Kinetics and Mechanism of the Homogeneous Olefin Disproportionation Reaction

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Abstract: Kinetic studies of the homogeneous disproportionation of 2-pentene to 2-butene and 3-hexene using a $L_2Mo(NO)_2Cl_2–R_xAlCl_{3-x}$ catalyst have shown the rate of disappearance of 2-pentene to be first order in catalyst and variable order in olefin. At low olefin:catalyst ratios the order is greater than one; at higher olefin:catalyst ratios the order is approximately one. These results are interpreted in terms of a mechanism involving stepwise, rapid reversible olefin complexation followed by a rate-determining disproportionation step. Activation energies of 6–7 kcal/mol were found for both 2-pentene and 4-nonene. A comparison of organoaluminum cocatalysts showed methylaluminum sesquichloride to give a more active catalyst than either ethylaluminum sesquichloride or ethylaluminum dichloride. A reaction intermediate involving a *cis*-diolefin–molybdenum complex is suggested. A description of the reaction pathway in terms of orbital transformations provides a rationale for the role of the metal in the catalysis.

The homogeneous disproportionation of olefins using catalysts based on tungsten hexachloride[1] and molybdenum and tungsten nitrosyl complexes[2] has been achieved. Details and mechanistic considerations of the WCl_6 catalyst system with internal olefins have appeared.[3] The scope of group VIB metal nitrosyl complexes which are suitable disproportionation catalysts and olefins which will react with these systems have been discussed.[4] The stereochemistry of the disproportionation of 2-pentene has been investigated using both WCl_6[3,5] and $(C_5H_5N)_2Mo(NO)_2Cl_2$ catalyst systems.[6]

During the last several years a great deal of interest in homogeneous catalysis has become evident. Because of the uniqueness of both the disproportionation reaction and our soluble catalyst system, the reaction was studied in detail. This paper reports the results of kinetic studies of the disproportionation reaction utilizing molybdenum nitrosyl catalysts and 2-pentene as a model olefin. A general mechanism for the reaction, based on these findings, is proposed.

Results

Treatment of the molybdenum nitrosyl complexes, $L_2Mo(NO)_2Cl_2$ ($L = C_5H_5N$, $(C_6H_5)_3P$, $(C_6H_5)_3PO$, etc.) with organoaluminum halides in chlorobenzene gives brown, homogeneous solutions which convert 2-pentene to 2-butene and 3-hexene. The reaction is reversible and attains a true thermodynamic equilibrium. This is shown by the fact that the same final distribution of olefins is obtained starting with either 2-pentene or an equimolar mixture of 2-butene and 3-hexene (Table I). The calculated equilibrium concentrations of the various olefins based on free energy data agree well with the experimental values. Table I shows the distribution of C_4, C_5, and C_6 olefins at 25°. As with the WCl_6 system,[3] thermodynamic equilibration of *cis* and *trans* isomers was observed with the present catalyst.[6]

Table I. Equilibrium Distribution of 2-Butene, 2-Pentene, and 3-Hexene

	Products, mol %						
Reactant(s)	2-Butene	2-Pentene	3-Hexene	Time, hr	Calcd mol %[a] C_4	C_5	C_6
C_5	23	50	27	6			
	24	50	26	24			
	24	50	26	30	27	46	27
$C_4 + C_6$	30	38	32	6			
	24	48	26	24			
	24	48	26	30			

[a] $\Delta F_f°$ data from F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, pp 475–476.

The catalyst requires a preformation period to reach maximum activity toward disproportionation. In curve A of Figure 1 the catalyst was allowed to form for 1 hr at room temperature before olefin addition; for curve B the catalyst preformation period was 0.5 hr at 0°. The two reactions were identical in all other respects. The S shape of curve B can be attributed to incompleteness of the catalyst formation reaction until *ca.* 1 hr reaction. This and other experiments indicate that the formation of catalyst in concentrations of $\sim 5 \times 10^{-3}$ *M* (based on Mo) requires 1–1.5 hr at room temperature. During this period of time the color of the catalyst solution changes from green to brown. Accompanying the color change is the disappearance of the two strong nitrosyl stretching bands at 1799 and 1689 cm^{-1} in the infrared spectrum in the case of $(C_5H_5N)_2Mo(NO)_2Cl_2$.[7]

Order in Catalyst. Numerous kinetic measurements on systems of the type $L_2Mo(NO)_2Cl_2–R_xAlCl_{3-x}$–2-pentene have served to emphasize the sensitivity of these catalysts to poisons. For this reason we have not attempted to evaluate actual rate constants but rather to compare parallel runs.

The effect of catalyst concentration on rate was investigated by preparing a solution of catalyst (from

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(1) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, **34**, 3327 (1967).

(2) E. A. Zuech, *Chem. Commun.*, 1182 (1968).

(3) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Am. Chem. Soc.*, **90**, 4133 (1968).

(4) E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *ibid.*, **92**, 528 (1970).

(5) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

(6) W. B. Hughes, *Chem. Commun.*, 431 (1969).

(7) W. B. Hughes, unpublished results.

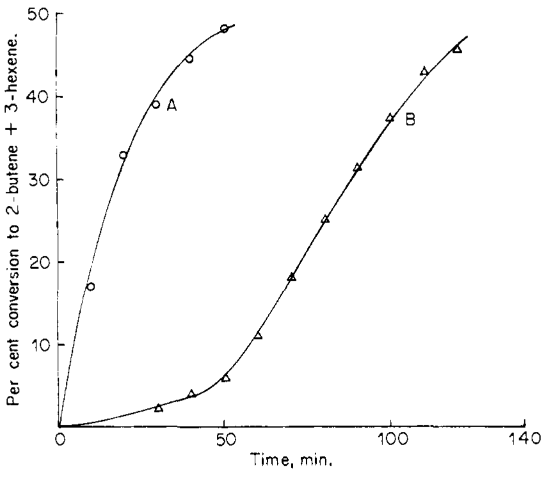

Figure 1.

$C_2H_5AlCl_2$ and $(C_5H_5N)_2Mo(NO)_2Cl_2$ in a 10:1 mol ratio) and reacting aliquots of 1 and 2 parts with equal quantities of 2-pentene after dilution to equal volume. Plots of per cent conversion to 2-butene and 3-hexene *vs.* time for three pairs of reactions are shown in Figure 2. The rates $-(\Delta C_5/\Delta t)$ were calculated from these plots over the interval 10–15% conversion. The relative catalyst concentrations and rates are gathered in Table II.

Table II. Variation in Rate with Catalyst Concentration

Reaction[a] no.	Relative catalyst concn[b]	$-(\Delta C_5/\Delta t) \times 10^{-2}$, mol l.$^{-1}$ min^{-1}
I-A	1	0.73
I-B	2	1.30
II-A	2	1.07
II-B	4	2.50
III-A	4	2.50
III-B	3	1.76

[a] All reactions were carried out at 0° in chlorobenzene with initial 2-pentene concentration of 0.58 mol l.$^{-1}$. [b] A catalyst concentration of 1 represents 2.08×10^{-3} mol l.$^{-1}$ of $(C_5H_5N)_2Mo(NO)_2Cl_2$.

Making use of eq 1[8] and the data of Table II we obtain n values of 0.84, 1.22, and 1.21 for reactions I, II

$$n = \frac{\log\left[-\left(\frac{\Delta C_5}{\Delta t}\right)_1\right] - \log\left[-\left(\frac{\Delta C_5}{\Delta t}\right)_2\right]}{\log\,[\text{catalyst}]_1 - \log\,[\text{catalyst}]_2} \tag{1}$$

and III, respectively, with an average value of 1.09. These results indicate that disproportionation is first order with respect to catalyst (we define the rate of disproportionation, R_{dp}, as $R_{dp} = -(\Delta C_5/\Delta t)$).

Order in Olefin. Similar experiments to the above were carried out to establish the order of the reaction with respect to olefin. Equal aliquots of catalyst solution were treated with various concentrations of 2-pentene. Table III summarizes the results obtained calculating the rates of disproportionation, $-(\Delta C_5/\Delta t)$, in the same manner as in Table II.

Using eq 1 with initial 2-pentene concentrations in place of catalyst concentrations and the data of Table III the n values given in the last column of the table were calculated. These results suggest that the order in olefin may vary with the olefin:catalyst ratio (*vide infra*).

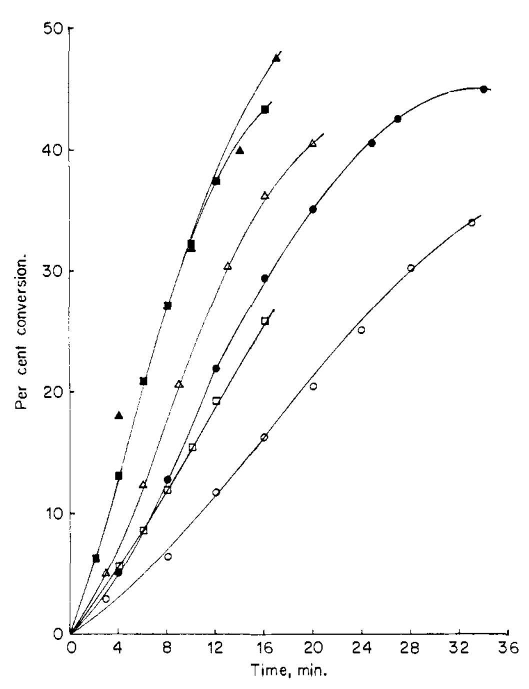

Figure 2. ○, I-A; ●, I-B; □, II-A; ■, II-B; ▲, III-A; △, III-B.

Table III. Variation in Rate with Olefin Concentration

Reaction no.[a]	[2-Pentene], mol l.$^{-1}$	[2-Pentene]/ $[(C_5H_5N)_2Mo(NO)_2Cl_2]$	$-(\Delta C_5/\Delta t) \times 10^{-2}$, mol l.$^{-1}$ min^{-1}	n
IV-A[b,e]	2.06	307	5.7	0.7
IV-B[b,e]	1.03	154	3.4	
V-A[b,e]	0.26	39	0.8	1.7
V-B[b,e]	0.52	78	2.6	
VI-A[c,f]	1.28	178	3.4	1.4
VI-B[c,f]	2.56	356	9.1	1.0
VI-C[c,f]	5.12	712	18.3	
VI-D[c,f]	2.56	356	9.1	
VII-A[d,g]	0.98	100	1.6	1.0
VII-B[d,g]	1.96	200	3.1	

[a] All reactions conducted at 0° in chlorobenzene. [b] Catalyst prepared from $(CH_3)_3Al_2Cl_3$ in a 3.8:1 mole ratio. [c] Catalyst prepared from $[C_2H_5AlCl_2]_2$ in a 3.8:1 mole ratio. [d] Catalyst prepared from $[C_2H_5AlCl_2]_2$ in a 7.7:1 mole ratio. [e] $[(C_5H_5N)_2Mo(NO)_2Cl_2] = 6.7 \times 10^{-3}$ mol l.$^{-1}$. [f] $[(C_5H_5N)_2Mo(NO)_2Cl_2] = 7.2 \times 10^{-3}$ mol l.$^{-1}$. [g] $[(C_5H_5N)_2Mo(NO)_2Cl_2] = 9.4 \times 10^{-3}$ mol l.$^{-1}$.

Comparison of Different Organoaluminum Compounds. The rates of 2-pentene disproportionation were measured using catalysts generated from different organoaluminum cocatalysts. The rates, $-(\Delta C_5/\Delta t)$, were calculated as above from plots of per cent conversion *vs.* time. The data are collected in Table IV.

At the same concentration methylaluminum sesquichloride gives a catalyst which is *ca.* three times more active than the analogous ethyl compound. The data also show that at a dimer concentration of 1.34×10^{-2} mol l.$^{-1}$ ethylaluminum sesquichloride gives essentially the same rate as does ethylaluminum dichloride at an equal concentration of monomer.

Effect of Organoaluminum Concentration. To determine the optimum Al:Mo ratio and thus obtain infor-

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[8] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, p 45.

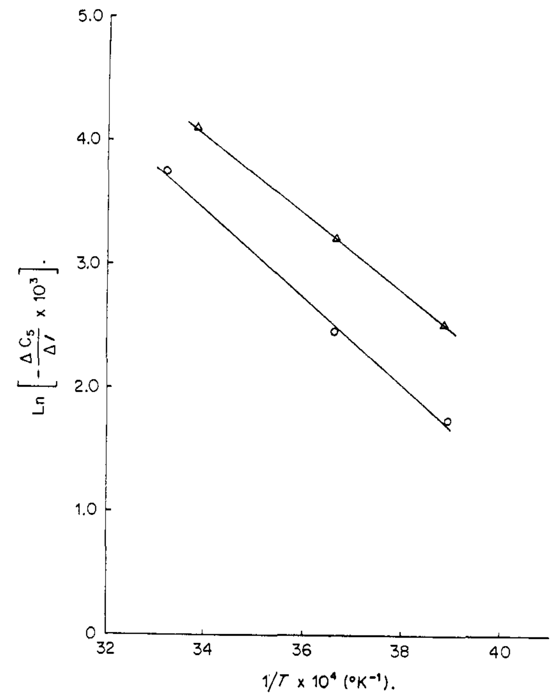

Figure 3. △, 2-pentene; ○, 4-nonene.

mation concerning the stoichiometry of the catalyst-formation reaction, a series of runs was made with increasing aluminum concentration and a fixed concentration of molybdenum. The results using a $C_2H_5AlCl_2$–$(C_5H_5N)_2Mo(NO)_2Cl_2$ catalyst are shown in Table V.

Table IV. Comparison of Different Organoaluminum Compounds

Reaction[a–c] no.	Organoaluminum reagent	$-(\Delta C_5/\Delta t) \times 10^{-2}$, mol l.$^{-1}$ min^{-1}
VIII	$(CH_3)_3Al_2Cl_3$[d]	2.80
IX[f]	$(CH_3)_3Al_2Cl_3$[d]	2.80
X	$(C_2H_5)_3Al_2Cl_3$[d]	0.84
XI[f]	$(C_2H_5)_3Al_2Cl_3$[d]	0.84
XII[f]	$(C_2H_5)_3Al_2Cl_3$[d]	0.93
XIII	$C_2H_5AlCl_2$[e]	0.70
XIV[f]	$C_2H_5AlCl_2$[e]	0.84

[a] All reactions conducted at 0° with initial 2-pentene concentration of 0.84 mol l.$^{-1}$. [b] Catalyst preformation periods were 2 hr except in XIII when it was 1.5 hr. [c] All reactions contained 0.1 g (0.25 mmol) of $(C_5H_5N)_2Mo(NO)_2Cl_2$. [d] Concentration was 1.34×10^{-2} mol l.$^{-1}$. [e] Concentration was 1.34×10^{-2} mol l.$^{-1}$. [f] Duplicate runs.

Table V. Effect of Organoaluminum Concentration

Reaction no.	Relative concentration	$[C_2H_5AlCl_2]/[(C_5H_5N)_2Mo(NO)_2Cl_2]$[a]	$-(\Delta C_5/\Delta t) \times 10^{-2}$, mol l.$^{-1}$ min^{-1}	
XV-A	1	3	0.28	
XV-B	1.3	4	0.53	0.62
XV-C	1.3	4	0.70	
XV-D	1.7	5	1.05	
XV-E	2.0	6	1.04	

[a] $[(C_5H_5N)_2Mo(NO)_2Cl_2] = 0.45 \times 10^{-2}$ mol l.$^{-1}$.

The rate increases systematically up to a 5:1 Al:Mo ratio suggesting at that level all the molybdenum complex has been converted to catalyst.

Activation Parameters. Activation parameters for the disproportionation of 2-pentene and 4-nonene were measured. The catalyst system was $(CH_3)_3Al_2Cl_3$–$(C_5H_5N)_2Mo(NO)_2Cl_2$ and $-(\Delta C_5/\Delta t)$ values were calculated over the interval of 10–15% conversion. The results are shown in Table VI and plotted in Figure 3.

Table VI. Effect of Temperature on Rate

Reaction no.	Olefin	Temp, °C	$-(\Delta C_5/\Delta t) \times 10^{-2}$, mol l.$^{-1}$ min^{-1}
XVI-A	2-Pentene	−15	1.23
XVI-B	2-Pentene	0	2.47
XVI-C	2-Pentene	23	6.00
XVII-A	4-Nonene	−16	0.57
XVII-B	4-Nonene	0	1.17
XVII-C	4-Nonene	28	4.25

The Arrhenius activation energies are 6.6 and 7.0 kcal/mol for 2-pentene and 4-nonene, respectively. The activation energy for the recently described rhodium-catalyzed conversion of quadricyclene to norbornadiene has been estimated to be 21 ± 5 kcal/mol.[9]

The enthalpies of activation were determined from plots of $\ln[-(\Delta C_5/\Delta t)/T]$ *vs.* $1/T$ and the rate constant, k, was obtained from the relation

$$k = \frac{-(\Delta C_5/\Delta t)}{[\text{catalyst}]_0{}^n[\text{olefin}]_0{}^m} \qquad (2)$$

where values for $-(\Delta C_5/\Delta t)$ are taken from Table VI (at 0°) and $[\text{catalyst}]_0$ and $[\text{olefin}]_0$ are the initial concentrations. At the olefin:Mo ratios used it is assumed that $n = m = 1$ and that $[\text{catalyst}]_0$ is equal to $[\text{Mo}]_0$. On this basis, the entropies of activation of both 2-pentene and 4-nonene were estimated to be −42 eu.

Stereochemistry. An examination of the disproportionation of *cis*- and *trans*-2-pentene in the early stages of reaction reveals that the reaction exhibits a high degree of stereoselectivity, *i.e.*, *cis*-2-pentene gives *cis*-2-butene and *cis*-3-hexene. Such selectivity has also been observed with other olefins.[4] A detailed discussion of the stereochemistry of disproportionation has appeared elsewhere.[6]

Discussion

Interpretation of Kinetic Results. We believe that the following type of mechanism best fits the present experimental results.

$$\text{cat} + \text{RHC{=}CHR}' \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{cat(RHC{=}CHR}') \qquad (3)$$

$$\text{cat(RHC{=}CHR}') + \text{RCH{=}CHR}' \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \text{cat(RHC{=}CHR}')_2 \qquad (4)$$

$$\text{cat(RHC{=}CHR}')_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \text{cat(RHC{=}CHR)(R}'\text{HC{=}CHR}') \qquad (5)$$

$$\text{cat(RCH{=}CHR)(R}'\text{HC{=}CHR}') \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \text{cat(RCH{=}CHR)} + \text{R}'\text{CH{=}CHR}' \qquad (6)$$

$$\text{cat(RCH{=}CHR)} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \text{cat} + \text{RCH{=}CHR} \qquad (7)$$

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

The following features of this mechanism should be pointed out. Olefin complexation occurs stepwise, (3) and (4), with $k_1 \neq k_2$ in general. Step 5 is the actual disproportionation reaction and is rate controlling. Steps 6 and 7 represent decomplexation of the product olefins. Similar equilibria were suggested in the tungsten system.[3] The complexation and decomplexation steps would be analogous to absorption and desorption on a heterogeneous catalyst surface. All reaction steps are reversible and, to a first approximation, all olefins are complexed and decomplexed with equal facility.

For a kinetic analysis of this mechanism only the first three steps will be considered and, since we will be dealing experimentally with the early stages of reaction, the reverse of step 5 will be neglected. To simplify the notation, the catalyst is represented by C, reactant olefin by S, and product olefins by P and P′. The mechanism may now be rewritten in abbreviated form as follows.

$$\mathrm{C} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{CS} \tag{8}$$

$$\mathrm{CS} + \mathrm{S} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{CS_2} \tag{9}$$

$$\mathrm{CS_2} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{CPP'} \tag{10}$$

We believe that complexation and decomplexation of olefin occur at rates significantly greater than the rate of disproportionation. Thus, the concentrations of the complexes CS and CS_2 can be obtained from the equilibrium expressions for steps 8 and 9.

$$[\mathrm{CS}] = \frac{k_1}{k_{-1}}[\mathrm{C}][\mathrm{S}] = K_1[\mathrm{C}][\mathrm{S}] \tag{11}$$

$$[\mathrm{CS_2}] = \frac{k_2}{k_{-2}}[\mathrm{CS}][\mathrm{S}] = K_1K_2[\mathrm{C}][\mathrm{S}]^2 \tag{12}$$

The rate of disproportionation, which is equal to $k_3[\mathrm{CS_2}]$, becomes

$$R_{\mathrm{dp}} = k_3K_1K_2[\mathrm{C}][\mathrm{S}]^2 \tag{13}$$

For comparison with the experimental data, it is necessary to have an expression for the rate, R_{dp}, in terms of initial catalyst, $[\mathrm{C}]_0$, and initial olefin, $[\mathrm{S}]_0$, concentrations. At time t, $[\mathrm{C}] = [\mathrm{C}]_0 - [\mathrm{CS}] - [\mathrm{CS_2}]$ and $[\mathrm{S}] = [\mathrm{S}]_0 - [\mathrm{CS}] - 2[\mathrm{CS_2}]$. Since the amount of catalyst is much smaller than olefin, $[\mathrm{S}] \approx [\mathrm{S}]_0$. Substituting these values into expressions 11 and 12 leads to the following expressions for the mono- and diolefin complex concentrations.

$$[\mathrm{CS}] = \frac{K_1[\mathrm{S}]_0\{[\mathrm{C}]_0 - [\mathrm{CS_2}]\}}{1 + K_1[\mathrm{S}]_0} \tag{14}$$

$$[\mathrm{CS_2}] = \frac{K_1K_2[\mathrm{C}]_0[\mathrm{S}]_0^2}{1 + K_1[\mathrm{S}]_0 + K_1K_2[\mathrm{S}]_0^2} \tag{15}$$

The initial rate of disproportionation, R_{dpo}, then becomes

$$R_{\mathrm{dpo}} = \frac{k_3K_1K_2[\mathrm{C}]_0[\mathrm{S}]_0^2}{1 + K_1[\mathrm{S}]_0 + K_1K_2[\mathrm{S}]_0^2} \tag{16}$$

It is assumed, in applying eq 16 to the experimental results, that the measured rates, $-(\Delta C_5/\Delta t)$, are close approximations to R_{dpo}. The rate expression predicts that R_{dpo} will be first order in catalyst at constant olefin concentration. The order with respect to olefin, at constant catalyst concentration, will be variable. At very high olefin concentration R_{dpo} will approach a zero-order dependence on olefin. At very low olefin concentration R_{dpo} will approach a second-order dependence. At intermediate concentrations the order will be influenced by the relative values of K_1 and K_2. If $K_1 > K_2$ then even at high olefin concentration the order could tend to level out at one. We believe that the data of Table III are in qualitative agreement with eq 16. In runs using the same organoaluminum cocatalyst and the same ratio of cocatalyst to Mo an increase in order at lower olefin:Mo ratios is observed. The results also show that in the range of *ca.* 100–700:1 olefin:Mo ratios the rate exhibits essentially a first-order dependence on olefin. We feel this indicates $K_1 > K_2$ which implies that formation of monoolefin complex is more facile than is formation of diolefin complex. The kinetic behavior is very much like that observed in enzymatic systems.[10]

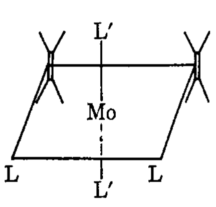

Figure 4.

The Reaction Intermediate. An important objective of research in homogeneous catalysis is the establishmet of a correlation between the geometrical structure and electronic states of a metal complex and the type of olefin reaction, if any, which the complex might catalyze. In this connection, two basic functions of the metal complex have been recognized for some time. First, the metal complex, through coordination, functions as a geometrical template which assures the proper orientation of the reactant molecules. Second, the bonding interactions of the metal system with the reactant olefin(s) result in a redistribution of electron density in the reactant(s). The present reaction is an excellent example of the role of the metal in homogeneous catalysis. The template effect in which three molecular species are brought together in a highly ordered manner is reflected in the high entropy of activation (*vide supra*). In the conversion of two 2-pentene molecules into 2-butene and 3-hexene, ΔF is close to zero; however, the reaction does not occur in the absence of a catalyst because of a high activation energy. In the presence of a catalyst E_a is relatively small. It is our purpose now to examine the course of the reaction in detail.

We suggest that the catalyst is a zerovalent molybdenum species and that the disproportionation of two olefins occurs *via* a molybdenum–diolefin[11] complex of the structure shown in Figure 4. A *cis*-diolefin complex intermediate has been proposed for the tungsten-catalyzed reaction.[3] At present, the identities of the ligands L and L′ are not known. The two reactant ole-

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(10) P. G. Ashmore, "Catalysis and Inhibition of Chemical Reactions," Butterworth and Co., Ltd., London, 1963, Chapter 4.

(11) The assumption of one molybdenum atom per catalyst molecule is made.

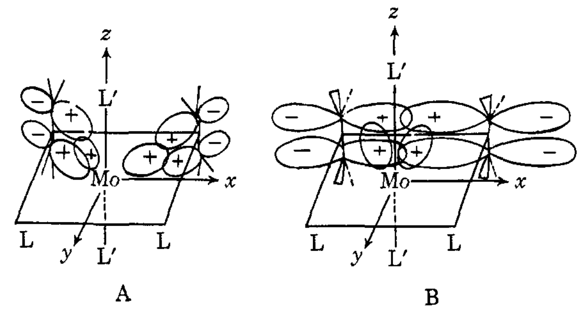

Figure 5.

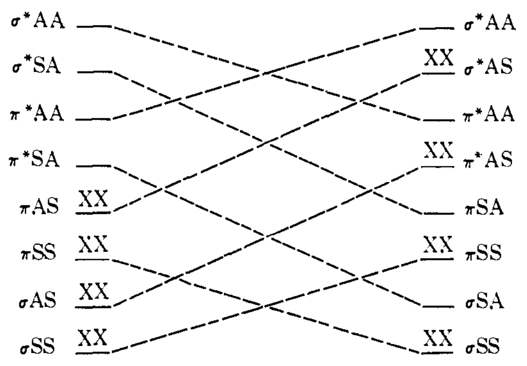

Figure 6. The first letter refers to the yz, the second to the xy plane of Figure 5.

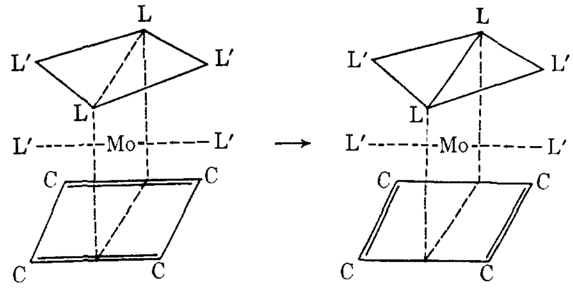

Figure 7.

fins occupy *cis* positions within the octahedron. The metal thus acts as a reaction template and in this manner overcomes the high entropy requirements of the reaction. The role of the organoaluminum component in catalyst formation and the significance of the 5:1 Al:Mo ratio are not clear; however, the function of the organoaluminum is most probably removal of the halide ligands, thereby creating vacant coordination sites.

The metal-olefin bonding is as usually depicted[12] with the olefinic bonds perpendicular to the plane of the molybdenum and the ligands L. The σ component of the Mo–olefin bond is formed by overlap of metal σ-type acceptor orbitals with olefin π^b orbitals (Figure 5A).

Orbital Transformations in Disproportionation. Disproportionation occurs by a disrotation of the two complexed olefins which results in positive overlap of the π^b orbitals which eventually become the product olefin σ bonds (Figure 5B). At the same time the σ bonds of the reactant olefins are broken and rehybridization to $p\pi$ orbitals occurs which forms the product π bonds.

A more formal and systematic description of this process may be obtained by making use of the concepts of molecular orbital symmetry conservation successfully applied by Hoffmann and Woodward to various types of electrocyclic reactions.[13] The orbital transformations which take place in disproportionation are shown in the correlation diagram of Figure 6. The σ and π orbital combinations are the same as those used previously in describing the cyclodimerization of two olefins.[13] The symmetry classifications of the combinations designate whether they are symmetric (S) or antisymmetric (A) with respect to the yz and xy planes of Figure 5. The correlation diagram makes clear the unfavorable nature of the uncatalyzed disproportionation reaction since electrons are introduced into antibonding orbitals.

Using the concepts of molecular orbital symmetry conservation, an interpretation of the role of the metal in the catalyzed olefin cyclodimerization reaction has been offered.[14] A similar rationale would apply in the present case. The important point is that the function of the metal is to provide, through complex formation, low energy molecular orbitals of the proper symmetry. Through use of d orbitals the metal can place electron density (so-called back donation) into incipient product bonding orbitals and withdraw into metal-based orbitals electron density from incipient product antibonding orbitals.

The above Mo–diolefin octahedral complex model, along with considerations of steric interactions between the two olefins in various orientations, correctly predicts the observed stereoselectivity of the reaction.[6] This gives credence to the reality of such an intermediate.

As a final note, we would like to suggest an alternate configuration for the Mo–diolefin intermediate, it being an Archimedian antiprism (Figure 7).[15] This structure can be easily obtained from the octahedral complex (dotted lines of Figure 7) by bending the ligands L′ into coplanarity with the ligands L (Figure 7). In fact, the intermediate complex may lie somewhere in between the two idealized geometries. This model results in a somewhat more symmetrical relationship of reactant and product olefins to the remaining ligands and to the molybdenum. In connection with this model, it is noteworthy that among the few metals which form eight-coordinated complexes are molybdenum, tungsten, and rhenium. Some of the more active disproportionation catalysts contain compounds of these metals. It is also tempting to suggest that with a given metal catalyst whether disproportionation or cyclodimerization of two olefins occurs depends upon the ability of the metal to form eight-coordinate structures. In intermediates of high coordination numbers the product olefins can be as easily bonded as the reactant olefins—this provides a driving force for disproportionation. Where bonding of product olefins is restricted because of geometry or available orbitals the incipient cyclobutane is lost from the coordination sphere of the metal. Most of the metals (Fe, Ni, Co)

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(12) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(13) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965).

(14) F. D. Mango and J. H. Schachtschneider, *ibid.*, 89, 2484 (1967).

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which catalyze cyclodimerization[16] are of the first transition series and hence favor lower coordination numbers.

Experimental Section

All experiments were carried out under an atmosphere of prepurified nitrogen in previously dried equipment. Reactions were conducted in either a conventional three-necked flask or 7-oz clear-glass beverage bottles sealed with perforated metal caps with a neoprene rubber liner.

Gas–liquid partition chromatography (glpc) analyses were performed on an F & M Model 720 or a Hewlett-Packard Model 5750 chromatograph, using a 10 ft × 0.25 in. copper tube column packed with 20% DC 200 silicone fluid on 35–80 mesh Chromosorb P. The chromatographs were run isothermally at *ca.* 100° with helium carrier gas flow rate of 100–200 ml/min. Areas were determined using a disk integrator.

The molybdenum complex, $(C_5H_5N)_2Mo(NO)_2Cl_2$, was prepared by the procedure of Cotton and Johnson.[17] The aluminum alkyls were purchased from Texas Alkyls and used without further purification. In catalyst preparation the aluminum alkyls were used as 1 *M* solutions in chlorobenzene. The chlorobenzene was Fisher or Mallinckrodt distilled from calcium hydride and stored over molecular sieves under nitrogen. The 2-pentene was Phillips pure grade and was purified by passage through a column of activated silica and magnesium oxide. The 4-nonene (n^{20}_{D} 1.4162) was from Aldrich Chemical Co. and used as received.

The following general procedure was used in all kinetic experiments. The molybdenum complex and chlorobenzene were placed in the reaction vessel. The solution of aluminum alkyl in chlorobenzene was injected into the mixture. The catalyst-formation reaction was generally allowed to proceed for 1–1.5 hr at room temperature with magnetic stirring. The reaction vessel then was placed in an insulated ice bath. After *ca.* 15 min the olefin was injected into the catalyst solution. Samples of the reaction mixture were taken *via* a 1-cc hypodermic syringe through a rubber septum on the side arm of the flask or through the rubber stopper of the bottle. The samples were immediately injected into a capped Diels–Alder tube containing water to terminate the reaction. In the experiments dealing with determination of the activation energies, the temperature was maintained to within ±0.5°.

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Mechanism of Copper(II) Oxidation of Reducing Sugars. I. Kinetics and Mechanism of Oxidation of D-Xylose, L-Arabinose, D-Glucose, D-Fructose, D-Mannose, D-Galactose, L-Sorbose, Lactose, Maltose, Cellobiose, and Melibiose by Copper(II) in Alkaline Medium

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Abstract: Kinetic studies of Cu^{II} oxidation of two pentoses, five hexoses, and four disaccharides have been carried out in alkaline medium. The reaction showed a first-order dependence with reducing sugar and alkali concentration, and the oxidation process is independent of Cu^{II} concentration in the case of all the reducing sugars. A single rate expression, $-d[Cu^{II}]/dt = k[S][OH^-]$, and one scheme of mechanism have been proposed. It is found that the rate of oxidation is the rate of enolization in the case of all the reducing sugars.

Kinetics of Cu^{II} oxidation of reducing sugars was first studied by Urech[2a] to elucidate the structure of the milk of sugar, in which, of course, he succeeded but did not put forward any detailed mechanism of the oxidation process. Thereafter, Singh, Krishna, and Ghosh[2b] studied the kinetics of oxidation of some hexoses and pentoses by alkaline cupric tartrate and citrate. They found that the rate of reaction is first order with respect to the reducing sugar and independent of Cu^{II} concentration, irrespective of the amount of complexing agents, and explained that observed rates of oxidation of reducing sugars correspond to their rates of enolization. Later, Marshall and Waters,[3] in their kinetic study of the oxidation of D-glucose, acetoin, and benzoin by alkaline Cu^{II} complexed with tartrate, citrate, and picolinate, etc., confirmed the result of Singh, *et al.*, and reported that the rates of enolization of acetoin and benzoin are greater than their rates of oxidation. They gave the rate expression as $-\,d[Cu^{II}]/dt = 2K_4[E]\cdot[Cu^{I}]$, and showed that cuprous chelate formation is the rate-determining step. Recently Wiberg and Nigh[4] have studied the oxidation of hydroxyacetophenone by Cu^{II} in buffered aqueous pyridine base in order to verify the ingenious explanation postulated by Marshall and Waters[3] and observed that the rate law is $v = K_1\cdot[\text{ketol}] + K_2[\text{ketol}][Cu^{II}]$. The first term of the right-hand side corresponds to the independently determined

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