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Catalysis of Symmetry-disallowed Reactions

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Opportunities for applying the principle of the conservation of orbital symmetry to catalytic processes are surveyed. Current views on the role of a transition metal in the catalysis of symmetry-disallowed reactions are reported, and possible mechanisms are discussed. Close attention is paid to the correlation of the catalytic activity of metal-containing catalysts with the electron configuration of the transition metal, the structure of the complex, and the nature of the ligands. Examples of catalytic reactions disallowed by the Woodward-Hoffmann rules—valency isomerisation of hydrocarbons, hydrogenation and disproportionation of alkenes, cyclo-oligomerisation—are considered in the light of ideas on concerted and stepwise mechanisms. A list of 137 references is included.

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I. INTRODUCTION

The study of catalysis as a method for conducting chemical processes has always made use of ideas developed in solid-state physics, organic, coordination, inorganic, and polymer chemistry, and enzymology. Many general theories of catalysis—physical, multiplet, semiconductor, supersaturation, etc. theories—were constructed in various historic periods on the foundation of advances in solid-state physics. From Sabatier to the present time the concept of intermediate compounds has been of the greatest assistance in the selection of new catalysts; such ideas were based on achievements in the preparation of various types of coordination and organometallic compounds. Generalisations such as the theory of "soft" and "hard" acids and bases, electronic theories developed in organic chemistry, etc. have proved extremely useful for catalysis. "Catalytic bionics"—whose aim is to create novel highly efficient and specific catalysts—has been constructed from data on the structure and the mechanism of the action of enzymes and the general principles of the action of biological catalysts.

One of the most important recent achievements of theoretical organic chemistry has been to elaborate rules for the conservation of orbital symmetry in concerted reactions (called the Woodward–Hoffmann rules). The directions of many chemical processes have been explained and predicted by means of these rules during recent years. It appeared useful to examine their application to the catalysis of reactions that are disallowed for

reasons of symmetry. Several possibilities of interpreting the mechanism of the process and describing (in isolated cases predicting) the nature of the action of a transition-metal catalyst are discussed for such important reactions as the valency isomerisation of hydrocarbons, the hydrogenation and disproportionation of alkenes, and cyclo-oligomerisation.

II. MAIN RULES FOR THE CONSERVATION OF ORBITAL SYMMETRY IN CONCERTED REACTIONS

The Woodward–Hoffmann rules[1-6] are based on the hypothesis that the direction of a synchronous reaction is determined by the symmetry of the highest occupied orbitals†. The view that these orbitals determine the reactivity of molecules had been expressed earlier by other workers. In this connection we must note the papers by Fukui and his collaborators on the theory of frontier electrons[13-15], which provide a basis for correlations between the position of the reaction centre and the maximum electron densities in the highest occupied orbitals and the lowest vacant orbitals of a molecule. Longuet-Higgins and Coulson[16,17] as well as Dewar[18] used the theory of perturbations to explain aromatic substitutions. The merits and defects of these methods have been analysed in detail in Salem's review[19].

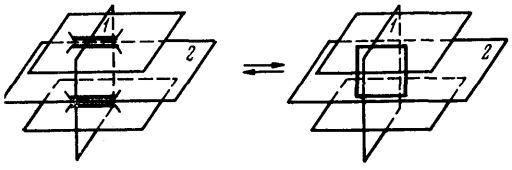


Figure 1. Symmetry elements for the coplanar combination of two ethylenic bonds to form cyclobutane.

The Woodward–Hoffmann method consists essentially in constructing correlation diagrams for the energy levels of products and reactants, and analysing them with respect to symmetry. If the symmetry of the highest occupied orbitals in the ground state of the products correlates with the symmetry of the ground state of the reactants, the reaction is thermally allowed. If the ground state of the products correlates with an excited state of the reactants, the reaction is thermally forbidden, but is allowed photochemically. The fundamental principle was formulated by Woodward and Hoffmann: "Orbital symmetry is conserved in synchronous reactions"[6].

Since we shall be interested mainly in synchronous cycloaddition and electrocyclic reactions, let us examine as example two correlation diagrams—of two ethylenic bonds for the cycloaddition, and of butadiene and cyclobutene for the cyclisation—for which purpose we make use of the arguments in Ref. 6. In the simultaneous combination of two ethylenic bonds to form a cyclobutane ring four π-levels of the two ethylene molecules, the latter lying in two parallel planes, and four σ-levels of cyclobutane are classified as symmetric *S* or antisymmetric *A* relative to the plane located midway between the carbon atoms of ethylene (plane *1* in Fig. 1) and the plane parallel to those of the molecules and located midway between them (plane *2*).

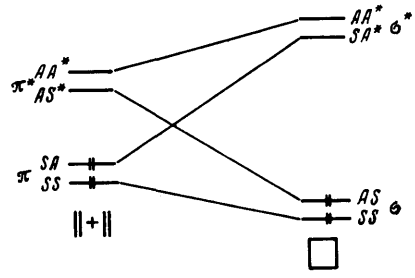


Figure 2. Correlation diagram of levels in the transition ethylene + ethylene → cyclobutane.

The correlation diagram for the transition ethylene + ethylene → cyclobutane shows (Fig. 2) that the reaction is thermally prohibited for reasons of symmetry, since the ground state of ethylene correlates with an excited state of cyclobutane. For reactions of this type the general rule of the conservation of symmetry can be written: reaction is thermally allowed provided that $m + n = 4q + 2$ (where m and n are the numbers of π-electrons in the reactants, and $q = 1, 2, 3, \ldots$); reaction is thermally forbidden for a system in which the number of electrons $m + n = 4q$.

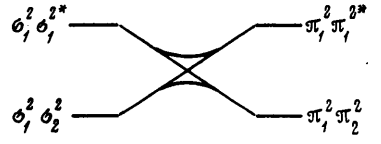


Figure 3. Diagram of states for cyclobutane and ethylene.

With forbidden reactions lines joining levels of similar symmetry intersect. Owing to electronic interaction, however, the system may cross from the adiabatic curve to the ground state of the product[20]. The diagram for the states of cyclobutane and two ethylene molecules shows that in this case symmetry prohibition is responsible for the high energy barrier opposing the transition ethylene + ethylene → cyclobutane (Fig. 3). No barrier due to symmetry is present with symmetry-allowed reactions (e.g. the Diels–Alder reaction).

A similar application of symmetry analysis to the cyclisation of butadiene (an electrocyclic reaction) shows[6]

†Numerous examples of concerted reactions obeying the rules of orbital symmetry (electrocyclic, sigmatropic reactions, cycloadditions, eliminations, etc.) are cited in Woodward and Hoffmann's monograph[6] as well as in reviews[7-12].

that conversion of a π-bond into a σ-bond may occur by either conrotatory or disrotatory motion of the ends of the molecule (Fig. 4). The corresponding symmetry elements are the axis of the molecule and a reflecting plane. The conrotatory path is thermally allowed with respect to symmetry, whereas the disrotatory path is forbidden (Fig. 5).

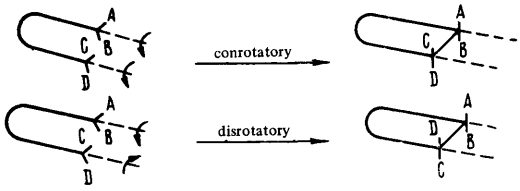


Figure 4. Conrotatory and disrotatory cyclisation of butadiene.

The general formulation of the prohibition rules for electrocyclic reactions is that the latter are thermally permitted with conrotatory motion if $k = 4q$ (where k is the number of π-electrons) and photochemically permitted when $k = 4q + 2$ (tne opposite relation applies with disrotatory motion).

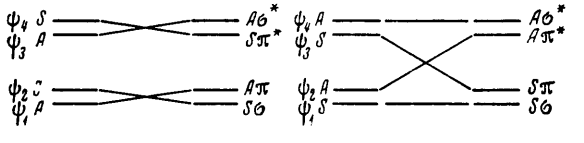


Figure 5. Correlation diagrams of levels for the transition butadiene → cyclobutane.

Correlation diagrams can be applied only to systems that possess symmetry. A different method of analysis was suggested for asymmetric systems [21]. A more general method (mapping) was proposed by Trindle [22] for a wide range of reactions, including those to which the Woodward–Hoffmann rules do not apply.

III. ROLE OF A TRANSITION METAL IN THE CATALYSIS OF SYMMETRY-DISALLOWED REACTIONS

Many symmetry-disallowed thermal reactions involving the cycloaddition of two ethylenic bonds with the formation of cyclobutane or the concerted opening of a cyclobutane ring (the valency isomerisation of strained σ-bonds, the disproportionation of alkenes, cyclo-oligomerisation) take place readily in the presence of complexes of transition metals. At the present time there is no generally accepted view on the role of the metal in catalysing such symmetry-disallowed reactions. The main problem consists in deciding whether such reactions are concerted or non-concerted (stepwise) in character.

A non-concerted mechanism involves essentially redox addition with formation of an intermediate complex, and can usefully be considered for specific examples of catalysed symmetry-disallowed reactions (Section IV). With a concerted mechanism the influence of the metal is apparent in a change in the symmetry of the highest occupied orbitals of the organic substrate.

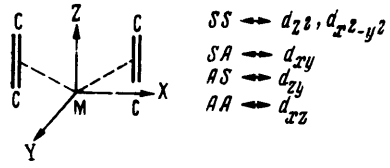


Figure 6. Metal–dialkene complex.

The correlation diagram (Fig. 2) shows that the orbitals of symmetry *SA* and *AS* play the main part in the concerted combination of two ethylenic bonds to form a cyclobutane ring. Occurrence of the thermal reaction requires conformity in symmetry between the ground states of cyclobutane and the two alkene molecules, which can be obtained by the mixing of metal and alkene orbitals in complexes of a transition metal with the alkene and with cyclobutane. Correlation diagrams for such complexes were first given by Mango and Schachtschneider [23] for the suprafacial $(2s + 2s)$‡ cycloaddition of two alkenes.

The concerted addition of two alkenes requires that their antibonding *AS* orbital should be populated (Fig. 2). Since the highest occupied ethylenic π-orbital is *SA*, formation of a metal–alkene complex involves transfer of an electron pair from this orbital to a metallic *d*-orbital of suitable symmetry, whereas an *AS** orbital obtains an electron pair from a *d*-orbital of the same symmetry (*AS*) [24,25].

Fig. 6 shows the symmetry relations between metal and alkene orbitals for a metal–dialkene complex in the given coordinate system. The interaction between metal and alkene orbitals results in their occupation in such a way that the symmetry-disallowed reaction ethylene + ethylene → cyclobutane becomes allowed in the presence of the metal, as follows from the correlation diagram (Fig. 7).

The ligand field of the non-reacting ligands has been disregarded in the construction of this correlation diagram: i.e. the diagram has been drawn for a metal–dialkene complex. In this case all the *d*-orbitals are degenerate. Nevertheless, the presence of non-reacting ligands creates a ligand field which splits the *d*-orbitals; this must be taken into account in studying the catalysis of symmetry-disallowed reactions [26]. Formation of an intermediate complex $ML_nAlkene_2$ in actual catalytic systems is accompanied by splitting of the *d*-levels, the degree of splitting and the distribution of the levels depending on the nature of the ligand and the structure of the complex. The symmetry of the highest occupied orbital of the complex is determined by its geometry. With strong ligand fields, where the splitting of the *d*-orbitals

‡Here and subsequently the symbols *s* and *a* denote suprafacial and antarafacial addition [7].

is large, the highest occupied orbital of the metal–cyclobutane complex may be of either *SA* or *AS* symmetry. Fig. 8 shows that the transition ethylene + ethylene → cyclobutane remains disallowed by symmetry: i.e. a ligand-field symmetry restriction operates in this case [26].

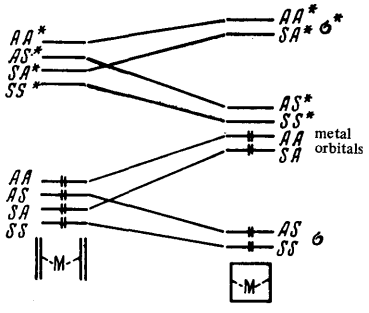


Figure 7. Correlation diagram for the conversion of the complexes metal–dialkene → metal–cyclobutane.

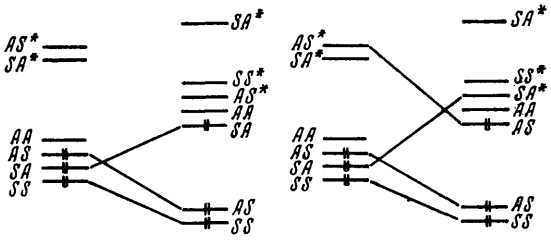


Figure 8. Correlation diagrams for the conversion of the complexes metal–dialkene → metal–cyclobutane for strong ligand fields.

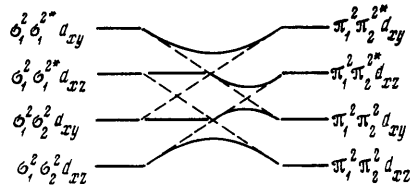


Figure 9. Diagram of states of metal–dialkene and metal–cyclobutane complexes.

The interaction between the orbitals of reactant and metal in electrocyclic reactions catalysed by transition metals produces the same effect as with cycloaddition of type 2 + 2.

A different view, that the metal acts by lowering the activation barrier to the disallowed reaction, not by changing the symmetry of the orbitals in the reactants, has been put forward by van der Lugt [27]. This view is supported by the correlation diagram of states for the concerted opening of the cyclobutane ring in the case of the square planar complex ML_2Cyclobutane and ML_2Alkene, where the metal has a d^8 shell. However, Mango has shown [28] that this example is a particular case of catalysis in which, owing to the effect of the ligand field, the splitting of the *d*-orbitals is such that the reaction remains disallowed by symmetry, but its activation barrier is greatly lowered by the mixing of the occupied orbitals with lower excited orbitals (Fig. 9).

IV. SYMMETRY-DISALLOWED REACTIONS CATALYSED BY TRANSITION-METAL COMPLEXES

Numerous examples of reactions, forbidden by the rules of the conservation of orbital symmetry but catalysed by transition metals, have become known since the publication of the Woodward–Hoffmann correlations [1–5]. They include the valency isomerisation of strained cyclic systems, the disproportionation and hydrogenation of alkenes, and also cyclo-oligomerisations. Examination of these catalytic reactions in the light of the conservation rules is extremely useful for determining the conditions under which such processes may be expected to occur.

Three views are currently held on the mechanism of symmetry-disallowed reactions catalysed by transition metals. Firstly, the reaction can be regarded as a concerted process of type 2 + 2, which becomes symmetry-allowed as a consequence of interaction between the electron levels of organic substrate and metal [26]. Another opinion [27] is that the introduction of orbitals of the metal intermediate in energy between the highest occupied and the lowest vacant orbital of the substrate lowers considerably the activation energy of the reaction, which remains symmetry-disallowed. Finally, a non-concerted process is possible, in which an organometallic intermediate is formed by oxidative addition of the metal to the substrate [29,30].

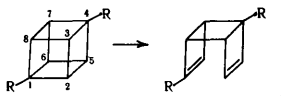
1. Valency Isomerisation of Strained Cyclic Systems

Valency isomerisations of cyclic systems having highly strained σ-bonds are of great interest among the symmetry-disallowed reactions known at the present time. While being in most cases "thermally forbidden" according the Woodward–Hoffmann rules, these reactions take place extraordinarily readily under mild conditions in the presence of compounds of transition metals; they are characterised also by high selectivity and by stereospecificity. Apart from the theoretical significance of valency isomerisations in developing the principle of the conservation of orbital symmetry, they are also useful for organic preparations, since they provide routes to the synthesis of several unique hydrocarbons (e.g. cuneane and semibullvalene).

Extraordinarily interesting examples of the catalytic valency isomerisation of strained σ-bonds are provided by cubane [31,32] and by homocubyl [33,34], 1,1′-bishomocubyl [33–38], and secocubane [39,40] systems, information on which has appeared quite recently. The very existence and the thermal stability of highly strained cubane compounds can probably be explained by the Woodward–Hoffmann rules, according to which thermal rearrangements of the type $\sigma 2a + \sigma 2a$ are not allowed for these molecules in the ground state.

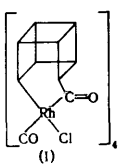
Ions and complexes of several transition and non-transition metals—rhodium, silver, palladium, copper, magnesium, zinc, iron, and mercury—have been examined as catalysts for the isomerisation of cubane and its derivatives. However, only silver(I), rhodium(I), and palladium(II) compounds were found to catalyse this

process, and their catalytic activity was varied and highly specific. In the presence of catalytic quantities of diene complexes of the type $(RhCl\,dien)_2$ (where diene represents norbornadiene, cyclo-octa-1,5-diene, or *syn*-tricyclo-octadiene) cubane undergoes rapid and quantitative isomerisation into *syn*-tricyclo-octadiene[31]:



This process can be regarded as a concerted opening of the cyclobutane fragment of type $\sigma 2s + \sigma 2s$, i.e. as concerted rupture of the $C_{(1)}-C_{(2)}$ and $C_{(5)}-C_{(6)}$ bonds allowed by the participation of a transition metal of suitable electron configuration (d^8), which donates electrons to antibonding cubane orbitals of appropriate symmetry. However, no experimental evidence in support of a concerted mechanism was obtained.

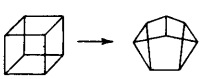
Cassar et al.[31] quote certain results indicating a non-concerted mechanism for the isomerisation of cubane into tricyclo-octadiene. The rate-determining step in this mechanism is the rupture of one carbon–carbon bond by the oxidative addition of the metal to the cubane. Oxidative addition is well known with rhodium and other d^8 complexes[29,30]. A non-concerted route is supported by kinetic data, the distribution of isomeric products from a monosubstituted cubane, and above all the isolation of an intermediate rhodium complex in the stoichiometric reaction of cubane with the dimer of the dicarbonylrhodium chloride. The tetrameric structure of the intermediate complex



(I)

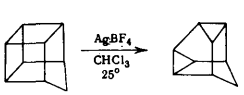
which corresponds to the tetragonal structure of the rhodium atom, is quite soundly based on its chemical reactions and infrared spectra[31].

The silver ion is an efficient catalyst for the isomerisation of cubane and its derivatives[32,34]. The valency rearrangement of cubane itself (catalysed by silver perchlorate in benzene) yields the saturated isomer cuneane (pentacyclo[3,3,0,$0^{2,4}$,$0^{3,7}$,$0^{6,8}$]octane), a representative of important natural ring systems (the cuneane molecule should be ~30–40 kcal mole^{-1} less strained than cubane):



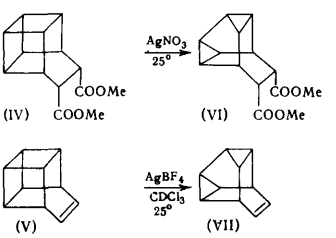
Cubane undergoes an analogous transformation under the influence of palladium(II) complexes (e.g. $[PdCl_2(C_6H_5CN)_2]$).[32]

The remarkable ability of the silver ion to promote symmetry-disallowed skeletal rearrangements is clearly apparent in the valency, isomerisation not only of cubane but also of its derivatives—homocubyl, 1,1′-bishomocubyl, and secocubane systems. In particular, homocubane (II) is converted in the presence of silver tetrafluoroborate into pentacyclo[4,3,0,$0^{2,4}$,$0^{3,8}$,$0^{5,7}$]nonane (III):[33]



(II) (III)

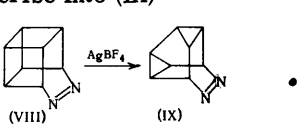
Although the homocubane structure is more strained than the pentacyclononane structure by about 45 kcal mole^{-1}, the purely thermal rearrangement ($\sigma 2a + \sigma 2a$) of (II) into (III) is not allowed by the Woodward–Hoffmann rules. The ease of the silver-catalysed process is probably due to mixing of the orbitals of the metal with the strained σ-orbitals of homocubane, resulting in the appearance of new occupied molecular orbitals, whose symmetry properties are compatible with the permitted isomerisation. Examples of the valency isomerisation of 1,1′-bishomocubyl derivatives are provided by the rearrangement of compounds (IV) and (V) into the corresponding pentacyclic isomers (VI) and (VII)[33–35]:



(IV) (VI) (V) (VII)

Formation of the pentacyclic diester (VI) has been observed also in thermal isomerisation. This suggests that here the effect of the transition metal is to lower the energy barrier to reaction, especially as four cyclobutane rings are converted into the thermodynamically more stable system comprising two cyclopropane and two cyclopentane rings. This reaction was not catalysed by compounds of mercury, copper, zinc, iron, and rhodium, nor by mineral acids.

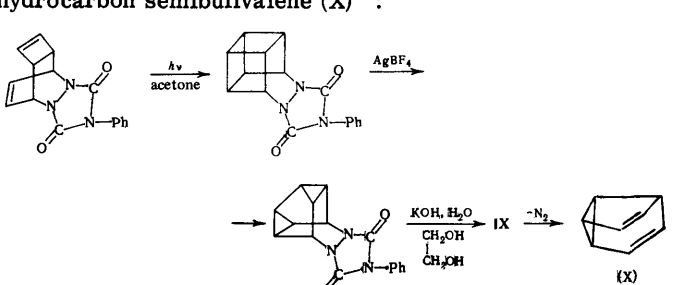
It is noteworthy that a redistribution of σ-bonds occurs with compound (V), while the π-bond of the cyclobutene ring, having a greater tendency to coordinate with a metal, remains unchanged[33]. Nevertheless, the azo-derivative (VIII) does not isomerise into (IX)



(VIII) (IX)

under conditions of catalysis by the silver ion, probably owing to the presence of the lone pairs of electrons on the nitrogen atoms, which interact readily with the metal[36].

The silver-catalysed rearrangement of 1,1′-bishomocubyl systems has been used for preparative purposes, in particular to obtain the hitherto almost inaccessible hydrocarbon semibullvalene (X)[36]:

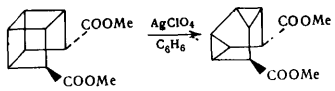


(X)

Although attempts to obtain this difficultly accessible hydrocarbon by the valency isomerisation directly of compound (VIII) were unsuccessful[36], use of its *NN*′-disubstituted derivatives (e.g. an *NN*′-diester) gave positive results[37].

The stereospecificity of catalytic valency isomerisations of cubane systems is excellently illustrated by the

silver-catalysed rearrangement of secocubane compounds[39,40]. Thus the *endo-endo*-diester (XI) gives a quantitative yield of the *endo-endo*-tetracyclo[3,3,0,$0^{2\ 8}$,$0^{4\ 6}$]-octane derivative (XII), and the *exo-exo*-diester is correspondingly converted into *exo-exo*-isomer[40]:



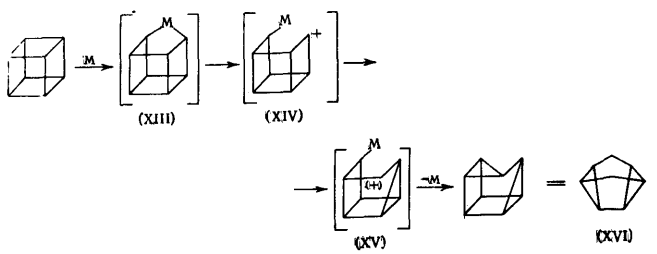
(XI) (XII)

Similar stereoselectivity has been observed also with tetra-substituted derivatives[39].

From the distribution of reaction products and a comparison of the rates of isomerisation of various *exo-endo*-isomers it is concluded[39] that substituted σ-bonds ($C_{(1)}$–$C_{(2)}$, $C_{(5)}$–$C_{(6)}$, $C_{(2)}$–$C_{(3)}$, and $C_{(4)}$–$C_{(5)}$) are not involved in the reaction. Furthermore, numerous examples of the isomerisation of homocubyl, 1,1′-bishomocubyl, and secocubane systems have shown convincingly that the presence of the $C_{(2)}$–$C_{(5)}$ bond is not necessary for the reaction.

The marked difference in catalytic properties shown by rhodium(I) compared with silver(I) and palladium(II) in the valency isomerisation of cubane and its derivatives cannot be explained in terms of electron configurations, since palladium(II) ($4d^8$) resembles silver(I) ($4d^{10}$) more closely than the isoelectronic rhodium(I) ($4d^8$). The reaction mechanism in this case is most probably determined by the oxidising properties of the metals or the effect of the ligand field.

The most general view of the valency isomerisation of cubane and related compounds catalysed by silver(I), palladium(II), and rhodium(I) has been given by Cassar et al.[41] on the basis of a non-concerted carbonium-ion mechanism involving a stage of oxidative addition:



(XIII) (XIV) (XV) (XVI)

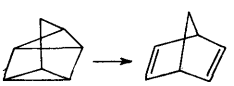
The oxidative addition of a metal ion (Ag^+, Pd^{2+}, or Rh^+) to the cubane molecule yields an organometallic adduct (XIII), which is obviously converted by the ions Ag^{2+} and Pd^{4+} into a cyclobutylcarbonium ion (XIV) (because of the strongly degenerate oxidative character of these metal ions). The ion (XIV) would in turn rearrange into the more stable cyclopropylcarbonium ion (XV). Subsequent reductive elimination of the metal ion should yield the final product, e.g. cuneane (XVI). In the case of catalysis by rhodium(I) further conversion of the organorhodium compound into a carbonium ion probably cannot occur owing to the lower oxidising power of rhodium(III)—compared with silver(II) and palladium(IV).

A stepwise mechanism is supported also by the influence of the positions and electronic effects of substituents on the rates of isomerisation of cubane systems[39,40,42]. Thus a linear free-energy correlation has been established[42] between the rate constants of the rearrangement of 1,4-disubstituted cubanes and the Taft polar δ* constants: rearrangement takes place more slowly the more negative is this constant (the greater the electron-repelling effect of the substituent). The closely similar rates of isomerisation of all stereoisomers of the secocubane ester (XI) and of reaction of the more strained dimethyl cubane-1,4-dicarboxylate probably indicate that electronic factors have a greater influence than geometric factors, which can be explained only in terms of a stepwise mechanism.

In spite of the above fairly convincing arguments in support of a non-concerted pathway for the valency isomerisation of cubane systems, interpretation of these reactions on the basis of a concerted mechanism cannot be finally rejected.

We can try to explain certain facts as due to the effect of the ligand field. The difference in catalytic activity between the isoelectronic palladium(II) and rhodium(I) is obviously associated, not with filling of the *d*-shells, but with the difference in the effects of the field due to the ligands (e.g. $[PdCl_2(C_6H_5CN)_2]$ and $[(RhCl\,dien)_2]$. Substitution of the ligands even in the rhodium complex may lead to a loss of activity towards the isomerisation of cubane (such an effect is produced in particular by replacing the diene ligands by triphenylphosphine ligands[31]). An intermediate complex of rhodium with cubane and its derivatives could be isolated only in the case of the dimer of carbonylrhodium chloride, which cannot be related to the specific properties of carbon monoxide as a ligand. Mango and Schachtschneider showed[26] that this ligand imposes a considerable ligand-field type of restriction on the concerted opening of the cyclobutane ring. They do not recommend the use of carbonyl-containing complexes as catalysts for valency isomerisations. The mechanism of the valency isomerisation of cubane and its derivatives catalysed by transition metals—silver(I), palladium(II), and rhodium(I)—has not yet been finally established. This problem may be solved when additional experimental results appear, and have been subjected to detailed analysis taking into account the orbital symmetry with the construction of correlation diagrams in each specific case.

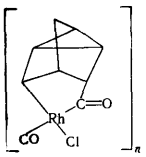
The conversion of quadricyclene into norbornadiene



is especially noteworthy among the valency isomerisations of strained cyclic systems disallowed by the Woodward–Hoffmann rules[43-45]. This skeletal rearrangement has been the object of the most thorough study of the dependence of the catalytic activity of transition-metal complexes on the filling of their *d*-shell and on the geometric configuration of the complexes[45]. The quantitative conversion of quadricyclene into norbornadiene has been effectively catalysed by mono- and di-alkene complexes of rhodium, palladium, and platinum—di-μ-chloro-dibicyclo-[2,2,1]hepta-2,5-dienedirhodium, di-μ-chloro-tetraethylenedirhodium, dichloro-cyclo-octa-1,5-dienepalladium, di-μ-chloro-bis-π-methylallyldipalladium, and dichloro-bicyclo[2,2,1]hepta-2,5-dieneplatinum—as well as by complexes of several transition metals with phthalocyanine and a tetraphenylporphyrin[45].

Two views are held on the mechanism of this reaction, as in the case of cubane: either the cyclobutane ring undergoes concerted opening, or a non-concerted process involves initial cleavage only of one carbon–carbon bond of the cyclobutane fragment by oxidative addition. A telling argument in support of a non-concerted mechanism is the formation of a rhodium complex of quadricyclene[43] by reaction of the dimer of dicarbonylrhodium chloride

with excess of quadricyclene. The structure of this complex



resembles that of the corresponding cubane complex (I).[31] However, a concerted mechanism is also quite likely, since the molecule could easily coordinate with the metal as a consequence of the π-character of the cyclopropane bonds common to the three- and four-membered rings[44].

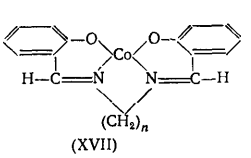
Table 1. Catalytic activity of square planar complexes of bivalent metals in the isomerisation of quadricyclene*.

Electronic structure	d^5	d^6	d^7	d^8				d^9		d^{10}
Metal ion	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Pt^{2+}	Rh^{1+}	Pd^{2+}	Cu^{2+}	Ag^{2+}	Zn^{2+}
	−	+	+	+	+	+	+	−	−	−

*+ = active; − = inactive.

Manassen has shown[45] that the ability of metals to catalyse the isomerisation of quadricyclene is primarily connected with the filling of the d-shell. Ions of metals with d^6, d^7, and d^8 electron shells are active in this process, whereas d^9 and d^{10} ions do not catalyse the reaction (Table 1). Such correlation is readily explained in terms of a concerted mechanism. In the d^8 complexes of rhodium, palladium, and platinum the d_{xy} orbital (i.e. the orbital of symmetry AS) should be vacant, or the highest unoccupied p-orbital should be quite close in energy to the occupied d-orbital. In the d^{10} complexes of copper(I) and silver(I) all the orbitals are occupied, and these ions are evidently incapable of catalysing the concerted opening of the cyclobutane ring.

The effect of ligands on the catalytic activity of the complexes (Section III) is due to splitting of the metal orbitals. In a study of complexes with quadridentate ligands (phthalocyanine, tetraphenylporphyrin, and certain Schiff bases) Manassen showed that a square planar configuration is the main condition for catalytic activity in the isomerisation of quadricyclene[45]. This configuration possesses vacant octahedral sites for the coordination of quadricyclene molecules with formation of an intermediate complex of symmetry such that concerted opening of the cyclobutane ring becomes permitted. As soon as the configuration of the catalytic complex ceases to be planar, the symmetry of the intermediate complex changes, and concerted opening of the ring remains symmetry-disallowed. For example, the most active catalyst for the rearrangement of quadricyclene was the square planar cobalt complex of a Schiff base



(XVII)

having $n = 2$. Complexes in which $n > 2$, whose configuration is non-planar, do not catalyse this isomerisation. Furthermore, the need for vacant octahedral sites in the square planar complexes is supported by the inhibition of their catalytic activity by pyridine bases, which are known to coordinate at octahedral sites in metal porphyrins[46].

Thus the important factor in the catalysis of symmetry-disallowed reactions is the field due to the ligands, together with the filling of the d-orbitals of the metal. On the whole the catalytic activity of each metal in concerted addition (or rupture of bonds) depends on its ability to form complexes of definite symmetry. That is why some metals possess catalytic activity, while others do not.

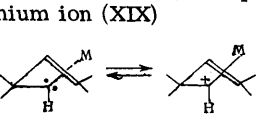
A detailed study has been made of the isomeric changes undergone by bicyclo[1,1,0]butane, which occurs as a structural unit in several polycyclic molecules. Available experimental results indicate that the direction of the valency isomerisation of bicyclobutanes catalysed by transition-metal complexes and ions is determined by the type of metal, the nature of the ligands, and also the positions of alkyl substituents in the bicyclobutane system.

Under the influence of the silver ion alkylated bicyclobutanes undergo almost quantitative and largely stereospecific conversion into dienes[47-50]. Thus *exo-exo*- and *endo-exo*-2,4-dimethylbicyclobutanes are converted mainly into *trans-trans*- and *cis-trans*-hexa-2,4-dienes respectively[47,48]. Under similar conditions 1,2,2-trimethylbicyclobutane yields not only hexa-2,4-dienes but also the corresponding vinylcyclopropane[49], whereas unsubstituted bicyclobutane is converted into butadiene[47].

Isomerisation proceeds differently in the presence of catalysts containing palladium[50,51]. Thus both 2,4- and 1,3-dimethylbicyclobutanes are converted under the influence of dichlorodibenzonitrilepalladium mainly into 2-methylpenta-1,3-diene[50]. Study of this complex together with bischloro-π-allylpalladium shows[51] that the nature of the ligand attached to the transition metal has a substantial influence on the direction of the isomerisation of bicyclobutanes. When small quantities (~ 0.2 mole %) of the catalyst are used, ligand exchange may occur during the reaction, which can lead to anomalous products[51].

In the presence of carbonyl complexes of rhodium, iridium, and ruthenium, alkylbicyclobutanes are converted into dienes and vinylcyclopropane. The structure and the proportions of the products are determined by the position of the alkyl substituents in the initial bicycle[50,52,53].

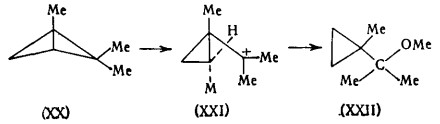
The mechanism of the valency isomerisations of the bicyclobutane system has been a matter of great debate. Several alternative mechanisms have been suggested. Paquette et al.[48,54] originally regarded the silver-catalysed rearrangement of bicyclobutanes into a 1,3-diene system as a concerted process of type $\sigma 2a + \sigma 2a$. However, later work[49,53,55,56] has led to rejection of a concerted mechanism for such processes. A silver–carbonium ion, resulting from rupture of the central $C_{(1)}$–$C_{(3)}$ bond of bicyclobutane followed by complex formation with the silver ion, was suggested[49] as intermediate. According to Gassman et al.[53] the intermediate compound is a transition-metal carbene complex (XVIII) in equilibrium with the hydride–carbonium ion (XIX)



(XVIII) (XIX)

These workers have since obtained[57,58] direct evidence that the interconversion (XVIII) ⟷ (XIX) is a stepwise

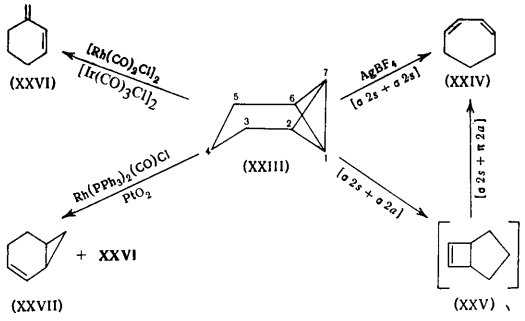
process involving successive rupture of the $C_{(1)}$–$C_{(2)}$ and $C_{(1)}$–$C_{(3)}$ bonds of bicyclobutane under the influence of the transition-metal complex. Formation of a cyclopropylmethyl cation (XXI) preceding appearance of the structures (XVIII) ⟷ (XIX) is supported by production of the corresponding methoxycyclopropane (XXII) from 1,2,2-trimethylbicyclobutane (XX) in the presence of bischlorodicarbonylrhodium in a strongly nucleophilic solvent (methanol):



(XX) (XXI) (XXII)

However, these workers [58] do not exclude the possibility of a different stepwise mechanism depending on the solvent.

The valency isomerisation of tricyclo[4,1,0,$0^{2,7}$]heptane (XXIII) is catalysed by a wide range of transition metals, the direction of the reaction being determined by the type of catalyst employed:

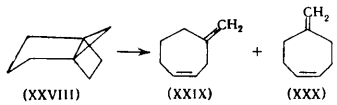


(XXVI) (XXIII) (XXIV) (XXVII) (XXV)

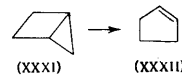
In the presence of silver tetrafluoroborate (XXIII) is converted rapidly and quantitatively into cyclohepta-1,3-diene (XXIV). [47,54] In view of the part played by the silver ion in several concerted processes, this reaction can be regarded as resulting from a symmetry-disallowed concerted ring opening of type $\sigma 2s + \sigma 2s$. With a non-concerted mechanism a two-step process can occur, involving as initial stage the thermally allowed rearrangement $\sigma 2s + \sigma 2a$ of (XXIII) to bicyclo[3,2,0]hept-6-ene (XXV) [59] followed by ring opening of type $\sigma 2s + \pi 2a$.

When (XXIII) isomerises in the presence of catalysts containing rhodium, iridium, platinum, ruthenium, palladium, and copper, the sole (or main) product is 3-methylenecyclohexene (XXVI), the yield of which is determined by the type of ligand [60,61]. Small quantities bicyclo[4,1,0]hept-2-ene (XXVII) are also formed. We must not overlook the fact that palladium(0), platinum(IV), and rhodium(I) were similar in their catalytic effects on this reaction, but the reason is still obscure. The ability of heterogeneous catalysts based on noble metals (PtO_2, Pd/C) to catalyse the isomerisation of tricycloheptane suggests that isomerisation is possible in their presence even during the hydrogenation of highly strained rings.

Examples of the valency isomerisation of polycyclic systems are the conversion of tricyclo[3,2,1,$0^{1,5}$]octane (XXVIII) into 4- and 5-methylenecycloheptenes (XXIX) and (XXX) [62] and the isomerisation of bicyclo[2,1,0]pentane (XXXI) into cyclopentene (XXXII) [63], which should take place in the presence of carbonyl complexes of rhodium, iridium, and ruthenium:



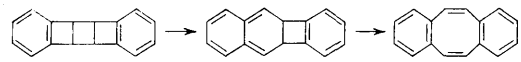
(XXVIII) (XXIX) (XXX)



(XXXI) (XXXII)

By analogy with the isomerisation of bicyclobutane and tricycloheptane the above changes are regarded [62] as stepwise processes with intermediate formation of a metal–carbene complex similar to structures (XVIII) ⟷ (XIX).

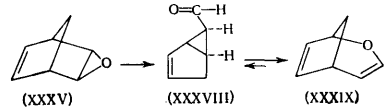
Several valency isomerisations involve the opening of a cyclobutene ring forming part of a bicyclic or tricyclic system. In the presence of silver ions at room temperature, for example, dibenzotricyclo-octadiene (XXXIII) isomerises to dibenzocyclo-octatetraene (XXXIV) [64–66]:



(XXXIII) (XXXIV)

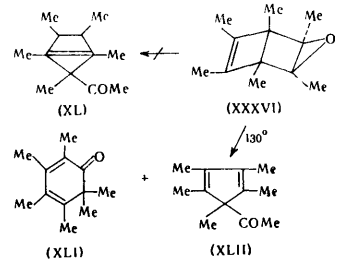
The forbidden disrotatory ring-opening (XXXIII) ⟷ (XXXIV) obviously becomes allowed thanks to the additional orbitals of the metal catalyst.

Papers have appeared recently [67,68] on the isomerisation of the epoxides of norbornadiene (XXXV), Dewar hexamethylbenzene (XXXVI), and cyclo-octatetraene (XXXVII). Under the influence of the dimer of dicarbonylrhodium chloride the first of these epoxides (XXXV) is converted quantitatively into the aldehyde (XXXVIII) and the cyclic ether (XXXIX):



(XXXV) (XXXVIII) (XXXIX)

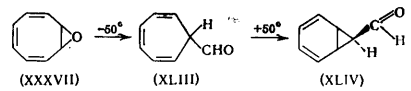
Thermal rearrangement of (XXXVI) is permitted and is a concerted process $\pi 2a + \sigma 2s + \sigma 2a$, which should yield the very strained cyclic system (XL). The actual products of thermal isomerisation, however, are the cyclohexadienone (XLI) and the cyclopentadienyl methyl ketone (XLII):



(XL) (XXXVI) (XLI) (XLII)

Catalytic isomerisation is more specific and gives mainly the latter product (XLII).

Cyclo-octatetraene epoxide (XXXVII) in the presence of the same rhodium complex is readily converted into the aldehyde (XLIII), which when heated to 50°C isomerises into the *exo*-aldehyde (XLIV) (probably as a result of disrotatory opening of the ring):



(XXXVII) (XLIII) (XLIV)

The rhodium-catalysed rearrangement of the epoxides (XXXV)–(XXXVII) is regarded [67,68] as a non-concerted process involving a step of oxidative addition to the metal with fission of a carbon–oxygen bond.

Despite the great attention paid to the valency isomerisation of strained cyclic systems catalysed by transition metals, it has not yet become generally accepted

whether the mechanism is concerted or stepwise. Sufficient experimental data are evidently not yet available to settle this question.

2. Disproportionation of Unsaturated Compounds

The disproportionation of a carbon–carbon double bond [69,70]

$$\begin{matrix} RCH{=}CHR' \\ RCH{=}CHR' \end{matrix} \rightleftarrows \begin{matrix} RCH \\ \| \\ RCH \end{matrix} + \begin{matrix} CHR' \\ \| \\ CHR' \end{matrix}$$

catalysed by transition-metal complexes, can be regarded as conforming to the Woodward–Hoffmann rules for the conservation of orbital symmetry [6]. The mechanism which is currently accepted involves intermediate formation of a "quasi-cyclobutane" four-membered ring (XLVI), which can break down in two ways with formation either of products or of the starting materials [71]:

$$\underset{\text{(XLV)}}{\begin{matrix} RCH{=}CHR' \\ RCH{=}CHR' \end{matrix}} \rightleftarrows \underset{\text{(XLVI)}}{\begin{bmatrix} RHC\text{——}CHR' \\ | \quad\quad | \\ RHC\text{-----}CHR' \end{bmatrix}} \rightleftarrows \underset{\text{(XLVII)}}{\begin{matrix} RCH \\ \| \\ RCH \end{matrix} + \begin{matrix} CHR' \\ \| \\ CHR' \end{matrix}}$$

Experiments with labelled alkenes confirmed [72–74] that redistribution of the double bonds took place via a four-centre state. Hence disproportionation can be regarded as a suprafacial cycloaddition (and cyclodecomposition) of type $\pi 2s + \sigma 2s$, disallowed by the Woodward–Hoffmann rules.

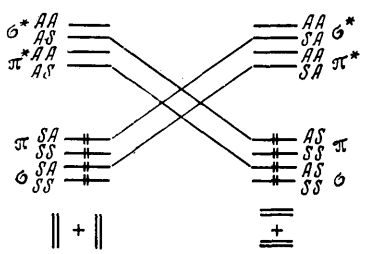
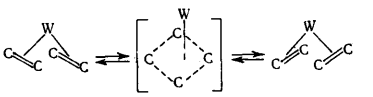


Figure 10. Correlation diagram for the disproportionation of alkenes.

The correlation diagram (Fig. 10) shows that occurrence of the reaction (XLV) → (XLVII) [26] requires that either orbitals of symmetry *SA** in the reaction products (XLVII) or those of symmetry *AS** in the initial alkenes (XLV) should be filled. Only under these conditions can the intermediate cyclobutane structure be formed, and then two new alkene molecules (Fig. 11).

The disproportionation of unsaturated hydrocarbons can take place under conditions of either homogeneous or heterogeneous catalysis [69,70]. Inspection of the correlation diagram shows (Fig. 11) that interaction of alkenes with a metal may make disproportionation a symmetry-allowed process provided that the metal–dialkene complex has lower filled orbitals of symmetry *AS* and *SA*. Satisfaction of this condition depends on the geometry of the intermediate complex and on the relative effect of the fields due to the unchanged ligands.

In the early work on homogeneous disproportionation Calderon et al. [75] assumed that the intermediate complex was a tetragonal pyramid on a square base formed by two alkene molecules, with the metal atom (tungsten) located at the vertex:



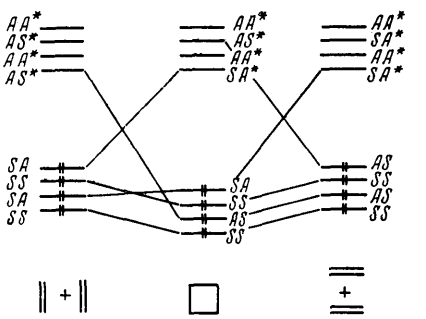


Figure 11. Correlation diagram for the transitions alkene → cyclobutane → alkene.

The position of the remaining ligands remained obscure. The double bonds were supposed to be weakened by coordination of the alkenes with the metal, so that exchange of the alkylidene groups became possible.

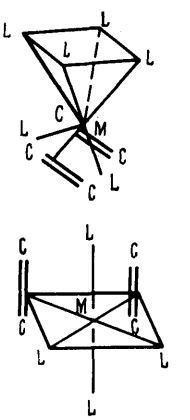


Figure 12. Possible structures of the intermediate metal–dialkene complex in disproportionation.

More precise geometries were suggested for the intermediate complex by Wang and Menapace [76] (for the catalytic system WCl_6 + n-C_4H_9Li) and also by Hughes [77] (for nitrosyl complexes of molybdenum). The intermediate complex can be regarded as an octahedron with the alkene ligands in the *cis*-position or as an Archimedean antiprism (Fig. 12).

Galdow and MacGregor [78] made calculations on the reactions alkenes → cyclobutane → alkenes [1] catalysed by d^6 and d^8 metals, and drew the corresponding correlation diagrams. They found that, in the presence of strong ligand fields and low-spin configurations, the most favourable geometry for the intermediate complex was (Fig. 13).

trigonal bipyramid (D_{3h}) ⇌ square pyramid (C_{4v}) ⇌ ⇌ trigonal bipyramid

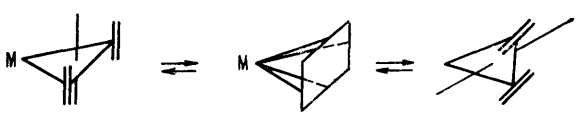
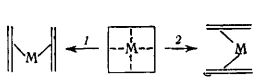


Figure 13. Geometry of the intermediate complex in the disproportionation of alkenes for low-spin d^6 and d^8 metal configurations.

A tetrahedral or square planar configuration imposes strong field restrictions on the redistribution of double bonds in alkenes. Quantum-mechanical calculations for d^6 and d^8 metals show [26,78] that the transition alkenes ⇌ ⇌ cyclobutane is impossible in the presence of a strong ligand field. With weak ligand fields, when splitting of the d-levels is small, such conversion is made possible by mixing of the orbitals of the ground state with lower excited orbitals.

Mango and Schachtschneider [26] constructed correlation diagrams, based on calculations by the extended Hückel method, for carbonyl and chloride complexes of iron and nickel. They examined square planar and tetrahedral configurations for the complexes ML_2alkene$_2$ and ML_2cyclobutane. They found that the transition dialkene ⇌ cyclobutane with preservation of the square planar configuration of the whole complex was restricted with respect to symmetry, since the ground state of the reactants correlated with an excited state of the products. The tetrahedral configuration showed no symmetry disallowance, but the cyclobutane ring can open only in one direction (*1* or *2*):

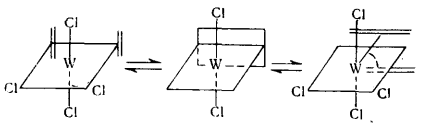


In particular, path *1* is symmetry-allowed for d^6 and d^8 metals, and path *2* for d^{10} metals.

When the complex contains a carbonyl ligand, the strong splitting of the d-orbitals results in the appearance of an energy barrier along the allowed path of the transition. Hence cycloaddition can be expected to occur—not disproportionation—when complexes with strong ligands are used as catalysts, since the latter process would require that the cyclobutane ring could break down in both directions. Such conditions can be achieved in weak ligand fields, where splitting of the d-orbitals is small.

Disproportionation of alkenes in the presence of the WCl_6 + RMgHal catalytic system [79] probably takes place by a four-centre mechanism, since a chloro-ligand does not produce strong fields. The reduction of tungsten hexachloride to the tetrachloride followed by coordination of two alkene molecules to the tungsten atom in the d^2 state suggests the transition

Alkenes ⇌ Cyclobutane ⇌ Alkenes



Attempts at the catalytic decomposition of cyclobutane into alkenes on disproportionation catalysts proved unsuccessful, which led Lewandos and Pettit [80,81] to suggest a four-centre mechanism of disproportionation but without cyclobutane as intermediate. They assumed the formation of a tetramethylene intermediate complex by interaction of the d-orbitals of the metal with four methylene orbitals of the alkene. This interaction is also severely restricted by symmetry: i.e. transitions are permitted only between orbitals of the same symmetry. Such interaction leads to formation of the four-centre system (XLVIII) (Fig. 14), which can break down to yield either (1) the initial substances or (2) disproportionation products.

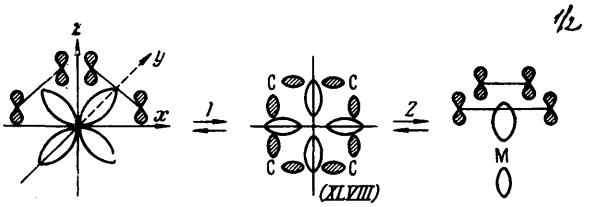


Figure 14. Possible mechanism of disproportionation.

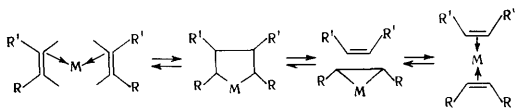
A significant difference between this mechanism and that involving formation of cyclobutane is that here the carbon σ-bonds of the initial alkenes are broken at the same time as the π-bonds. Coordination of the tetramethylene intermediate with the metal takes place at four sites: i.e. the metal must be in a low state of oxidation. Pettit [81] supports his hypothesis by results for the disproportionation of pent-2-ene and non-4-ene under the influence of an arene–$W(CO)_3$ complex. It is suggested that, when tricarbonyltungsten is used, the removal of one carbonyl group is the decisive factor in formation of the tetramethylene–$W(CO)_2$ complex, since only in this case does the tungsten have four vacant coordination sites. Disproportionation does not take place in the presence of excess of carbon monoxide, owing to an insufficient number of free sites for coordination of the tetramethylene complex.

In the Reviewers' opinion a configuration of the intermediate M–alkene complex that is unfavourable for the alkene ⇌ cyclobutane transition is obtained with excess of carbon monoxide, and furthermore carbonyl produces a strong ligand field. The existence of a tetramethylene complex as intermediate also seems improbable, since the proposed [81] symmetry analysis will not give satisfactory results for the simultaneous disproportionation of alkenes with an inner and a terminal double bond.

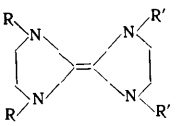
All the above mechanisms for the disproportionation of alkenes presuppose, independently of the structure of the intermediate complex, that the process is concerted.

Recently, however, data have appeared indicating that this reaction may have a non-concerted mechanism, as postulated earlier by Cassar et al.[31]

Formation of a metal ring as intermediate has been suggested[82]:



Carbene complexes have been isolated as intermediates (under the influence of rhodium(I) complexes)[83] in the disproportionation of "electron-rich" alkenes of the type



Thus the mechanism of the disproportionation of alkenes still remains a matter of controversy.

3. Hydrogenation of Alkenes

Special interest attaches to application of the conservation rules of orbital symmetry to a process of such theoretical and practical importance as the catalytic hydrogenation of unsaturated compounds in the presence of transition-metal complexes. Although many papers (including reviews[84-87]) have been published on homogeneous catalytic hydrogenation, many aspects of the reaction mechanism and of the action of the catalysts remain matters of debate. In particular, the sequence of the interrelated stages of activation of molecular hydrogen and activation of the substrate has not been established. Convincing explanations of the selective action of complex catalysts have not appeared.

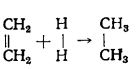
In the Reviewers' opinion, regarding catalytic hydrogenation as the concerted addition of molecular hydrogen to the double bond of an alkene allows us to postulate that the first stage of homogeneous hydrogenation is complex formation between alkene and metal. The selectivity of the action of complex catalysts should be related to the way in which the unsaturated substrate is coordinated with the metal.

Uncatalysed hydrogenation

The uncatalysed hydrogenation of a carbon–carbon double bond can occur in two ways. A free-radical mechanism involves dissociation of the hydrogen molecule followed by addition of the hydrogen atoms at the double bond:

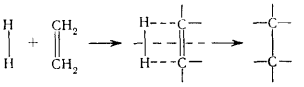
$$H_2 \rightarrow H + H$$
$$CH_2=CH_2 + H \rightarrow CH_3-CH_2^{\cdot}$$
$$CH_3-CH_2 + H \rightarrow CH_3-CH_3$$

The hydrogen molecule may undergo concerted addition to the alkene:

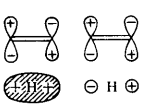


The first of these mechanisms is symmetry-allowed[88,89] according to the Woodward–Hoffmann rules[6], but the reaction has a high activation barrier owing to the large dissociation energy of the hydrogen molecule (104 kcal mole^{-1}). Extreme conditions—high temperatures and pressures—are therefore necessary for the uncatalysed hydrogenation of alkenes[90].

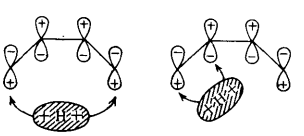
The second pathway—concerted addition—presupposes formation of an intermediate four-centre state followed by simultaneous cleavage of H–H and C=C bonds with formation of new C–H bonds:



Monoalkenes and alkenes having non-conjugated multiple bonds, like the hydrogen molecule, belong to the D_{nh} point group; the highest occupied orbitals in the ground state are the A_{1g} orbital of hydrogen and the B_{3u} orbital of the alkene. In the transition state for concerted addition (four-centre configuration, point group C_{2v}) the highest occupied orbitals have symmetry A_1 and B_2, while the B_{3u} orbital passes into B_1 and is an excited orbital. Thus the ground state of the reactants correlates in symmetry with an excited state of the intermediate configuration, so that the concerted addition of hydrogen to monoalkenes and alkenes having isolated double bonds is disallowed by symmetry[88,89]. According to the Woodward–Hoffmann rules[6] thermally forbidden reactions can be accomplished photochemically. Hence the photochemical hydrogenation of alkenes is fully able to occur by a four-centre mechanism:



The hydrogenation of conjugated dienes is symmetry-allowed when hydrogen adds at the 1,4 (or 2,3) positions, and disallowed in the case of 1, 2 (or 3, 4) addition[88,89]:

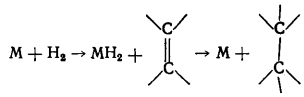


Catalytic homogeneous hydrogenation of alkenes

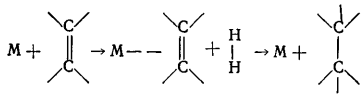
Homogeneous hydrogenation is currently regarded as being generally a stepwise process with successive addition of hydrogen atoms to the double bond of an alkene. The first stage is assumed to be activation of molecular hydrogen by its interaction with the metal (homolytic fission with formation of a mono- or a di-hydride or heterolytic fission with formation of a monohydrate). The H–H bond can be weakened both by transfer of electrons from a filled *d*-orbital of the metal to an antibonding orbital of the hydrogen molecule[91] and by redistribution of electron density between an occupied bonding orbital of the hydrogen molecule and a vacant orbital of the metal[87,92]. Aspects of the activation of molecular hydrogen by simple and complex ions of transition metals have been discussed in detail[84,85,87,91].

The possibility of the concerted addition of a hydrogen molecule to a carbon–carbon double bond was first pointed out by Pearson[88,89]. As already mentioned, a symmetry-forbidden reaction may become allowed by the participation of a transition metal[23]. If catalytic hydrogenation is regarded as a concerted process, three possible reaction paths can be distinguished—(1) formation

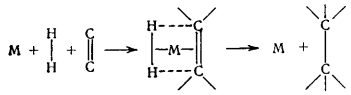
of a complex MH_2 and its subsequent interaction with the substrate



(2) formation of a metal–alkene complex followed by its interaction with hydrogen



and (3) simultaneous coordination of hydrogen and alkene molecules with the metal followed by interaction of hydrogen with the alkene in the complex



The formation of two new carbon–hydrogen bonds in the hydrogenation of a double bond requires the preliminary interaction of an unoccupied orbital of the hydrogen molecule A_{1u} with an occupied orbital of the alkene B_{3u} or of an occupied orbital of hydrogen A_{1g} with a free orbital of the alkene B_{2g}. In the absence of a transition metal such interaction between orbitals of the hydrogen molecule and of the substrate is symmetry-forbidden. When a hydrogen or an alkene molecule coordinates with a metal, interaction of a filled d-orbital of the metal with an unoccupied orbital of the molecule (Fig. 15) removes the symmetry restriction, independently of the geometry of the resulting complex. In both cases the given fragment of the complex has symmetry C_{2v}. With simultaneous coordination of hydrogen and alkene molecules with a metal concerted addition is impossible if the two molecules lie in the same plane (Fig. 15). Departure from a planar configuration may bring one hydrogen atom closer to the alkene molecule than the other, in which case there is no sense in considering a concerted process.

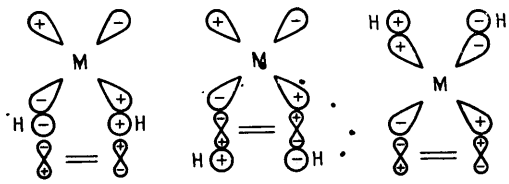
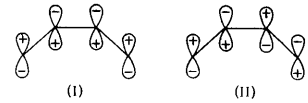


Figure 15. Possible intermediate configurations in the catalytic hydrogenation of alkenes.

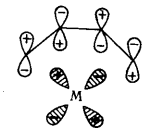
Thus, depending on the suggested mechanism for homogeneous hydrogenation, the metal either activates molecular hydrogen (in the stepwise scheme) or changes the symmetry of the highest occupied orbitals of the reactants by interaction with the substrate, so that the forbidden reaction becomes allowed (concerted addition).

Regarding the hydrogenation of a double bond as a concerted process will explain the selective action of transition-metal complexes in the hydrogenation of conjugated dienes. As mentioned above, addition of a hydrogen molecule at the 1,4 (or 2,3) positions is a symmetry-allowed process. Such addition should result in monoalkenes having an internal double bond. The effect of the metal catalyst is then merely to lower the activation barrier without changing the symmetry of the system [27,93].

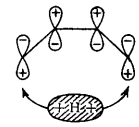
Conjugated dienes have two antibonding π-orbitals



Coordination of the diene with a metal and formation of a dative bond take place when the orbital (II) interacts with a filled d-orbital of the metal

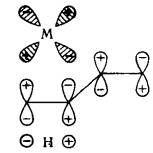


It has been shown in the formation of a metal–butadiene complex that the electron density is displaced from the periphery towards the centre of the diene molecule [93]. The antibonding π-orbital (I) remains vacant, but is allowed by its symmetry to interact with a filled σ-orbital of hydrogen: i.e. addition of hydrogen will occur at the 1,4 positions to form monoenes having an internal double bond



Thus interaction of a metal with a substrate does not change the symmetry of the highest occupied orbitals involved in the formation of carbon–hydrogen bonds, but merely removes the energy difference between them.

A different pattern is found in the hydrogenation of conjugated dienes at the 1,2 positions. As with monoalkenes, the concerted addition of a hydrogen molecule to this double bond is symmetry-forbidden. Interaction of the substrate with a metal may make the 1,2-addition symmetry-allowed, but only provided that coordination of the diene with the metal occurs only at the site of the hydrogenated bond. Thus the electron density of the metal–diene bond would be displaced towards the end of the diene molecule:



In this case the reaction products should be terminal alkenes.

The high selectivity exhibited by complexes of metals of the fourth period in the hydrogenation of conjugated dienes to monoalkenes (Table 2) is evidently connected with the mode of coordination of the diene molecule with the metal. When chromium and vanadium complexes are used as catalysts, for example, monoenes with a terminal double bond are almost completely absent from the products [98,99,101], which must definitely be related to the paucity of complexes of these metals with monoenes

and non-conjugated alkenes. The hex-2-ene and hex-3-ene obtained by the hydrogenation of hexadienes in the presence of tricarbonylchromium do not isomerise, which probably indicates the inability of these metals (especially of chromium) in a particular state of oxidation to coordinate alkenes at only one double bond.

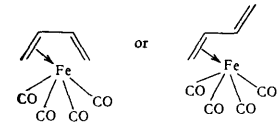
Table 2. Hydrogenation of conjugated dienes in the presence of complex catalysts.

Catalyst	Substrate	Hydrogenation product	Yield, %	Ref.
$CoCl_2$—KCN(CN/Co>6)	butadiene	but-1-ene	80—85	95
$CoCl_2$—KCN(CN/Co<5,5)		*trans*-but-2-ene		
		cis-but-2-ene	86	
$CoH(Ph_2PEt)_2$	butadiene	but-1-ene	11	96
		cis-but-2-ene	50	97
$Co(acac)_3 + Et_2AlCl + Ph_2PPr$	butadiene	*cis*-but-2-ene	38.7	
		but-1-ene	39.7	
$(C_5H_5)_2Cr(CO)_3$	isoprene	2-methylbut-2-ene	95	98
$PhCOOCH_2Cr(CO)_3$	hexa-1,3-diene	*cis*-hex-2-ene	66	99
		cis-hex-3-ene	40	
$PhCOOCH_2Cr(CO)_3$	hexa-2,4-diene	*cis*-hex-2-ene	90	99
		cis-hex-3-ene	10	
$PhCOOCH_2Cr(CO)_3$	methyl sorbate	methyl *cis*-hex-3-enoate		99
$RuCl_2$	isoprene	2-methylbut-2-ene		100
		3-methylbut-1-ene		
$(C_5H_5)_2VCl_2$	isoprene	2-methylbut-2-ene	97	101
$FeCl_3 + PPh_3 + AlEt_3$	butadiene	butadiene	22	102
		but-2-ene	13	
		but-1-ene	56.9	
		butane	83	
Ru-N-phenylanaline	isoprene	isopentane	8.4	103
		3-methylbut-1-ene	15.4	
		2-methylbut-1-ene	40.7	
		2-methylbut-2-ene	35.4	

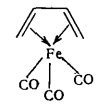
The possibility of the concerted addition of a hydrogen molecule to conjugated dienes at both the 1,4 and 1,2 positions can be illustrated by the hydrogenation of butadiene in the presence of pentacyanocobalt [94,95,104-115]. Kwiatek et al. [95] showed that the composition of the hydrogenation products depends on the CN/Co ratio. When the ratio is ≤ 5.5 the main product is *trans*-but-2-ene (70–86%), but dominant formation of but-1-ene (80–85%) takes place at ratios > 6. Such variation in the yields of the isomers was explained [95,107,115] by the possible formation of π-allyl and σ-allyl intermediate complexes at low and high ratios respectively.

An explanation of the above results in terms of concerted addition is that, at low ratios of the cyanide ion to cobalt, butadiene is probably coordinated on the complex ion $[Co(CN)_5]^{3-}$ (the activity of this ion has been demonstrated) [116-118], and a complex is formed in which the electron density of the metal–diene bond is localised in the region of the second and third carbon atoms of the diene: i.e. the diene acts as a bidentate ligand. In this case addition of hydrogen at the 1,4-positions will be symmetry-allowed, with the formation of but-2-ene. At high ratios an additional coordination site of the metal is occupied by a cyano-group ($[Co(CN)_6]^{4-}$ is probably formed), and the diene can be coordinated only through one double bond (the butadiene acts as a unidentate ligand). Addition of hydrogen at the 1,2-bond then becomes symmetry-allowed, with the predominant formation of but-1-ene.

Some support for the above arguments is provided by the existence of a butadiene complex of iron tetracarbonyl, in which the diene behaves as a unidentate ligand:



Nevertheless, butadiene occupies two coordination sites in the iron tricarbonyl complex:



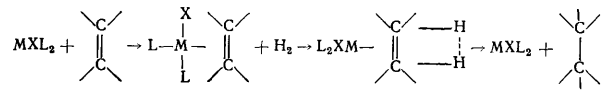
Considering the hydrogenation of a carbon–carbon double bond as a concerted process enables us to suggest complex formation between metal and alkene as the first stage in homogeneous hydrogenation. This view may be supported by several experimental results on the hydrogenation of monoalkenes and non-conjugated dienes in the presence of individual complexes of transition metals and complex organometallic compounds (catalysts of the Ziegler–Natta type).

The first stage in the hydrogenation of alkenes on phosphine complexes of rhodium and iridium is the detachment of one phosphine group, i.e. the freeing of one coordination site [119-121]:

$$MX(PPh_3)_3 \rightleftarrows MX(PPh_3)_2 + PPh_3$$

The second stage would be complex formation between the metal and one of the reactants, to give either the metal hydride or a metal–alkene complex.

The hypothesis that a dihydro-complex of the metal is an intermediate in this reaction was based on the isolation of iridium dihydride [122,123]. In a kinetic study of the hydrogenation of ethylene in the presence of hydrocarbonyltristriphenylphosphineiridium, however, Burnett and Morrison [124] found that the trihydrocarbonylbistriphenylphosphineiridium formed is an inhibitor of the reaction. Kinetic data on the hydrogenation of dimethyl maleate [125] indicate that the first stage is formation of an iridium complex of the substrate, which then reacts with hydrogen. Kinetic investigations of the hydrogenation of alkenes in the presence of chlorotristriphenylphosphinerhodium and hydrocarbonylbistriphenylphosphinerhodium also led Wilkinson et al. [126-128] to regard formation of a metal–alkene complex as the initial stage (the kinetic order with respect to the alkene varies from the first to zero). These results suggest concerted addition of hydrogen by the scheme



Complex organometallic catalysts of the Ziegler–Natta type are active in the hydrogenation of monoalkenes and non-conjugated dienes [84,85]. The decrease in reducing power of the organoaluminium component in the sequence

$$(AlEt_3 \geqslant Al(i\text{-}Pr)_3 > AlEt_2Cl > AlEtCl_2 > Al(OEt)Et_2)$$

leads to a fall in the catalytic activity of the system [129]. The sequence of transition metals with respect to their activity in catalysing the hydrogenation of alkenes is

$$Co \geqslant Ni > Fe > Mn \simeq Cr > V > Ti$$

i.e. their efficiency increases with increase in the number

of *d*-electrons. The calculated overlap integrals of the metal–alkene bond showed [130] that the energy of this bond diminishes in the same sequence

$$Ni<Co<Fe<Mn<Cr<V<Ti.$$

Hence the formation of a metal–alkene complex is an important stage in the hydrogenation of an isolated double bond, and permits the concerted addition of hydrogen.

No selectivity is observed when Ziegler–Natta catalysts are used in the hydrogenation of conjugated dienes [102,131]: monoenes having internal and terminal double bonds and also alkenes can be found among the reaction products. The whole process can be represented by the scheme

$$\text{Diene} + M \rightarrow (M\text{-Diene}) + H_2 \begin{cases} \nearrow M\text{-Monoene-1} \\ \searrow M\text{-Monoene-2} \end{cases} \xrightarrow{H_2} \text{Alkane} + M.$$

The absence of selectivity is probably due to the possibility of coordinating the resulting monoalkenes with Group IV metals in a low state of oxidation.

4. Cyclo-oligomerisations

Among cyclo-oligomerisations of alkenes catalysed by transition-metal complexes that of butadiene is of the greatest scientific and practical interest. This reaction can be regarded as a concerted addition, in contrast to polymerisation, which involves closing the chain at the third unit. Concerted addition is supported by the fact that the larger and intermediate rings are formed by the polymerisation of butadiene only on strong dilution, whereas cyclo-oligomerisation takes place only at high concentrations of the monomer.

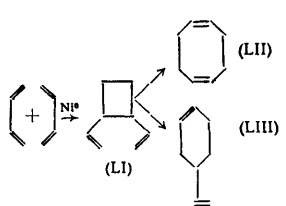
The formation of cyclododecatriene and cyclo-octatetraene from butadiene is symmetry-disallowed, 2 + 2 + 2 and 2 + 2. In the presence of a transition metal, e.g. nickel, this process becomes allowed, thanks to the coordination of butadiene on the metal and the formation of complexes of π-allyl type [132–135]



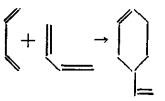
(XLIX) (L)

which have been isolated [134–136].

Heimbach and Brenner [133] studied the dimerisation of butadiene on nickel complexes, and found that, in the presence of zerovalent nickel, butadiene is converted via divinylcyclobutane (LI) mainly into cyclo-octa-1,5-diene (LII) together with some 4-vinylcyclohexene (LIII):



Up to 40% of (LI) appears among the reaction products at low concentrations of butadiene. Reaction of butadiene with isoprene in the presence of the same catalysts yields cyclododecatriene [134], which can also be explained by concerted addition. The formation of (LIII) can be regarded as resulting from the symmetry-allowed interaction of two π-bonds of one butadiene molecule with one π-bond of a second molecule:



The low yield of (LIII) is probably connected with the small probability of such relative orientation of the molecules. If the number of coordination sites is limited, the action of the metal may be to facilitate such orientation and form a complex of type



In particular, examples are known [132,135] in which the introduction of an additional ligand (e.g. triphenylphosphine or carbonyl) leads to the formation solely of (LIII). Vinylcyclohexene is also the sole product of the oligomerisation of butadiene in the presence of rhodium complexes in solvents of high complexing power (e.g. dimethylformamide) [137].

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