Electron Deficient Compounds. II. Relative Energies of ``Half Bonds''

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Electron Deficient Compounds. II. Relative Energies of "Half-Bonds"*

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It is suggested that the tendency to make use of all low energy orbitals is the underlying principle of electron-deficient bonding. Simple theoretical arguments, limited to the special case of two electrons and three orbitals, are given to show that this principle is a direct consequence of quantum-mechanical theories of valence.

Two half-bonds are shown to be of lower energy than a single bond plus an unused low energy orbital in most cases. The tendency to form half-bonds should be most important in symmetrical cases, and particularly where the electronegativities of all atoms involved are equal, e.g., the boron hydrides and H_3^+.

Certain consequences of the proposal to the fields of organo-metallic compounds, catalysis, and molecular rearrangements are pointed out. It is suggested that at low temperatures complexes may exist between molecules with excess orbitals and molecules with no unshared pairs.

I N recent papers structures of such diverse compounds as boron hydrides, trialkylaluminum dimers,[1] the tetramethylplatinum tetramer,[1,2] certain interstitial compounds,[1,3] and metallic hydrides[4] are discussed in terms of a bonding in which a non-metallic atom uses one orbital and one electron pair to form more than one interatomic link. Except in range of application the type of bonding suggested differs only in details from earlier suggestions,[5] but it is pointed out that common to all compounds in which this electron-deficient bonding occurs are a metal atom with more low energy orbitals than valence electrons combined with atoms or groups containing no unshared pairs. It has been suggested that the non-metal "overextends" the use of its orbitals in order to use effectively all the low energy orbitals of the metal.[1]

Electron-deficient bonding is not really rare in chemistry. It occurs quite generally where the above condition is fulfilled.[6] It would, therefore, be a serious fault in modern theories of valence if they were merely reconcilable with electron-deficient bonding.

In this paper it is pointed out that both the molecular orbital and Heitler-London theories of valence lead naturally to the conclusion that "normal" structures which leave low energy orbitals unused are unstable with respect to electron-deficient bonding in which all the low energy orbitals are used. The tendency to use all low energy orbitals is, in our view, the underlying principle of electron-deficient bonding.[7] Rather than

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[1] R. E. Rundle, J. Am. Chem. Soc. **69**, 1327, 2075 (1947).

[2] R. E. Rundle and J. H. Sturdivant, J. Am. Chem. Soc. **69**, 1561 (1947).

[3] R. E. Rundle, Acta Crystallographica **1**, 180 (1948).

[4] R. E. Rundle, J. Am. Chem. Soc. **69**, 1719 (1947).

[5] See for example, B. Eistert, Zeits. f. physik. Chemie **B52**, 202 (1942); H. Longuet-Higgins and R. Bell, J. Chem. Soc. 250 (1943); K. Pitzer, J. Am. Chem. Soc. **67**, 1126 (1945); A. D. Walsh, J. Chem. Soc. 89 (1947); R. Mulliken, Chem. Rev. **41**, 207 (1947), and earlier works referred to in these papers. An entirely different proposal has been made by Pitzer and H. Gutowsky, J. Am. Chem. Soc. **68**, 2204 (1946).

[6] Further examples of electron-deficient bonding are discussed by H. Schlesinger and A. Burg, Chem. Rev. **31**, 1 (1942) and by S. Bauer, Chem. Rev. **31**, 43 (1942). Metals are examples of highly electron-deficient bonding, as discussed from several points of view. See Frederick Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chapters VII–X, and L. Pauling, J. Am. Chem. Soc. **69**, 542 (1947).

[7] This principle has not been recognized. For example, predicted structures for tetramethylplatinum, and even trimethylplatinum chloride [L. C. Pauling (*The Nature of the Chemical Bond*, hereafter N.C.B., Cornell University Press., Ithaca, 1st Edition, 1939), p. 90; and E. Cox and K. Webster, Zeits. f. Krist. **90**, 561 (1935)] took no account of the fact that four normal bonds to platinum would leave two low energy platinum orbitals unused. Indeed, even after the structure was known, no immediate reason for the structure was apparent. See N.C.B., 2nd Edition (1940), p. 120.

Pitzer's suggestion (see reference 5) for the boron hydrides, though satisfactory for the lower hydrides, leaves low energy bonds orbitals unused for the higher hydrides, and hence is in

electron-deficient structures being exceptional, it is molecules of the trimethylboron type, which possess unused low energy orbitals that are exceptional. Presumably these molecules exist with apparently unused low energy orbitals only because an enhanced hyperconjugation *does* make use of the extra orbital,[8] and because polymerization through electron-deficient bonds is inhibited for steric reasons.[1]

The present discussion will be limited to the simple case in which the stability of a structure containing one normal bond and one excess orbital is compared with a structure consisting of two half-bonds (bonds containing half an electron pair, or of bond number $\frac{1}{2}$ in Pauling's nomenclature).[6] The reason for this limitation is first, one of simplicity. However, it has been shown that where the number of excess orbitals is relatively small, the resulting electron-deficient bonds can generally be discussed in terms of half-bonds.[1] This is the most localized type of electron-deficient bond and might well be expected to occur frequently. As in the case of ordinary structures, where added stability is to be gained by delocalization of bonds, or where resonance among several bond structures is a factor, localized single bonds are not sufficient to describe the system, so the picture presented below, limited to half-bonds, will sometimes be too simple for the description of electron deficient compounds, *e.g.*, the higher hydrides of boron, where the number of excess orbitals becomes relatively large.[9] We have already had to use a somewhat more complex discussion to arrive at bonds of number two-thirds in tetramethylplatinum and certain interstitial compounds.[1] In the case of metals, where the number of excess orbitals is large, the delocalization of bonds proceeds to such an extent that entirely different discussions are needed.[6]

A QUANTUM-MECHANICAL CONSIDERATION OF THE ENERGY OF HALF-BOND PAIRS

Half-bonds occur in pairs in electron-deficient (or, better, excess orbital) structures. The system, A—B—A, with one electron pair, may be thought of as resonating between the principal contributing structures I and II. This system, composed of two electrons with paired spins and three atomic orbitals, has frequently been suggested for this situation.[2,5] We shall inquire as to the relative energy of the resonating system as compared with I or II individually.

$$A\text{—}B \quad A' \quad \text{I} \qquad\qquad A \quad B\text{—}A' \quad \text{II}$$

Ignoring exchanges between A and A', and assuming equal exchanges between A and B and A' and B, a

molecular orbital treatment gives the secular Eq. (1).[10] To make all the β's equal,

$$\begin{vmatrix} q_A - W & \beta & 0 \\ \beta & q_B & \beta \\ 0 & \beta & q_A - W \end{vmatrix} = 0 \qquad (1)$$

the orbital which B uses in the half-bonding must be equally directed toward A and A'. This will generally require the use of a bidirectional orbital, such as a p-orbital, or a symmetrical orbital, such as an s orbital.[2] The use of an unidirectional orbital, such as a tetrahedral sp^3 orbital, would require that this orbital be directed symmetrically between A and A', and this would generally lead to poor overlap and poor binding to both A and A', although with a small bond angle, A—B—A', such binding may be possible.[9]

The solutions of Eq. (1) are

$$W = (q_A + q_B)/2 \pm \sqrt{2}\beta + \Delta^2/8\sqrt{2}\beta, \qquad (2)$$

and

$$W = q_A \qquad (3)$$

where $\Delta = q_A - q_B$.

For a two-electron system, both electrons may be put in the lowest state, so that

$$W = q_A + q_B + 2\sqrt{2}\beta + \Delta^2/4\sqrt{2}\beta. \qquad (4)$$

For structure I_A or II_A above,

$$W = q_A + q_B + 2\beta. \qquad (5)$$

For the case that Δ is small, the resonance energy,

$$W_R = 0.828\beta. \qquad (6)$$

An *HLSP*-type treatment, and various refinements of the simple treatment, have been made for H_3^+ by Hirschfelder, Eyring, and Rosen.[11] Their Wang-type treatment of the resonating system

$$\text{H—H H} \qquad\qquad \text{H H—H}$$

leads to a binding energy of about 130 kcal./mole, *versus* about 90 kcal. for the Wang treatment of H_2. This is about a 40 percent increase, in good agreement with the simple *MO* treatment above. If long bond and ionic terms

$$\overline{\text{H H}}\ \text{H III} \quad \text{H }\ddot{\text{H}}\text{ H IV} \quad :\text{H H H V} \quad \text{H H H: VI}$$

are included, the binding energy increases to 150 kcal./mole. In the later treatment III and IV are of more importance than V and VI, and the exchange integrals they introduce are much like the single electron exchange integrals encountered in H_2^+. The latter are

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disagreement with the principle given above. Where all low energy orbitals are not used, Pitzer's suggested structures appear to be incorrect (see reference 9). His suggestions for the trialkyl-aluminum dimers makes use of the fourth orbital of aluminum.

[8] See R. Mulliken, reference 5.

[9] S. Bauer, J. Am. Chem. Soc. **70**, 115 (1948); and J. Kasper, C. Lucht, and D. Harker, J. Am. Chem. Soc. **70**, 881 (1948).

[10] Here β and q are the usual exchange and Coulomb integrals respectively. The symbols used follow those of L. C. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 381 ff.

[11] J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. **4**, 130 (1936).

important only if the electronegativities of the atoms involved are approximately equal. Consequently, in cases where electronegativities are unequal, the first approximation is probably a better estimate of the increased stabilization than the latter.

The most stable form of H_3^+ appears to be a triangle with two shorter and one longer sides.[12] This corresponds to further delocalization of the bonding and an increased bond energy of 20 kcal./mole. It seems likely that here the spherical symmetry of the s orbitals of hydrogen, which permit good overlap in all directions, aids in the further delocalization, but will be less important in most other cases.

If A and A' of I and II are not equivalent, and if the energy of a normal A—B bond is quite different from the A'—B bond energy, then only I or II will be important. In this case we should expect little stabilization by delocalization of the bonding.

From the above we should expect symmetrical cases with all atoms having equal electronegativities, e.g., H_3^+ and the boron hydrides, to be most favorable for half-bonds, but all symmetrical cases should be favorable. Unsymmetrical half-bonds are favorable only if the normal bonds A—B and B—C are not greatly different in bond energy.[13]

As noted, the fractional bonds in the proposed bridge structure for diborane should be especially strong. The bridge structure is now supported by the Raman spectrum interpretation of Bell and Longuet-Higgins,[14] by the infra-red study of Price,[15] by the electron diffraction of the presumably similar molecule, tetramethyldiborane,[16] and by the critical examination of other structural information by Pitzer.[5]

The heat of formation of BH_3 should be approximately zero, since the electronegativities of boron and hydrogen are essentially equal.[17] Hence, the heat of formation of B_2H_6 may be ascribed to the extra energy involved in forming the equivalent of two half-bond pairs. (The four-membered ring in B_2H_6 undoubtedly involves some further delocalization of the bonds, but for reasons previously noted,[18] it seems likely that the electron density is concentrated primarily in the B—H ligands, which are then approximately half-bonds.)

For the reaction

$$2B(s) + 3H_2(g) = B_2H_6(g), \quad \Delta H = -44 \text{ kcal.}[19]$$

The comparison should be made for single-bonded reactants as gases forming single-bonded products as gases, so that under these circumstances ΔH should be even more negative by about 8 kcal. Hence, the energy of the bridge system exceeds that of two ordinary B—H bonds by more than 50 kcal. Since a B—H bond must have a strength of the same order of magnitude as a C—H or an N—H bond, (70–80 kcal.), or perhaps less,[20] we may conclude that the half-bond pair is better than the single bond by nearly 30 percent, possibly more if the B—H bond is weak, as Walsh has suggested. This is close to the amount of added stabilization expected from the above calculations.

For less favorable, unsymmetrical A—B—C bonds, one can get some indication of strength from the fact that there are no known molecules whose parts are held together by one such bond. Since for gaseous molecules at room temperature, $T\Delta S°$ of dimerization will be of the order of -10 to -15 kcal./mole, one may conclude that bonds of this type are stabilized by energies of less than that amount, leading to unfavorable free energies of dimerization. Since normal bonds have energies of the order of 40–90 kcal., the half-bond pair in this case does not exceed normal bonds by more than 15–25 percent. However, they are strong enough that asymmetric fractional bonds appear to exist in tetramethylplatinum.[1]

Though the data on strengths of half-bonds which can be presented are as yet meager, the above values of half-bond energies seem to substantiate the general deductions from the simple treatment presented above, $i.e.$, half-bond energies appear to be relatively greatest for symmetrical cases in which the electronegativities of the three elements in the half-bond pair are equal (the boron hydrides and H_3^+) and to be least for unsymmetrical half-bonds.

It is interesting to note the similarities and differences between electron-deficient bonding and ordinary, single bonds. If A and B each have a stable orbital, then by suitable combination of the two orbitals two new orbitals may be obtained, one of lower and one of higher energy than either of the original orbitals. If only two electrons are involved, $i.e.$, if the system is deficient two electrons under the four necessary to fill all orbitals, then it will be energetically advantageous for the electron pair to occupy the lower, combined orbital, or bonding orbital. In this sense, electron deficiency is necessary for any covalent bonding.

In a system of three atoms, each with an orbital, it is generally possible to obtain, by linear combination of three atomic orbitals, a bond orbital which is lower in

[12] J. Hirschfelder, J. Chem. Soc. **6**, 795 (1938).

[13] This point of view is somewhat different from that of A. D. Walsh (see reference 5) who suggested that weak bonds should be electron donors to good electron acceptors, which would seem to suggest electron-deficient bonds should result in cases where the normal bond A—B is weak and the bond B—C is strong. Actually asymmetric fractional bonds are almost unknown.

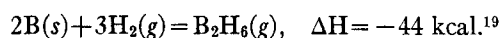[14] R. Bell and H. Longuet-Higgins, Proc. Roy. Soc. **A183**, 357 (1945).

[15] W. C. Price, J. Chem. Phys. **15**, 614 (1947).

[16] W. Shand, J. Chem. Eng. News, **24**, 2950 (1946) has found that tetramethyldiborane has a bridge structure. Hence, at least for this molecule, the ethane structure is ruled out.

[17] See reference 10, Chapter II.

[18] See reference 1, p. 2075.

[19] Roth, Borger, and Bertrand, Ber. **70**, 971 (1937).

[20] See reference 13.

energy than any one of the atomic orbitals or any combination of only two. Of course, at the same time two other orbitals of higher energy are obtained. If the system has only two electrons, i.e., if there is a deficiency of four electrons, then it will be energetically advantageous for the system to use the linear combinations of three orbitals for the electron pair.

We might expect that in cases of greater electron deficiency, limited mainly to metals, four or five or more atomic orbitals may be combined to give a single-bond orbital of lower energy than any atomic orbital or any combination of fewer bond orbitals. In this case, if the electron deficiency is great enough, one electron pair may bond a large number of atoms together through this combination of orbitals. This is compatible with the point of view outlined both by Pauling, and by quantum-mechanical treatments of metals, where the "orbitals" belong to the metal aggregate as a whole.[6]

In any case, a localized bond point of view must be approximate, and it will not be surprising if in electron-deficient compounds, now described in terms of half-bonds, more complicated terms will have to be added. It is our feeling, however, that, as in the case of "normal" molecules, the localized picture of the bonding will serve as a close enough approximation to permit the drawing of conclusions concerning the molecules in which electron-deficient bonding is to be expected, the relative importance of this bonding, and, combined with the directional properties of orbitals, something about configurations in electron-deficient structures.

CONSEQUENCES OF THE PROPOSAL

It appears possible from the above discussion to predict that in nearly all symmetrical cases, and in some unsymmetrical cases, a half-bond pair is to be preferred to a single bond plus an unused low energy orbital. One can now hope to predict where other electron-deficient structures are to be found, and these predictions may be expected to furnish the severest tests of the present proposal.

The largest single field for electron-deficient structures is probably to be sought in organometallic compounds, since metals quite generally have more low energy orbitals than valence electrons, and organic groups have no unshared pairs. As an example, we may cite the case of trimethylgold which has recently been prepared, but whose structure is still unknown.[21] Trivalent gold has four stable bond orbitals, the dsp^2 orbitals, leading to four bonds directed toward the corners of a square. Trimethylgold must be expected to have a square configuration, with four interatomic links to gold, in spite of the fact that the "normal" compound would involve only three bonds. Possible structures, for example, include a tetramer, A, planar

[21] H. Gilman and L. Woods, J. Am. Chem. Soc. 70, 550 (1948).

except for hydrogens, where one-third the methyl

A　　　　　　　　　　　B
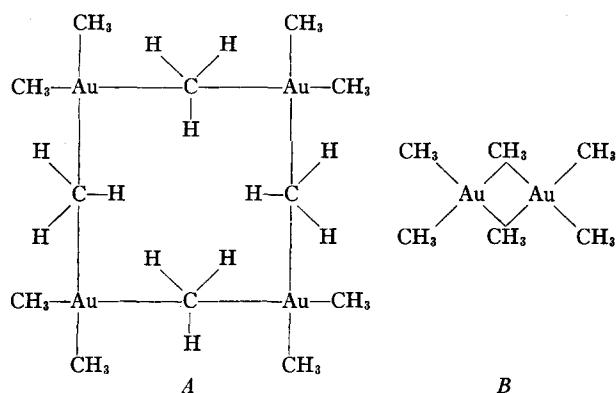
groups bridge gold atoms together, using a p orbital for the bridge. The bridging methyl group might then be planar, using sp^2 carbon orbitals for the three bonds to hydrogen. The methyl groups outside the ring should be normal. Alternately, a planar dimer, B, with more conventional methyl groups may exist.

It should be noted that low energy orbital is a relative term. It appears that if orbitals are of low enough energy to be used in accepting unshared pairs to form coordinate link bonds they may be low enough in energy to lead to the formation of electron-deficient bonds in most cases. It will not be surprising, however, if the exact limits do not coincide in the two instances, and, indeed, one might expect the requirements on the orbital to be more severe for the formation of electron-deficient bonds than for the formation of coordinate links.

One might now also expect certain molecules with excess orbitals, e.g., trimethylboron, boron trifluoride, to form complexes with certain molecules containing no unshared pairs. Since such complexes would generally contain unsymmetrical half-bonds, they may be expected only at low temperatures where entropy considerations are relatively unimportant. Since molecules which do not dimerize in spite of excess orbitals usually contain extra stabilization of one type or another (hyperconjugation in the case of trimethylboron, double-bond character of the B—F bonds in boron trifluoride), it may be difficult to demonstrate such complex molecules. Success may depend upon choosing molecules in which this excess stabilization is slight.

Complexes between molecules with excess orbitals and molecules with no unshared pairs are not of trivial interest. Catalysts are frequently metals or compounds with excess orbitals (BF_3, $AlCl_3$, etc.). It is well known that repulsive forces leading to high activation energies result from interactions of filled electron shells. Hence, compounds which may accept electrons should behave as catalysts. It is, of course, recognized in the case of compounds with unshared pairs that catalysts may operate by combining with reagent molecules through the unshared pairs. It would appear that they may act similarly on compounds with no unshared pairs.

It is of interest that rearrangements of the hydrides of boron have already been compared with cracking and alkylations of hydrocarbons in the presence of $AlCl_3$.[22] The former contains its own excess orbitals, while the latter needs an outside agent. Moreover, the hydrides of boron react with Si_2H_6 to give SiH_4 and boron even at comparatively low temperatures (115°).[23] The breaking of an Si—Si bond at this temperature indicates a relatively low activation energy, and a half-bond intermediate appears to be an attractive possibility. Trimethylaluminum appears to react with saturated hydrocarbons (Apiezon grease),[24] and again, this reaction seems understandable if a molecule with no unshared pairs is able to form at least an unstable intermediate involving partial transfer of electrons to the excess orbital through the formation of fractional bonds.

Finally, the Whitmore mechanism for molecular rearrangement involves an intermediate with unused bond orbital. The intramolecular character of the migration and the preservation of optical activity centers during the migration suggest that the migrating group is bound to two atoms by one electron pair in the intermediate, rather than existing with an unused orbital. A similar situation obtains in *trans*-addition to a double bond, and here a form of electron-deficient bonding of the positive ion intermediate has already been suggested.[25] The present discussion would indicate that it is natural that the electron-deficient intermediate should somewhat stabilize itself by forming enough fractional bonds to use all low energy orbitals. In both addition and migration this can be accomplished by bonding one group by one electron pair to two other atoms.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. A. J. Stosick with whom he has discussed the major portion of this paper.

[22] H. I. Schlesinger and A. B. Burg, Chem. Rev. **31**, 4 (1942).
[23] A. Stock, *Hydrides of Boron and Silicon* (Cornell University Press, Ithaca, 1933), p. 150.
[24] N. Davidson and H. Brown, J. Am. Chem. Soc. **64**, 319 (1942).

[25] C. C. Price, *Reactions at Carbon-Carbon Double Bonds*, Interscience Publishers, Inc., New York, N. Y., 1946, Chapt. II. See also A. D. Walsh, J. Chem. Soc. 89 (1947) and M. Dewar, *ibid.*, 406 (1946) who express similar ideas concerning mechanisms of molecular rearrangements.

The Relative Reaction Velocities of Isotopic Molecules

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The rate constants for competitive reactions of isotopic molecules are considered from the theory of "absolute rates" and the collision theory. Formulas are derived for the ratio of the rate constants and the difference in the activation energies for reactions of isotopic molecules. The difficulties in the *a priori* calculation of relative rates are pointed out and discussed.

In general the rate constant for the light molecule will be greater than that of the heavy molecule. It is shown that the maximum ratio in the rates occurs when the isotopic atom is essentially free in the activated complex. The conditions for the rate constant of the heavy molecule to exceed that of the light one are formulated.

It is shown that the difference in activation energies covers the range from zero to the difference in the differences in the zero-point energies of the reacting molecules and their respective activated complexes.

INTRODUCTION

AMONG the interesting and important chemical differences between two isotopic atoms or molecules is their difference in reaction rates. One of the goals of any theory of reaction rates is to calculate these differences precisely. Experimental determination of relative reaction rates of isotopic molecules can aid in understanding the mechanism of a reaction and testing different approaches to the problem of reaction rates.

Eyring[1] and Evans and Polanyi[2] have treated the general problem of reaction rates from a statistical viewpoint. The method has come to be known as the "theory of absolute rates." The assumptions, applications and limitations of the theory have been discussed in detail.[3] Several of the early applications of the theory were to reactions involving hydrogen and deuterium atoms and molecules.[4-6] In these applications the rate constants of each reaction were calculated explicitly after an evaluation of the potential energy surface of

[1] Henry Eyring, J. Chem. Phys. **3**, 107 (1935).
[2] M. G. Evans and M. Polanyi, Trans. Farad. Soc. **31**, 875 (1935).

[3] See S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).
[4] L. Farkas and E. Wigner, Trans. Farad. Soc. **32**, 708 (1936).
[5] J. O. Hirschfelder, H. Eyring, and B. Topley, J. Chem. Phys. **4**, 170 (1936).
[6] A. Wheeler, B. Topley, and H. Eyring, J. Chem. Phys. **4**, 178 (1936).