178. *The Use of* 3d *Orbitals in Certain Valency States of the Carbon Atom and Other First-row Elements.*
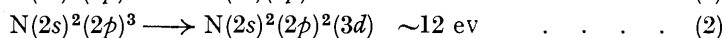
By R. J. GILLESPIE.

The possibility that carbon and nitrogen utilise their $3d$ orbitals in bond formation in certain molecules is discussed. The conditions are considered under which higher valency states involving these orbitals are formed and it is shown that the promotional energies involved are probably not prohibitively large. On the basis of the assumption that carbon can utilise one or more of its $3d$ orbitals for bond formation under suitable circumstances, the transition state of a bimolecular substitution reaction at a saturated carbon atom, the transition state of a carbonium ion rearrangement, and the electronic structure of certain metal alkyls are discussed in detail. The possibility that other first-row elements also utilise their $3d$ orbitals in bond formation is also briefly considered.

IT is usually assumed that the elements of the first period of the Periodic Table cannot expand their outer octets when combining with other atoms, thus utilising their $3d$ orbitals, as these orbitals are supposed to lie at a very high energy level with respect to the $2s$ and the $2p$ orbitals. It is suggested here, however, that the promotional energy involved is not necessarily so large as to make the use of $3d$ orbitals quite impossible, and that in suitable circumstances carbon, and possibly nitrogen, if not other first-row elements, may make some use of these oribtals and thus achieve a covalency of greater than four.

The promotional energy needed to reach various valency states of an atom can in most cases be calculated approximately from spectroscopic data. Such values, however, apply to the free atom and not to the atom in a state of combination. As we shall show later, the values for the free atom and the combined atom may be quite different. Unfortunately we have no direct information about promotional energies for combined atoms.

We shall first calculate the promotional energies needed to reach the quinquevalent state of a free nitrogen atom and a free negative carbon atom C^- and compare them with the promotional energies needed to reach the quinque- and sexa-valent states of phosphorus and sulphur respectively, thereby showing in a rather rough way that the energy involved in the case of carbon is not prohibitive. We can obtain the information we require from spectral data for the nitrogen atom.

We have that

$$N(2s)^2(2p)^3 \longrightarrow N(2s)(2p)^4 \quad \sim 11 \text{ ev} \quad . \quad . \quad . \quad . \quad . \quad (1)^*$$

$$N(2s)^2(2p)^3 \longrightarrow N(2s)^2(2p)^2(3d) \quad \sim 12 \text{ ev} \quad . \quad . \quad . \quad . \quad (2)$$

There is no experimental value for the transition

$$N(2s)^2(2p)^3 \longrightarrow N(2s)(2p)^3(3d) \quad . \quad . \quad . \quad . \quad . \quad (3)$$
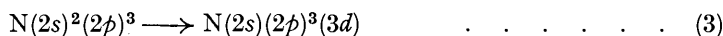
so let us assume as a first approximation that the energy involved is (1) + (2), *i.e.*, 23 ev. This procedure must, however, overestimate the energy of this transition, as (1) involves the energy of repulsion of two electrons in the same $2p$ orbital whereas the summed process (3) does not. Thus our first estimate of 23 ev will probably be too large by several electron-volts. Let us therefore assume process (3) to involve ~ 20 ev.

The ground state of the negative carbon atom has the configuration $(2s)^2(2p)^3$. If one of the $2s$ electrons is promoted to a $3d$ level, the quinquevalent configuration $(2s)(2p)^3(3d)$ is obtained. We can obtain the energy associated with this promotion by multiplying the value 20 ev obtained above for the analogous promotion in nitrogen by $Z'_C{}^{-2}/Z'_N{}^2$ where Z'

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* The spectroscopic data used in this paper have been taken from " Atomic Energy Levels " by Charlotte E. Moore, Circular No. 467 of Nat. Bureau Stand.

is the effective nuclear charge, *i.e.*, $Z - s$, where s is the screening constant. We have, using Slater's rules,

$$Z'_N = 3 \cdot 9 \text{ and } Z'_{O-} = 2 \cdot 9$$

Hence we find $\quad\quad C^-(2s)^2(2p)^3 \longrightarrow C^-(2s)(2p)^3(3d) \quad \sim 11 \text{ ev}$

The electron affinity of the carbon atom is 1 ev, and therefore we have

$$C(2s)^2(2p)^3 \longrightarrow C^-(2s)(2p)^3(3d) \quad \sim 10 \text{ ev}$$

Now the values given above are for the lowest energy terms of the various electronic configurations. Hence the energies of 10 ev obtained for the formation of the $C^-(2s)(2p)^3(3d)$ configuration from the carbon atom in its ground state and of 20 ev for the formation of the $N(2s)(2p)^3(3d)$ configuration from the free nitrogen atom in its ground state apply, strictly, to the lowest energy terms of these configurations. The actual valency states will be linear combinations of all the atomic states with these configurations and would be expected to lie at 2—3 v above the lowest energy state.

The tetrahedral sp^3 valency state of carbon is known to be at 7 ev above the ground state. Hence we may conclude that the additional energy needed to reach the quinquevalent state from the tetrahedral state is very approximately 6 ev. For nitrogen, the additional energy needed to reach the quinquevalent state from the tervalent ground state is of the order 23 ev.

We may now consider the promotional energies associated with the formation of the quinquevalent state of the phosphorus atom from the tervalent state, and the sexavalent state of sulphur from the bivalent state, both these higher valency states being known in stable compounds. For the phosphorus atom we have

$$P(3s)^2(3p)^3 \longrightarrow P(3s)(3p)^4 \quad \sim 8 \text{ ev}$$
$$P(3s)^2(3p)^3 \longrightarrow P(3s)^2(3p)^2(3d) \quad \sim 9 \text{ ev}$$

Hence, adopting the same procedure as for nitrogen, we have

$$P(3s)^2(3p)^3 \longrightarrow P(3s)(3p)^3(3d) \quad \sim 17 \text{ ev}$$

This method overestimates the actual energy involved as explained earlier and a fair estimate for the transition

$$P(3s)^2(3p)^3 \longrightarrow P(3s)(3p)^3(3d)$$

appears to be ~ 13 ev. Again, this is the energy of formation of the lowest atomic state with this configuration, and the actual valence state may be several volts higher, *i.e.*, ~ 16 ev.

For the sulphur atom we have

$$S(3s)^2(3p)^4 \longrightarrow S(3s)^2(3p)^5 \quad \sim 9 \text{ ev} \quad\quad\quad\quad (4)$$
$$S(3s)^2(3p)^4 \longrightarrow S(3s)^2(3p)^3(3d) \quad \sim 9 \text{ ev} \quad\quad\quad\quad (5)$$

therefore $\quad\quad S(3s)^2(3p)^4 \longrightarrow S(3s)^2(3p)^2(3d)^2 \quad \sim 18 \text{ ev}$

hence by the summation procedure employed above

$$S(3s)^2(3p)^4 \longrightarrow S(3s)(3p)^2(3d)^2 \quad \sim 27 \text{ ev}$$

In this case the repulsion term arising from placing an electron in an orbital already containing one electron is involved in both (4) and (5), but with opposite sign, hence to a first approximation no correction is required. An upward correction of several volts will, however, be needed because the valency state of the sulphur atom will be several volts higher than the lowest atomic state of the same configuration. Thus the formation of the sexavalent state of sulphur from the bivalent state involves a promotional energy of approximately 30 ev.

In all cases where an atom has several valency states the energy of formation of the higher states is partly offset by the formation of additional bonds. However, when reasonable values are taken for the energies of formation of these additional bonds it still appears that the actual promotional energies cannot be so great as the above calculations indicate; if they were so great, stable molecules would not be formed by these higher-valency states. Thus, for example, the energy of the reaction

$$PCl_3 + 2Cl \longrightarrow PCl_5$$
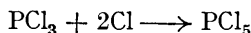
is 78 kcal. (Syrkin and Diatkina, " The Structure of Molecules," Butterworth, London, 1950, p. 261). If we take the energy of formation of the new bonds as a first approximation to be the same as in PCl_3, *i.e.*, 75 kcal. (Syrkin and Diatkina, *op. cit.*), then apparently the actual promotional energy needed to reach the quinquevalent state of phosphorus from the tervalent state is $(2 \times 75) - 78 = 72$ kcal. ~ 3 ev. This value is to be compared with the value ~ 16 ev calculated above for the free atom. If we take the value 16 ev for the promotional energy to be correct, then we must assume that the energy of formation of each of the additional bonds is ~ 10 ev. It seems more reasonable, however, to assume that the energies of formation of the P–Cl bonds are not vastly different in the two cases, and that we must allow for the effect of the presence of the chlorine atoms on the promotional energy needed to reach the quinquevalent state.
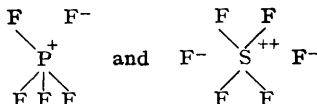
The higher valencies of atoms such as phosphorus and sulphur are only stabilised by combination with very electronegative atoms such as fluorine, oxygen, and chlorine, and we can therefore draw the conclusion that the perturbing effect of these atoms on the central phosphorus or sulphur atom is to considerably stabilise (*i.e.*, lower the energy of) their higher (*e.g.*, 3*d*) orbitals or, more accurately, certain combinations or hybrids of these orbitals with lower valency orbitals. When sulphur, for example, combines with a very electronegative atom such as fluorine, the bonds that are formed are polar in the sense $\overset{\delta+}{S}\text{–}\overset{\delta-}{F}$. An approximate way of describing this is to say that the bond electrons are occupying a molecular orbital composed of a sulphur atomic orbital that projects strongly in the direction of the fluorine atom and a fluorine atomic orbital that is fairly well localised in the region of the fluorine nucleus. In the case of sulphur hexafluoride the situation is best described in terms of sulphur atomic orbitals by saying that the electrons occupy the six sp^3d^2 hybrid orbitals which project strongly along the six octahedral directions. It is evident that the energy of the electrons in these octahedral orbits will be much lower for the sulphur atom surrounded by six fluorine or other electronegative atoms than for the free sulphur atom, since these electronegative atoms will stabilise the octahedral configuration in which the sulphur electrons are at a relatively large distance from the nucleus.
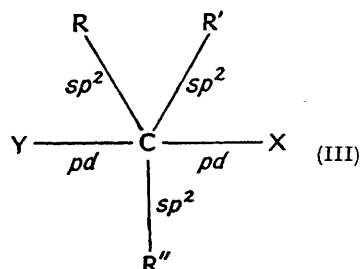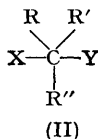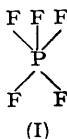
In general, we may say that the perturbing effect of electronegative atoms on the energy levels of an atom with which they are combined is to lower considerably the energy of certain hybrid orbitals which may involve the participation of orbitals which lie at a relatively high energy level in the free atom. It can be shown by a consideration of the simple case of the hydrogen atom that the perturbing effect of an adjacent positive charge (which is equivalent, of course, to an electronegative atom) is to make the most stable orbital for the hydrogen electron not a pure 1*s* orbital but a 1*s*–2*p* hybrid orbital although the 2*p* orbital lies at 10 ev above the 1*s* (Pritchard and Skinner, *J.*, 1951, 945). These authors remark that " The very significant contribution of the $2p^2$ orbitals to the bonding in H_2^+ and the lesser but nevertheless important contribution in H_2 should be stressed. The relatively large energy separation of the 1*s* and 2*p* atomic orbitals of the H atom is seen to present a barrier insufficient to prevent an appreciable mixing of these orbitals when bond formation occurs. As a consequence, it is reasonable to expect that hybridisation occurs more frequently than not, for in general the energy separations between neighbouring orbitals in atoms other than hydrogen are not larger than in the hydrogen atom itself."

It is perhaps relevant that phosphorus and sulphur are not always regarded as utilising their 3*d* orbitals in the formation of compounds such as phosphorus pentafluoride and

sulphur hexafluoride. It has often been suggested that their structures are resonance hybrids of structures such as

$$
\begin{array}{ccc}
F \quad F^- & & F \quad F \\
\diagdown \quad \diagup & & \diagdown \quad \diagup \\
P^+ & \text{and} \quad F^- \quad S^{++} \quad F^- \\
\diagup \quad | \quad \diagdown & & \diagup \quad \diagdown \\
F \quad F \quad F & & F \quad F
\end{array}
$$

implying that the phosphorus and sulphur atoms make use of their $2s$ and $2p$ orbitals but not of their $3d$ orbitals to form four covalent bonds which resonate among the five or six postions (cf. Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 2nd Edn., 1940, p. 93). This does not, however, seem to be a completely satisfactory representation of the electronic structure of the molecules as it implies a complete delocalisation of the bonding electrons, whereas by assuming the participation of a d orbital in the bonding we retain the idea of a localised bond. A better description of the phosphorus penta-fluoride molecule would appear then to be that given above, which in "resonance language" may be considered as a resonance hybrid of the above ionic structures and *in addition* the covalent structure (I) in which the phosphorus atom utilises five orbitals for bond formation, one of which remains empty in each of the ionic structures. One of these five orbitals must be a $3d$ orbital.

$$
\begin{array}{ccc}
F \quad F \quad F & & R \quad R' \\
\diagdown | \diagup & & \diagdown \diagup \\
P & & X{-}C{-}Y \\
\diagup \quad \diagdown & & | \\
F \quad F & & R'' \\
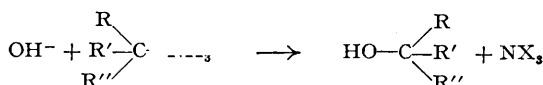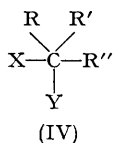\text{(I)} & & \text{(II)}
\end{array}
$$

(III)

Thus we have seen that the promotional energies involved in the formation of the higher-valency states of the free phosphorus and sulphur atoms are very large and that the energies associated with the use of $3d$ orbitals by nitrogen and carbon are only of the same order. It has been pointed out that these higher-valency states are only found in combination with very electronegative atoms and an explanation for this has been given. It does not seem unreasonable therefore to suggest that in similar circumstances carbon and nitrogen may be able to use $3d$ orbitals in bond formation. We shall show that the assumption that carbon can do so leads to a more satisfactory description than is given by current formulations of the transition state of a bimolecular substitution reaction at a saturated carbon atom, the transition state of a carbonium ion rearrangement, and the electronic structure of certain metal alkyls. The possibility that nitrogen is quinquevalent in some of its compounds is also further discussed.

The Transition State of a Bimolecular Substitution at a Saturated Carbon Atom.—It is suggested that the transition state of a bimolecular substitution reaction at a saturated carbon atom can be satisfactorily described as an unstable compound of quinquevalent carbon. We imagine that the carbon atom is using five orbitals for bond formation, one $2s$, three $2p$, and one $3d$. In contrast to the current resonance picture of the transition state all five atoms or groups are to be regarded as attached to the central carbon atom by ordinary electron-pair bonds. In a completely symmetrical case where all five attached atoms or groups are identical the carbon orbitals will hybridise to form $5sp^3d$ hybrids. However, in the usual case, *e.g.*, (II) where R, R', and R'' are H or alkyl groups and X and Y are electro-negative atoms or groups (*e.g.*, OH, Cl, or F), it seems more likely that the CRR'R'' bonds will be changed merely from tetrahedral sp^3 bonds in the initial state to trigonal sp^2 bonds in the transition state, while the d orbital will be shared between the polar C–X and C–Y bonds, which will be formed from two collinear pd hybrids on the carbon atom (see III). The carbon atom has a formal negative charge but its actual charge will be very small as the highly projecting pd orbitals will cause most of the charge to be in the region of the X

and Y atoms. The nature of these pd hybrid orbitals is further discussed in the Appendix (p. 1012).

If the presence of the two electronegative atoms or groups, X and Y, can sufficiently lower the energy of the two pd hybrid orbitals involving the use of the carbon $3d$ atomic orbitals, then this appears to be a satisfactory description of the transition state alternative to the generally accepted resonance theory. It should be emphasised perhaps that we are not here considering a stable compound but one for which the promotional energy needed to reach the quinquevalent state is not quite counterbalanced by the energy gained from the formation of a new bond. The difference between these two energy values corresponds to the activation energy of the reaction, that is, the energy of formation of the transition state.

An alternative description of the transition state (IV) is apparently possible. However, the fact that inversion of configuration invariably accompanies substitution shows, as is well known, that (III) is actually more stable than (IV). That this should be so is not immediately obvious, as any permutation of the five atoms or groups among the five trigonal bipyramidal postions will minimise filled orbital repulsions. Hence, to a first approximation at least (IV) should have the same energy as (III). Electrostatic repulsions may be of some importance and in the case, for example, where C–X and C–Y are both highly polar in the same sense we might expect that (III) would be a more stable arrangement than (IV). Electrostatic interactions are, however, not the determining factor as is shown by the fact that inversion occurs in the case :

$$\text{OH}^- + \text{R}'\!\!-\!\!\underset{\substack{| \\ \text{R}''}}{\overset{\substack{\text{R} \\ |}}{\text{C}}}\text{- - - -}_3 \longrightarrow \text{HO}\!\!-\!\!\underset{\substack{\backslash \\ \text{R}''}}{\overset{\substack{\text{R} \\ /}}{\text{C}}}\!\!-\!\!\text{R}' + \text{NX}_3$$

In the hope of gaining a little more insight into the problem let us now examine more closely the nature of the orbital that the central carbon atom uses in the two cases. It is reasonable to assume that the strength and nature of the CRR′R″ bonds will be little altered in the formation of the transition state. They will therefore be formed either from sp^3 orbitals of the central carbon atom or from orbitals with a similar bond-forming power. In configuration (III) the CRR′R″ bonds have been described as being formed from trigonal sp^2 hybrids on the central carbon. It is known that these form bonds of a strength similar to, or slightly greater than, sp^3 hybrids. The weaker and polar C–X and C–Y bonds are formed from two collinear pd hybrid orbitals. In configuration (IV) the CRR′R″ bonds cannot be planar trigonal hybrids, and it seems most reasonable to assume
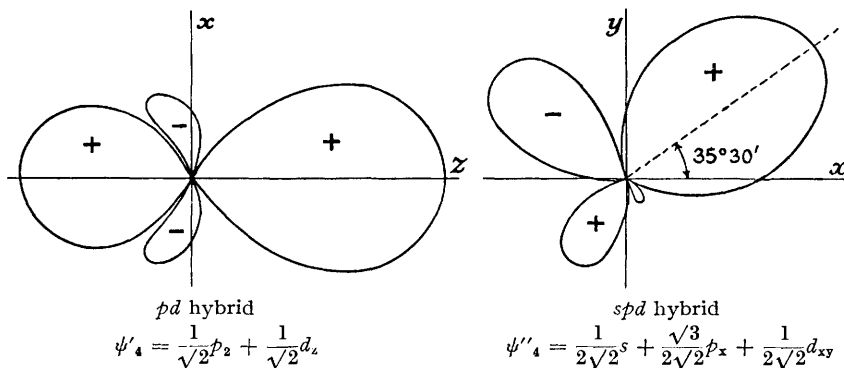

(V)   (VI)   (VII)
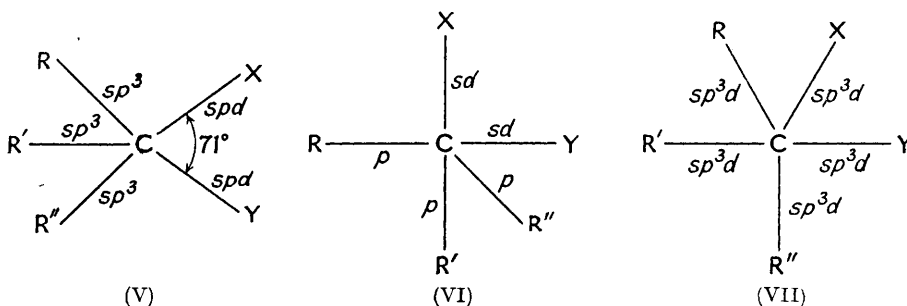
that they will be little changed from the initial state, being formed from approximately sp^3 tetrahedral hybrids. This leaves one sp^3 orbital to be hybridised with an appropriate $3d$ orbital to form two equivalent orbitals to be used in bond formation with X and Y. It can be shown (see Appendix) that two orthogonal and normalised orbitals may be formed that are quite strongly directed along two axes at 71° to each other. Hence they will form two polar C–X, C–Y bonds at an angle of approximately 71°. Thus configuration (IV) for the transition state may be more exactly represented by (V). The angle between the C–X and C–Y bonds may only be increased by increasing the amount of s character in the orbitals

forming these bonds and thus appreciably decreasing the strength of the CRR′R″ bonds. In the limiting case where $\angle$XCY $= 90°$ there are two alternative but equally unsatisfactory descriptions of the transition state. In one case the CRR′R″ bonds could be described as pure p orbitals which are therefore at right angles, and the C–X and C–Y bonds as two sd hybrids also at right angles (VI). In the other case all the bonds may be described as nearly equivalent sp^3d hybrids with a trigonal bipyramidal arrangement (VII). Neither description is satisfactory because in both cases the orbitals forming the CRR′R″ bonds are considerably changed and the bonds correspondingly weakened. It is clear that if the transition state is to have the configuration (IV) it cannot have the symmetrical trigonal bipyramidal arrangement but must have the rather less symmetrical arrangement (V).

We are now in a position to estimate the relative stabilities of (III) and (IV). This will depend primarily on the relative strengths of the C–X and C–Y bonds and the relative magnitude of filled orbital repulsions in the two cases. The strength of the C–X, C–Y

FIG. 1.

pd hybrid

$$\psi'_4 = \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{2}}d_z$$

spd hybrid

$$\psi''_4 = \frac{1}{2\sqrt{2}}s + \frac{\sqrt{3}}{2\sqrt{2}}p_x + \frac{1}{2\sqrt{2}}d_{xy}$$

bonds will depend on the overlapping power of the orbitals used by the carbon atom to form these bonds : they are pd hybrids for (III) and spd hybrids for (IV), as described above and in more detail in the Appendix. Their shapes are shown in Fig. 1.

Without a detailed calculation of overlap integrals, a qualitative consideration of the shapes will serve to convince us that the pd orbital used in (III) probably has a better overlapping power than the spd orbital used in (IV). The negative portions of the orbital which reduce the effective overlapping ability of the positive portions are relatively larger and more unfavourably situated in the spd orbital than in the pd. (The largest and most strongly projecting lobe of the orbital which will be responsible for bond formation has been arbitrarily assigned the positive sign in Fig. 1.) Hence we should expect the pd hybrid orbital to form rather stronger bonds than the spd hybrid. Moreover it is not unreasonable to assume that filled orbital repulsions will be minimised in a symmetrical trigonal bipyramidal arrangement of the transition state and that in any arrangement involving smaller bond angles there may be energetically important repulsions between the atoms concerned. We have seen that configuration (III) may have this symmetrical bipyramidal arrangement, but that configuration (IV) must have a less symmetrical arrangement involving a small bond angle of $\sim70°$. Hence it is not unreasonable to suppose that filled orbital repulsions will be greater in (IV) than (III). Thus we have two reasons for concluding that configuration (IV) will be less stable than (III).

The Transition State of a Carbonium Ion Rearrangement.—Rearrangements in which a methyl or other alkyl group in a carbonium ion migrates from one carbon atom to an adjacent one occur quite readily. This can be represented :
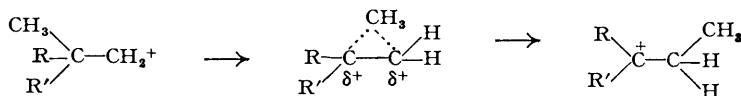
It appears that the transition state of this rearrangement can be more satisfactorily described in terms of the view-point developed in the preceding discussion than in terms of resonance between (VIII) and (IX) according to the current view. This description

(VIII) ... (IX)

implies that the migrating methyl group utilises a sp^3 tetrahedral orbital to overlap with orbitals on the two carbon atoms that are presumably nearly pure p orbitals, as shown in Fig. 2. This arrangement of orbitals, however, gives rise to only rather poor overlap and hence rather weak bonds. Thus, if we are to describe the bonds in this transition state in terms of combinations of appropriate atomic orbitals, the sp^3 tetrahedral orbital on the carbon atom of the migrating methyl group would not appear to be suitable for our purpose. An electron on the carbon atom of this methyl group will be strongly attracted by the two adjacent positively charged carbon atoms and will therefore be largely concentrated in two regions of space directed towards these carbon atoms. It will not be suitably described by placing it in a tetrahedral sp^3 orbital. Such an orbital is appropriate
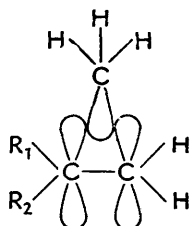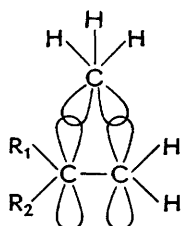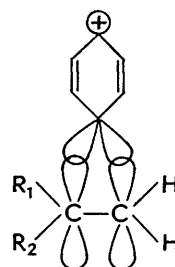
FIG. 2.   FIG. 3.   FIG. 4.

for the description of a bond in the case where a carbon atom is bound to four others, but not when it is bound to five. In the latter case one of the several sets of spd hybrids discussed earlier will be more appropriate, in particular that illustrated in (V). The C–H bonds of the migrating methyl group will be formed from tetrahedral sp^3 orbitals, and the carbon atom of the methyl group will be linked to the carbon atom it is leaving and the one it is joining by bonds formed by the overlap of its two hybrid spd orbitals at an angle of 70° to each other with p orbitals on the two carbon atoms (Fig. 3). This arrangement of orbitals appears to give better overlap and hence stronger bonds than in the preceding resonance description. The spd hybrid orbitals used in this case are stabilised by the presence of the two adjacent positively charged carbon atoms. There are, of course, not sufficient electrons available for both the bonds joining the migrating methyl group to the rest of the molecule to be full electron-pair bonds. To a first approximation there is available only an average of one electron for each of these bonds. However, a small amount of delocalisation of the C–H-bond electrons of the migrating methyl group, which can alternatively be described as a type of hyperconjugation, will lead to an increase in the average number of electrons in these bonds and thus help to increase their strength. It is interesting to note that the transition state for the migration of a phenyl group can be described in a quite similar fashion although, because of the unsaturation of the phenyl group, this does not necessitate the utilisation of a carbon $3d$ orbital. A carbon atom of the migrating phenyl group can utilise two sp^3 tetrahedral orbitals to overlap with the p orbitals on the two adjacent carbon atoms, and the positive charge may be largely accommodated in the phenyl group (Fig. 4). The transition state should therefore be correspondingly more stable and a phenyl should migrate more readily than a methyl group.

The Structure of Certain Metal Alkyls.—The alkyl derivatives of certain metals exist in polymeric forms whose structures have proved difficult to formulate on ordinary valency considerations. Thus, for example, trimethylaluminium forms a stable dimer $Al_2(CH_3)_6$

and dimethylberyllium an infinite linear polymer [Be(CH$_3$)$_2$]$_n$.   Considerable evidence has accumulated recently that in both these cases the metal atoms are held together by two bridge methyl groups just as two bridge chlorine atoms hold the two aluminium atoms together in Al$_2$Cl$_6$ (Longuet-Higgins, *J.*, 1946, 139; Pitzer and Gutowski, *J. Amer. Chem. Soc.*, 1946, **68**, 2204; Kohlrausch and Wagner, *Z. physikal. Chem.*, 1942, B, **52**, 185; Rundle, *J. Chem. Physics*, 1949, **17**, 671; Brockway and Davidson, *J. Amer. Chem. Soc.*, 1941, **63**, 3287; Skinner and Sutton, *Nature*, 1945, **156**, 601).   We can then write the structure of the alkyl-aluminium and -beryllium polymers as :
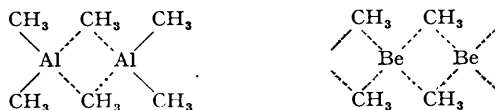
where the bridge bonds whose nature is uncertain are indicated by broken lines.   Very recently this structure for dimethylberyllium has been fully confirmed by a complete *X*-ray investigation of the solid (Snow and Rundle, *Acta Cryst.*, 1951, **4**, 348).

Various suggestions have been made concerning the electronic structure of these molecules (cf. Longuet-Higgins, *loc. cit.*; *J. Amer. Chem. Soc.*, 1947, **69**, 1327; Davidson, Kingill, Skinner, and Sutton, *Trans. Faraday Soc.*, 1940, **36**, 1212; Skinner and Sutton, *loc. cit.*; Burawoy, *Nature*, 1945, **155**, 269), the most reasonable of which appears to be the resonance formulation,
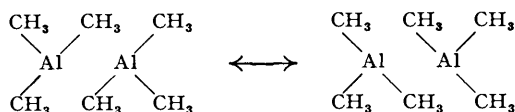
This implies that an sp^3 orbital on the carbon atom of a bridge methyl is overlapping equally with sp^3 orbitals from each of the aluminium atoms (Fig. 5), forming two localised molecular orbitals each containing two electrons and bonding three nuclei (Al, C, and Al). This does not, however, seem a very satisfactory description of the electronic arrangement; for the overlap of the orbitals oriented in this way cannot be particularly good and would only lead to the formation of rather weak bonds, particularly since there is only an average of one electron available for each Al–C bond in the bridge.   Much stronger bonds would be formed if the carbon atoms of the bridge methyl groups could utilise orbitals strongly
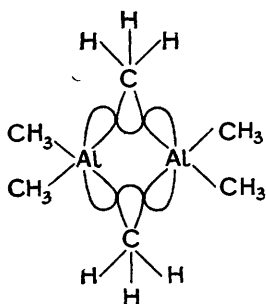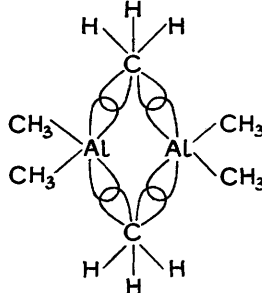
FIG. 5.

FIG. 6.

directed towards the aluminium atoms.   The two *dsp* orbitals described earlier and illustrated in (V) are the orbitals required.   If the aluminium orbitals are tetrahedral and therefore ∠CAlC = 109°, the ∠AlCAl must be 71° if the ring is assumed to be planar, which is in fact the angle between these two *dsp* hybrids.   Good end-on overlap of the carbon *dsp* orbitals and the aluminium tetrahedral sp^3 orbitals can thus be achieved and strong bonds formed.   It is suggested therefore that the electronic arrangement of the Al$_2$(CH$_3$)$_6$ molecule can best be represented as in Fig. 6.   Of course, this and similar

molecules are electron-deficient, and there are not enough electrons for all the bonds to be full electron-pair bonds. In the structure shown above, each of the four bridge bonds contains only one electron. However, a small amount of delocalisation of the C–H bonds of the bridge methyl groups will considerably increase the electron density in the Al–C bonds and hence increase their strength. In fact, if the C–H bonds of the bridge methyl groups are regarded only as 2/3 bonds, then each of the Al–C bonds may be written as a full electron-pair bond, *e.g.*,
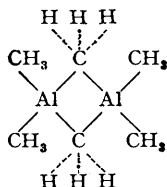
The Be(CH$_3$)$_2$ linear polymer may be formulated similarly (see Fig. 7).

Although recent spectroscopic evidence (Kohlrausch and Wagner, *loc. cit.*) has shown that the bridge structure is almost certainly correct, an early interpretation of the electron-diffraction data (Brockway and Davidson, *loc. cit.*) rejected this type of structure because it predicted a very short Al–Al distance with the ∠CAlC considerably greater than the ∠AlCAl. This is, however, what our formulation requires.

Very recently, from a complete *X*-ray investigation of the dimethylberyllium polymer, Rundle and Snow (*loc. cit.*) have shown that it consists of infinite chains having the structure shown above with ∠BeCBe = 66° and ∠CBeC = 114°, in good agreement with our predictions.

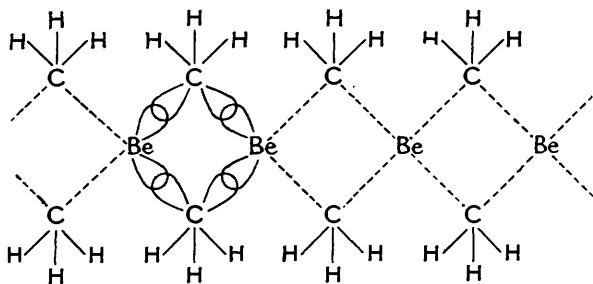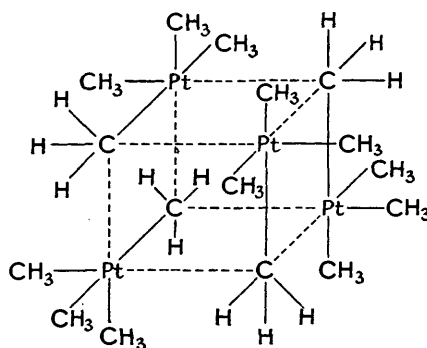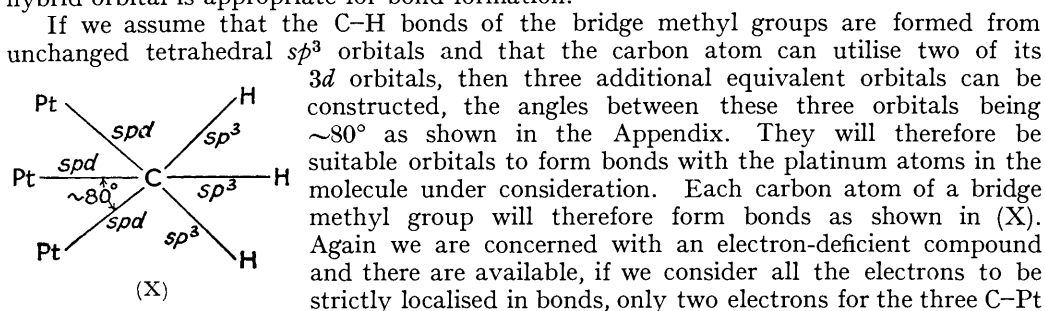Fig. 7.   Fig. 8.

Many aluminium compounds exist in stable polymeric forms and this can be attributed to the very strong tendency of an aluminium atom in a normal tervalent compound to use its empty *p* orbital for bond formation. In the direction of this vacant *p* orbital the aluminium nucleus is very little shielded by the valency electrons and hence *in this direction* the aluminium atom can be regarded as having a very high electronegativity. We should then expect an aluminium atom to pull electrons very strongly into its vacant *p* orbital and, as is well known, the aluminium atom in tervalent aluminium compounds forms a strong bond with any atom that has a lone pair of electrons. Thus in the dimeric aluminium alkyls we should expect that the perturbing effect of the strongly electronegative aluminium atoms on the energy levels of the carbon atoms of the bridge alkyl groups will be to lower the energies of any orbitals that are strongly directed towards the aluminium atoms. The presence of the aluminium atoms makes it easier for the carbon atoms of the bridge alkyl groups to make use of the *dsp* hybrid orbitals. Quite similar considerations apply to the Be(CH$_3$)$_2$ polymer, the beryllium atom in the monomer having a very strong tendency to utilise its two empty *p* orbitals.

The structure of tetramethylplatinum presents an even greater problem in terms of conventional ideas of valency. An *X*-ray investigation of the solid compound (Rundle

and Sturdivant, *J. Amer. Chem. Soc.*, 1947, **69**, 1561) has shown the presence of tetrameric molecules with the cubic arrangement shown in Fig. 8. The stability of this tetramer can be attributed to the great tendency of quadrivalent platinum to utilise its two empty d orbitals and form six octahedral d^2sp^3 bonds. According to the resonance formulation the C–Pt bond formed by the bridge methyl groups can have one of three positions. This implies that the carbon atom of the methyl group is utilising a tetrahedral sp^3 orbital directed along one of the cube diagonals which overlaps equally with a d^2sp^3 octahedral orbital on the platinum atom, thus forming a partly localised molecular orbital containing two electrons and linking together four nuclei. The amount of overlap that can be achieved by the atomic orbitals in this way appears to be very small and unable to lead to strong bond formation, especially since there is only one electron pair available for sharing between three bonds. It would appear that stronger C–Pt bonds would be formed if the carbon atoms of the bridge methyl groups could utilise orbitals more strongly directed towards the platinum atoms. Now when a carbon atom is linked to four other atoms, some form of sp^3 hybrid orbitals is appropriate for bond formation; when it is linked to five other atoms, as in the examples previously discussed, some form of sp^3d hybrid orbital is appropriate for bond formation.

If we assume that the C–H bonds of the bridge methyl groups are formed from unchanged tetrahedral sp^3 orbitals and that the carbon atom can utilise two of its 3d orbitals, then three additional equivalent orbitals can be constructed, the angles between these three orbitals being $\sim80°$ as shown in the Appendix. They will therefore be suitable orbitals to form bonds with the platinum atoms in the molecule under consideration. Each carbon atom of a bridge methyl group will therefore form bonds as shown in (X). Again we are concerned with an electron-deficient compound and there are available, if we consider all the electrons to be strictly localised in bonds, only two electrons for the three C–Pt bonds formed by one carbon atom. However, this number may be increased by a small amount of delocalisation of the electrons of the C–H bonds of the bridge methyl groups. If we assume that each of these is only a 2/3 bond, then **16** electrons are available for **12** Pt–C bonds which bind together 8 atoms. Thus there is the equivalent of one electron-pair bond per atom, and the stability of the molecule is no longer surprising. The energy of the sp^3d^2 hybrid orbitals used by the carbon atom of the bridge methyl group is lowered sufficiently for these orbitals to be of some importance by the great electronegativity of the surrounding platinum atoms in the directions of their unfilled sp^3d^2 orbitals.

Quinquevalent Nitrogen.—It seems possible, although perhaps not nearly as probable as for carbon, that nitrogen may sometimes be quinquevalent. The non-existence of compounds with the electronegative halogens such as nitrogen pentachloride can be attributed partly to the rather large promotional energy involved in attaining the quinquevalent state and partly perhaps to steric factors, that is, to considerable repulsions between the five attached atoms. However, although the promotional energy and filled orbital repulsions may be too large to allow the utilisation of spd hybrid orbitals for the formation of strong σ-type single bonds, these factors may not prevent the utilisation of these orbitals in the formation of the weaker π-type components of double bonds with oxygen, in compounds where filled orbital repulsions will also be considerably smaller; such a case is nitric acid, for which we might write the structure $H–O–N\langle{}^O_O$. This formulation implies that the nitrogen atom utilises sp^2 hybrids to form three σ-bonds to oxygen atoms and two pd hybrids to form π-bonds to two of the oxygen atoms. There are good reasons for thinking that the oxides and other oxy-compounds of the second-row elements phosphorus and sulphur contain double bonds, and not co-ordinate or semi-polar bonds, as has been accepted for many years, having structures such as $O{=}S\langle{}^O_O$ and $HO{-}P{=}O$ (with HO, HO) involving the

use of 3d orbitals (Hunter, Phillips, and Sutton, *J.*, 1945, 146; Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **200**, 409).

It is difficult to know whether structures involving 3d orbitals actually make any important contribution to the structure of oxygen-containing nitrogen compounds, but on the basis of promotional energies alone we cannot state that such structures are of no importance.

Other First-row Elements.—It is unlikely that other first-row elements have a valency shell of more than eight electrons in any of their compounds. In fact, there are exceedingly few compounds in which this is even possible. In a very few compounds oxygen is apparently four-covalent, *e.g.*, " basic " beryllium acetate, $Be_4O(CH_3 \cdot COO)_6$, and ether complexes of certain alkoxyboron dichlorides [such as $(BCl_2 \cdot OEt)_2Et_2O$] but it seems rather improbable that it has a valency shell of more than eight electrons even in these compounds. This is, however, not unreasonable as the elements preceding carbon have insufficient electrons unless they acquire improbably large formal negative charges, while the promotional energies associated with the use of 3d orbitals in oxygen and fluorine will be even greater than for nitrogen, which, as we have seen, is considerably greater than for carbon.

APPENDIX

Let us consider the nature of the orbitals that may be formed using one s, three p, and one d orbital. We shall neglect any difference in the radial parts of the wave functions and consider only their angular parts. We have then

$$\psi_s = 1$$

$$\psi_{p_x} = \sqrt{3} \sin \theta \cos \phi$$

$$\psi_{p_y} = \sqrt{3} \sin \theta \sin \phi$$

$$\psi_{p_z} = \sqrt{3} \cos \theta$$

$$\psi_{d_{xy}} = \frac{\sqrt{15}}{2} \sin^2 \theta \sin^2 \phi$$

$$\psi_{d_z} = \frac{\sqrt{5}}{2} (3 \cos^2 \theta - 1)$$

Assuming that the orbitals have a trigonal bipyramidal arrangement, we can represent the set of five orbitals by the following wave functions :

$$\psi_1 = \frac{\sin \alpha}{\sqrt{3}} s + \frac{\sqrt{2}}{\sqrt{3}} p_x - \frac{\cos \alpha}{\sqrt{3}} d_z$$

$$\psi_2 = \frac{\sin \alpha}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y - \frac{\cos \alpha}{\sqrt{3}} d_z$$

$$\psi_3 = \frac{\sin \alpha}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y - \frac{\cos \alpha}{\sqrt{3}} d_z$$

$$\psi_4 = \frac{\cos \alpha}{\sqrt{2}} s + \frac{1}{\sqrt{2}} p_z + \frac{\sin \alpha}{\sqrt{2}} d_z$$

$$\psi_5 = \frac{\cos \alpha}{\sqrt{2}} s - \frac{1}{\sqrt{2}} p_z + \frac{\sin \alpha}{\sqrt{2}} d_z$$

where α is a variable parameter.

In the special case when $\alpha = \pi$ we have

$$\psi_1' = \frac{1}{\sqrt{3}} s + \frac{\sqrt{2}}{\sqrt{3}} p_x$$

$$\psi_2' = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y$$

$$\psi_3' = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_z - \frac{1}{\sqrt{2}} p_y$$

$$\psi_4' = \frac{1}{\sqrt{2}} p_z + \frac{1}{\sqrt{2}} d_z$$

$$\psi_5' = \frac{1}{\sqrt{2}} p_z - \frac{1}{\sqrt{2}} d_z$$

Thus in this case there are three equivalent sp^2 bonds in a plane and two equivalent axial pd bonds [cf. (III)]. ψ_4' has been plotted as a polar diagram in Fig. 1. By choice of a suitable value of α, that is by a mixing of s and d in all five orbitals, they may be made more nearly equivalent than in the above special case, as has been envisaged in (VII).

If, instead of considering the five orbitals to have a regular bipyramidal arrangement, we make the restriction that three of them are tetrahedral sp^3 orbitals, then the set of five orbitals can be represented by the following wave functions.

$$\psi_1'' = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x + \frac{\sqrt{2}}{\sqrt{3}}p_z$$

$$\psi_4'' = \frac{1}{2\sqrt{2}}s + \frac{\sqrt{3}}{2\sqrt{2}}p_x + \frac{1}{\sqrt{2}}d_{xy}$$

$$\psi_2'' = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x - \frac{1}{\sqrt{6}}p_z + \frac{1}{\sqrt{2}}p_y$$

$$\psi_5'' = \frac{1}{2\sqrt{2}}s + \frac{\sqrt{3}}{2\sqrt{2}}p_x - \frac{1}{\sqrt{2}}d_{xy}$$

$$\psi_3'' = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x - \frac{1}{\sqrt{6}}p_z - \frac{1}{\sqrt{2}}p_y$$

ψ_4'' has been plotted as a polar diagram in Fig. 1. The main maximum of ψ_4'' occurs at $\psi = 35° 30'$, and hence the angle between the directions of the main maxima of ψ_4'' and ψ_5'', and hence between the bonds formed by these orbitals, is $71°$, since ψ_5'' is the mirror image of ψ_4'' in the xz plane.

We may also briefly consider the nature of the orbitals that may be formed by use of one s, three p, and two d orbitals with the restriction that three of the orbitals are tetrahedral sp^3 orbitals. We find that the set of six orbitals may be represented by the following wave functions :

$$\psi_1 = \frac{1}{2\sqrt{3}}(s + p_x + p_y + p_z) + \frac{\sqrt{2}}{\sqrt{3}}d_z$$

$$\psi_2 = \frac{1}{2\sqrt{3}}(s + p_x + p_y + p_z) - \frac{1}{\sqrt{6}}d_z + \frac{1}{\sqrt{2}}d_{x-y}$$

$$\psi_3 = \frac{1}{2\sqrt{3}}(s + p_x + p_y + p_z) - \frac{1}{\sqrt{6}}d_z - \frac{1}{\sqrt{2}}d_{x-y}$$

$$\psi_4 = \frac{1}{2}(s + p_x - p_y - p_z)$$

$$\psi_5 = \frac{1}{2}(s - p_x + p_y - p_z)$$

$$\psi_6 = \frac{1}{2}(s - p_y - p_x + p_z)$$

The angle between the three orbitals, ψ_1, ψ_2, and ψ_3, will be equal and between $71°$ and $90°$, *i.e.*, $\sim80°$.