

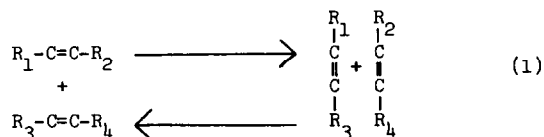
A PROPOSED MECHANISM FOR THE METAL-CATALYSED
DISPROPORTIONATION REACTION OF OLEFINS

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The discovery¹ of the metal-catalysed disproportionation² reaction of olefins (eq. 1) has evoked interest both because of the unique character of the reaction and because of its potential use in organic synthesis.³ Furthermore it has been shown that the disproportionation of olefins may proceed with astonishing facility⁴ despite the fact that in the absence of the metal the overall reaction represents a forbidden process according to the Woodward-Hoffmann rules governing concerted reactions.⁵ The role the metal plays is therefore clearly intriguing.

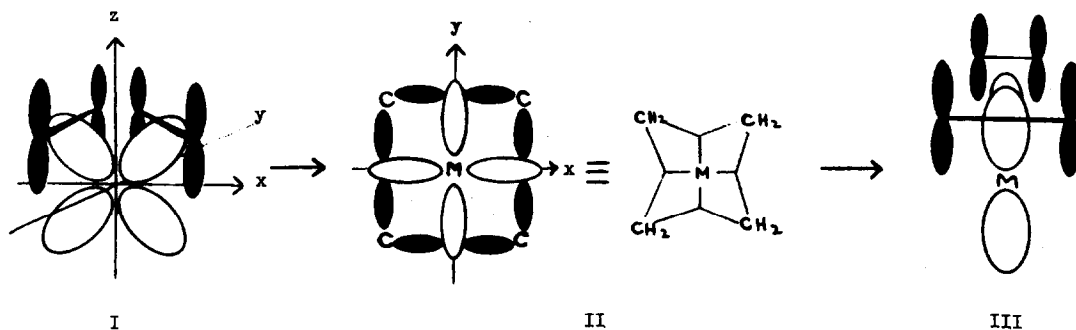


Concerning the course of the disproportionation reaction it has been tentatively suggested that in the presence of the metal the two olefins combine to form a complex, variously referred to as "quasicyclobutane,"⁶ "pseudocyclobutane,"⁷ "adsorbed cyclobutane,"⁸ or "cyclobutane"^{4,9} complexes. Depending on the direction of cleavage these systems could then regenerate either the initial or the disproportionated olefins. These proposals adequately account for the products of the reaction though a precise description of the nature of the intermediate remains to be given. The results of the present study in which disproportionation, cyclobutane formation and its cleavage have each been observed with the same olefin-metal system suggest that the four carbon atoms of the intermediate are not to be considered as a cyclobutane ring.

Since one molecule of cyclobutane has very closely the same free energy of formation as two molecules of ethylene (the two values are identical at 175°), it seems reasonable to suppose that if the disproportionation reaction of ethylene with itself were to proceed via a transition state resembling cyclobutane, then cyclobutane should be one of the products; especially as there can exist no strong bond between cyclobutane and the metal. We find

that treatment of ethylene with molybdena on Al_2O_3 (a known disproportionation catalyst¹) does indeed produce cyclobutane but only in extremely low yields (<0.1%). In contrast, under similar conditions, ethylene undergoes the disproportionation reaction with itself to an extent that at least 35% of the molecules present enter into a reaction which leads to the disproportionation products. This value was obtained through the use of monodeuteroethylene and by measuring the amount of $\text{C}_2\text{H}_2\text{D}_2$ produced in the reaction; isotope effects having been neglected. Furthermore, cyclobutane reacts with the catalyst under similar conditions to produce ethylene but again only in extremely low yields (3%). It is clear that the activation barriers for the two reactions (disproportionation versus cyclobutane formation and cleavage) are different and that different transition states must therefore be involved.

Since the only orbital symmetry treatments, suggested as applicable to the olefin disproportionation reaction,¹⁰ involve an intermediate in which a metal coordinated ligand consists of four carbon atoms connected by sigma bonds, our experimental observations (vide supra) suggest consideration of other orbital symmetry "allowed" pathways. As an alternative explanation we propose that the ethylene molecules first react with the metal to form a bis-ethylene π complex I which reorganizes to a multicentered organometallic system II in which the bonding is most conveniently described as resulting from the interaction of a basic set of metal atomic orbitals and four methylenic units, a more detailed molecular orbital description of which is given below. Retraction of the system II along the x axis leads to starting materials while separation along the y axis leads to disproportionated products.



With reference to the axes given in structure (I) the symmetry elements which are retained in the conversion of I to III via the complex II are reflection in the yz and xz planes. The molecular orbitals which can be constructed from the set of two basic orbitals of methylene, ψ and θ , together with the orbitals of the metal giving the appropriate symmetry with which these ligand orbitals can combine, are given in Fig. I.

The molecular orbitals of the starting bis-olefin metal complex, together with the orbitals of the same symmetry into which they transform in the complex (II), are listed in Table I. In this table the symbol $\overset{4}{\rightarrow}$ denotes forward coordination of a total of 4 electrons from filled ligand orbitals to empty metal orbitals while $\overset{4}{\leftarrow}$ denotes back donation of 4 electrons from filled metal orbitals to empty ligand orbitals; the symbols S and A refer to the symmetry property of reflection in the yz and xz planes.

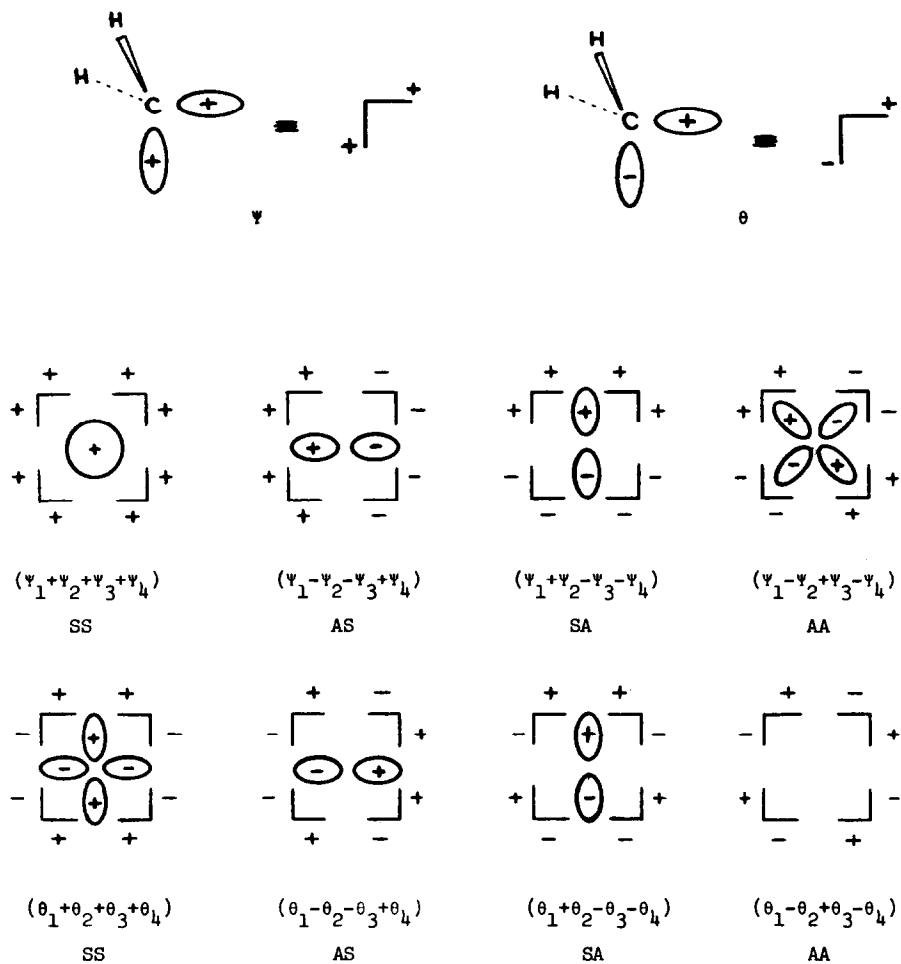


Fig. 1. The molecular orbitals of the tetramethylene ligand and the metal orbitals with which they combine in the complex II. The system is viewed down the z axis with the metal atom lying below the plane of the four carbon atoms.

TABLE I

Conversion of the molecular orbitals of complex I to complex II according to their symmetry properties.

Symmetry	Olefin-Metal Complex		Tetramethylene-Metal Complex
SS	$(\pi_1 + \pi_2) \xrightarrow{4} s$ $(\sigma_1 + \sigma_2) \xrightarrow{4} d_{x^2-y^2}$	\rightarrow	$(\psi_1 + \psi_2 + \psi_3 + \psi_4) \xrightarrow{4} s$ $(\theta_1 + \theta_2 + \theta_3 + \theta_4) \xrightarrow{4} d_{x^2-y^2}$
AS	$(\pi_1 - \pi_2) \xrightarrow{4} d_{xz}$ $(\sigma_1 - \sigma_2) \xrightarrow{4} p_x$	\rightarrow	$(\psi_1 - \psi_2 - \psi_3 + \psi_4) \xrightarrow{4} d_{xz}$ $(\theta_1 - \theta_2 - \theta_3 + \theta_4) \xrightarrow{4} p_x$
SA	$(\pi_1^* + \pi_2^*) \xleftarrow{4} d_{yz}$ $(\sigma_1^* + \sigma_2^*) \xleftarrow{4} p_y$	\rightarrow	$(\psi_1 + \psi_2 - \psi_3 - \psi_4) \xleftarrow{4} d_{yz}$ $(\theta_1 + \theta_2 - \theta_3 - \theta_4) \xleftarrow{4} p_y$
AA	$(\pi_1^* - \pi_2^*) \xleftarrow{2} d_{xy}$ $(\sigma_1^* - \sigma_2^*) \xleftarrow{2} d_{xy}$	\rightarrow	$(\psi_1 - \psi_2 + \psi_3 - \psi_4) \xleftarrow{2} d_{xy}$ $(\theta_1 - \theta_2 + \theta_3 - \theta_4) \xleftarrow{2} d_{xy}$

Of key importance is the fact that in the conversion to the complex (II) the AS and SA orbitals, initially involved as forward coordination and back donation bonds of the bis-olefin metal complex, now become completely equivalent; this is apparent from simple inspection of Fig. I. The remaining orbitals of the complex II are either symmetrical or antisymmetrical about both the xz and yz planes. Therefore reversion to the bis olefin complex is equally probable along the y or x directions leading to disproportionated olefins or starting olefins respectively.

In this argument we have neglected the interaction of other ligands which could remain on the metal during the reaction; however while these will of course affect the energetics of the process and make the molecular orbital description more complicated, it can be shown that it need not necessarily affect the basic argument presented here.

The distinct difference between the previously proposed orbital symmetry pathway¹⁰ and the scheme presented here is that in the former case the initial sigma bonds of the two ethylene molecules remain unaffected, and the pi bonds are transformed into the new sigma bonds affecting cyclization. In the scheme presented here, the carbon-carbon sigma bonds of the initial olefins are being ruptured concurrently with the pi bonds, so that a cyclobutane molecule is never realized.¹¹

Acknowledgements

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