

% were examined. Redistilled tetralin and reagent-grade benzene were added to the 30,000 c.s. silicone polymer and gel determinations made on samples of the irradiated solutions. In all cases, the gel yields are based on the polymer content of the original solution. From the corrected gel yields for doses in the range 10 to 40 Mr., the equivalent dose, D' , was determined from Fig. 1 of the preceding paper. In Fig. 3 the suppression of crosslinking, D'/D , is shown as a function of the amount of diluent.

Compared to the mercaptans, described in the previous section, tetralin is much less effective in retarding crosslinking. Thus, at 10 weight % (tetralin ≈ 0.75 mole/l., butyl mercaptan ≈ 1.1 mole/l.), the D'/D ratios are 0.4 and 0.1, respectively, for tetralin and *n*-butyl mercaptan. Benzene is even less effective than tetralin. From

Fig. 3 it can be seen that it requires 50% benzene (6.4 mole/l.) to produce the same suppression of crosslinking, $D'/D = 0.25$, as only 20% tetralin (1.5 mole/l.). The fact that, on either a weight or a molar basis, considerably more benzene than tetralin is required to suppress crosslinking suggests that such factors as hydrogen transfer and radiation yield of radicals, both of which should be higher for tetralin than for benzene, are more important than "protection" by energy transfer to aromatic solvent molecules in this polymer system.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, UNIVERSITY PARK, LOS ANGELES, CALIFORNIA]

Electronegativity, Non-bonded Interactions and Polarizability in the Hydrogen Halides and the Interhalogen Compounds

BY RONALD F. BROWN

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The dissociation energies of the compounds in the title have been corrected for non-bonded interactions by an empirical scheme. The corrected values were used to calculate the electronegativities for the five elements. A new scale of electronegativity is proposed based upon the ionization energy of hydrogen. Using the charges predicted by the electronegativity values and the charges calculated from dipole moments of the hydrogen halides, inductive charge transmission coefficients were obtained and shown to be related to the molecular geometry and to the longitudinal polarizabilities of the bonds.

Despite wide usage and acceptance, the concept of electronegativity and the relationship to ionic character have remained obscure. We propose to introduce two factors, inductive charge transfer and non-bonded interactions, in considering the problem. By correction of the experimental dissociation energies for a series of diatomic molecules for non-bonded interactions it looked to be possible to use Pauling's¹ method to calculate a set of electronegativity differences from which a revised set of electronegativities could be obtained. In order to be of value, such a set should show very little, if any, inconsistency between differences in electronegativity taken from the set as compared with those calculated from the corrected dissociation energies.² With such electronegativity values, a comparison with the charges as calculated from dipole moments could be made and a transmission coefficient for charge transfer (or partial neutralization of charge across a given bond) calculated. Such transmission coefficients should bear a relationship to the geometry of the molecule as should the longitudinal polarizability of the bond. This program has been carried through, and considering the simplicity of the model the results have been surprisingly satisfactory.

(1) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, p. 80, 82, 88.

(2) See Table III in M. L. Huggins, *THIS JOURNAL*, **75**, 4123 (1953), for an example of the lack of concordance even in the revised electronegativities proposed by Huggins, but using experimental dissociation energies.

It seems to be commonly agreed that non-bonded interactions exist in those molecules in which filled orbitals lie in proximity to each other. Such interactions have been used successfully in estimating the enthalpy and entropy of hydrocarbons,³ and Mulliken⁴ has considered the halogen molecules from the viewpoint that negative bond order is the counterpart in l.c.a.o. m.o. theory of nonbonded repulsions in v.b. theory. Such a repulsion in a halogen-halogen bond (absent or weak in a hydrogen-halogen bond) should weaken the bond.⁴ According to v.b. theory non-bonded interactions exist not only between lone pairs on adjacent atoms but also between every electron on one atom and every electron of like spin on the other. Of these non-bonded interactions, those between electrons in orbitals of like symmetry (both σ , or both π^+ or both π^-) are repulsions, and these are often strong, just as between two lone pairs one on each atom. Non-bonded attractions occur between electrons of unlike symmetry and on different atoms (σ_A , π_B attractions, π_A^+ , π_B^- attractions). The net effect of the non-bonded interactions not involving lone pairs on each atom may be and is fairly large. Magnitudes of terms of this sort have been discussed by Mulliken⁵ who gives earlier references. Since the approach used here has been empirical,

(3) K. S. Pitzer, *ibid.*, **70**, 2140 (1948); **72**, 4493 (1950).

(4) R. S. Mulliken, *ibid.*, **77**, 884 (1955); *J. Chem. Phys.*, **23**, 2343 (1955).

(5) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

we have assumed only that a repulsion exists in all the compounds considered except in hydrogen and hydrogen halides. The crude method used glosses over any of the finer details.

In order to set up a reasonable, though empirical, method of estimating the magnitude of such an effect, use was made of a correction term A/r_{AB}^n such that the repulsion energy, R_{AB} is set equal to $-D_{AB}A/r_{AB}^n$, in which A is a constant and D_{AB} is the experimental dissociation energy of the substance AB. The interatomic distance was used for r_{AB} since the p orbitals lie parallel to each other at that distance. The exponent n , analogous to the Born exponent (note that the correction term is similar in form to the Be^2/r^n term used to express the repulsion energy term in the equation for crystal energy)⁶ was chosen by the use of equation 1 in which Z is an atomic number. This equation

$$n_{AB} = 2 + \sqrt{Z_A + Z_B} + \sqrt{Z_A - Z_B}; Z_A \geq Z_B \quad (1)$$

was selected after experimentation with a number of other relations between n and Z failed to reproduce the values of n_{AB} ordinarily used such as 7 for neon-neon like ionic repulsions, 9 for argon-argon like ionic repulsions, etc.⁶ The calculated values of n_{AB} for the interhalogen compounds are listed in Table I along with the values of r_{AB} used and the calculated values of r_{AB}^n .

TABLE I
VALUES OF n_{AB} AND $(\sigma - 1)_{AB}$ FOR $A = 1.9741$

Cmpd AB	n_{AB}^a	$r_{AB}, \text{\AA}^b$	r_{AB}^n	$\frac{(\rho - 1)_{AB}}{-(R/D)_{AB}}$
FF	6.243	1.418	8.852	0.223000
FCI	9.927	1.628	126.31	.015629
FBr	13.732	1.759	2334.0	.000846
FI	16.507	1.915	45482	.000043
ClCl	7.831	1.988	217.24	.009087
ClBr	13.454	2.138	27533	.000072
ClI	16.367	2.324	986500	.000002
BrBr	10.367	2.283	5206.3	.000379
BrI	15.623	2.478	1,436,100	.000001
II	12.296	2.667	172760	.000011

^a The exponent n in r^n was calculated from equation 1.

^b All bond distance values are from L. E. Sutton, ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

A serious criticism of the correction term used here is that if the repulsion energy is at all sizable, the experimental bond length should be longer than normal, and the correction term less than it otherwise would be. This might be taken care of by the use of a modified Morse equation in which an extra exponential repulsion term is introduced or by corrections to the existing exponential repulsion term. A plot of such a modified equation should fit the experimental dissociation energy and bond distance while the absence of the modifying terms would represent the case in which the extra repulsion is not present and which should lie below and to the left of the modified plot. Efforts were made along this line, but since such an approach required a knowledge of the variation of r_{AB} with D_{AB} which in turn required that the Morse function be dependable at distances from the minimum where it is

(6) Ref. 1, pp. 507, 509.

known to be inaccurate, and since we failed to find reasonable criteria for the needed arbitrary factors, no satisfactory results were obtained. It has been found⁷ that the power term form is at least as good as the Morse form exponential in other instances. Since the case of fluorine would be the most seriously in error by the approach used here, the fluorine molecule was used as a fixed point in the selection of the constant, A , with the expectation that the error so introduced for the other molecules would be small because of the magnitude of the resulting r_{AB}^n .

Since the dissociation energy, D , is taken with a positive sign, R is negative, and a normal bond energy, N , may be defined from the relation $D_{AB} = N_{AB} + R_{AB}$. In this manner one may consider the normal bond energy as being that which would be calculated from covalent and ionic canonical forms if all other effects were eliminated, all other effects including, among other things, non-bonded repulsions, hybridization, conjugation, etc., so that $D = N + R + H + C + \dots$. Here, for the diatomic molecules being considered, all terms but R are neglected. For convenience in calculation, another term was defined, $\rho_{AB} = (N/D)_{AB} = (D - R)/D$ so that $(\rho - 1)_{AB} = -(R/D)_{AB}$ which is tabulated in Table I.

An innovation introduced at this point is a redefinition of Pauling's¹ Δ' which he used as $\Delta'_{AB} = D_{AB} - \sqrt{D_{AA}D_{BB}}$, the primed delta being used to distinguish the use of the geometric mean from the plain delta as used for the arithmetic mean. Instead of using the experimental dissociation energies, D , we use the normal bond energies, or

$$\Delta'_{AB} = N_{AB} - \sqrt{N_{AA}N_{BB}} = \rho_{AB}D_{AB} - \sqrt{\rho_{AA}\rho_{BB}D_{AA}D_{BB}} \quad (2)$$

Pauling then proceeded to divide Δ or Δ' by an arbitrary constant (23.06, the number of kilocalories in an electron-volt), to take the square root, and use the result as the difference in electronegativity between "A" and "B." If we follow such a procedure as well and if the electronegativities of a series of elements lie in the order $E_A > E_B > E_C$, then equation 3 follows.⁸

$$\sqrt{\Delta'_{AC}} = \sqrt{\Delta'_{AB}} + \sqrt{\Delta'_{BC}} \quad (3)$$

In order to use this equation, the constant A the numerator in the correction term, was evaluated by selecting an arbitrary value of 0.1 for $(\rho_{FF} - 1)$. This in turn corresponded to an arbitrary value for A from which a value of $(\rho_{AB} - 1)$ and Δ'_{AB} could be evaluated for every other interhalogen compound. Then (3) was used to find the discrepancy in the equality between the left- and right-hand sides of the equation for all possible "ABC" sequences. The process was repeated by selecting a new arbitrary value, say 0.2 for $(\rho_{FF} - 1)$, and finding a new series of discrepancies by the use of (3). It soon became evident that most of the discrepancies decreased rapidly as $(\rho_{FF} - 1)$ increased, soon changed sign and began to increase in the opposite direction. By interpolation $(\rho_{FF} - 1) = 0.22300$

(7) E. C. Baughan, *Trans. Faraday Soc.*, **53**, 1046 (1957); **55**, 736 (1959).

(8) C. A. Coulson, "Valence," Oxford University Press, London, 1952, p. 133. Note that any divisor used is eliminated in equation 3.

was found to fit equation 3 for $\sqrt{\Delta'_{\text{FBr}}} = \sqrt{\Delta'_{\text{FCl}}} + \sqrt{\Delta'_{\text{ClBr}}}$, and $A = 1.9741$. Table I lists the values of $(\rho_{\text{AB}} - 1)$ calculated for $A = 1.9741$. However, it turned out that some of the discrepancies remained, specially after the hydrogen halides were considered in which $D_{\text{HH}} = N_{\text{HH}}$, and $D_{\text{HX}} = N_{\text{HX}}$ were used. This meant that an estimate of error needed to be made for most of the $\sqrt{\Delta'_{\text{AB}}}$ values. Instead, the procedure was reversed and values of the dissociation energies needed to give no discrepancies in applying equation 3 were calculated on the assumption that the D_{AB} values of all the elements (except hydrogen) and compounds were subject to experimental errors of the order of up to 0.4 kcal. This was done by assuming an experimental error, δ , in D_{FF} of 0.2 kcal., so that $D^*_{\text{FF}} = 38.006$ kcal. instead of $D_{\text{FF}} = 37.806$ kcal. Using all other D_{AB} values as given, δ values or discrepancies were calculated for the three interhalogen fluorine compounds by the use of equation 3. Next, a value of $D^*_{\text{ClCl}} = 58.084$ instead of $D_{\text{ClCl}} = 57.884$ was used, returning to $D_{\text{FF}} = 37.806$ kcal., and keeping all other D_{AB} values as given. Then δ values for the three interhalogen compounds containing chlorine were calculated. In turn, the D value of BrBr, II, and each hydrogen halide was increased by 0.2 kcal. and the δ values for the corresponding interhalogen compounds determined. The results were set up in a table from which it was found that, by assigning values of δ as shown in Table II to the D_{AB} values for the halogens and hydrogen halides and calculating the δ values for the interhalogen compounds as given in Table II, the largest δ value was 0.453 for FI, all others being less. Since an accuracy of better than 0.4 kcal. seldom is claimed for D_{AB} determinations (the values used in Table II to three decimal places were taken from tables which required comparison from one temperature to another for a given substance), the agreement is excellent for the purpose of obtaining a consistent set of differences proportional to electronegativity differences, namely $\sqrt{\Delta'_{\text{AB}}}$. The values of D used in Table II were taken from recent compendia and checked with later reports. The consistency of the whole set of calculations tends to sustain the reliability of the values used. That a consideration of non-bonded repulsions should give rise to such concordance of $\sqrt{\Delta'_{\text{AB}}}$ values, crude though the method is, verifies the correctness of the approach used. It is of interest to note that the magnitude of R falls rapidly with increase in size of the atoms, being -8.431 kcal. for F-F, -0.528 for Cl-Cl, -0.952 for F-Cl, -0.052 for F-Br, and practically negligible for all the others, although even the value of -0.004 for Cl-Br is necessary in order to give a perfect fit.

So long as no quantitative use was made of electronegativity values, E , the original scale proposed by Pauling has remained in use even though many efforts have been made to improve the precision of the assignments.⁹ Now, with the more consistent values available, for five elements at least, it would be useful to change the scale to one in which a difference in electronegativity would give the charges

(9) See, for example, (a) ref. 2 and (b) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

on the atoms which arise from this cause alone, that is, apart from atomic and homopolar dipole effects and before the operation of inductive charge transfer comes into play. At first, Pauling¹ converted Δ into electron volts before taking the square root, $(E_{\text{B}} - E_{\text{A}}) = \sqrt{\Delta/23.06}$, and then selected values of E to satisfy approximately the various differences in electronegativity. Later on he arbitrarily selected 30 kcal. as the divisor for Δ' . We propose a scale by dividing Δ' by the energy of the hydrogen atom (the ionization energy of hydrogen) before taking the square root. With our proposal, the assumption is made that the difference in electronegativity becomes equal to the charge, x_{AB} , or

$$E_{\text{B}} - E_{\text{A}} = x_{\text{AB}}/x_{\text{H}} = \sqrt{\Delta'/I_{\text{H}}} = 0.05645 \sqrt{\Delta'} \quad (4)$$

This may be shown to be numerically and dimensionally consistent as follows. Squaring (4) gives $x^2_{\text{AB}}/x^2_{\text{H}} = \Delta'/I_{\text{H}}$. But $I_{\text{H}} = -e^2x^2_{\text{H}}/2r_{\text{H}} = 313.85$ kcal. Substituting for I_{H} , $x^2_{\text{AB}}/x^2_{\text{H}} = -2\Delta'/r_{\text{H}}/e^2x^2_{\text{H}}$ from which it is found that $\Delta' = -e^2x^2_{\text{AB}}/2r_{\text{H}}$ which is the energy necessary to separate to an infinite distance the charges x_{AB} and $-x_{\text{AB}}$ from a common center of density but at a radius equal to the Bohr radius, $r_{\text{H}} = 0.5292$ Å. Hence, the division of Δ' by I_{H} is a means of comparing x_{AB} and x_{H} under identical conditions. Since x_{H} is the electronic charge, namely one, the ratio $x_{\text{AB}}/x_{\text{H}}$ is numerically equal to the charge, x_{AB} , on an atom in the bond but is dimensionless. In effect (4) represents a normalization of electronegativity differences¹⁰ such that if the origin of the scale be properly chosen no value of E will exceed one.

In order to set the origin for the scale, the electronegativity of hydrogen was calculated as the average of the ionization energy and electron affinity as originally suggested by Mulliken and extended by Moffitt.^{9b} This average of 165.94 kcal. was divided by I_{H} to give $E_{\text{H}} = 0.5287$. Hydrogen was chosen because no complications concerning valence states intrude and the average value is relatively reliable. The use of the $E_{\text{B}} - E_{\text{A}}$ values from Table II allows the evaluation of $E_{\text{F}} = 0.9872$, $E_{\text{Cl}} = 0.8107$, $E_{\text{Br}} = 0.7723$ and $E_{\text{I}} = 0.7018$ to be made.

Table III presents a comparison of electronegativity values on the basis of the old convention and on the basis proposed here. The various scales are comparable but the differences are noticeable. The principal difference is the higher values in the proposed scale for E_{Cl} , E_{Br} and E_{I} while E_{F} and E_{H} are nearly the same as on the Pauling or Huggins lists. The Mulliken and Moffitt list is lower in general than the other three even if E_{H} is given a high value as in column 4. This probably reflects the uncertainties involved in the calculation of the valence state energy by their method for the halogens.

(10) One should inquire into the use of the enthalpy change for the reaction $\text{H-H} \rightarrow \text{H}^+\text{H}^-$ (no change in internuclear distance) as a normalizing factor. Although attractive at first glance because it represents a change from an almost pure covalent bond to an ionic bond, the objection lies in "almost pure," namely the H-H bond energy contains some ionic terms, etc., while the enthalpy change itself is not known with precision. If, however, one were to use a value of 176 kcal. for this purpose, then $E_{\text{H}} = 0.9428$, and the $E_{\text{B}} - E_{\text{A}}$ values in Table II should be multiplied by 1.3354 so that $E_{\text{F}} - E_{\text{H}}$, for example, would become 0.6123, and $E_{\text{F}} = 1.5551$. As a result $E_{\text{F}} - E_{\text{N}_\text{A}}$ would certainly be greater than unity.

TABLE II

Cmpd. AB	NORMAL BOND ENERGIES ^a AND ELECTRONEGATIVITY DIFFERENCES										
	$D_{AA},^b$ kcal.	$\delta_{AA},^d$ kcal.	$N_{AA},$ kcal.	$D_{BB},^b$ kcal.	$N_{BB},$ kcal.	$D_{AB},^c$ kcal.	$\delta_{AB},^d$ kcal.	$N_{AB},$ kcal.	$\Delta',$ kcal.	$\sqrt{\Delta'}$	$(E_B - E_A)^*$
HF	104.180	None	104.180	37.806	46.237	135.193	0.200	135.393	65.989	8.123	0.4585
HCl	104.180	None	104.180	57.884	58.612	103.095	None	103.095	24.953	4.995	.2820
HBr	104.180	None	104.180	46.070	46.087	87.510	0.400	87.910	18.618	4.315	.2436
HI	104.180	None	104.180	36.084	36.384	71.372	-.400	70.972	9.405	3.067	.1731
ClF	57.884	0.200	58.612	37.806	46.237	61.265	-.374	61.843	9.785	3.127	.1765
BrF	46.070	None	46.087	37.806	46.237	60.312	.303	60.667	14.505	3.808	.2149
IF	36.084	0.300	36.384	37.806	46.237	67.035	-.453	66.585	25.570	5.057	.2854
BrCl	46.070	None	46.087	57.884	58.612	52.201	.232	52.437	0.463	0.680	.0384
ICl	36.084	0.300	36.384	57.884	58.612	50.334	-.435	49.899	3.719	1.929	.1089
IBr	36.084	0.300	36.384	46.070	46.087	42.511	-.004	42.507	1.558	1.249	.0705

^a See the text for definition. ^b D for the elements from D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," No. 18 of Advances in Chemistry, American Chemical Society, Washington, D. C., 1956. ^c D for the hydrogen halides from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular of N.B.S. 500, U.S.G.P.O., Washington, D. C., 1952. D for the interhalogen compounds from W. H. Evans, T. R. Munson and D. D. Wagman, *J. Research Natl. Bur. Standards*, **55**, 147 (1955). ^d See text; δ_{FF} is zero. ^e $E_B - E_A = 0.05645 \sqrt{\Delta'} = \sqrt{\Delta'}/I_H$.

TABLE III

COMPARISON OF ELECTRONEGATIVITY VALUES AND SCALES								
Paul- ing ^a	Hug- gins ^b	M and M ^c	This paper ^d	Paul- ing ^e	Hug- gins ^e	M and M ^e	This paper	
F	4.0	3.90	3.91	4.000	1.01	0.94	0.907	0.9872
Cl	3.0	3.15	3.00	3.285	0.76	.76	.696	.8107
Br	2.8	2.95	2.76	3.129	.70	.71	.640	.7722
I	2.5	2.65	2.56	2.844	.63	.64	.594	.7018
H	2.1	2.20	2.28	2.142	.53	.53	.529	.5287

^a Ref. 1, p. 60. ^b Ref. 2. ^c H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955), the values they give in e.v. calculated by the method of Mulliken and Moffitt multiplied by 1/3.15. ^d Our scale values multiplied by 4.0519 in order to give $E_F = 4.00$. ^e Values from columns 2, 3 and 4 multiplied by a factor such that $E_H = 0.5287$ in each.

Another comparison is made in Table IV by displaying $E_B - E_A$ values calculated in three different ways, namely, (1) by means of the arithmetic mean from D values, (2) by means of the geometric mean from D values and (3) by the use of N values through the geometric mean as proposed in this paper. Alongside are shown the $E_B - E_A$ differences calculated from the last 4 columns of Table III. In going from the arithmetic mean method, column 2, Table IV, to the geometric mean method, column 3, all the differences in electronegativities are increased. Then the use of N values, column 4, results in a small decrease and illustrates the effect of including the repulsion and experimental error corrections as compared to column 3. None of the older electronegativity scales, column 5, 6 and 7, gives complete agreement with any of the calculated differences, columns 2, 3 and 4. The scale proposed in this paper fits exactly with column 5, but it was set up to do so. Nevertheless, the deviations of the previous scales from a good fit are demonstrated.

The charges set up in a diatomic molecule by electronegativity differences are neutralized partially by inductive transfer of the charge difference across the bond. The actual situation is more complex than this because of the presence of homopolar terms, etc. Nevertheless, let us define a transmission coefficient as $a = (x_B - x_{B_0})/(x_A - x_{B_0})$ in which x_A and x_B are the final charges on A and B after transmission of charge has occurred, and x_{A_0} and x_{B_0} are the initial charges as set up by electronegativity differences and other forces.

Then $x_B = x_{B_0} + a(x_A - x_{B_0})$ and $x_A = x_{A_0} - a(x_A - x_{B_0})$. These equations may be solved to give $x_A = (x_{A_0} + ax_{B_0})/(1 + a)$ and $x_B = (ax_{A_0} + x_{B_0})/(1 + a)$. In a diatomic molecule $x_{A_0} = -x_{B_0}$, so that

$$x_A = -x_B = x_{A_0}(1 - a)/(1 + a) \quad (5)$$

If "a" is thought of as a measure of charge transfer, then the ratio $(1 - a)/(1 + a)$ may be set equal to T which will serve as a coefficient to measure charge retained. We shall let x_A , as measured from dipole moments, $\mu_{AB} = er_{AB}x_A$, serve as a measure of ionic character.

As has been discussed elsewhere,¹¹ the dipole moment may be considered to be a sum of individual moments (see eq. 6) in which μ_{AB} is the measured

$$\mu_{AB} = \mu_E + \mu_0 + \mu_H + \mu_P \quad (6)$$

dipole, μ_E is an "ionic" term which we will equate to $er_{AB}(E_B - E_A)$, μ_0 is the "overlap" or "homopolar" term which arises from a difference in size of A and B, μ_H is the "hybridization" or "atomic" term originating in a change in center of density on a given atom with hybridization, while μ_P is a polarizability term which often is neglected. If our proposed scale of electronegativities is to be of any value, it is necessary to evaluate the other terms and show that μ_{AB} may be reproduced with some accuracy. As a first approximation we shall assume that μ_H is zero for the compounds considered here even though Mulliken¹² has discussed the bond energy of fluorine in terms of repulsions and of the other halogens in terms of partial d hybridization. This leaves μ_0 and μ_P to be accounted for. If x_0 and T are capable of being estimated, then, since a moment equals $er_{AB}x$, (6) may be rewritten as 7.

$$x_A = x_E + x_0 + 0 + x_P \quad (7)$$

Here, $x_E = E_B - E_A$, $x_P = (T - 1)(E_B - E_A + x_0)$, so that $x_A = T(E_B - E_A + x_0)$ and $x_{A_0} = E_B - E_A + x_0$ as used in (5).

Our calculation of x_0 depends upon another way of considering a moment. Following Gordy,¹¹ con-

(11) R. S. Mulliken, *J. Chem. Phys.*, **3**, 573 (1935), and W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 290, and references given by them, as well as B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955), and ref. 8, p. 102.

(12) R. S. Mulliken, *THIS JOURNAL*, **77**, 884 (1955).

TABLE IV
COMPARISON OF METHODS OF CALCULATING ELECTRONEGATIVITY DIFFERENCES

Cmpd. AB	$E_B - E_A^a$	$E_B - E_A^b$	$E_B - E_A^c$	$E_B - E_A^d$	$E_B - E_A^e$	$E_B - E_A^f$	$E_B - E_A^g$
HF	0.4523	0.4804	0.4585	0.48	0.41	0.378	0.4585
HCl	.2651	.2847	.2820	.23	.23	.167	.2820
HBr	.1986	.2410	.2436	.17	.18	.111	.2436
HI	.0629	.1790	.1731	.10	.11	.065	.1731
ClF	.2068	.2148	.1765	.25	.18	.211	.1765
BrF	.2420	.2433	.2149	.31	.23	.267	.2149
IF	.3096	.3097	.2854	.38	.30	.313	.2854
BrCl	.0267	.0423	.0384	.06	.05	.056	.0384
ICl	.1033	.1215	.1089	.13	.12	.102	.1089
IBr	.0676	.0744	.0705	.07	.07	.046	.0705

^a Calculated from D_{AB} values in Table II by use of the arithmetic mean, $E_B - E_A = 0.05645 \sqrt{D_{AB} - 1/2(D_{AA} + D_{BB})}$.

^b Calculated from D_{AB} values in Table II by use of the geometric mean, $E_B - E_A = 0.05645 \sqrt{D_{AB} - \sqrt{D_{AA}D_{BB}}}$. ^c Calculated from N_{AB} values as in Table II. ^d From the differences in Pauling's values of electronegativity as given in column 6 of Table III. ^e From Huggin's values as given in column 7 of Table III. ^f From Mulliken and Moffitt values as given in column 8 of Table III. ^g From this paper as given in column 9 of Table III.

sider the atoms A and B linked along the z axis (to avoid confusion since x refers to electronic charge) with the origin at the mid-point, C. If $r_A < r_B$ (bond radii of atoms) then a point D to the left of C represents the juncture of the radii and would be the center of density of the pair of electrons in the bond if no other effects were in operation. Thus $z_A' = r_A - r_{AB}/2$ is the distance from C to D in the negative direction, and $\mu_A' = 2ez_A'$. In effect this regards a dipole moment as having a constant charge ($2e$) and a variable distance (z_A'), in contrast to the former scheme in which $\mu_A' = er_{AB}x_A'$ in which the distance is constant and the charge variable. This gives $2z_A' = r_{AB}x_A'$, so that $x_A' = z_A'/(r_{AB}/2)$, or any variable charge, x , is related to the variable distance, z , through the factor $1/(r_{AB}/2)$. It turns out that x_A' is of such magnitude that it could not be used in place of x_0 in (7). Consequently it was necessary to find a reasonable method of reducing the size of x_A' . This was done by assuming that z_0 is the height of the cylinder of radius $r_{AB}/2$ and of a volume equal to that of the cylinder of height z_A' and radius $z_A'/2$. This gives $x_0 = 2(z_A'/r_{AB})^3$. By defining $r_A = r_{AB}r_{AA}/(r_{AA} + r_{BB})$, which makes r_A proportional to r_{AA} such that $r_A + r_B = r_{AB}$, z_A' becomes equal to $r_{AB}(r_{AA} - r_{BB})/2(r_{AA} + r_{BB})$ and

$$x_0 = 0.25[(r_{AA} - r_{BB})/(r_{AA} + r_{BB})]^3 \quad (8)$$

This allowed " T " and " a " to be calculated from (7) and (5). The results are presented in Table V. It is seen that the results are quite reasonable. Furthermore if one attempts a least squares fit to the equation, $a_{AB} = P + Qr_{AB}^2$, for the hydrogen halides, one obtains $P = -0.2044$ and $Q = 0.2491$. Using these constants to recalculate a_{AB} from r_{AB}^2 ; $a_{HF} = 0.005$, $a_{HCl} = 0.2005$, $a_{HBr} = 0.2936$ and $a_{HI} = 0.4396$ are obtained in very good agreement with those given in the table. Even more interesting, if a_{AB} is set equal to unity, $(r_{AB}^2)_{a=1} = 4.8356$. This suggested itself as being 4.8029 or that $(r_{AB}^2)_{a=1}$ is numerically equal in area in \AA^2 to $e \times 10^{10}$ esu. Also, $1 - 4.8029/4 = -0.2007$ in close agreement with P . Such being the case, equation 9 was used without attaching any special signifi-

$$a_{AB} = -0.2007 + m_{AB}r_{AB}^2/8 \quad (9)$$

cance to the use, at present, of e . That a_{AB} should

be a function of r_{AB}^2 may be partially justified in that $1/a_{AB}$ may be considered to be analogous to a resistance which in turn should be proportional to a length, r_{AB} , and perhaps proportional to a function of density (of electronic charge?) which involves a term $1/r_{AB}^3$. The coefficient " m " seems to be a type of bond factor since $m_{HH} = 4$, $m_{HX} = 2$, $m_{XY} = 1$ were the values used and correspond of course to sigma-sigma, sigma-pi and pi-pi bonding. Table VI shows the concordance of this independent calculation of a_{AB} by demonstrating that μ_{AB} may be calculated knowing only the electronegativities and bond distances by the use of equations 7, 8 and 9.

TABLE V
CALCULATION OF x_A , x_0 , T_{AB} AND a_{AB}

Cmpd. AB	μ_{AB}^a	x_A^b	x_E^c	x_0^d	T_{AB}^e	a_{AB}^f
HF	1.94	0.4400	0.4585	-0.0076	0.9759	0.0122
HCl	1.08	.1764	.2820	-.0238	.6832	.1882
HBr	0.78	.1149	.2436	-.0331	.5458	.2938
HI	0.38	.0492	.1731	-.0450	.3841	.4450
ClF	0.88	.1125	.1765	.0012	.6330	.2248
BrF	1.29	.1527	.2149	.0032	.6999	.1765
IF			.2854	.0071		
BrCl	0.57	.0555	.0384	.0001	1.4419	
ICl	0.65	.0583	.1089	.0008	0.5317	.7082
IBr	1.2	.1008	.0705	.0001	1.4290	

^a Values of μ are in Debye units; for HF, HCl, HBr, HI and IBr from C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N.Y., 1955, p. 244, which also lists $\mu_{ICl} = 1$; for ClF, BrF, BrCl and ICl from Gordy, *et al.*, ref. 11, p. 361. ^b $x_A = \mu_{AB}/er_{AB}$; r_{AB} from Table I. ^c $x_E = E_B - E_A$. ^d Calculated from eq. 8. ^e $T_{AB} = x_A/(E_B - E_A + x_0)$. ^f $a_{AB} = (1 - T_{AB})/(1 + T_{AB})$. Since T_{AB} and a_{AB} have limits of zero and 1, the values of T_{BrCl} and T_{IBr} are impossible. All calculations were carried out to five decimal places and the rounded off values are reported.

Furthermore, if the longitudinal polarizability, l_{AB} , of a bond be set equal to the volume of the cylinder of height r_{AB} and radius $r_{AB}/2$, it is found

$$l_{AB} = m_{AB} \pi r_{AB}^3/4 \quad (10)$$

that equation 10 agrees very well with the available data, as shown in Table VI. LeFèvre¹³ has proposed a more general equation, $l_{AB} = A + Bd^3$, in which d is related to r_{AB} , r_A and r_B depending upon

(13) R. J. W. LeFèvre, *Proc. Chem. Soc.*, 283 (1958).

TABLE VI
 CALCULATED RESULTS OF a_{AB} , μ_{AB} , l_{AB} AND λ_{AB}

Cmpd. ^a AB	a_{AB} ^b	a_{AB} , ^c calcd.	μ_{AB} ^d	μ_{AB} , ^e calcd.	l_{AB} ^f	l_{AB} , ^g calcd.	S_{AB} ^h	λ_{AB} ⁱ	$\frac{\lambda^2 - 1}{1 + \lambda^2 + 2\lambda S}$
HF	0.0122	0.0100	1.94	1.95		1.22	0.300	1.878	0.447
HCl	.1882	.2057	1.08	1.04	3.1	3.26	.490	1.323	.186
HBr	.2938	.2991	0.78	0.77	4.2	4.44	.495	1.226	.135
HI	.4450	.4457	.38	0.38	6.6	6.53	.500	1.126	.079
FCI	.2247	.1306	-.88	-1.07		3.39	.220	0.846	-.136
FBr	.1765	.1860	-1.29	-1.26		4.27	.235	.833	-.147
FI		.2577		-1.59		5.52	.240	.811	-.167
ClBr	.7082	.3707	-0.57	-0.18		7.68	.295	.977	-.018
ClI		.4738	-0.65	-.44		9.85	.300	.951	-.039
BrI		.5668	-1.2	-.23		11.95	.305	.975	-.019
HH		.0746			0.7	1.28	.75		
FF		.0506				2.24	.17		
ClCl		.2933			6.6	6.17	.29		
BrBr		.4508				9.35	.30		
II		.6884				14.90	.31		

^a The compounds have been arranged such that $Z_A \leq Z_B$ as required for the use of S_{AB} and λ_{AB} . ^b From Table V as calculated from observed μ_{AB} . ^c From eq. 9. ^d From Table V, other values which have been given are $\mu_{HCl} = 1.03$, $\mu_{ClI} = 1$. From the use of eq. 6, 7, 8 and 9. ^e l_{HH} from Smyth, note a, Table V, p. 409. All others from K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940). Also see ref. 13. ^f From eq. 10, l in (Å).³ ^g R. S. Mulliken, *THIS JOURNAL*, **72**, 4493 (1950). S_{FBr} , S_{FI} , S_{ClBr} , S_{ClI} , S_{BrBr} and S_{BrI} interpolated. ^h From eq. 13. ⁱ Calculated from data in the Table; see text.

the structure. Designed for application to organic compounds, he finds $l_{HCl} = 2.8$, $l_{HBr} = 3.8$ and $l_{HI} = 5.4$, so that eq. 10 appears to be superior for our purposes.

Combining equations (9) and (10) leads to (11), which illustrates the complex relationship which exists between a_{AB} and l_{AB} .

$$a_{AB}/l_{AB} = [0.5 - 0.8028/m_{AB} r_{AB}^2]/\pi r_{AB}^2 \quad (11)$$

Since the dipole moment may also be expressed as equal to the product of the longitudinal polarizability and a force field, $\mu_{AB} = l_{AB}G_{AB} = (m\pi r_{AB}^3/4)(eT(E_B - E_A + x_0)/r_{AB}^2)$, the dipole moment also was calculated in this fashion. It was found that the results differed from those presented in Table VI by a constant factor, $4/m_{AB}\pi$. Since the force field supposedly is external to the system upon which it is acting, the system having a longitudinal polarizability which measures the response of the system by way of producing a dipole moment, it is not surprising that the charge which produces the field $T(E_B - E_A + x_0)$, and the charge resulting from the polarizability response should differ by such a factor. In fact, it is difficult to see why the equation should fit at all.

Since others¹⁴ have shown that relationships exist between force constants, electronegativity and bond lengths, and since inductive charge transfer, longitudinal polarizability and dipole moments have been related to electronegativity and bond lengths here, the empirical inter-correlations of bond properties for diatomic molecules are nearly complete although bond shortening awaits more clarification.

The equation for a dipole moment as derived from m.o. theory should be examined in the light of our calculations. Following Coulson,¹⁵ equation 12

$$\mu_{AB} = 2ez_{AB} = 2e \left[\frac{r_{AB}/2(\lambda_{AB}^2 - 1) + 2\lambda_{AB}x_0}{1 + \lambda_{AB}^2 + 2\lambda_{AB}S_{AB}} \right] \text{ or } \quad (12)$$

$$x_A = (\lambda_{AB}^2 - 1 + 2\lambda_{AB}x_0)/(\lambda_{AB}^2 + 1 + 2\lambda_{AB}S_{AB})$$

(14) See G. R. Somayajulu, *J. Chem. Phys.*, **28**, 814 (1958), for a recent example and references to earlier work.

(15) Ref. 8, p. 102.

is easily derived from which it is equally easy to derive a formula for λ_{AB} , equation 13, the values of which are given in Table VI. The term λ_{AB} is used¹⁶ as a measure of polarity of the orbital, in

$$\lambda_{AB} = [-x_0 + S_{AB}x_A + \sqrt{(x_0 - S_{AB}x_A)^2 + 1 - x^2}]/(1 - x_A) \quad (13)$$

simple form $\psi_{AB} = \psi_A + \lambda_{AB}\psi_B$, or $\lambda_{AB} = C_B/C_A$. Some effort was made to assign various terms in the numerator of (12), as being proportional to x_E or other component charges. However, no coordination was found as shown by the values of $\lambda^2 - 1$, listed in the last column in Table VI and which do not fit with any of the component charges as given in equation 7 and Table V. However, Mulliken as well as Parr and Pariser have considered the problem of inductive charge transfer in relation to electronegativity and partial charge neutralization from a theoretical standpoint¹⁷ and propose that such a separation is possible. In view of the complex relationship between λ_{AB} , x_A , x_0 and S , such a partition of $\lambda_{AB}^2 - 1 + 2\lambda_{AB}x_0$ into additive portions bearing a simple relationship to x_E , x_0 and x_P seems difficult at best.

In conclusion, if the empirical relations given here have any validity, then the polarizability term, x_P , is rather more important, and the overlap term, x_0 , is less important in contributing to the dipole moment than has been thought.¹⁸ Also the usage of inductive charge transfer of the charges produced by electronegativity difference and homopolar effects as the polarizability term (equation 6 and 7) should clarify the meaning of ionic character, reserved to x_A , as apart from the electronegativity character as shown by x_E .¹⁹ The elec-

(16) Ref. 8, p. 71.

(17) R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949); G. R. Parr and R. Pariser, *J. Chem. Phys.*, **23**, 711, 2343 (1955). See also ref. 19.

(18) Coulson, ref. 8, p. 146, gives -1 as the homopolar dipole in HCl, whereas we find 1.73, -0.15 and -0.54 for μ_E , μ_0 and μ_P .

(19) Ref. 1, p. 98, for example. It is of interest that J. K. Willmshurst, *J. Chem. Phys.*, **30**, 561 (1959), and previous papers found it necessary to propose that ionic character be equated to $(E_A - E_B)/(E_A + E_B)$ as a consequence of using the old electronegativity scale

tronegativity scale proposed here may merit general adoption because of the simple relationship with

and neglecting polarizabilities. It should be noted that this definition predicts a greater ionic character for a given electronegativity difference as the sum of the electronegativities decreases.

charge, inductive transmission of charge and dipole moment.

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Isotope Effects in Deuterium Oxide Solution. I. Acid-Base Equilibria

BY C. A. BUNTON AND V. J. SHINER, JR.¹

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It is suggested that the deuterium oxide solvent isotope effect on aqueous acid dissociation constants arises principally from changes in zero-point energy associated in turn principally with changes in hydrogen bonding strength and number on dissociation. These considerations lead to a simple quantitative method of estimating the isotope effect on acid-base equilibrium constants; this shows good agreement with experiment.

Solvent deuterium isotope effects are an important tool for the determination of the mechanism of reactions, particularly those catalyzed by acids and bases; *e. g.*, the observation that some acid catalyzed reactions are faster in deuterium than in protium oxide often is used as evidence that the conjugate acid of the reactant is an intermediate formed in an equilibrium step.

Understanding of these kinetic isotope effects can only follow our understanding of isotope effects upon reaction equilibria. This latter topic is the subject of this paper, which will be followed by another dealing with the more complex problems set by solvent kinetic isotope effects. We discuss equilibria first because the knowledge of initial and final state structure makes possible experimental justification of our treatment. In discussions of mechanism the structure of the transition state represents an additional unknown which leads to additional uncertainties and controversy.

The general theoretical considerations involved in the treatment permit qualitative predictions about isotope effects on acid-base equilibria. In addition, by choice of certain simple rules and the acceptance of assignment of certain vibrational frequencies a simple model is set up which provides generally satisfactory quantitative explanations of such effects.

It has long been known that protium oxide has a larger self dissociation constant than deuterium oxide^{2,3} and that dissociation constants of weak acids are larger in water than in deuterium oxide, the isotope effect being larger the weaker the acid.^{4,5} It has been suggested that these differences are related to the smaller zero point energy of the dissociated proton relative to a covalently bonded hydrogen.^{2,3,6}

This difference of dissociation constants gives a ready explanation for the greater rate in deuterium oxide (by factors up to 3) of those acid catalyzed

reactions in which the rate depends on an equilibrium concentration of the conjugate acid of the reactants.⁶

By making certain reasonable approximations one can express the deuterium isotope effect upon a reaction equilibrium constant, between the initial state having a sum of the vibration frequencies for the isotopically substituted hydrogen atoms, $\Sigma\nu_H$, and a final state having a corresponding sum $\Sigma\nu_H'$, by the expression⁷

$$\Sigma\nu_H - \Sigma\nu_H' = 12.53 T \log K_H/K_D$$

The dissociated proton exists in water solution as the hydronium ion, H_3O^+ ,⁸ which is strongly hydrogen bonded to three adjacent water molecules. Recently the vibration frequencies of this ion in solution have been assigned.⁹ The stretching vibration frequencies of the hydronium ion in concentrated solution lead to a broad band centered at 2900 cm^{-1} , appreciably lower than the corresponding absorption of water, 3400 cm^{-1} . This difference, however, of itself is not sufficient to explain the deuterium isotope effect upon the autoprotolysis of water, $K_{H_2O}/K_{D_2O} = 6.5$.¹⁰ Further it gives no explanation of the dependence of relative acid dissociation constants in water and deuterium oxide upon the strength of the acid.

The clue which leads to a general explanation of these observations is the fact that the ratio K_{H_2O}/K_{D_2O} for the dissociation of acids decreases as the acid becomes stronger. Since all acids partially dissociate in water to the hydronium ion and a con-

(7) This equation, an approximation of a more exact and general formulation of the effect of isotopic substitution on reaction rate published by Bigeleisen (see ref. 18), involves the assumption that all of the isotope effect is due to zero-point energy differences and that the reduced mass relationship holds between the vibration frequencies of hydrogen and deuterium. For further discussion of these approximations see A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *THIS JOURNAL*, **80**, 2326 (1958). Explicitly neglected are any isotopic entropy effects, tunnelling and anharmonicity. Within the accuracy of the present calculations these limitations should not be serious.

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