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Ionic Character and the Dipole Moment of Chemical Bonds. Calculations of the Dipole Moment of HCl*

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The method of assigning the ionic character of chemical bonds by the use of the dipole moment is examined for the case of hydrogen chloride. Using both the atomic orbital and the LCAO molecular orbital approximation, the ionic character of HCl is calculated. Not only do the values so calculated seem unreasonable from energy considerations, but the calculated rate of change of dipole moment with respect to internuclear distance does not agree with the experimentally observed infra-red intensity. This discrepancy is due to the large dipole moment associated with the covalent bond. Although the results for a purely covalent compound are in agreement both with the dipole moment, and the

infra-red intensity, if the dipole is assumed to have the orientation Cl^+H^- , this assumption is discredited by the fact that one would have to assume more ionic character for HBr than HCl. If we make the assumption that $s-p$ hybridization occurs, these difficulties are removed. It is shown that the dipole moment of the purely covalent molecule is a very sensitive function of the amount of hybridization, and the covalent molecule can have almost any reasonable dipole moment. Thus it is shown that there are difficulties which must be surmounted before one can use dipole moments to obtain ionic character.

INTRODUCTION

PAULING¹ has given a method for obtaining the ionic character of chemical bonds from electronegativity data. This method is based on the correlation of the electronegativities of the hydrogen halides with their ionic character as obtained from the dipole moments.²

The purpose of this paper is to discuss the method of obtaining ionic character from dipole moments, especially the nature of the dipole moment of a covalent molecule.

There have been other attempts to calculate dipole moment of HCl from wave functions.^{3,4} Coulson⁵ has calculated the dipole moment of the C-H bond in methane using the molecular orbital approximation.

By approximating the wave functions of the electrons in HCl, it is possible to calculate the ionic character from the dipole moment μ . Then by assuming that the ionic character does not vary appreciably with internuclear distance for small displacements, it is possible to calculate $\partial\mu/\partial d$, where d is the internuclear distance. One can compare this with the experimental infra-red intensity.⁶ It is thus possible to obtain a check on the ionic character obtained.

The results show that there are difficulties that must be explained before one can use dipole moments to obtain ionic character. The dipole moment of the covalent bond is hard to determine. On the simple picture of a pure p bond it is of the order of -1 debye unit (using the atomic orbital approximation), i.e., the hydrogen negative. When $s-p$ hybridization is taken into effect,

values up to $+2$ debye units can be found depending on the amount of hybridization.

ASSUMPTIONS

In the calculation of the dipole moment the following assumptions are made:

1. Polarization of the non-bonding electrons is neglected.
2. The wave functions are assumed to be hydrogen-like functions with screening constants obtained from Pauling and Sherman.⁷
3. The change of ionic character for small changes in interatomic distance can be neglected.

GENERAL FORMULAS

The dipole moment μ is given by Eq. (1) where e is the electronic

$$\mu = ed - e \sum_i \bar{z}_i, \quad (1)$$

charge, d is the internuclear distance, and \bar{z}_i is the average value of z (defined with the chlorine at the origin and the z axis along the bond) for the i th electron and the sum is taken over all the electrons. The first term is due to the proton and the second to the electrons.

If we now assume that all the electrons except the two bonding electrons have their average position at the chlorine nucleus, i.e., no polarization or hybridization of the non-bonding electrons, then Eq. (1) becomes

$$\mu = ed - 2e\bar{z}_b, \quad (2)$$

where \bar{z}_b is the average value of z for each bonding electron.

To obtain \bar{z}_b it is necessary to know the wave function for the two bonding electrons, ψ_b (assuming that the complete wave function is a product-type function of all the other electrons).** Then \bar{z}_b is given by Eq. (3).

$$\bar{z}_b = \left[\int |\psi_b|^2 z_1 d\tau_b \right] / \left[\int |\psi_b|^2 d\tau_b \right]. \quad (3)$$

⁷ Pauling and Sherman, *Zeit. f. Krists.* **81**, 1 (1932).

** If the wave function were completely antisymmetrized, then one would have to include small terms involving overlap of non-bonding orbitals with the H orbital.

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¹ Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York), p. 69-75.

² See reference 1, p. 46.

³ Wall, *J. Am. Chem. Soc.* **62**, 800 (1940).

⁴ Mulliken, *J. Chem. Phys.* **3**, 573 (1935).

⁵ Coulson, *Trans. Faraday Soc.* **38**, 433 (1942).

⁶ Bourgin, *Phys. Rev.* **32**, 237 (1928).

TABLE I. Table of calculated values of \bar{z} for the bonding electrons, dipole moments, $\partial\bar{z}/\partial d$ and $(1/e)\partial\mu/\partial d$ for the various types of bonds, and comparison with the results quoted by Rollefson.*

| | \bar{z}_b (Bohr radii) | μ (Debye units) | $\frac{\partial\bar{z}_b}{\partial d}$ | $\frac{1}{e}\frac{\partial\mu}{\partial d}$ |
|--|--------------------------|---------------------|--|---|
| Atomic orbital pure covalent bond | 1.402 | -0.98 | 0.358 | 0.283 |
| Molecular orbital pure covalent bond | 1.541 | -1.69 | | |
| Atomic orbital mixed ionic covalent | 0.989 ^b | +1.10 | 0.150 | 0.700 |
| Molecular orbital mixed ionic covalent | 0.989 ^b | +1.10 | 0.158 | 0.784 |
| Experimental values | | $\pm 1.10^a$ | | ± 0.197 |

* See reference 11.

^b Ionicity chosen so as to fit dipole moment value of +1.10 debye units

It is normally assumed that the chlorine part of the wave function involved in the bonding is a $3p_z$ function (hereafter called p) and that the hydrogen part of the function is a $1s$ function centered around the hydrogen nucleus (hereafter called h). Using the atomic orbital approximation,⁸ the wave function for the bonding electrons is given by (4).

$$\psi_b^{\text{cov}} = p(1)h(2) + h(1)p(2). \quad (4)$$

If we make the LCAO molecular orbital approximation, then we obtain⁹ (5):

$$\psi_b^{\text{cov}}(1, 2) = [p(1) + h(1)][p(2) + h(2)]. \quad (5)$$

These are wave functions for purely covalent bonds. We must take ionic character into account. In the atomic orbital approximation this means adding a term representing an ionic structure.

$$\psi_b = \psi_b^{\text{cov}} + \lambda p(1)p(2). \quad (6)$$

For the molecular orbital case we put in a factor to show that the electron spends more time around the chlorine nucleus.

$$\psi_b^{\text{cov}} = [\lambda^1 p(1) + h(1)][\lambda^1 p(2) + h(2)]. \quad (7)$$

It is possible to calculate λ or λ^1 from the observed dipole moment. This type of calculation has been done before, mainly by Pauling,² Wall,³ and Mulliken.^{10, 4}

Pauling² and also Wall³ assumed that purely covalent HCl would have no dipole moment, in other words, $\bar{z}_b = d/2$. Mulliken^{10, 4} estimated that the electrons on the average would be at the end of the covalent radius. This would lead to a dipole moment of about -2.5 debye units (the hydrogen end being negative). Neither

⁸ See, for example, Pauling and Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

⁹ For a recent review of the molecular orbital method see Coulson, *Quart. Rev.* **1**, 144 (1947).

¹⁰ Mulliken, ONR Report (1948). Formulas are given here for the dipole moment as a function of ionic charge, overlap moment, etc. We are grateful to Professor Mulliken for an interesting discussion of this report (to be published in *J. de Chim. Phys.*), and for criticism of this paper.

of these very different assumptions is in accord with the results of the following analysis.

IONIC CHARACTER OF HCl ON THE ASSUMPTION OF P BONDS

To obtain \bar{z}_b for a purely covalent bond, it is necessary to substitute Eqs. (4) and (5) into Eq. (3).

$$\bar{z}_b^{\text{cov}} = \frac{\int [p(1)h(2) + p(2)h(1)]^2 z_1 d\tau_1 d\tau_2}{\int [p(1)h(2) + p(2)h(1)]^2 d\tau_1 d\tau_2}. \quad (8)$$

$$\bar{z}_b^{\text{cov}} = \frac{\int [p(1) + h(1)]^2 z_1 d\tau_1}{\int [p(1) + h(1)]^2 d\tau_1}. \quad (9)$$

On expanding and using the following definitions and equations:

$$\int p(1)^2 z_1 d\tau_1 = 0; \quad \int h(1)^2 z_1 d\tau_1 = d. \quad (10)$$

$$\int p(1)^2 d\tau_1 = \int h(1)^2 d\tau_1 = 1. \quad (11)$$

$$\int p(1)h(1) d\tau_1 = S; \quad \int z_1 p(1)h(1) d\tau_1 = M. \quad (12)$$

Then

$$\bar{z}_b^{\text{cov}} = [d + 2MS] / [2 + 2S^2]. \quad (13)$$

$$\bar{z}_b^{\text{cov}} = \frac{d + 2M}{2 + 2S}. \quad (14)$$

If we assume ionic character, substituting Eqs. (6) and (7) in Eq. (3), we obtain the following answers for \bar{z}_b :

$$\bar{z}_b = \frac{d + 2MS + 2\lambda M}{2 + 2S^2 + \lambda^2 + 4\lambda S}, \quad (15)$$

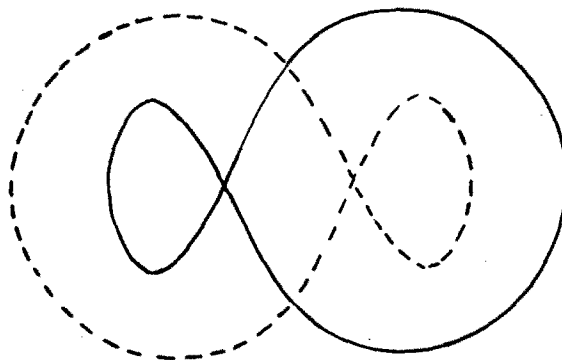


FIG. 1. Schematic representation of bonding (—) and non-bonding (---) s - p hybridized orbitals.

or

$$\bar{z}_b^1 = \frac{d + 2\lambda^1 M}{1 + (\lambda^1)^2 + 2\lambda^1 S}. \quad (16)$$

Therefore, for all these cases it is only necessary to calculate the overlap integrals

$$S = \int h(1)p(1)d\tau_1, \quad \text{and} \quad M = \int h(1)p(1)z_1 d\tau_1.$$

It is at this point that the present study deviates from those of previous investigators. Both Pauling² and Wall³ implicitly assumed S small so that $\bar{z}_1 \rightarrow d/2$. Mulliken¹⁰ overestimated the effect of overlap of the functions and thus obtained a large negative value for μ cov.

S and M were calculated using hydrogen-like wave functions with a screening constant of 6.5.

Numerically:***

$$S = 0.4833, \\ M = 1.078.$$

Substitution of these values into Eqs. (13) and (14) leads to

$$\bar{z}_b^{\text{cov}} = 1.402 \text{ (Bohr radii)}, \\ \bar{z}_b^{1 \text{ cov}} = 1.541 \text{ (Bohr radii)}.$$

Substitution of these values into Eq. (2) gives

$$\mu_{\text{cov}} = -0.98D, \\ \mu_{\text{cov}}^1 = -1.69D.$$

If we assume a value for μ of $+1.10$ debye units,¹¹ then \bar{z}_b would equal 0.989 Bohr radii. With this assumption we can calculate λ and λ^1 from Eqs. (15) and (16)

$$\lambda = 1.14, \\ \lambda^1 = 1.96.$$

These values of λ and λ^1 seem much too high from energy considerations.² Furthermore, allowance for polarization of the non-bonding electrons would give an even more negative covalent dipole, and one would have to use even larger λ 's to compensate for this.

CHECK WITH $\partial\mu/\partial d$

Differentiating Eq. (2), one obtains

$$\partial\mu/\partial d = e - 2e\partial\bar{z}_b/\partial d.$$

We get $\partial\bar{z}/\partial d$ by differentiating Eqs. (15) and (16) so it is necessary to calculate $\partial S/\partial d$ and $\partial M/\partial d$

$$\partial S/\partial d = -0.120, \quad \partial M/\partial d = -0.189.$$

On substituting these values into the formulas, one obtains the following results, assuming λ and λ^1

*** These two integrals and similar ones for HBr, were calculated by Professor E. B. Wilson, Jr., and checked by the author. The author is grateful to Professor Wilson for lending him his unpublished manuscript.

¹¹ R. Rollefson and A. N. Rollefson, Phys. Rev. 48, 779 (1935). The sign is not determined experimentally.

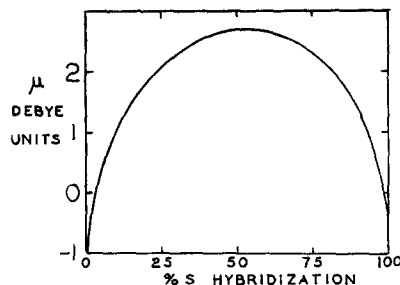


FIG. 2. Dipole moment of covalent HCl as a function of s -hybridization.

constant.

$$\partial\bar{z}_{\text{cov}}/\partial d = 0.3583, \\ \partial\bar{z}/\partial d = 0.150, \\ \partial\bar{z}^1/\partial d = 0.108,$$

and, on further substitution,

$$1/e[\partial\mu_{\text{cov}}]/[\partial d] = +0.2834, \\ 1/e\partial\mu/\partial d = 0.700, \\ 1/e\partial\mu^1/\partial d = 0.784.$$

The experimental value of $1/e[\partial\mu/\partial d]$ is ± 0.197 (as obtained from an effective charge of 0.93×10^{-10} e.s.u.). These results are summarized in Table I. It is important to note that the rather dubious assumption that λ and λ^1 remain constant on stretching has been made.

From these results one would conclude that highly ionic p bonds are not possible. However, the results are in good agreement with an almost purely covalent compound if we assume that the dipole moment is negative. But if the actual dipole moment were negative one would expect that the calculated value of μ_{cov} for NBr would be smaller than that for HCl since the actual dipole moment of HBr is smaller than that of HCl. This is not the case (as is shown below) so that one would have to assume more ionic character for HBr than HCl, an assumption which seems unreasonable and which, therefore, discredits the idea that the moment is negative.

DIPOLE MOMENT OF COVALENT HBR

Using the same method as used for HCl with a $4P_z$ wave function and a screening constant of 8.90, the values of S and M were found to be 0.492, and 1.362 Bohr radii, respectively. These lead to a dipole moment of -1.40 debye unit, using the atomic orbital approximation.

Since a negative dipole moment is caused by the difference in size of the atoms, this result is not surprising. We, therefore, can eliminate the possibility that HCl has a negative dipole moment.

ASSUMPTION OF S - P HYBRIDIZATION

As pointed out by Mulliken¹⁰ s - p hybridization would improve our results. The atomic orbitals for a hybridized bond are shown schematically in Fig. 1.

We now have to consider dipole moments of the non-bonding s electrons. Qualitatively we can say these are two electrons in the non-bonding orbital while there is one on the average in the bonding orbital. The large negative value of \bar{z} for the non-bonding electrons would lead to a more positive dipole moment. This effect was first discussed by Coulson⁵ and is most responsible for his calculated negative value of the C-H dipole moment.[†]

Now we assume that the chlorine part of the wave function for the bonding electrons is

$$\psi_{cl} = a^{\frac{1}{2}}s + (1-a)^{\frac{1}{2}}p,$$

which leads to the following result for ψ_b on the atomic orbital approximation

$$\psi_b = [a^{\frac{1}{2}}s(1) + (1-a)^{\frac{1}{2}}p(1)]h(2) + h(1)[a^{\frac{1}{2}}s(2) + (1-a)^{\frac{1}{2}}p(2)],$$

where s is a $3s$ function centered at the chlorine nucleus.

The wave function for the non-bonding hybridized electron is

$$\psi_{nb} = [1-a]^{\frac{1}{2}}s - a^{\frac{1}{2}}p.$$

Equation (2) must now be modified

$$\mu = ed - 2e\bar{z}_b - 2e\bar{z}_{nb}.$$

We now substitute the wave function to obtain the average value of \bar{z}_{nb}

$$\bar{z}_{nb} = \int z(\psi_{nb})^2 d\tau = -2[a(1-a)]^{\frac{1}{2}}P,$$

where

$$P = \int s p z d\tau = \frac{3[6]^{\frac{1}{2}}}{Z}$$

Bohr radii from atomic wave functions. By the same method as in Eq. (13)

$$\bar{z}_b = \frac{d + 2[(a^{\frac{1}{2}}M^1 + (1-a)^{\frac{1}{2}}M)(a^{\frac{1}{2}}S^1 + (1-a)^{\frac{1}{2}}S)] + 2[a(1-a)]^{\frac{1}{2}}P}{2 + 2(a^{\frac{1}{2}}S^1 + (1-a)^{\frac{1}{2}}S)^2},$$

where $S^1 = \int s h d\tau = 0.4744$, and $M^1 = \int s h z d\tau = 0.7395$. The first term is caused by the hydrogen orbital, the second by the overlap, and the third by the chlorine orbital.

The dipole moment of a purely covalent HCl is plotted as a function of the hybridization in Fig. 2. We can see that the moment is a very sensitive function of the amount of hybridization. Therefore, because of this great dependence on hybridization, it is only possible to say that hybridization probably takes place, and that the ionic character is difficult to determine.

SUMMARY OF RESULTS AND CONCLUSIONS

The assumption of pure p bonds for the chlorine wave function of HCl leads to ionic character that is inconsistent both with energy considerations and with the experimental result for $\partial\mu/\partial d$. The main discrepancy is due to the large negative value of the covalent contribution to the dipole moment, arising from the fact that the bonding electrons are closer to the hydrogen nucleus than to the chlorine nucleus. In fact the results for pure p bonds would suggest that the actual value of the dipole moment might well be negative, since the calculated value for $\partial\mu/\partial d$ agrees with the experimental value. However, when the covalent dipole of HBr is calculated, it leads to a more negative value. To fit a negative value of μ it would be necessary for HBr to have greater ionic character than HCl. This does not appear reasonable.

These difficulties are removed if $s-p$ hybridization is considered. Then, although the dipole moment of the

bonding electrons is made even more negative, it is more than balanced out by the "atomic" dipole caused by the non-bonding electrons. Now almost any value of dipole moment could be accounted for with purely covalent HCl. A value for the ionic character could be obtained from approximate energy data, and the amount of hybridization could be adjusted so as to fit the dipole moment. However, for the calculation of $\partial\mu/\partial d$, the assumption would have to be made that the amount of hybridization as well as ionicity would stay constant upon stretching. This assumption does not seem reasonable. Consequently, dipole moments do not give a good method for determining ionic character of bonds. The simple picture here presented shows that even in the case of HCl with the very simple assumptions made, the dipole moment is so sensitive to bond hybridization that interpretations are difficult.

However, it is reasonable to assume that the bond in covalent chlorine is not a pure p bond and that some hybridization must occur.¹⁰ This has been suggested by Townes and Dailey¹² who examined the quadrupole coupling constant data for other molecules. A pure p function will probably not represent accurately such properties of the molecule as the dipole moment or quadrupole coupling constant with any great degree of accuracy. Whether the additional complication of $s-p$ hybridization gives a useful picture depends on whether one can predict with it any useful properties of the molecule.

ACKNOWLEDGMENT

The author wishes to thank Professor E. Bright Wilson, Jr., under whom this work was carried out, for his guidance and helpful advice.

¹² Townes and Dailey, J. Chem. Phys. (to be published).

[†] In Coulson's case there is no overbalancing effect from the other electrons since they are involved in other bonds. For HCl the actual moment of the bond is more negative but the moment of the non-bonding electrons balances it out.