as an atomic property and believes[3] that it is virtually constant, even for different oxidation states of any one element. Thus, he quotes electronegativities of iron as, 1.8 (Fe^{2+}) or 1.9 (Fe^{3+}); of copper as 1.9 (Cu^+) or 2.0 (Cu^{2+}); and of tin as, 1.8 (Sn^{2+}) or 1.9 (Sn^{4+}).[11] This conclusion seems somewhat surprising on the basis of the Mulliken definition, since one hardly expects ionization potential and electron affinity, or even their sum, to be the same for different oxidation states, and, hence, demands closer examination, particularly because differences of electronegativities have been noted by many authors.

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