A Theoretical Investigation of Ziegler-type Catalysis. Part I. Soluble Catalyst Systems

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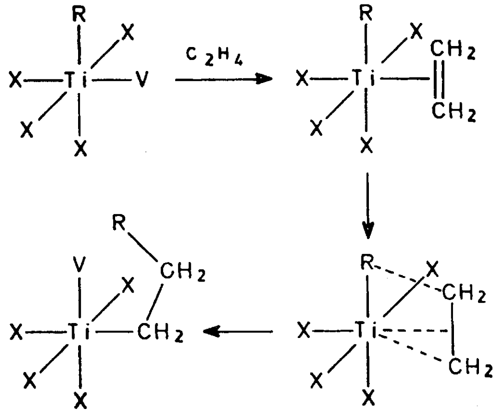
A theoretical investigation of the Cossee mechanism for Ziegler-type catalysis has been made by use of the all valence electron self-consistent field method. The electronic structure of a titanium–aluminium–ethylene complex was studied, as well as the sequence of steps in which ethylene inserts into a titanium–methyl bond. The study of the olefin complex reveals that (*a*) the titanium–olefin bond has no retrodative character and the antibonding π^* orbital of ethylene acquires little stability as a result of interaction with the titanium *d* orbitals; (*b*) the titanium–methyl σ-bond is localised almost completely in the highest bonding level of the olefin complex and the contribution to it from the metal atom is almost pure *d* in character; (*c*) the $>AlR_2$ group in a molecular catalyst seems merely to function as a substrate which maintains a high co-ordination number at the titanium site. Calculations on the reaction co-ordinate show that the methyl group can migrate from its site to join the ethylene molecule without becoming detached from the titanium atom and that the d_{yz} orbital functions as a 'transfer agent'. This, and a study of the total energy changes over the co-ordinate, lead to a new rationale of the mechanism of catalysis and the existence of vacant sites.

ZIEGLER's important discovery[1] of a catalyst system for the low-temperature polymerisation of olefins has led to a vast amount of experimental work, dealing with almost every aspect of the family of catalysts. There have been numerous suggestions[2] as to the mechanism, perhaps the most favoured being that due principally to Cossee.[3] At its most general, this mechanism envisages that a titanium compound (*e.g.*, solid titanium trichloride) is first alkylated by an alkyl-aluminium derivative. With ethylene as monomer, the sequence of steps shown in Scheme 1 then follows. The formation of a vacant site (V) in the octahedral co-ordination sphere of the titanium atom, the initial co-ordination of an ethylene molecule, and the migration of the alkyl group R are the principal features of this mechanism. This basic suggestion has now been extended and appears to be receiving wide acceptance.[4] In conjunction with the reaction scheme, Cossee[3] has also constructed a tentative orbital sequence for the active titanium site. This scheme is essentially qualitative and there has been no other attempt to



Scheme 1 Cossee's mechanism for Ziegler catalysis

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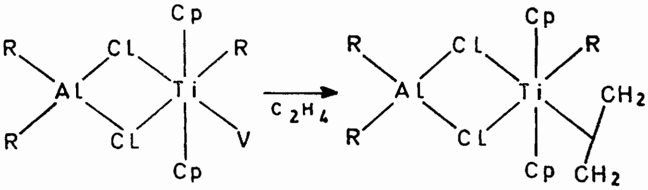
[1] K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.*, 1955, **67**, 541.

[2] *E.g.*, see Review by J. Boor, *Makromol. Rev.*, 1967, **2**, 115.

[3] P. Cossee, 'The Stereochemistry of Macromolecules,' ed. A. D. Ketley, Marcel Dekker, New York, 1967, vol. I, ch. 3, p. 145.

[4] A. K. Ingberman, I. J. Levine, and R. J. Turbett, *J. Polymer Sci., Part A*-1, 1966, **4**, 2781; J. W. Begley and F. Penella, *J. Catalysis*, 1967, **8**, 203.

discuss quantitatively the electronic structure and energy levels of the intermediate complexes. The Cossee scheme can be extended to a description of the 'soluble catalysts'.[5] Systems such as the couple $(cp)_2TiCl_2$ and R_3Al [(cp) = cyclopentadienyl] also show catalytic properties and, in this case, the intermediates are suggested to occur as in Scheme 2.



SCHEME 2 'Soluble' catalyst system based on a Ti^{IV} compound

Clearly theoretical rationalisation of the electronic structures of the intermediate complexes on a quantitative basis, and the way in which their geometries may change, is highly desirable. Unfortunately, the catalysts based on solid titanium trichloride are not, at present, amenable to a *full* theoretical treatment but the molecular (*i.e.*, the 'soluble') catalysts can be treated by quantum chemical methods of intermediate sophistication. We have, therefore, carried out a series of self-consistent field, all-valence electron calculations specifically directed towards solving some of the problems inherent in the catalytic process. We hope also thereby to throw some light on other catalytic processes.

It is impossible to attempt to evaluate the feasibility of *all* the model mechanisms which have been put forward. Hence we have restricted our attention to Cossee's scheme and this paper focuses on the 'soluble' type of catalyst. In a future paper, the catalyst based on a model of solid titanium trichloride will be examined. For the 'molecular' catalyst we have calculated molecular energy levels and have determined their nature for a large number of stages in a reaction co-ordinate involving the migration of the alkyl group. Charge distribution over the atoms of the system was also evaluated but, more important, electron-density contours for the system in transition were obtained. The points which we have specifically considered are (*a*) the nature of the 'vacant site' on titanium, (*b*) the bonding between ethylene and titanium, (*c*) the function of the $>AlR_2$ group, (*d*) the driving force for the migration of the alkyl group, and (*e*) the reason for the low activation energy for the process.

Broadly, our conclusions are in accord with those of Cossee[3] although there are certain important points of disagreement. Further, much which was previously speculative is now quantified.

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[5] G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, 1971, **10**, 105.

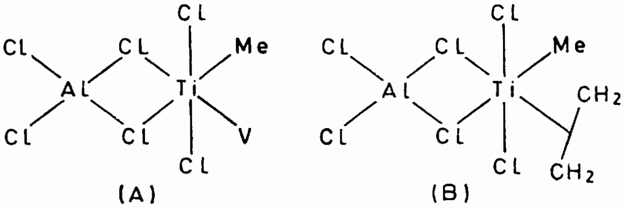
[6] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc.* (*A*), 1971, 3654.

[7] K. A. Levison and P. G. Perkins, *Theoret. Chim. Acta*, 1969, **14**, 206.

With regard to the existence of a vacant site on the titanium at some point in the mechanism, we find that it is not necessary to postulate this. The complex in which the alkyl group lies between two octahedral sites has the lower energy and a mechanism in which an incoming ethylene molecule displaces this on co-ordination is shown to be possible.

CALCULATIONAL METHODS

The 'soluble' or molecular catalyst systems were first investigated. The specific system studied arises from the combination of $TiCl_4$ and $MeAlCl_2$ and envisages an intermediate complex (A) in which the methyl group and the vacant site lie *cis* with respect to each other. The first



Stereochemistry of the initial ethylene complex

calculation was performed on the hexaco-ordinate complex having ethylene in the vacant site. Henceforth this will be referred to as the 'initial ethylene complex' (B). Chlorine atoms were substituted for the cyclopentadienyl groups of Scheme 2 in order to reduce the overall number of basis orbitals and hence simplify the calculation. The theoretical method was a greatly modified version of the CNDO scheme and has been fully discussed.[6] Parameterisation for all the atoms except titanium has been detailed:[7] 3*d* orbitals were neglected on both aluminium and chlorine but were, of course, included for titanium. There has been some speculation as to the oxidation state of titanium in these catalysts[2] but for the purpose of the calculation no *a priori* assumption of the metal oxidation state is required. The input parameters for titanium were: diagonal Hamiltonian matrix elements; 4*s*, 6·07 eV; 4*p*, 3·35 eV; 3*d*, 5·58 eV; the one-centre two-electron repulsion integral was accorded the single value 9·00 eV for all titanium orbitals.

Since there have been relatively few calculations of this degree of sophistication on transition-metal compounds, the method cannot yet be said to have been fully tested. In a separate study[8] on titanium tetrachloride the ground- and a number of the excited-state electronic structures, including extensive configuration interaction, were calculated. Briefly, these calculations afforded excellent agreement between the calculated molecular orbital energy levels and the experimental photoelectron spectrum[9] of the compound. Moreover, the calculated electronic spectrum exhibited very satisfactory agreement with the seven bands observed in the experimental spectrum.[10] This result is better than has been previously achieved in calculations on this compound.

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[8] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *Theoret. Chim. Acta*, submitted for publication.

[9] P. A. Cox, S. Evans, A. Hamnett, and A. F. Orchard, *Chem. Phys. Letters*, 1970, **7**, 414; J. C. Green, M. L. H. Green, P. J. Joachim, A. F. Orchard, and D. W. Turner, *Phil. Trans.*, 1970, *A*, **268**, 111.

[10] A. Viste and H. B. Gray, *Inorg. Chem.*, 1964, **3**, 1113.

In addition, an extensive series of pilot calculations was performed on the initial ethylene complex (B). In these tests the parameters necessary to the calculation (orbital exponents, repulsion integrals, valence-state ionisation potential, and bond lengths and angles) were varied by small amounts. This was done to assess the sensitivity of the calculation to these parameters. For brevity, no detailed results of these computations are given but we can state simply that no essential change in the interpretation of the basic calculations arises from this treatment.

The geometry selected for the initial ethylene complex is given in Table 1. Since no direct structural measurement has been carried out on this compound, the bond lengths and angles chosen are either those which have been measured for related molecules or reasonable values were assumed. The site symmetry for the titanium atom is assumed to be purely octahedral and the ethylene positioned so that the molecule is coplanar with the Al–Ti bridged ring. The carbon atoms are numbered thus: those on ethylene are C(1) and C(2) and the methyl carbon is C(3).

TABLE 1

Geometry of the initial ethylene complex

Al–Cl (br.)	0·230 nm [a]
Cl (br.)–Al–Cl (br.)	90° [a]
Ti–Cl (br.)	0·230 nm [a]
Ti–Cl (term.)	0·230 nm [b]
Ti–C (methyl)	0·215 nm [c]
Ti–C (ethylene)	0·249 nm [b]
C–C	0·136 nm [b]
C–H (all)	0·110 nm [b]

[a] G. Natta, P. Corradini, and I. W. Bassi, *J. Amer. Chem. Soc.*, 1958, **80**, 755. [b] Assumed value. [c] I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccoola, *J. Amer. Chem. Soc.*, 1971, **93**, 3787.

Each intermediate in the reaction co-ordinate has $3N - 6$ degrees of freedom, and optimisation of the geometry at each point by calculation is obviously impossible. Hence, we focused attention on the concerted movement of the carbon atoms of the olefin and the alkyl group. Thus the aluminium–titanium–chlorine skeleton and the C–H bond lengths were kept fixed and the ethylene and the methyl groups were moved in straight lines in a concerted fashion. These conditions are, of course, approximations but we do not believe them to be too severe, since most changes would be expected to occur in the region of the active site.

Eleven points were studied on the reaction co-ordinate, the first being the initial ethylene complex (B) and the last the species in which a propyl group is situated in a *cis*-position relative to a vacant site. In the ' reaction ' the C=C, Ti–CH_3, and Ti–C_2H_4 bond distances were varied in ten equal steps between the initial and final geometric situations.

In a normal SCF calculation the ' trial guess ' of the Fock matrix for the first cycle of iteration is generally the extended Hückel matrix. In the present calculations, except for the first point on the reaction co-ordinate, a final SCF Fock matrix is available which is a good approximation to the needed starting matrix for the next calculation. Hence, instead of using an extended Hückel matrix to start a new SCF calculation, the Fock matrix for the previous calculation was used. By this technique, far fewer iterations are needed to attain self-consistency and, since the self-consistency test can be made more severe, more accurate results can be obtained. All calculations were carried out on the Strathclyde University ICL 1905 computer, by use of the programme system SYMPROG.[6]

RESULTS AND DISCUSSION

A priori it would be expected that most changes would occur on the alkyl carbon and titanium atoms as the reaction proceeded. Moieties distant from the reaction site would be expected to be little perturbed and act only as ' fine tuners ' for the main features of the electronic structure. We are here referring mainly to the distribution of electronic charge but it would also be expected that the energies of all molecular orbitals (except those localised on the reacting centres) would only ' ripple ' slightly as a result of the geometric changes. This argument is based on perturbation theory which, in the context of LCAO theory, dictates that the change in energy of a molecular orbital brought about by perturbation at a specific atom is proportional to the squares of the coefficients of the atomic orbital participating in the particular molecular orbital.[11]

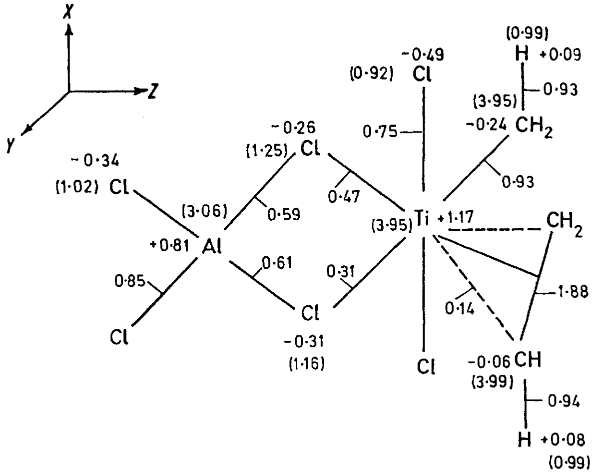

FIGURE 1 Charge distribution in the initial ethylene complex

Electronic Structure of the Initial Ethylene Complex.—Because of the central position the electronic structure of the initial ethylene complex occupies in the interpretation of the process, the bonding and orbital pattern for this complex will be considered in some detail before the reaction co-ordinate is discussed. The results are most conveniently dealt with under four headings. In certain of these categories reference to the charge distribution and derived quantities will be made and hence Figure 1 presents the relevant data. Numbers in parentheses are valencies. Although in this complex, only the terminal chlorine atoms bonded to titanium and aluminium are genuinely equivalent, there are several pairs which are similar in their environment. Hence, in Figure 1, the computed quantities are not shown where they differ insignificantly from those of similar atoms.

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[11] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.

The titanium–olefin bond. The most widely quoted formulation of the transition metal–olefin bond is that due to Chatt and Duncanson.[12] In this model, bonding to the metal is suggested to arise from σ donation of the π bonding electrons of the olefin, whilst, synergically, a back transfer of electron density from metal to the antibonding π^* orbital of the olefin takes place. This is obviously theoretically possible and it is therefore of some interest to examine our results in order to try to identify these two effects and to assess their importance. First, however, it is necessary to discard a number of contributions to the relevant molecular orbitals. In a molecule of this size and complexity, no molecular orbital exists which is wholly assignable to a particular bond or interaction. Hence, we can only construct a correlation diagram for the Ti–olefin bond by ignoring certain contributions to these molecular orbitals which are not relevant to the bond in question. Essentially the atomic orbitals on titanium can be split into three sets: (i) a group which σ bond to the π electrons of ethylene; $4s$, $4p_z$, $3d_{x^2-y^2}$, and $3d_{z^2}$; (ii) those which π bond to the π^* of ethylene; $4p_y$ and $3d_{yz}$; and (iii) a non-bonding set; $4p_x$, $3d_{xz}$, and $3d_{xy}$.

Table 2 lists the relevant density matrix elements between the carbon $2p_z$ orbital (π-type in ethylene) and the titanium bases. The overlap weighted σ-bond total is far greater (*ca.* 20 times if the third significant figure is used) than that of the π-type bond. Of the two atomic orbitals on Ti that can π bond to the ethylene's π^* orbital, p_y is used up in σ and π bonding to aluminium and chlorine and overlaps poorly with the carbon p_z. The d_{yz} orbital, whilst overlapping slightly better, is of less favourable energy to bond in this fashion. On the other hand, s and d_{z^2} on Ti overlap sufficiently well to give good bonds. The $d_{x^2-y^2}$ orbital overlaps poorly with the carbon p_z, as expected from the geometry, and this interaction is unimportant.

TABLE 2

Density matrix elements in the Ti–C bond

$\sigma = 2p_z$	$P_{\lambda\sigma}$	$P_{\lambda\sigma}S_{\lambda\sigma}$ †
$\lambda = 4s$	0·12	0·02
$4p_x$	0	0
$4p_y$	0·01	0·00
$4p_z$	0·01	−0·00
$3d_{x^2-y^2}$	0·04	−0·00
$3d_{xz}$	0	0
$3d_{z^2}$	−0·22	0·02
$3d_{yz}$	−0·02	0·00
$3d_{xy}$	0	0

† $S_{\lambda\sigma}$ is the overlap matrix element between orbitals λ and σ.

One of the postulates of the Cossee mechanism is that, of the four olefin–metal *p–d* orbitals, two are filled or partly filled, namely, the $\pi\sigma$ and $\pi^*\pi$ bonds. Figure 2 is a simplified correlation diagram for the Ti–olefin bond. It is seen that the olefin π^* and the $3d_{yz}$ orbitals are little displaced from their positions in the 'free' components. In fact, the $3d_{yz}$–π^* orbital is very strongly polarised towards the titanium atom and is unoccupied. The lack of perturbation of the ethylene is also shown up well by the normal valencies (for definition of 'valency' see Armstrong, Perkins, and Stewart[13]) which the carbon and hydrogen atoms adopt. We therefore conclude that the π component of the bonding between ethylene and titanium (*i.e.*, the 'back donation' to the π^* of ethylene) is unimportant in this case and this is not surprising when the relative energies of the two sets of orbitals are compared.

This conclusion disagrees with Cossee's postulation that one of the $3d$ orbitals ('t_{2g}' of an octahedral titanium complex) is considerably stabilised by interaction with the ethylene π^* orbital. Since this is one of the pivotal points in Cossee's explanation of the catalysis, we must seek an alternative explanation for the activation of the titanium alkyl–carbon bond in the catalytic process (if, of course, this is a necessary step). The discussion of this point is postponed to a stage when the entire mechanism can be viewed.

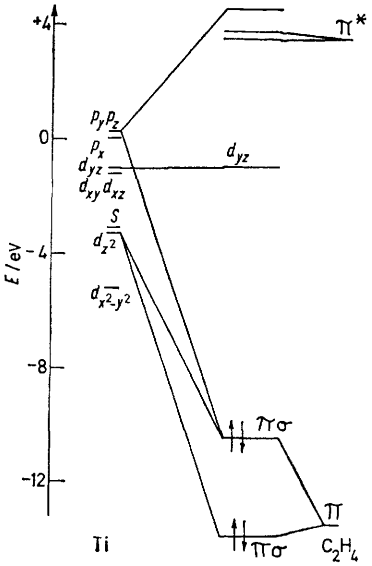

FIGURE 2 Correlation diagram for the titanium–ethylene bond

The titanium–methyl carbon bond. Examination of the bonding patterns in the complex shows that the bonds to titanium can be divided as follows: first, the Cl–Ti bonds are built largely from the $4s$ and $4p$ orbitals on titanium and these need not be considered further in detail. Secondly, the methyl–titanium bond shows a bond order (Figure 1) which is close to unity in the complex. It is remarkable and highly significant that the contribution to this quantity from titanium is almost pure $3d$ in nature whilst the carbon orbitals involved are essentially the $2s$ and $2p$, which can be regarded as a hybrid of '*sp*' type.

Energies and character of the molecular orbitals. One of the most valuable features of such a calculation is that the one-electron molecular energies are given quantitatively with a degree of reliability and it is not

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[12] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.

[13] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *Theoret. Chim. Acta*, submitted for publication.

necessary to conjecture on their position in the energy scale or their character. In this system there are 56 valence orbitals, of which 34 are filled. For brevity and clarity we propose to discuss only a few of these and it is fortunate that they divide well into groups in which separable contributions are readily distinguished.

First, a group of ten bonding levels lie between −20·0 and −48·0 eV: these are concerned solely with the chlorine 3*s* and carbon 2*s* orbitals together with bonding hydrogen contributions. A second set, lying between −9·5 and −18·0 eV, are built from essentially the 3*p* orbitals on chlorine. The highest bonding orbital involves chiefly the Ti–Me bond and we shall discuss this in detail later. Of the virtual orbitals the lowest-lying group (5 levels) arise mainly from the titanium *d* orbitals whilst above this, and of less interest, are those in which the 4*s*, 4*p* of titanium, the aluminium orbitals, and the antibonding *s* and *p* contributions from the chlorine figure. Finally, a narrow band of essentially C–H antibonding levels lie at high energies.

Table 3 provides data relevant to the important energy levels which cluster around the bonding–antibonding gap. The gap itself is not small and amounts to *ca.* 8 eV. Undoubtedly the most important orbital in our sequence is ψ_1, the highest filled. This is built mainly from the titanium $d_{x^2-y^2}$ and d_{z^2} and the methyl carbon $2p_y$ and 2*s* orbitals: other contributions to this orbital are either not important (*e.g.*, the participation of the carbon $2p_x$ and $2p_z$) or are vanishingly small. The two titanium *d* orbitals in question may conveniently be regarded as a linear combination giving rise to a d_{y^2} orbital directed towards the methyl group: similarly, the alkyl-carbon orbitals form an *sp*-type hydrid oriented towards titanium.

TABLE 3

Highest filled and lowest virtual orbitals of the initial ethylene complex, ψ_n

n	E_n/eV	Main character of orbital
1	−8·95	Ti–C bond
2	−9·46	p_x orbitals of terminal chlorines on Al
3	−9·89	p_x orbitals of terminal chlorines on Ti
4	−10·29	All *p* orbitals on all chlorines plus p_z on Ti
−1	−0·83	d_{yz} on Ti
−2	−0·72	d_{xz} on Ti
−3	−0·71	d_{xy} on Ti
−4	−0·17	d_{z^2} on Ti and p_y on C(3) σ*
−5	+0·20	$d_{x^2-y^2}$ on Ti and p_y on C(3) σ*

The three lowest unfilled orbitals are near-degenerate and possess strong d_{xy}, d_{xz}, and d_{yz} character respectively. Of these, d_{yz} can interact with the ethylene π system but, as aforestated, this particular interaction is weak and the molecular orbital is only slightly lower in energy than the other two. The d_{xz} orbital cannot partake in any titanium–carbon bonding at all. The next two virtual levels, ψ_{-4}, ψ_{-5} are significant in that they are antibonding between the metal and the methyl carbon and are, in addition, relatively close to the three unfilled *d* orbitals in energy. Preliminary calculation of the first triplet excited state of the complex, configuration interaction being neglected, leads to a value of 1·40 eV, and there are a number of states lying in this area. States of this energy are too far removed from the ground-state for extensive Boltzmann population although, if populated, they would be effective in labilising the Ti–Me bond, since two of the orbitals of the group involved in the lower excited states (ψ_{-4}, ψ_{-5}) have antibonding character across this link. The excited states will be discussed elsewhere.[14]

Our conclusions about the energy ordering of the orbitals are in some ways essentially similar to those of Cossee.[3] Thus, we also find that (i) the Ti–alkyl bond is strongly localised in the highest filled orbitals, (ii) two of the 't_{2g} set' remain virtually non-bonding whilst the third (d_{yz}) is lowered in energy by interaction with the ethylene π system. We depart from Cossee's interpretation when *quantitative* aspects of the scheme are considered: we do not believe that the weak lowering of d_{yx} by interaction with ethylene (*ca.* 0·1 eV) can account for the dramatic experimental observations. This does not argue that labilisation of the Ti–C by thermal population of the excited states is of no consequence but we relegate it to second-order. No doubt this type of factor is responsible for the 'fine tuning' of the reaction by different attached groups. Accordingly, we later present an alternative rationale of the mechanism of the reaction.

Charge distribution. The total electron populations, atom–atom bond orders, and atomic valencies[13] are shown in Figure 1. The electronic configuration of titanium in the complex is calculated to be $4s^{0\cdot38}\,4p^{0\cdot78}\,3d^{1\cdot67}$. Most of the *d*-orbital population is resident in the d_{z^2} and $d_{x^2-y^2}$ orbitals and, further, it is interesting that the 4*p* orbitals become appreciably occupied.

In the complex the titanium and aluminium atoms assume overall positive charges. This is as would be expected from chemical intuition. The Ti–Me bond is quite strongly polarised with electrons moving towards the latter group, whilst the ethylene molecule is barely changed electronically at all: this is consistent with the transient nature of the bonding to titanium in such an active complex. Both the carbon and hydrogen atoms exhibit their classical valencies and the 'double-bonding' character of the C–C moiety remains virtually unaltered. The titanium and aluminium atoms show very low valencies and this is particularly interesting as they are co-ordinated to six and four groups respectively. This matter will not be pursued further here; a forthcoming paper[15] will examine more generally the significance of the valencies of atoms having high co-ordination number in their compounds.

The Reaction Co-ordinate.—Having characterised the starting complex, we now examine how the calculated quantities discussed above change as the nuclei move in the reaction.

Orbital energies. Figure 3 illustrates the modifications

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[14] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Dalton*, submitted for publication.

[15] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *Theoret. Chim. Acta*, submitted for publication.

to the energy scheme which are brought about by the migration of the alkyl group. At the left-hand side of the diagram are the orbital energies of the initial ethylene complex, whilst the right-hand side shows those of the propyl-substituted species having a vacant site. The abscissa on Figure 3 simply gives the number of the calculation (*N*) which is keyed directly to an intermediate geometry in which both ethylene and the methyl group have changed position. As before, to avoid unnecessary complication, attention will be concentrated on only those molecular orbitals which lie immediately adjacent to the energy gap. Whilst recognising that all other orbitals play some part in the reaction scheme, their role is minor.

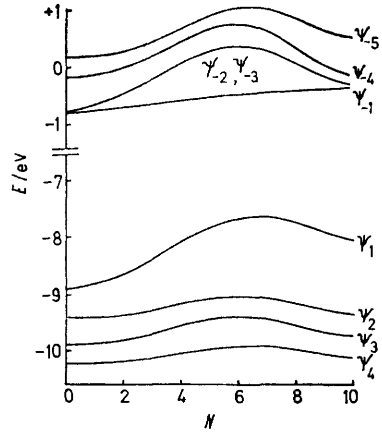


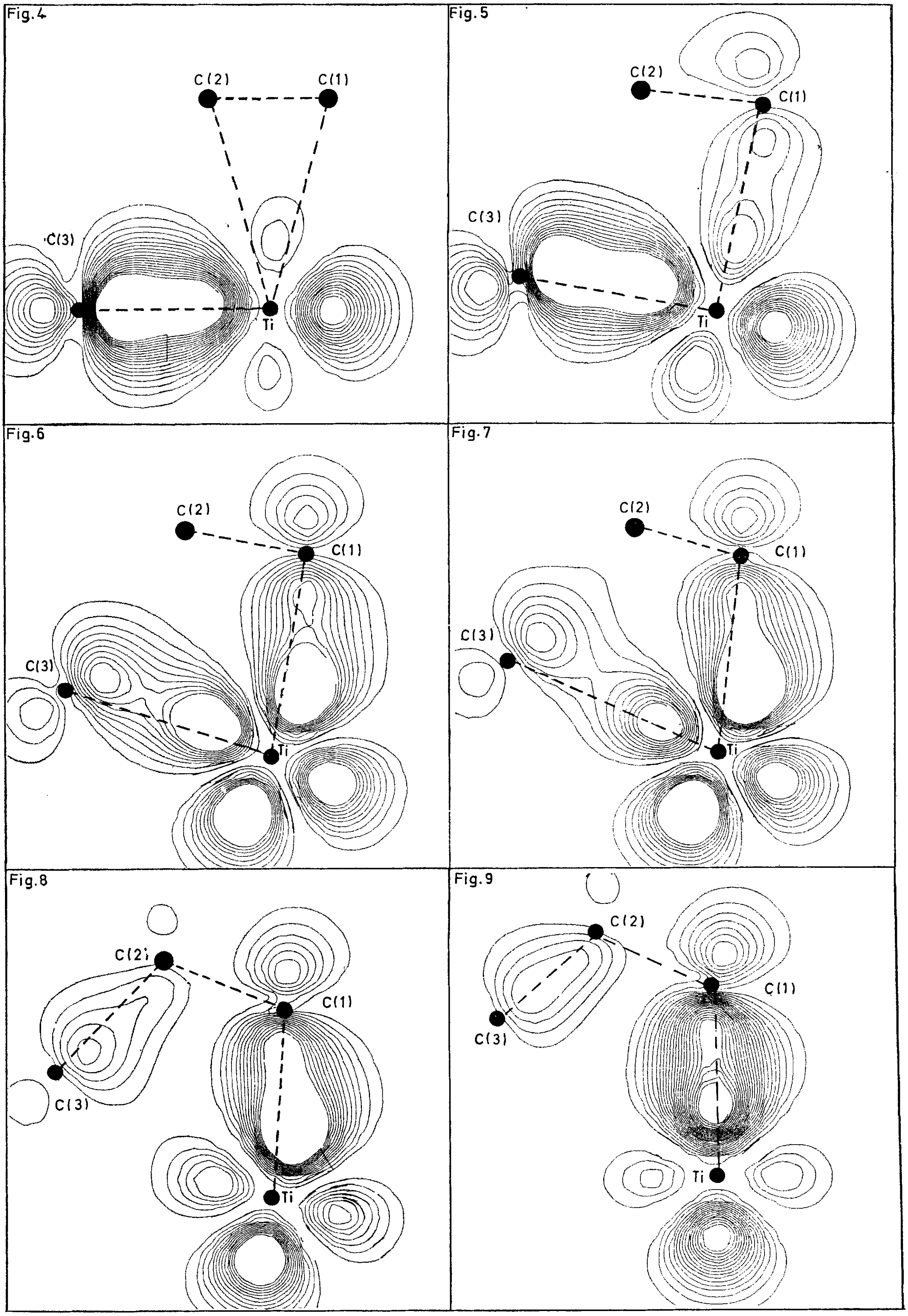
FIGURE 3 Orbital energies over the reaction co-ordinate

First, the orbitals ψ_2, ψ_3, and ψ_4 all remain localised on the chlorines and we do not need to consider them further. The orbital ψ_1, which governs the Ti–Me bond, is raised in energy by migration of the methyl group and passes through a maximum before decreasing to a new position in the propyl species. Now, the propyl species is one where we consider a vacant site to be positioned *cis* to the alkyl group and, if we assume that alkyl-chain growth does not change appreciably the orbital energy level ψ_1, then Figure 3 (right to left) describes what happens to the Ti–alkyl carbon energy level when an ethylene is accepted on the vacant site. It is seen that this co-ordination *stabilises* the M–C bonding orbital. Further, if the unfilled orbitals ψ_{-1} to ψ_{-4} are studied, then the energy gap between ψ_1 and all these increases. This added to Cossee's picture in that ψ_{-1} appears to be stabilised by co-ordination of ethylene but ψ_1 is also lowered in energy. Cossee did not, at the time of his writing, make any assertion of the effect of ethylene on ψ_1. Whilst, in the absolute sense, the increase of the energy gap (by *ca.* 0·4 eV) does not militate against labilisation of the M–C bond by thermal excitation of electrons, it does suggest that the initial co-ordination of ethylene to the vacant site is not a critical prerequisite for the catalysis, as when the groups start to move the energy gap is depressed anyway. Perhaps the most significant point which develops from this is that it calls into question the significance and existence of the ' vacant site ' in the catalysis. This point is discussed in more detail later.

Orbital character. The changes which occur in the nature of the orbital ψ_1 are striking and they lead to rationalisation of alkyl-group migration. As soon as the methyl group commences movement, then the new symmetry of the situation induces bonding (previously forbidden) between the methyl carbon and the d_{yz} orbital. Since the latter is already weakly overlapping with the ethylene π^* orbital, its involvement in the bonding to methyl brings about a threefold result: it activates the M–C bond, links it to ethylene and, at the same time, helps to populate the antibonding orbital of the latter. As the migration proceeds, the mixing-in of d_{yz} increases to a point where two lobes of the orbital are bonded, one each to C(1) and C(3). After this point its contribution decreases and the orbital ψ_1 reverts to being constituted from virtually a pure titanium d_{z^2} orbital, pointing now, however, to the ethylene carbon C(1). Figures 4—9 illustrate these stages pictorially through electron-density contour plots of the orbital.[6] In Figure 4 the M–C bond is clearly seen as being built from a d_{y^2} orbital and a carbon *sp*-type hybrid. In this diagram the position of ethylene is marked since ψ_1 has no contribution from either C(1) or C(2) at this stage. As the migration proceeds, the d_{y^2} and the carbon *sp* hybrid orbitals contract away from each other and both begin to extend towards the ethylene molecule (Figure 5). After the transition state (Figures 5 and 6), the d_{yz} lobe to methyl contracts completely and a new M–C bond has formed. This is again of d_σ–p_σ type (Figure 7) but it is now directed to the C(1) carbon atom of the ethylene moiety. At the same time, p_σ–p_σ overlap has developed between the migrating methyl and C(2) of ethylene (Figure 9).

Figure 10 shows the contributions to the M–C bond and the way in which they change quantitatively during the migration. The increase and decrease in importance of the d_{yz} contribution to the orbital ψ_1 and the way in which this function acts as a link between the d_σ contribution on the left-hand side (initial complex) and on the right (propyl species) stands out clearly. In Figure 11 the important bond-order changes in the active moieties which are involved in the reaction are shown quantitatively. In this diagram, the transition state reveals itself as a multiple crossing point in the middle of the reaction sequence.

In summary, the main features which are brought out by this study are that (i) *at all stages* the methyl group and the ethylene can remain bonded to the titanium atom and hence no energy for bond-breaking is required; (ii) the d_{yz} orbital acts as a transfer agent, which enables the methyl group to leave its position and to link to a carbon atom of the co-ordinated olefin; (iii) we do not really need to consider initial labilisation of the M–C bond by thermal excitation, since there is never any substantial loss in Ti–C bonding energy as



FIGURES 4—9 Electron-density contours for stages in the reaction co-ordinate

the methyl group migrates; (iv) the whole process is accompanied by only minor changes in the orbital energies of the complex.

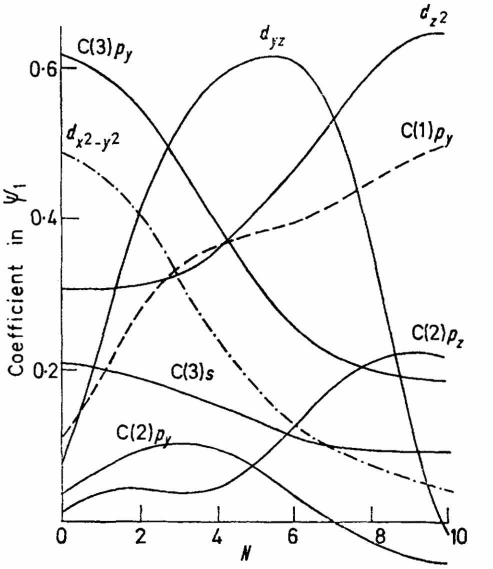


FIGURE 10 Orbital contributions to the M–C bond

It is now of interest to consider the question of how the reaction could be initiated. A clue to this is given by the charge distribution. This shows the olefin to be weakly positive, while the methyl carbon is strongly negative. There is, in addition, weak bonding between the carbons C(2) and C(3) (not shown in Figure 1). This initial situation thus predisposes atoms C(2) and C(3) towards stronger interaction and the migration could then be set in motion thermally by population of appropriate vibrations. This interpretation is strengthened if we study the *total* molecular energy of the system on going from the initial ethylene complex to the final propyl-containing product: this quantity undergoes a substantial decrease over the reaction co-ordinate. The driving force for the reaction should be the tendency for the system to go to the state of lowest electronic energy (*i.e.*, the propyl species). Moreover, because the methyl group is able to transfer to the ethylene without significant loss of bonding energy, there is virtually no activation-energy barrier to the migration. This is consistent with the phenomenon of catalysis.

We can also comment usefully on the effect of weakening the initial titanium–alkyl bond, either by the nature of the alkyl group itself or by altering the terminal groups on the aluminium atom. If we accept that the driving force for migration is the extra stability conferred on the system by the formation of a new C–C σ bond, then weak Ti–alkyl bonding will clearly help to maximise the energy difference between the initial ethylene complex and the species formed after migration. However, our calculations suggest that, in any case, there need be no barrier to initiation of the reaction.

Role of the $>$AlR$_2$ *Group.*—The orbitals of the aluminium atom or the terminal groups do not exercise any first-order effect on the important energy levels of the species involved in the process. However, it is of critical importance that the symmetry of the titanium site be such that the titanium–alkyl bond can be localised in a labile molecular orbital which has considerable *d* character. Although we have not investigated a range of symmetries, it seems that a trigonal bipyramidal or octahedral site symmetry may achieve this result best. This suggests that the most important role fulfilled by the $>$AlR$_2$ group is to partake in bridge bonding with the titanium, thus compelling it to adopt a high co-ordination number.

Existence of the Vacant Site.—All the reasoning advanced heretofore has assumed that, at least transiently, a vacant site will exist on the titanium atom at some point in the catalytic process. We now question this assumption, to see whether there is an acceptable modification of the mechanism which does not require the vacant site. The first question therefore is whether the propyl species having a vacant site is more stable than one in which the propyl group is placed equivalently in the trigonal plane so that the titanium atom adopts trigonal bipyramidal site symmetry. Intuitively, one would expect the latter geometry to be the more stable but the point was checked by a series of total-energy calculations in which the propyl group was moved from the 'octahedral' to the 'trigonal bipyramidal' position. Figure 12 is a plot of the total energy of the system against the angle of rotation of the Ti–C bond from the 'octahedral' position. The trigonal bipyramidal situation corresponds therefore to the 45° angle of rotation. Figure 12 shows that the symmetrically placed propyl group gives rise to the situation of lowest energy.

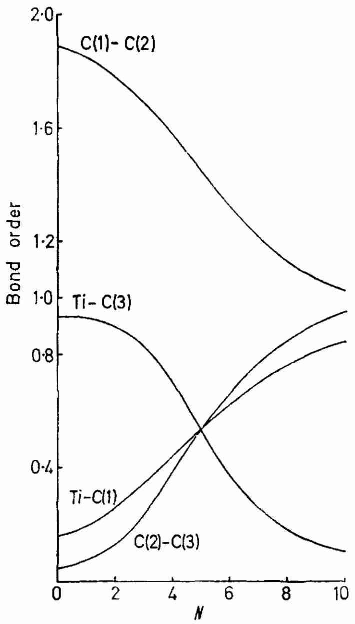


FIGURE 11 Bond-order changes over the reaction co-ordinate

In fact, the bottom of the well is almost parabolic, indicative of very uniform repulsion from either of the two conformations having vacant sites. The situation arises from the minimisation of nuclear–nuclear repulsion, since no bond forms between propyl and chlorine and all interactions are repulsive.

Now, as stated, the total energy of the initial ethylene complex is decreased by migration of the methyl group to the ethylene to form a propyl group, and is further decreased by adoption of the trigonal bipyramidal conformation. We now argue thus: the most energetically favourable conformation for a species containing *only* an alkyl group is one where the site symmetry of titanium is trigonal bipyramidal. When an ethylene molecule arrives at the active titanium site for co-ordination, the energy of the alkyl-containing system must first be raised by moving the alkyl group and creating a transient vacant site (although it should be noted that a concerted addition–rotation does not require that a site should ever be freed). The energy released by ethylene co-ordination then re-lowers the energy of the whole system and more than compensates for the reorganisation at the titanium site. Although we do not know the intrinsic energy of co-ordination of an olefin to a titanium atom accurately, we do know that the overall heat generated in the reaction between a titanium compound, *e.g.*, $TiCl_4$, and an olefin, is small.[16] Nevertheless, there is clear evidence of complex formation in such mixtures [17] and, if this is accepted, it means that the intrinsic energy of olefin bonding is essentially equal to the reorganisation energy of $TiCl_4$ to the appropriate geometry in the olefin complex.[18] Now the reorganisation energies of $TiCl_4$ from tetrahedral to other geometries, based on the trigonal bipyramid and the octahedron, have been calculated [18] and are both greater than the energy difference between the last two geometries. The maximum energy change is also essentially the octahedral–trigonal bipyramidal reorganisation energy. This is less than that for the reorganisation from tetrahedral to either of the other geometries, a quantity which, we have argued, is essentially the same as the intrinsic co-ordination energy of an ethylene molecule. Hence, we opine that the intrinsic C_2H_4–Ti co-ordination energy is sufficient to shift the alkyl group and reorganise the site symmetry of the titanium atom in a ' soluble ' catalyst from trigonal bipyramidal to octahedral. Since the energy released by olefin co-ordination is partly used up in shifting the growing alkyl group, it qualifies in a sense as ' activation energy '.

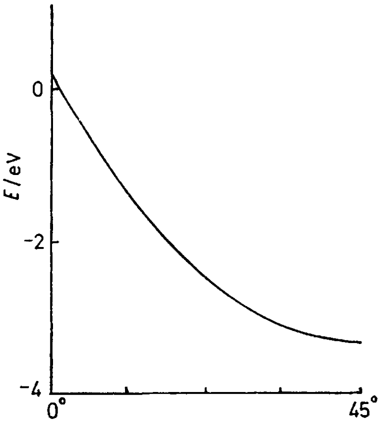


FIGURE 12 Total energy change between ' octahedral ' and ' trigonal bipyramidal ' site symmetry at titanium

Finally, since alkyl migration is energetically favoured, then clearly after initial olefin co-ordination the reaction runs sequentially downhill energy-wise.

An important secondary consequence of our postulation of the electronic stability of the trigonal bipyramidal titanium site is that the next incoming olefin molecule can attack from *either* side of the growing alkyl group. This will help to account for a high pre-exponential factor in the rate equation, since the symmetry of the mechanism is greatly enhanced. Further, it argues cogently that stereospecific mechanisms of polymer growth which rely on the generation of vacant sites in certain positions are invalidated. This section of the paper is in no way at variance with the work described in earlier sections, since the migration of the methyl group *after* ethylene co-ordination was studied. It does suggest, however, a concerted mechanism in which an ethylene molecule attacks and, as the alkyl group moves away, is transferred to it *via* the *d* orbitals. This could also be accompanied by concomitant approach of a second ethylene molecule. We believe, however, that a more complex mechanism of this kind would not induce any basic differences in the electronic rearrangements in the process suggested in this paper.

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