**576.** *The Role of* 3d-*Electrons in Valency States of First-row Elements.*

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Gillespie (*J.*, 1952, 1002) has suggested that 3d-orbitals may contribute to valency states of carbon in certain electron-deficient compounds. It is now shown that any such contributions leave the general configuration of the valency electrons unchanged.

GILLESPIE (*J.*, 1952, 1002) recently suggested that 3d-orbitals may contribute to certain valency states of first-row elements in general, and of carbon in particular. In the present paper the problem is investigated in more detail and it is shown that a flaw in Gillespie's argument invalidates most of his conclusions.

The point can be made most clearly by referring to one of the specific problems discussed by Gillespie : the structure of the triangular non-classical ion (I), derived from CH_3^+ and a symmetrical olefin. Structures of this type appear as intermediates in carbonium-ion rearrangements (cf. Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3274), and they have been interpreted (Dewar, *J.*, 1946, 406) as co-ordination compounds (π-complexes) of the olefin acting as donor to the alkyl cation as acceptor, as in (II). According to this view the two electrons taking part in the dative bond occupy a molecular orbital formed from the $2p$ atomic orbitals that contribute to the π-bond of the olefin, and a single tetrahedral, hybrid atomic orbital of the methyl carbon atom. (This is equivalent to earlier representations in terms of resonance theory; see Dewar, *Bull. Soc. chim.*, 1951, **18**, 71c, for a review and references.) The orbitals concerned, and their mode of overlap, are indicated in (III). Gillespie now suggests that the orbitals of the methyl group involved in the formation of (I) are not a single sp^3 hybrid as in (III), but a pair of sp^3d hybrids (χ_1, χ_2) (IV) formed by further hybridisation of the tetrahedral sp^3 atomic orbital with a $3d$ atomic orbital. His argument is that the difference in energy between the sp^3 atomic orbital and an unoccupied $3d$ atomic orbital of carbon is small enough to allow interaction, and that the resulting sp^3d atomic orbitals can overlap much more efficiently with the olefinic p orbitals than can the single sp^3 hybrid.
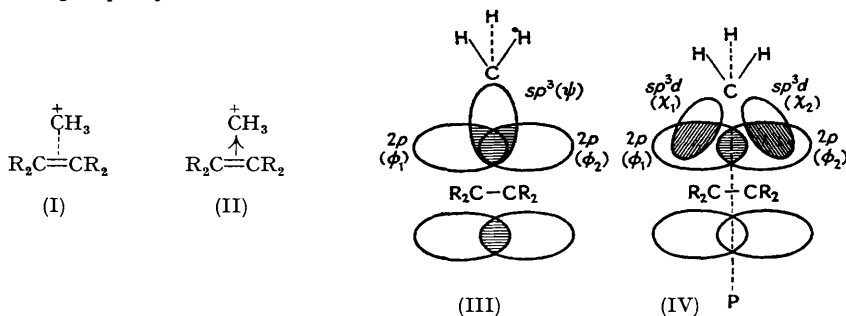
Gillespie did not analyse the fate of the two electrons that bond the three carbon atoms in (I). It is evident that no one of the three possible classical structures (V)—(VII), corresponding to the possible modes of overlap in (IV), can represent the system; it must be depicted as a hybrid of these structures, possibly with others in addition. The flaw
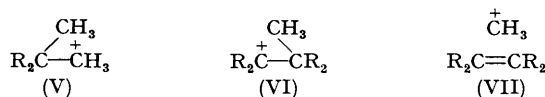
in Gillespie's argument lies in the fact that when the system is so depicted, the net contribution of the $3d$ orbital vanishes identically. Gillespie's suggestion, although at first sight attractive, is therefore fundamentally incorrect. The same flaw invalidates his con-

6 N

clusions concerning other electron-deficient systems (beryllium, aluminium, and platinum methyls); here again carbon $3d$ orbitals cannot be involved in the way Gillespie suggested.

The valence-bond treatment of this system is relatively complicated and involves factors not considered by Gillespie. The problem will therefore first be discussed in terms of molecular-orbital theory, wherein the possible role of the $3d$ orbitals will become clearer. The results obtained also serve as a guide in the subsequent valence-bond treatment of (I).

It will be assumed throughout that the normal σ-bonds in (I), *i.e.*, the C–H and C–R bonds, and the σ-component of the R_2C–CR_2 bond, are formed by localised pairs of electrons; this conventional assumption is reasonable since any delocalisation of the σ-electrons can lead only to small second-order effects (*i.e.*, hyperconjugation). It will also be assumed * (cf. Dewar, *loc. cit.*) that the $R_2C\cdot CR_2$ group in (I) is coplanar, the central pair of carbon atoms having sp^2 hybridisation, and that the methyl-carbon atom lies on the two-fold axis of symmetry perpendicular to the plane containing the groups R. The two carbon atoms, C, in the grouping $R_2C\cdot CR_2$ will be referred to as the *basal* carbon atoms, and that in the methyl group as the *apical* carbon atom. With these assumptions, (I) has two planes of symmetry: one (P) perpendicular to the line joining the basal carbon atoms, and one (Q) containing the basal and the apical carbon atoms [see (IV)]. These three carbon atoms are linked by a delocalised pair of electrons, and it is the configuration of these electrons that is to be studied.

In the molecular-orbital representation, this pair of electrons occupies a single molecular orbital. The atomic orbitals available for constructing this are the two unhybridised $2p$ orbitals [ϕ_1, ϕ_2 in (IV)] of the basal carbon atoms, and an sp^3 hybrid orbital (ψ), and the set of five $3d$ orbitals, of the apical carbon atom.

Since these five $3d$ orbitals form a complete set, there is no loss in generality if an arbitrary orthogonal set is chosen; for any $3d$ orbital of the apical carbon atom will be expressible as a linear combination of orbitals from any such set. The usual choice, which will be quite suitable here, is a set of five real orbitals defined with respect to cartesian co-ordinates. For the present purpose it will be convenient to arrange the orbitals so that each is either symmetric or antisymmetric with respect to inversion in either of the planes P, Q. Accordingly the intersection of P and Q is taken to be z-axis, P the yz-plane, and Q the xz-plane. The symmetry properties of the corresponding set of $3d$ orbitals are shown in the Table. The orbital explicitly considered by Gillespie is the one described here as $3d_{xz}$.

Orbital	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	$3d_{x^2-y^2}$	$3d_{z^2}$	ϕ^+	ϕ^-	ψ
Behaviour on reflection in } { P	—	—	+	+	+	+	—	+
Q	—	+	—	+	+	+	+	+

The orbitals ϕ_1, ϕ_2 do not conform to the symmetry of the molecule, and it is convenient to replace them by an equivalent pair of " symmetry orbitals " ϕ^+, ϕ^- defined by

$$\phi^+ = 2^{\frac{1}{2}}(\phi_1 + \phi_2); \quad \phi^- = 2^{\frac{1}{2}}(\phi_1 - \phi_2) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The symmetry properties of ϕ^+ and ϕ^-, and of the sp_3 hybrid orbital ψ, are also shown in the Table.

Now the average electron distribution in a molecule must conform to the symmetry of the field in which the electrons move. Since the nuclear field in (I) is symmetric with respect to reflection in P and Q, so also must be the average electron distribution. Consequently the wave function of the electrons must be either symmetric or antisymmetric, the electron distribution being symmetric in either case since it is given by the square of the wave function. The required three-centre molecular orbital Φ must therefore be either symmetric or antisymmetric with respect to reflection in P, Q. But Φ is being constructed from orbitals each of which has that kind of symmetry; it is then easily seen that Φ will be of the required type only if it is composed of orbitals all of exactly the same symmetry type.

Since moreover at least one of the orbitals ϕ^+, ϕ^- must contribute to Φ if electrons in Φ are to bond all three carbon atoms C in (I), and since both ϕ^+ and ϕ^- are symmetric with respect to reflection on Q (see Table), the orbitals $3d_{xy}$, $3d_{yz}$ cannot contribute to Φ. The

* This assumption does not affect the argument that follows; ϕ_1, ϕ_2 [in (IV)] could equally be hybrid orbitals.

remaining orbitals can be classified as symmetric or antisymmetric depending on their behaviour on reflection in P :

$$\left.\begin{array}{ll} \text{Symmetric} & 3d_{x^2-y^2},\, 3d_{z^2} \\ \text{Antisymmetric} & 3d_{xz} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
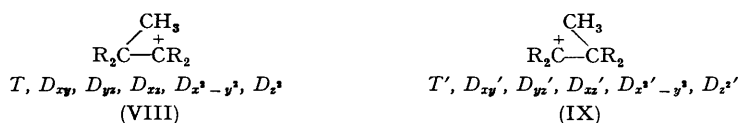
Φ must be represented as a linear combination of orbitals from one or other of these sets, but not both.

It is evident that the molecular orbital of lowest energy (*i.e.*, Φ) will be symmetric, for the lowest symmetric orbital will have no nodes, whereas the lowest antisymmetric orbital necessarily has one node (in the plane P). Moreover, the low-energy atomic orbital ψ can contribute only to symmetric molecular orbitals. Therefore the only $3d$ orbitals that can contribute to Φ are the symmetric orbitals $3d_{x^2-y^2}$ and $3d_{z^2}$.

This immediately disposes of Gillespie's suggestion that the bonding of the apical carbon is through hybrids of ψ with the antisymmetric orbital $3d_{xz}$. The latter orbital cannot contribute at all to the ground state of (I). Contributions by the symmetric $3d$ orbitals, while possible, would not alter the general situation; for hybrids of such orbitals with ψ would have the same general shape as ψ itself and would not overlap any better than ψ with the basal p orbitals ϕ_1, ϕ_2. Whether or not these symmetric $3d$ orbitals do in fact make a significant contribution to the ground state of (I) is a question which could be answered only by detailed calculations of prohibitive difficulty. On general grounds it seems very unlikely that such contributions can be appreciable in view of the high energy of the $3d$ orbitals and in view of the fact that their inclusion would not increase the orbital overlap. But the type of d orbital hybridisation considered by Gillespie is definitely ruled out by considerations of symmetry.

The valence-bond representation will now be discussed. The structure (I) is then depicted as a hybrid of the structures (V), (VI), and (VII). According to Gillespie, the C–CH_3 bond in (V) or (VI) is formed through a sp^3d hybrid orbital of the apical carbon atom. The d component of this orbital can be represented as a linear combination of the standard d orbitals (see Table). If t is written for the relevant sp^3 orbital of the apical carbon atom, the bonds are then formed by td^5 hybrid orbitals of that atom.

Now if the C–CH_3 bond in (V) is formed by such a hybrid, (V) can in turn be represented as a hybrid of the six structures (VIII) in each of which the C–CH_3 bond is formed by one or other of the six " pure " orbitals (t or d). Likewise, (VI) can be represented as a hybrid of the six structures (IX). (T, D_{xy}, etc., denote structures derived from the atomic orbitals t, d_{xy}, etc.).

$$\begin{array}{cc} \begin{array}{c} CH_3 \\ \diagup\ + \\ R_2C\!-\!CR_2 \\ \end{array} & \begin{array}{c} CH_3 \\ +\ \diagdown \\ R_2C\!-\!CR_2 \\ \end{array} \\ T,\, D_{xy},\, D_{yz},\, D_{zx},\, D_{x^2-y^2},\, D_{z^2} & T',\, D_{xy}',\, D_{yz}',\, D_{zx}',\, D_{z^2-y^2}',\, D_{z^2}' \\ \text{(VIII)} & \text{(IX)} \end{array}$$

The bond eigenfunctions Φ, Φ' of (V) and (VI) are then given by

$$\left.\begin{array}{l} \Phi = aT + \sum\limits_r b_r D_r \\[2mm] \Phi' = a'T' + \sum\limits_r b_r'D_r' \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the total eigenfunction Ψ of (I) by

$$\begin{aligned} \Psi &= c\Phi + c'\Phi' + c''\Phi'' \\ &= (acT + a'c'T') + \sum\limits_r (b_r c D_r + b_r'c'D_r') + c''\Phi'' \quad . \quad . \quad . \quad (4) \end{aligned}$$

where the a's, b's, and c's are algebraic coefficients and Φ'' is the bond eigenfunction of (VII).

Now Ψ must be either symmetric or antisymmetric with respect to inversion in P; it follows that

$$ac = \pm\, a'c'\,; \quad b_r c = \pm\, b_r'c' \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Therefore, (4) can be written in the form

$$\Psi = m(T \pm T') + \Sigma_r n_r(D_r \pm D_r') + c''\Phi'' \quad . \quad . \quad . \quad . \quad (6)$$

The structures T, D_r, etc., can therefore enter Ψ only as the " symmetry eigenfunctions " $(T \pm T')$, $(D_r \pm D_r')$. Also for reasons given earlier, all the contributing symmetry eigenfunctions must be of the same symmetry type, and since Φ'' is itself symmetric it can contribute only if Ψ is symmetric.

Let us denote the twelve symmetry eigenfunctions by $(X_r \pm X_r')$, derived from atomic orbitals ξ_r where ξ_r is t or one of the five $3d$ orbitals. $(X_r \pm X_r')$ can be factored into a series of products of σ-bond eigenfunctions, a spin term for the pair of electrons forming the central C–C bonds, and the corresponding space eigenfunction. Since the two former sets of factors will be common to all the functions in Ψ, attention can be confined to the space eigenfunction of the delocalised pair of electrons. In the case of $(X_r + X_r')$ and $(X_r - X_r')$ these functions, x_r, x_r' can be expanded as

$$\begin{aligned}
x_r &= 2^{\frac{1}{2}}\{(\phi_1{}^1\xi_r{}^2 + \phi_1{}^2\xi_r{}^1) + (\phi_2{}^1\xi_r{}^2 + \phi_2{}^2\xi_r{}^1)\} \\
&= 2^{\frac{1}{2}}\{(\phi_1{}^1 + \phi_2{}^1)\xi_r{}^2 + (\phi_1{}^2 + \phi_2{}^2)\xi_r{}^1\} \\
x_r' &= 2^{\frac{1}{2}}\{(\phi_1{}^1\xi_r{}^2 + \phi_1{}^2\xi_r{}^1) - (\phi_2{}^1\xi_r{}^2 + \phi_2{}^2\xi_r{}^1)\} \\
&= 2^{\frac{1}{2}}\{(\phi_1{}^1 - \phi_2{}^1)\xi_r{}^2 + (\phi_1{}^2 - \phi_2{}^2)\xi_r{}^1\}
\end{aligned} \quad \Bigg\} \quad . \quad . \quad . \quad . \quad (7)$$

where the superscripts as usual distinguish between the electrons occupying the various atomic orbitals. From (7) it is seen that x_r, x_r' have the form of simple bond eigenfunctions for bonds formed between the atomic orbital ξ_r and the symmetry orbitals ϕ^+, ϕ^- [cf. eqns. (1)]. Now a bond can be formed by two orbitals only if they have the same symmetry. Since ϕ^+ and ϕ^- are symmetric with respect to inversion in Q, only those symmetry eigenfunctions can contribute to Ψ which are derived from orbitals ξ_r, symmetric with respect to inversion in Q. Consequently the symmetry eigenfunctions derived from the orbitals $3d_{xy}$ or $3d_{yz}$ can be eliminated at once, since they do not correspond to structures with a bond between the apical carbon and one basal carbon atom. Of the remaining pairs of symmetry eigenfunctions $(X_r \pm X_r')$, only one in each case is acceptable for the same reason. The surviving eigenfunctions may now be classified according to their behaviour on reflection in P:

Symmetric $\quad (T + T')$, $(D_{x^2-y^2} + D'_{x^2-y^2})$, $(D_{z^2} + D_{z^2}')$ $\Big\}$ $\quad . \quad . \quad . \quad . \quad (8)$

Antisymmetric $(D_{xz} + D_{xz}')$

Since the functions contributing to Ψ must be either all symmetric or all antisymmetric, it is evident that $(T + T')$ and $(D_{xz} + D_{xz}')$ cannot both contribute. Consequently the relevant orbitals of the apical carbon atom in (I) cannot be td_{xz} hybrids, as Gillespie supposed.

It is evident that the ground state of (I) must be symmetric, not only because many more structures can contribute to a symmetric state, but also because the symmetric structures include $(T + T')$ and Φ'' which must on energetic grounds be the most important. Both the molecular-orbital and valence-bond treatments agree on this point, and a comparison of expressions (2) and (6) shows that they also agree on the orbitals which can contribute to (I), on the orbitals which can contribute to symmetric states of (I), and on the orbitals which can contribute to antisymmetric states.

The difficulty in applying the valence-bond method to this problem lies in distinguishing between pairs of symmetry eigenfunctions $(X_r + X_r')$ and $(X_r - X_r')$. One or other member of each pair will be symmetric with respect to inversion in P, and it is not at all evident why each symmetric member should not be able to contribute to Ψ.

The argument given above shows, however, that one member of each pair must be rejected since it does not correspond to a bonded structure. The flaw in Gillespie's argument is evident; his structures for (V) and (VI) correspond in the present terminology

(neglecting algebraic factors) to $(T + D_{xz})$ and $(T' - D_{xz}')$; the final eigenfunction Ψ' for (I) then reduces (numerical factors being neglected) to

$$\Psi' = (T + T') + (D_{xz} - D_{xz}') + \Phi'' \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and the contribution of the second term in fact vanishes.

These arguments may easily be extended to the other electron-deficient molecules considered by Gillespie, in particular beryllium, aluminium, and platinum methyls. In each case there can be no contribution to the ground state by the particular d orbitals invoked by him. The only d orbitals that can contribute are ones which do not significantly alter the symmetry of the tetrahedral sp^3 orbitals with which hybridisation is supposed to occur, and such contributions cannot therefore have any significant effect on the efficacy of orbital overlap.

It may be noted that these criticisms of Gillespie's suggestions do not apply to systems containing additional electrons. Thus the transition state of a Stevens rearrangement formally resembles (I), but with CH_3^- replacing CH_3^+; here there are two additional delocalised electrons which must occupy a molecular orbital of higher energy than Φ. Of the two lowest orbitals available, one is in fact antisymmetric with respect to inversion in P. If the extra electrons occupy this orbital, a contribution by the $3d_{xz}$ orbital would be possible. The same is true of the transition state for a $S_N 2$ reaction where two of the four delocalised electrons occupy an orbital of symmetry appropriate to d interaction. Note that in these cases classical structures are not electron-deficient; in the case of (I), or of the metal methyls mentioned above, at least one atom has an incomplete valency shell in any classical structure.

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