329. *Orbital Hybridisation and Some Other Considerations concerning the Transition State of Bimolecular Organic Substitution Reactions.*

By V. Gold.

The plausible orbital hybridisations in the transition state of bimolecular organic substitution reactions can be divided into two classes : (i) those in which a *p*-electron contributes to the binding of three atomic centres, and (ii) those in which only two-centre binding by electron pairs need be postulated. The first category is approximated by the case of substitution at a saturated carbon atom, and the second one by that of aromatic substitution. Substitution at the carbon atom of vinyl or carbonyl groups probably involves an intermediate structure about which it should in principle be possible in some cases to adduce more exact information by stereochemical experiments.

In this paper the quantum-mechanical picture of the directional properties of single and multiple carbon bonds is applied to a discussion of the connection between electronic arrangement and bond directions in the transition state of bimolecular substitution reactions at a carbon atom and hence the stereochemical course of such reactions. This approach has been indicated by other workers, notably Hughes, Ingold, and their collaborators (*e.g.*, *J.*, 1937, 1256; 1941, 608), for the cases of substitution at a saturated carbon atom or in a benzene ring, but has not so far received a more comprehensive development.

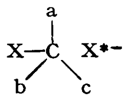
The common feature of all bimolecular substitution reactions—homolytic, nucleophilic, or electrophilic—is the condition that in the transition state the substitution centre must be linked to one atomic nucleus more than in the initial and the final state of the reaction. The combination of this obvious requirement with the postulates that the reactions are electronically " adiabatic " and that the potential energy of the transition state is to be a minimum, forms the basis of the following discussion. It is found that the accepted principles of bonding and hybridisation are adequate for at least a qualitative discussion. For the present no attempt has been made to assess the energy changes involved in the formation of the transition states and thus to decide between possible alternative structures of the transition state.

Substitution at a Saturated Carbon Atom.—It is found that bimolecular substitution invariably leads to optical inversion of configuration whenever such a test is possible (Hughes, *Trans. Faraday Soc.*, 1938, **34**, 202). In the transition state of the reaction

$$\mathrm{X{\cdot}C\vdots a\ b\ c + X^{*} \longrightarrow a\ b\ c\vdots C{\cdot}X^{*} + X}$$

(all electric-charge signs of the species involved being omitted), the groups X and X* must therefore lie on opposite sides of the surface containing the points C, a, b, c. It is usually accepted that the points X, C, and X* will, in the absence of unsymmetrical steric hindrance, be collinear, and that, apart from a slight deviation caused by the possibility of a potential hollow near the saddle point (Gorin, Kauzmann, Walter, and Eyring, *J. Chem. Physics*, 1939, **7**, 633), X and X* will be equidistant from C and hence C, a, b, and c will tend to be coplanar. The hybridisation must then be such that three equal coplanar bonds (to a, b, c) and two, possibly weaker, equal bonds in the direction perpendicular to the plane of this set of three bonds can be formed. The only hybridisation of *s*- and *p*-electrons which can lead to three strong coplanar bonds is the sp^2 arrangement as assumed for the σ-bonds in ethylene, and we may conclude that the electron contributed towards the binding of the nuclei X and X* is the remaining p-electron. As far as this argument goes the problem is the same irrespective of the electric charges of the reaction partners, although this will affect the electron distribution within the bond formed.

In terms of valency-bond representations—which may sometimes be found preferable for the statement of these structures, since they take explicit account of the restrictions on electronic configurations imposed by the Pauli principle—the transition state, for the example of nucleophilic substitution, may be said to be made up of the mesomeric structures



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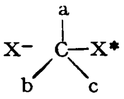
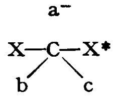
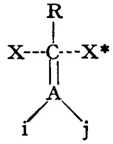


The question arises (as has been privately pointed out to the author by Professor Coulson) whether the weakness of bonds in the transition state can really be thought to be localised in the bonds C–X and C–X*. Valency-bond terminology being used, this raises the problem whether structures such as (I) make an appreciable contribution to the mesomeric transition state. (The hybridisation of the collinear X–C–X bonds would be sp, leaving two pure p-orbitals for the bonding of b and c.)

(I.)



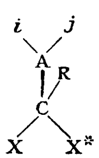


(II.)

Such structures would certainly be unimportant in the case of nucleophilic replacements such as the hydrolysis of alkyl halides and, in any case, it seems reasonable in the first approximation to assume that it is the bonds which are formed and broken and must pass through bond lengths which are inappropriate to normal bonds, are the ones which contain most of the weakness of bonding in the transition state.

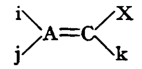
Substitution at a Singly-unsaturated Carbon Atom.—The transition state must in this case involve a 4-co-ordinated carbon atom and planar square or tetrahedral arrangements of the bonds are therefore reasonable alternatives. The planar structure may be written as (II), (where A is some atom which can be doubly bound to carbon, and i, j is the representation for some unsymmetrical attachment to A) with the entering and ejected groups again tending to be collinear with the central carbon atom. By analogy with the case of substitution at a saturated carbon atom, this is the structure generally assumed for the transition state for ester hydrolysis and similar reactions. The corresponding hybridisation would be sp for the collinear R–C–A σ-bonds, one p-electron would take part in the formation of the π-bond between C and A, and the remaining p-electron would again be contributed towards the weak links to the two groups involved in the substitution.

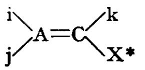
The extreme alternative structure is a regular tetrahedral disposition of the groups about the central carbon atom. As it is unlikely that a p-electron could effectively help to bind three nuclei which are far from collinear, it is probable that the usual sp^3 hybridisation would apply, the bond C–A assuming single-bond character (see figure).



It is of course possible and, in fact, probable that the true state of affairs lies somewhere between these two extremes. It is important to note that the relative contributions of the two forms towards the real structure * may in principle be assessed by stereochemical experiments and that a discussion of this problem is not fundamentally unverifiable. The planar transition state would lead to complete *geometrical* inversion during the reaction, *i.e.*, conversion of (III) into (IV). In the tetrahedral structure, the bond C–A is single and free to rotate, apart from factors outside the bond which may impede or prevent this rotation. The regular tetrahedral transition state should therefore lead to an equilibrium mixture of the isomers. If it is true

(III.)





(IV.)

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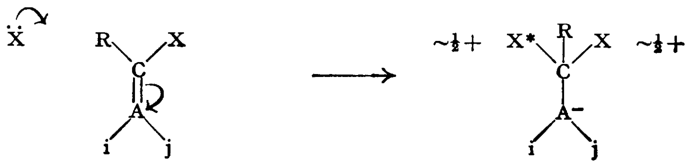
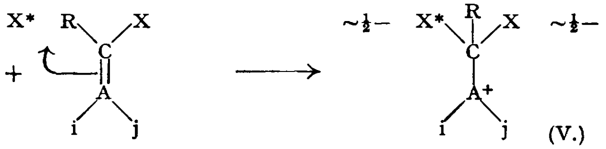
* The terms " resonance " or " mesomerism " between the two forms should be used with caution since the forms differ, not only with respect to their electron distributions, but also with respect to the position of the nuclei.

that this structure makes an appreciable contribution (*i.e.*, that the transition state is non-planar) it can be predicted that the geometrical inversion accompanying these reactions will not be complete. So far, substitution reactions involving the replacement of X do not seem to have been observed in cases where $i \neq j$ and where this test would be possible. Only few cases of substitution in vinyl systems are known, and their mechanism is uncertain (cf. Taft, *J. Amer. Chem. Soc.*, 1949, **70**, 3364). The most important group of substitution reactions at singly unsaturated carbon atoms is that of carbonyl compounds, such as the hydrolysis reactions of esters, acid chlorides, and anhydrides and, naturally, in this group no configurational evidence concerning the steric course of the reaction is possible.

The formulation of the tetrahedral structure may be discussed a little further. The electrical nature of the reagent will determine how single-bond character is acquired by the bond C–A. If X* is nucleophilic (*i.e.*, supplies its own electron pair towards bond formation, like OH^- or R_3N) the Pauli principle will require a pair of electrons to leave the shell of the carbon atom and in the simplest case they will become localised on the atom A, *i.e.*,

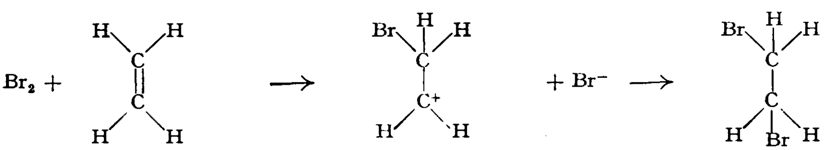


(the charges being relative to the initial electrification of the reagents). It is known that carbon has a low electron affinity and this rarely permits the formation of negative ions of the type $\bar{C}R_3$, whereas oxygen-containing anions $\bar{O}R$ are very stable. For this reason the fact that vinyl compounds (A = carbon) undergo nucleophilic substitution reactions only with the greatest difficulty, in contrast to the facility of such reactions for carbonyl compounds (Aij = oxygen), may perhaps be advanced as an argument for the importance of the contribution of the tetrahedral transition-state structure in which the necessity for such a charge separation occurs. Dewar ("Electronic Theory of Organic Chemistry," Oxford, 1949, p. 117) has dismissed the tetrahedral transition state in favour of the planar one for the case of ester hydrolysis, on the grounds that its formation would involve a prohibitive loss of resonance energy, and has stated that the particular reactivity of carbonyl compounds is due to the interaction of the *p*-electrons of the entering and ejected groups with the C=O π-orbital, *i.e.*, that these groups are linked to the central carbon atom by *partial double* bonds. However, such conjugation would be more and not less likely in the case of the unreactive vinyl compounds—since C=O π-bonds are more localised than C=C π-bonds (Coulson, *Trans. Faraday Soc.*, 1946, **42**, 106)—so that this factor by itself is an unlikely explanation of the reactivity of esters and related compounds.



(V.)

Conversely, electrophilic reagents would produce the transition state (V), a structure which should be feasible when A is a carbon atom but less favourable for carbonyl compounds. The formula will be recognised also as a more general representation of the labile intermediate formed during the two-stage addition reactions of olefins, *e.g.*,



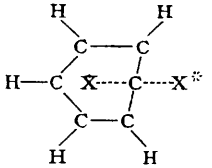
(VI.)

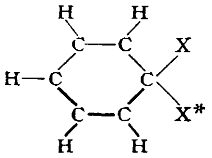
for a review see Gwyn Williams, *Trans. Faraday Soc.*, 1941, **37**, 755). Since it is known that these intermediates are molecular species capable of independent, albeit short-lived, existence, the most stable configuration of (V) will also have this property, *i.e.*, *it* cannot be the transition state (cf. Taft, *loc. cit.*). The intermediate corresponds to a potential hollow near the saddle-point for the energy profile of the substitution reaction. In the cases where this hollow exists, the transition state of the substitution reaction is the most energised configuration during the formation or decomposition of the intermediate, but inasmuch as the saddle-point is not far removed from the hollow, the *main* valency directions will be the same in the two cases. For reactions in which such an intermediate is formed, the final product should always be the equilibrium mixture of the geometrical isomers, and a measurement of the contribution of the planar form is not possible, but in this case it would not be expected to be important since the intermediate has a tetrahedral structure.

Whether the labile intermediate of the formula (VI) will complete reaction by elimination of one of the groups X or by addition of another group on the opposite side of the double bond is quite irrelevant in this connection. We may also note that a potential hollow near the saddle-point, corresponding to an intermediate, has been established in only a few cases (as in the two-stage halogen addition or the unimolecular elimination reactions (*E*1) and, for instance, there is no evidence for its existence in nucleophilic substitution reactions.

Substitution at an Aromatic Carbon Atom.—This is really a sub-group of the previous class of substitution reactions, the initial hybridisation being the same trigonal sp^2 arrangement. However, the discussion is simpler in this case, since the strict analogue (VII) of the first alternative structure of the last section is planar and clearly sterically impossible and need not be considered further.

(VII.)



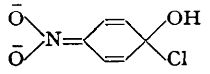


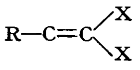
(VIII.)

A tetrahedral structure has often, in the past, been assumed for this transition state (VIII) and, indeed, would appear to be the only one possible for a bimolecular aromatic substitution reaction, by whatever type of reagent (Hughes, Ingold, *et al.*, *J.*, 1941, 608). It involves the destruction of the benzene ring conjugation, the conjugated system left over being a pentadienyl frame bearing the appropriate electric charge according to whether the groups X, X^* donate, accept, or supply a share of the bonding electrons. Wheland's calculations (*J. Amer. Chem. Soc.*, 1942, **64**, 900) of the stability of the transition state for different kinds of aromatic substitution are based on this assumption (see also Waters, *J.*, 1948, 727, and Dewar, *J.*, 1949, 463). The electrical repulsion between entering and ejected groups may somewhat widen the angle between these bonds, although the resulting utilisation of the electrons would necessarily be less complete, and for this reason we may probably discount a transition state in which approach and ejection of the groups take place in the direction at right angles to the plane of the benzene ring. The hybridisation would in this case be either *sp* for the collinear $X{-}C{-}X^*$ bonds and *p* σ-bonds to the neighbouring carbon atoms in the ring, or else $X{-}C{-}X^*$ could be bound by a single *p*-electron, leaving the trigonal sp^2 hybridisation for the two bonds in the ring and the third trigonal orbital unused.

Since the electric charge must, in the tetrahedral transition state, reside on an atom other than those becoming attached to or detached from the benzene ring, nucleophilic substitution occurs only in those benzene derivatives where a better location than a carbon nucleus is available for it, as in *p*-chloronitrobenzene (but not in the *m*-derivative) where structures such as (IX) will be important. On similar reasoning, the chlorine atom in chloroquinones should be hydrolysable.

(IX.)





(X.)

The considerations of the last section concerning the occurrence of addition reactions are valid. We may quote one small item of evidence which suggests that the formation of a labile reaction *intermediate* [analogous to (VI)] may occur in certain substitution reactions. Price and Arntzen (*J. Amer. Chem. Soc.*, 1938, **60**, 2835) have shown that bromine addition and the replacement of hydrogen by bromine in aromatic hydrocarbons follow the same unusual kinetic law, from which they concluded that the rate-determining stage was in each case the formation of a cation intermediate. In terms of energy surfaces, the problem whether the proton abstraction in aromatic nitration *is* (Bennett, Brand, James, Saunders, and Williams, *J.*, 1947, 474) or *is not* (Hughes, Ingold, and Reed, *J.*, 1950, 2428) kinetically significant is then equivalent to the question whether the pass between the " products valley " and the saddle hollow, or that between the " reactants valley " and the saddle hollow is higher in any one particular case.

Substitution at an Acetylenic Carbon Atom.—The *only* feasible structure of the transition state—charge designations being again omitted—is in this case (X), but here again most reagents bring about addition rather than substitution.

A Classification.—The possible transition-state structures may be divided into two extreme classes: (i) those in which a *p*-electron is involved in three-centre binding (called, for brevity, a $p\theta$ electron) and, therefore, increased *s*-character in the remaining valencies, and (ii) those in which the groups involved in substitution are held by near-normal valencies, when the multiplicity of one bond is reduced (the effect may be relayed by conjugation to other bonds) and the *p*-character of the remaining σ-valencies is increased, as summarised in the table.

	Transition-state hybridisation :	
Initial hybridisation.	(i).	(ii).
sp^3	$(sp^2) . p\theta$	—
$sp^2 . p\pi$	$(sp) . p\pi . p\theta$	(sp^3)
$sp . (p\pi)^2$	—	$(sp^2) . p\pi$

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