dimethyl ether exhibited no longer the characteristic property of the original substance, to give dark-red solutions in alkali.

Summary

With the exception of α-vinylnaphthalene itself, substituted α- and β-vinylnaphthalenes do not exhibit dienic properties toward maleic anhydride or similar substances.

A number of 9-vinylphenanthrenes have been prepared and their physical and chemical behavior have been studied. Most of them add maleic anhydride forming higher polycyclic systems, as expected. Surprisingly, 9-cyclohexenylphenanthrene and 9,9′-diphenanthryl do not behave like true dienes; this is ascribed to the special steric arrangement of the respective molecules.

The reaction of several substances with alkali metals has been studied.

In two cases, Tschugaeff's classical method for the preparation of ethylenes failed, giving the corresponding saturated systems.

REHOVOTH, PALESTINE RECEIVED MARCH 4, 1937

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 603]

A Quantitative Discussion of Bond Orbitals

BY LINUS PAULING AND J. SHERMAN

Six years ago, in the course of the development of the quantum mechanical theory of directed valence,[1] a very simple method of discussing the bond-forming power of an atomic bond orbital (one-electron orbital wave function) in its dependence on the angular distribution of the orbital was formulated.[1b,2] The fundamental assumption of the method is that in the case of bond orbitals with the same or nearly the same radial part of the wave function the magnitude of the angular part of an orbital along the bond axis (that is, in the direction of the other atom) is a measure of its relative bond-forming power. The bond-forming power or strength S of an s orbital (normalized to 4π), defined in this way, is 1, that of a p orbital is 1.732, and that of the best bond-forming hybrid sp orbital (called a tetrahedral sp bond orbital) is 2.

In order to obtain information as to the extent to which the bond strength S of an orbital can be considered a qualitative measure of its bond-forming power and also as to the quantitative relation between the energy of a bond and the strengths of the bond orbitals involved in its formation, we have now carried out the thorough discussion of various sp and spd one-electron bonds between identical atoms.

Description of the Method

We discuss a system comprising two atomic nuclei or kernels (nuclei and completed inner shells of electrons), with residual charge $+e$, and one electron, which forms a one-electron bond between the two atoms. The energy integral $E = \int \psi^* H\psi d\tau / \int \psi^*\psi d\tau$ is evaluated for various internuclear distances to give an energy function for each choice of the wave function ψ. This wave function is assumed to be of the form $c(\psi_A + \psi_B)$, ψ_A and ψ_B being similar atomic bond orbitals for atoms A and B and c a normalization constant. The functions ψ_A and ψ_B are formed by linear combination of central-field atomic orbitals. However, in discussing s-p hybridization, we do not use $2s$ and $2p$ hydrogen-like orbitals, inasmuch as these differ somewhat in their radial parts; instead, in order to obtain results bearing directly on the effect of angular distribution of the orbital on its bond-forming power, we use the same radial function for $2s$ as for $2p$. As a result of this simplification of the radial function, the energy of the $2s$ orbital is changed from the hydrogen-like value, a term $l(l+1)/r^2$ being introduced by the kinetic energy operator acting on the radial function, and not canceled by the angular function. In order to achieve sp degeneracy we omit this term, as well as the corresponding term in the sp exchange integrals. In a later section there is then discussed the case in which the s and p orbitals correspond to different energy values. Similarly in discussing M orbitals we use the

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[1] (a) J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931); (b) L. Pauling, THIS JOURNAL, **53**, 1367 (1931).

[2] See also R. Hultgren, *Phys. Rev.*, **40**, 891 (1932), for extended applications of the method, J. H. Van Vleck, *J. Chem. Phys.*, **3**, 803 (1935), for a discussion of the relation between directed bond orbitals and molecular orbitals, and C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **33**, 104 (1937), for a brief discussion of the criterion of maximum overlapping.

same radial function for 3*s* and 3*p* as for 3*d*, and omit the extra terms introduced by the kinetic energy operator.

The radial wave functions used are thus the hydrogen-like 2*p* and 3*d* functions, $R_{21}(r)$ and $R_{32}(r)$, for all orbitals of the *L* and *M* shells, respectively; the symbols ψ_{2s}, ψ_{2p} and ψ_{3s}, ψ_{3p}, ψ_{3d} represent these multiplied by the angular parts 1 (for *s*), $\sqrt{3}\cos\theta$ (for *p*), and $\sqrt{5/4}\,(3\cos^2\theta-1)$ (for *d*), rather than the usual hydrogen-like orbitals. The *z*-axis for each atom points along the internuclear axis toward the other atom.

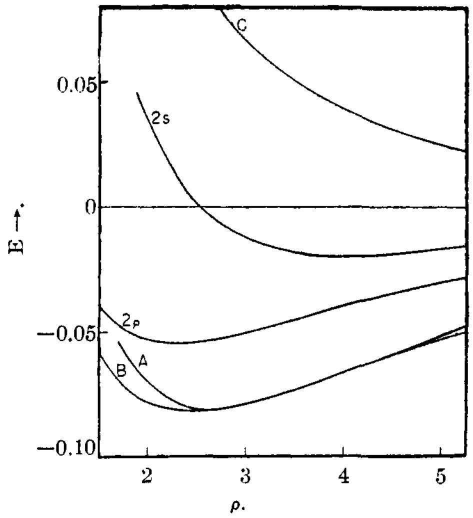

Fig. 1.—Energy curves for one-electron bonds involving 2*s*-2*p* hybridization.

The effective atomic numbers in the radial wave functions cannot be evaluated by minimizing the energy integral, because of neglect of inner shells. In all the calculations reported the effective atomic numbers were given the value 1.

This investigation involved the evaluation of thirty integrals and the computation of numerical values for each of them for values of $\rho = r_{AB}/2a_0$ at intervals of 0.5 from 1.5 to 5.0 for *L* orbitals and from 2.0 to 7.5 for *M* orbitals. The work is straightforward, though laborious, and involves no new methods. In this paper we shall discuss only the results of the calculations.

Bond Orbitals Formed by *s*-*p* Hybridization

An atomic bond orbital $\psi = a\psi_s + b\psi_p$ can be varied from a pure *s* orbital to a pure *p* orbital by varying the ratio of the coefficients *a* and *b*. Energy curves calculated for one-electron bonds between similar orbitals on two atoms, as functions of $\rho = r_{AB}/2a_0$, with r_{AB} the internuclear distance, are shown for various choices of the bond orbitals in Figs. 1 and 2, Fig. 1 representing *L* orbitals and Fig. 2, *M* orbitals. The curves A represent bonds formed by tetrahedral orbitals, with the ratio b/a equal to $3^{1/2}$. The curves B represent the strongest bonds which can be formed by *s*-*p* orbitals, the ratio of b/a being so chosen for each value of ρ as to minimize the energy integral. The curves C correspond to orbitals which are orthogonal to those for curves B; they represent the maximum repulsion given by *s*-*p* orbitals.

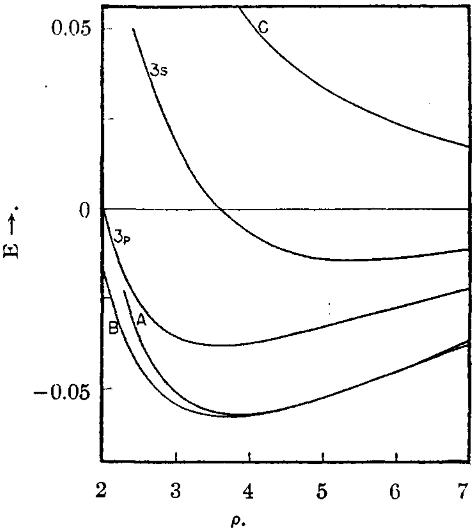

Fig. 2.—Energy curves for one-electron bonds involving 3*s*-3*p* hybridization.

The most striking characteristic of the figures is the close approximation of the tetrahedral-orbital curves (A) to the curves for strongest bonding (B), the difference being very small over the ranges 2.5 to 4.5 in ρ for *L* orbitals and 4 to 6 for *M* orbitals. This shows the extent to which the original simple treatment, which ascribes to tetrahedral orbitals the maximum bond-forming power, is applicable. Similar information is provided by Fig. 3, in which the ratio b/a for the orbitals corresponding to the curves B is shown; in each case this ratio differs from the value for tetrahedral orbitals, 1.732, by less than about 20% over a range of values of about 2 for ρ, beginning with the equilibrium value.

The internuclear distance at which the best bond orbitals are tetrahedral orbitals is in each case somewhat larger than the equilibrium distance given by the minimum of the energy curve. It is possible that in actual molecules the repulsion of inner shells increases the equilibrium internuclear separations toward the values at which the simple treatment of the strengths of bond orbitals is accurate. The results of the present investigation show that even without this effect the simple treatment can be used for qualitative and rough quantitative arguments.

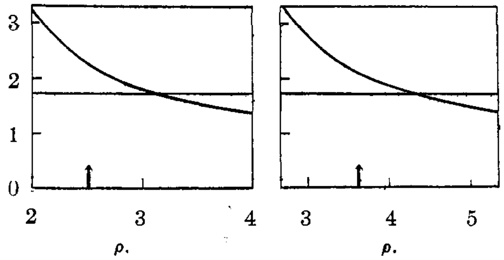

Fig. 3.—The ratios of coefficients of p and s orbitals in best s-p bond orbitals (left, L orbitals; right, M orbitals).

Bond Energies.—It is seen that the bond energies (given by the minima of the curves of Figs. 1 and 2) for s, p, and tetrahedral bonds are in the approximate ratios 1:3:4. (The actual values, in units e^2/a_0, are 0.020, 0.054, and 0.082, respectively, for L orbitals, and 0.014, 0.037, and 0.057, respectively, for M orbitals.) These ratios are the squares of the bond strengths S introduced in the simple treatment, as given by the expression $S = (a + \sqrt{3}\, b)/(a^2 + b^2)^{1/2}$. A further test of the suggested relation $D = kS^2$ connecting the bond energy D with the strength S of the two bond orbitals involved is shown in Fig. 4. The dashed curves in this figure represent S^2 for $2s$–$2p$ and $3s$–$3p$ bond orbitals (with shifted vertical scales) as a function of the coefficient a from 0 to 10, b being placed equal to $10 - a$. With this normalization S^2 increases from 3 at $a = 0$ (p orbitals) to a maximum of 4 at $a = 3.66$ (tetrahedral orbitals) and then decreases to 1 at $a = 10$ (s orbitals). The solid lines show the calculated one-electron-bond energy D with the scale changed by a factor making the energy of the best bond 4. It is seen that in each case the curve for D/k approximates the S^2 curve closely throughout the range, again showing the good approximation provided by the simple treatment.

The results suggest that for bonds between atoms with unlike orbitals ψ_A and ψ_B the bond energy is given by the expression $D = kS_AS_B$, being proportional to the product of the strengths of the two orbitals. The energy of a bond for ψ_A with ψ_B would then be the geometrical mean of the bond energies for ψ_A with ψ_A and ψ_B with ψ_B. This is of significance in connection with a related case. In a discussion of the partial ionic character of covalent bonds[3] the postulate was made that the energy of a normal covalent single bond between unlike atoms A and B is the algebraic mean ${}^1/_2(D_{AA} + D_{BB})$ of the bonds between like atoms of the kinds involved. The discussion above indicates that this postulate should be replaced by a similar postulate[4] with $(D_{AA}D_{BB})^{1/2}$ in place of ${}^1/_2(D_{AA} + D_{BB})$. In case that the bond energies D_{AA} and D_{BB} do not differ greatly in value, there is only a very small difference between their geometric and algebraic means (which for 3 and 4, for example, are 3.46 and 3.50, respectively); and for this reason the arguments based on the earlier postulate are in general valid with the new one. The new postulate is superior to the old in some ways, leading to better agreement with thermal data. In the

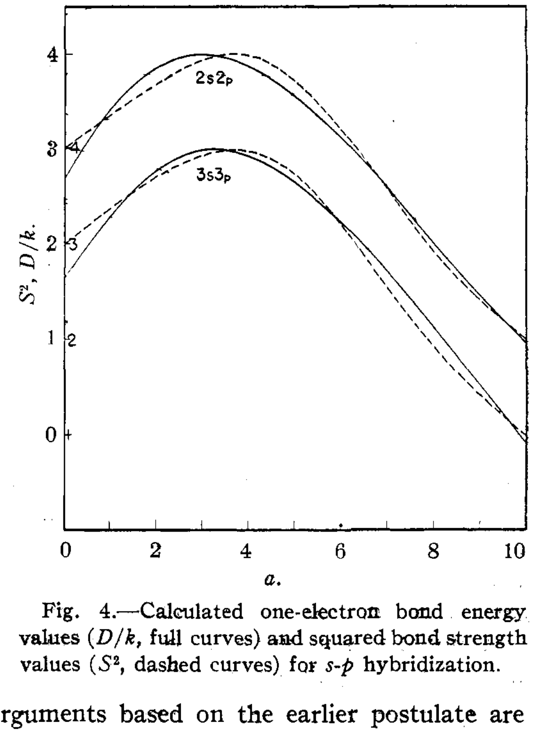

Fig. 4.—Calculated one-electron bond energy values (D/k, full curves) and squared bond strength values (S^2, dashed curves) for s-p hybridization.

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[3] L. Pauling and D. M. Yost, *Proc. Nat. Acad. Sci.*, **18**, 414 (1932); L. Pauling, THIS JOURNAL, **54**, 3570 (1932).

[4] The new postulate is presumably accurate in simple cases, such as for bonds between univalent atoms. For multivalent atoms a complication is introduced by the usual choice of the normal states of separated atoms as the origin for energy measurements, inasmuch as this changes in an erratic manner with change in term character (especially multiplicity) from row to row of the periodic system. It is probable that better results would be obtained for multivalent atoms by using as the energy of a bond the energy required to break that bond and dissociate the molecule into two parts, rather than a fraction of the energy required to dissociate the molecule completely into atoms. At present, however, accurate values of the energy required to break one bond alone in a molecule are not available.

earlier discussion use was made of the equation $D_{AB} = {}^1/_2(D_{AA} + D_{BB}) + \Delta$, in which Δ, the contribution of ionic character to the bond energy, should always be greater than or equal to zero. A few exceptions to this were noted. In case that the new postulate is used, $D_{AB} = (D_{AA}D_{BB})^{1/2} + \Delta'$, these cases are no longer troublesome, all values of Δ' being positive. For the carbon–iodine bond, which alone of those discussed in the earlier work gave a negative value for $\Delta(-0.12$ e. v.), the values $D_{CI} = 2.45$ e. v., $D_{CC} = 3.60$ e. v., and $D_{II} = 1.54$ e. v., lead to the positive value $\Delta' = +0.10$ e. v. Another case in which the original postulate is invalid has been pointed out by Mulliken.[5] From the values $D_0 = 4.45$ e. v. for H_2 and 1.14 e. v. for Li_2, algebraic additivity would give as a lower limit for D_0 for LiH the value 2.80 e. v., to be increased by Δ in case that the bond has some ionic character. The experimental value of D_0 for LiH is about 2.59 e. v.; this shows a discrepancy with the old additivity postulate of 0.2 e. v., and, as emphasized by Mulliken, the discrepancy is really somewhat larger, since the Li–H bond has without doubt some ionic character. The trouble is remedied by the new postulate, which gives 2.25 e. v. as the geometric mean of the values of D_0 for H_2 and Li_2; this leads to 0.34 e. v. for Δ', corresponding to a reasonable difference in electronegativity of hydrogen and lithium. Sodium hydride and potassium hydride provide similar cases. With $D_0 = 0.76$ e. v. for Na_2, the old postulate gives $D_0 = 2.61$ e. v. $+ \Delta$ for NaH, which is incompatible with the experimental value 2.24 e. v.; whereas the new postulate leads to 1.84 e. v. $+ \Delta'$, corresponding to the reasonable value 0.40 e. v. for Δ'. With $D_0 = 0.51$ e. v. for K_2, the old and new postulates give 2.48 e. v. $+ \Delta$ and 1.51 e. v. $+ \Delta'$, respectively, for D_0 for KH; the experimental value is 1.91 e. v., which is incompatible with the first but compatible with the second of these, leading to 0.40 e. v. for Δ'. The sequence of values $\Delta' =$ 0.34, 0.40, and 0.40 e. v. for LiH, NaH, KH, respectively, shows to some extent the increase expected because of the increasing electropositive character of the alkali metals with increasing atomic number; it is possible that this effect would be shown more clearly if more reliable values of D_0 were available.

Interatomic Distances.—The equilibrium internuclear distances (at which the energy curves have their minima) are given for $2s2p$ and $3s3p$ bonds by the curves of Fig. 5, showing the dependence of ρ_0 on the coefficient a in the hybrid orbital $a\psi_s + b\psi_p$, with $b = 10 - a$. It is seen that addition of a very small amount of s to a p orbital causes ρ_0 to decrease slightly, its minimum value being at $a = 1$, which corresponds to a state of the atom which is about 1% s and 99% p (the ratio of a^2 to b^2 being ${}^1/_{81}$). With further increase in a the equilibrium distances increase monotonically toward their values for s bonds.

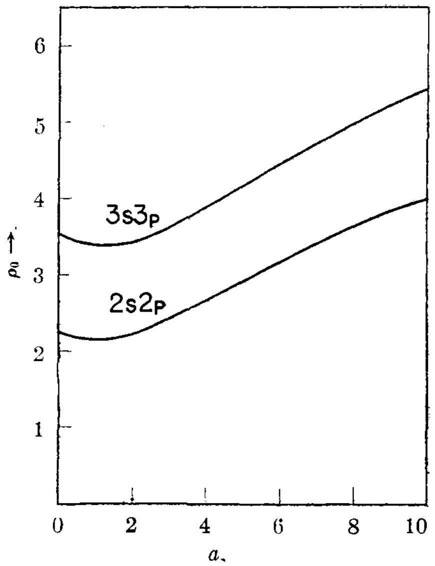

Fig. 5.—Dependence of equilibrium internuclear distance on nature of bond orbitals.

Comparison of Figs. 4 and 5 shows that there is no simple relation between bond energy and equilibrium internuclear distance for s-p bonds, the minima in ρ_0 and the maxima in D occurring for much different values of a. There is, indeed, no reason to expect bond energy to depend in a simple way on bond distance, and the non-existence of a monotonic dependence is shown directly by the fact that in many diatomic molecules r_0 has smaller values for excited states than for the normal states. In a recent discussion of single-bond–double-bond resonance Penney[6] has assumed a simple monotonic relation between bond distance and bond energy; such a relation may of course be valid in special cases, but its validity cannot be assumed in general without justification.

Bond Orbitals Formed by *s-p-d* Hybridization

The results of the calculation of one-electron bond energies for orbitals of the type $a\psi_{3s}$ +

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(5) R. S. Mulliken, *Phys. Rev.*, **50**, 1028 (1936).

(6) W. G. Penney, *Proc. Roy. Soc.* (London), **A156**, 306 (1937).

$b\psi_{3p} + c\psi_{3d}$ are shown in Fig. 6. The contour lines for the diagram 6a indicate values of $S^2 = (a + \sqrt{3}\,b + \sqrt{5}\,c)^2/(a^2 + b^2 + c^2)$, the values of a, b, and c determining the hybrid wave function being given by triangular coördinates (normalized to $a + b + c = 10$). The maximum value of S^2, 9, corresponding according to the simple treatment to the best *spd* bond orbital, occurs[1b] at $a = 2.01$, $b = 3.49$, $c = 4.50$. From this point the bond strength falls off at about the same rate in all directions. In the diagram 6b the contour lines represent similarly the calculated values of the bond energy (in units $0.022\ e^2/a_0$). It is seen that the function corresponds only roughly to S^2, the approximation being much less close than for *s-p* hybridization. The general behavior of the energy surface is similar to that of the S^2 surface; its maximum, however, is shifted by a large amount, lying near the *p-d* line. A study of the energy calculations suggests that this lack of agreement with the simple treatment is to be attributed to the occurrence for small values of ρ of negative values for the overlapping integral between a $3p$ orbital of one atom and a $3d$ orbital of the other. It is possible that in actual molecules the repulsion of inner shells increases the equilibrium values of ρ in such a way as to cause the bond energies to be more nearly proportional to S^2 than for the calculations presented here. It is, indeed, found that at a constant value of ρ in the neighborhood[7] of 4 to 6 the calculated energy curves for hybrid orbitals are closely proportional to S^2, the proportionality being nearly exact at $\rho = 5.5$.

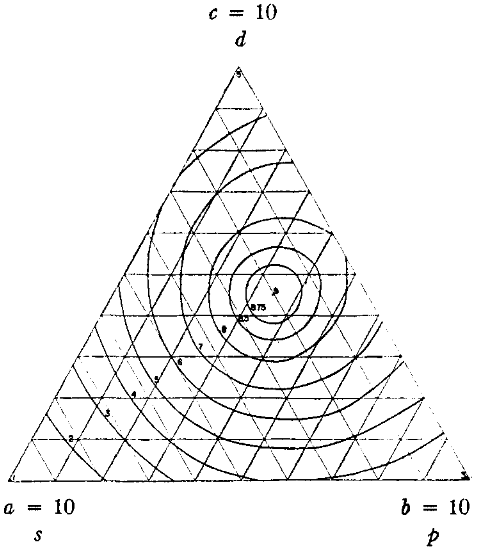

Fig. 6a.—Contour diagram of S^2 (square of bond strength of orbital) for *s-p-d* hybridization.

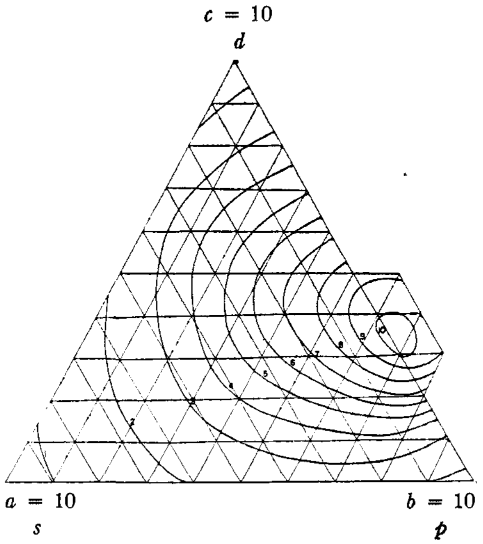

Fig. 6b.—Contour diagram of D/k (calculated one-electron bond energy divided by a constant) for *s-p-d* hybridization.

We conclude that qualitative arguments regarding *s-p-d* hybridization can be safely based on the simple bond-strength treatment, but that this treatment cannot be expected to have the same quantitative significance in this case as for *s-p* bond orbitals.

The Lithium Molecule-Ion

In the preceding calculations the orbitals $2s$ and $2p$ have been assigned the same energy value. In the lithium atom the $2p$ level lies 1.84 e. v. above the $2s$ level, as indicated by the horizontal lines (corresponding to a lithium ion and a lithium atom in the ^2P or ^2S state at large internuclear distance) in Fig. 7. We can take this *s-p* separation into account by adding 1.84 e. v. to H_{pp} and making corresponding changes in the other integrals which occur in the secular equation. The two roots of the secular equation are represented by curves B and C of Fig. 7. Curve C, the upper of the two roots, represents the interaction of a lithium ion and an excited lithium atom; according to this simple treatment only a weak bond is formed, the curve being repulsive to about $\rho = 7$, at which the bond energy is about 0.3 e. v.

Curve B, representing the combination of a lithium ion and a normal lithium atom to give a

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(7) The minima of the energy curves occur at about $\rho = 4$ or 5 except in the region around $a = 0$ to 2, $b = 4$ to 6, $c = 2$ to 5, where values as low as 2 or 2.5 are found.

normal lithium molecule-ion, has its minimum value at $\rho = 2.85$, corresponding to the equilibrium internuclear distance $r_e = 3.02$ Å. The value found for the bond energy D_e is 1.19 e. v. This energy value is in good agreement with that calculated by James[8] by a reliable method, 1.27 e. v., and the value of r_e agrees well with that estimated by James, 3.0 Å. The agreement provides one more example showing the surprisingly good approximations yielded by very simple treatments of molecular problems such as that reported in this paper.

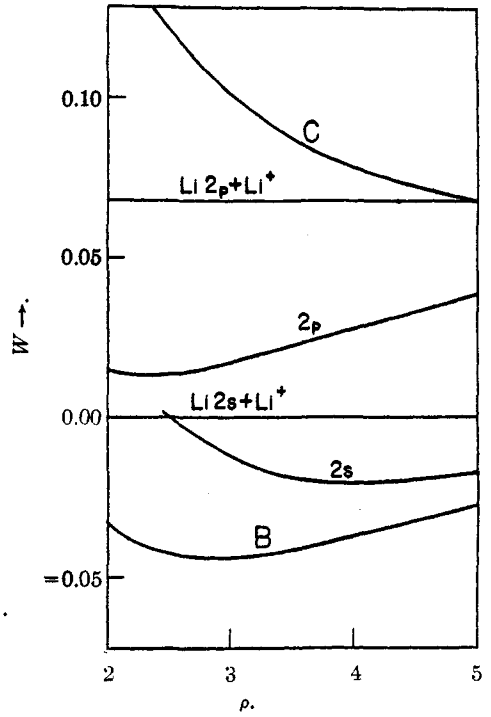

Fig. 7.—Energy curves for the lithium molecule-ion, with consideration of the s-p separation.

Although the s-p separation is nearly twice as large as the bond energy, there occurs extensive hybridization of the bond orbitals: at the equilibrium internuclear distance the bond orbitals are composed nearly equally of ψ_s and ψ_p, the ratio b/a being 0.92 (Fig. 8). This hybridization increases the bond energy by more than 100%, from 0.54 e. v. for a pure s bond (Fig. 7) to 1.19 e. v. The contribution of ψ_p and the value of the bond energy are of course smaller than they would be for zero s-p separation ($b/a = 1.9$ and $D = 2.16$ e. v. at $r = 3.0$ Å.). It may be pointed out that the ratio $b/a = 1$ corresponds to a bond angle of 180° for two equivalent orbitals.

James also carried out a treatment of the lithium molecule-ion with use of $2s$ orbitals and explicit consideration of the four K electrons, obtaining the energy value -0.304 e. v. at $r = 2.98$ Å. (this being not necessarily the minimum point of the curve). Our curve for an s bond similarly gives a very small energy value, -0.22 e. v., at this value of r. The calculations described above indicate that the principal source of inaccuracy in these treatments is the assumption that the bonds are s bonds, and that the consideration of s-p hybridization makes a great improvement.

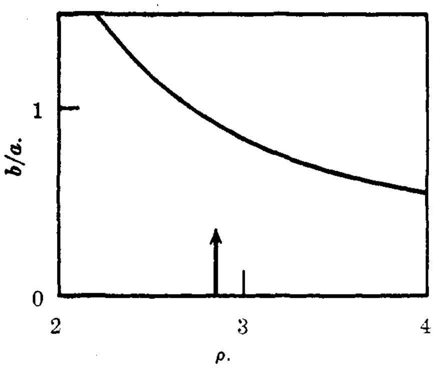

Fig. 8.—The ratio of coefficients of p and s orbitals for the normal state of the lithium molecule-ion.

A Test of the Validity of Simple Methods of Discussing Resonance.—In the quantum mechanical treatment of chemical problems, especially those involving the resonance of molecules among several valence-bond structures, many simplifying assumptions are made in order that the solution of the equations involved may become practicable. An important one of these assumptions, that the orthogonality integral $\Delta_{\mathrm{I\,II}} = \int \psi_{\mathrm{I}}\psi_{\mathrm{II}}d\tau$ for two wave functions corresponding to two structures I and II can be neglected and the secular equation written in the form

$$\begin{vmatrix} H_{\mathrm{I\,I}} - W & H_{\mathrm{I\,II}} \\ H_{\mathrm{I\,II}} & H_{\mathrm{II\,II}} - W \end{vmatrix} = 0 \qquad (1)$$

rather than

$$\begin{vmatrix} H_{\mathrm{I\,I}} - W & H_{\mathrm{I\,II}} - \Delta_{\mathrm{I\,II}}W \\ H_{\mathrm{I\,II}} - \Delta_{\mathrm{I\,II}}W & H_{\mathrm{II\,II}} - W \end{vmatrix} = 0 \qquad (2)$$

can be tested for the system just discussed, the lithium molecule-ion. The functions I and II are the s-bond and p-bond functions, respectively. The curves B and C of Fig. 2 represent

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(8) H. M. James, *J. Chem. Phys.*, **3**, 9 (1935). No experimentally determined values for r_e and D_e have been reported.

the two roots of Equation 2 for zero *s-p* separation and the curves B and C of Fig. 7 the roots of Equation 2 with 1.84 e. v. *s-p* separation. To test the extent to which neglect of $\Delta_{\mathrm{I\,II}}$ can be compensated by suitable choice of values of the energy exchange integral $H_{\mathrm{I\,II}}$, we may evaluate $H_{\mathrm{I\,II}}$ as a function of ρ by substituting for $H_{\mathrm{I\,I}}$ and $H_{\mathrm{II\,II}}$ in Equation 1 their values as given by curves 2*s* and 2*p*, respectively, of Fig. 2 and choosing values of $H_{\mathrm{I\,II}}$ which cause curve *B* of this figure to represent the low root of the equation. The expression for $H_{\mathrm{I\,II}}$ found in this way can then be used to evaluate the low root of Equation 1 for the case of 1.84 e. v. *s-p* separation. It is found that over the range 2.5 to 3.5 for ρ curve C as calculated in this way differs from the curve given by Equation 2 by less than 0.05 e. v. (4% of the bond energy). This provides some justification for the use of Equation 1 in place of Equation 2 for rough calculations in which the magnitude of the exchange integral is determined empirically.

We are indebted to Dr. S. Weinbaum and Mrs. M. R. Lassettre for assistance with the calculations described in this report.

Summary

Theoretical energy curves for one-electron bonds between two atoms are calculated for bond orbitals formed by hybridization of 2*s* and 2*p* orbitals, 3*s* and 3*p* orbitals, and 3*s*, 3*p*, and 3*d* orbitals, the same radial part being used for the orbitals in a set. It is found that for *s-p* hybridization the bond energy is closely proportional to S^2, with S the magnitude of the angular part of the bond orbital in the bond direction. This relation is less satisfactorily approximated in the case of *s-p-d* hybridization.

It is shown that the energy of a normal covalent bond A-B between unlike atoms is probably represented more closely by the geometric mean of the bond energies for A-A and B-B than by their arithmetic mean.

The energy of the one-electron bond in the lithium molecule ion is calculated with consideration of the *s p* separation to be 1.19 e. v., and the hybrid bond orbital involved is shown to involve about equal contributions from the 2*s* and 2*p* orbitals of the lithium atom.

PASADENA, CALIF. RECEIVED JUNE 1, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Mechanism of the Dehydration of Calcium Sulfate Hemihydrate. II. Observations with Large Crystals

BY HARRY B. WEISER AND W. O. MILLIGAN

In the first communication[1] under this title it was demonstrated that: (1) contrary to the conclusions of Linck and Jung, Balarew, Gibson and Holt, and others, the dehydration curve of calcium sulfate hemihydrate has a definite step indicating that the compound is a true chemical hydrate and not a zeolite; (2) contrary to the conclusions of Jung, Ramsdell and Partridge, Caspari, Gallitelli, Onorato, and others, calcium sulfate hemihydrate and dehydrated hemihydrate (soluble anhydrite) are not identical in structure as evidenced by the existence of characteristic differences in the X-radiograms of the two substances.

At about the same time that the above results were reported, Caspari,[2] in a second paper, reached diametrically opposite conclusions from an X-ray examination of large crystals of hemihydrate grown from a nitric acid solution. In the first place, he claims that the proposed arrangement of three molecules of calcium sulfate in a hexagonal unit cell will not suit a definite hydrate of the composition $CaSO_4 \cdot 0.5H_2O$; and in the second place, he states that X-ray rotation spectrograms of the opaque anhydrous pseudomorph obtained by dehydrating the so-called hemihydrate were in every way identical with those of the original hemihydrate.

In view of these conflicting reports, it becomes a question of fact whether macrocrystals of hemihydrate such as used by Caspari behave the same or differently from microcrystals obtained by dehydration of $CaSO_4 \cdot 2H_2O$. The following experiments attempt to answer this question.

Experimental

Preparation of Large Crystals of $CaSO_4 \cdot 0.5H_2O$.—To prepare large crystals Caspari dis-

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[1] Weiser, Milligan and Ekholm, THIS JOURNAL, **58**, 1261 (1936).

[2] Caspari, *Proc. Roy. Soc.* (London), **155**, 41 (1936).