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SYMMETRY CONTROL AND TRANSITION METAL CATALYSED REACTIONS

by

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Several examples have recently been reported which indicated that pericyclic reactions which are symmetry-forbidden by the Woodward-Hoffmann rules[1] should become allowed under the influence of appropriate transition metal complexes.[2-4]

A theoretical explanation for the contradictory course of pericyclic reactions under the influence of transition metals has been proposed by Mango and Schachtschneider[5] and by Pettit et al.[6]. It was suggested that certain metal systems containing orbital configurations of the prerequisite energy may render thermally forbidden pericyclic reactions allowed. In the absence of the transition metal an occupied and an empty molecular orbital of the organic substance cross, but this crossing can be compensated by a crossing of the orbitals of the transition metal in the opposite way and consequently the forbidden reaction should become an allowed one.

Now, if one considers the experiments described, the stereochemistry of the starting material for all reactions investigated was such that the allowed reaction could not proceed for steric reasons. Therefore, it can only be concluded from the experiments that the energy of activation of a forbidden reaction is lowered by the intervention of the transition metal, but whether the reaction becomes symmetry allowed or remains forbidden is still an open question.

One may wonder that so little attention has been paid to the fact that experimentally the same catalytic influence has been observed for d^8 and d^{10} metal systems (Hogeveen and Volger[3] report a value of 11.7 kcal/mole for the lowering of the energy of activation for a d^8 system while Pettit[7] reports 15 kcal/mole for a d^{10} system). A correlation diagram reveals, however,

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(1) R.B. Woodward and R. Hoffmann, Angew. Chemie, 81 (1969) 797.

(2) H. Hogeveen and H.C. Volger, J.Am.Chem.Soc. 89 (1967) 2486.

(3) H.C. Volger and H. Hogeveen, Rec. Trav. Chim. 86 (1967) 830;
H.C. Volger and M.M.P. Gaasbeek, Rec. Trav. Chim. 87 (1968) 1290.

(4) W. Merk and R. Pettit, J.Am.Chem.Soc. 89 (1967) 4787.

(5) F.D. Mango and J.H. Schachtschneider, J.Am.Chem.Soc. 89 (1967) 2484;
Tetrahedron Letters (1969) 4813.

(6) W. Merk and R. Pettit, J.Am.Chem.Soc. 89 (1967) 4788.

(7) R. Pettit, H. Sugahara, J. Wristers and W. Meek, Disc. of Far. Soc., 47 (1969).

that the explanation in terms of the "forbidden - to - allowed" concept[5,6] under the influence of transition elements cannot be applied to rationalize the effectiveness of d^{10} systems. Therefore it seems worthwhile to look for an alternative explanation of the role of the metal ion in the dramatic enhancement of the rate of a forbidden reaction. In this communication we shall show that instead of orbital symmetry considerations other factors are in fact much more important for the catalytic effect of transition metals.

Let us consider the reaction of a cyclobutane ring to form two ethylene molecules. The correlation diagrams of the orbitals and the states[8] are shown in Fig. 1 on the left-hand and the right-hand side, respectively. The orbitals are classified according to their symmetry with respect to the two planes of symmetry preserved during the reaction. (AS, for example, means antisymmetric and symmetric with respect to the XY-plane and the XZ-plane, respectively.) It will be seen from Fig. 1 that if there were no configuration interaction the electronic ground state of cyclobutane would end up in a doubly excited state of the two ethylene molecules, as shown in the figure by a dotted line, and, consequently, the reaction is symmetry forbidden.

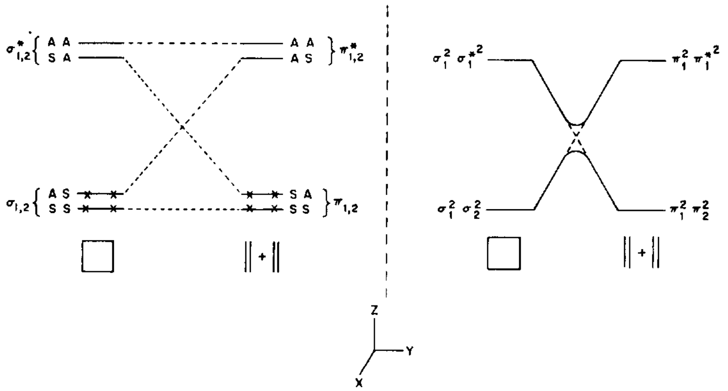

FIGURE 1

The correlation diagrams of the orbitals and the states for the interconversion of cyclobutane and two ethylene molecules. The symmetry of all states drawn in this figure is SS.

In order to clarify our point of view with respect to the role of a transition metal in forbidden reactions we will consider now the same organic reaction catalysed by a d^8 transition metal as an example. Although the actual geometry of the complex is quite uncertain, the square planar arrangement of cyclobutane and two other ligands (L) around the d^8 transition metal (e.g. the rhodium catalyst used by Hogeveen and Volger for the ring opening of quadricyclene[2]) seems to be the most reasonable one.

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(8) H.C. Longuet-Higgins and E.W. Abrahamson, J.Am.Chem.Soc. 87 (1965) 2045.

In this complex all d orbitals except the d_{xy} are occupied by two electrons. The correlation diagrams of the orbitals and the states for the interconversion of cyclobutane and two ethylene molecules under the influence of a d^8 transition metal in a square planar complex are shown in Fig. 2.

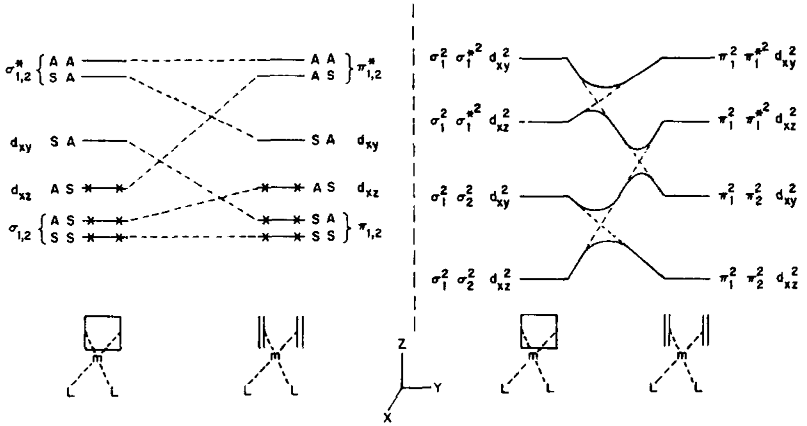

FIGURE 2

The correlation diagrams of the orbitals and the states for the interconversion of cyclobutane and two ethylene molecules under the influence of a d^8 transition metal in a square planar complex. In order to simplify the figure merely two d orbitals (d_{xy} and d_{xz}) of the transition metal are shown. The other d orbitals correlate with themselves and therefore need not concern us here. In addition, the s and p orbitals of the metal have been omitted. The symmetry of all states drawn in this figure is SS.

Since the electronic configuration of the ground state of the starting material without configuration interaction still correlates with a doubly excited configuration of the product, the conclusion to be drawn from Fig. 2 is that the reaction remains symmetry-forbidden in the presence of the transition metal. In addition, the doubly excited configuration is essentially the same as in Fig. 1. The role of the metal in accelerating the reaction, however, becomes clear by comparing the correlation diagrams of the two figures. In both cases the ground state of the starting material passes over adiabatically into the ground state of the product, because of the interaction with a doubly excited configuration. In the absence of the transition metal this doubly excited configuration is situated within the organic molecule and therefore very high in energy. In Fig. 2, however, the configuration interaction takes place with a doubly excited configuration of the transition metal and this configuration is certainly much lower in energy. In this way the organic molecule profits by the excited electronic configurations of the transition metal and consequently the activation energy is lowered as compared with the uncatalysed reaction.

The same reasoning can be applied to the catalytic influence of d^{10} systems. The introduction of energy levels of the metal in between the highest occupied levels and the lowest unoccupied levels of the organic system affords a sufficient explanation of the catalytic activity of the transition metal. Whether or not the metal p orbitals are included in the considerations does not change the explanation of the catalytic function of the metal.

According to the reasoning developed in this paper, orbital symmetry seems not relevant for explaining the lowering of the energy of activation of forbidden reactions catalysed by a transition metal. It may very well be, however, that orbital symmetry becomes important again in those concerted catalysed reactions which are free to proceed in two ways, an allowed and a forbidden one, but such reactions have not been investigated up to the present.

Amsterdam, 20th April 1970