the total birefringence has been resolved into components coming from crystalline and amorphous orientation.[32] It was found, for example, that about two-thirds of the birefringence of low-density polyethylene comes from the crystalline contribution. For static deformation, this fraction is not affected very much by thermal treatment.

The dynamic birefringence, measured on a vibrating sample as with the previous measurements, is much more revealing.[9,10,12,33] The birefringence response is conveniently expressed in terms of the strain-optical coefficient, K, the derivative of birefringence with respect to strain. Since the birefringence differs in phase from the applied strain, K is also a complex quantity with a real and imaginary part.

The variation of the real part of the strain-optical coefficient, K', with temperature at a frequency of 1 Hz is shown in Figures 9 and 10 for heat-treated and quenched low-density polyethylene. While the value of K'' for the heat-treated sample passes through a maximum at about 60°, a maximum for the quenched sample occurs below 20°.

The crystalline and amorphous contributions to K' may be obtained by differentiating the preceding equations for birefringence with respect to strain. The only terms which vary with strain are the orientation functions. This gives the orientational compliances which may be evaluated from the dynamic X-ray studies.

The values of K'_{cr} and K'_{am} calculated in this way

are included in Figures 9 and 10.[30] It is seen that the most of the birefringence of the heat-treated sample comes from the amorphous contribution. In fact, the crystalline contribution is negative at low temperatures. For the quenched sample, however, the crystalline and amorphous regions contribute about equally to K'.

Further Studies

These studies have been carried out for a particular polyethylene sample and are now being extended to the study of other samples of polyethylene as well as other polymers. Attempts are being made to directly measure amorphous orientational changes from the observation of infrared dichroism of bands arising from amorphous regions.[34,35] Also attempts are being made to observe crystalline orientational changes during relaxation at constant length.[36,37] It is hoped that the interpretation of such experiments will help with the understanding of the physical properties of these important materials.

(33) S. Onogi, D. A. Keedy, and R. S. Stein, *J. Polym. Sci., Part A-2*, **5**, 1079 (1961).

(34) Y. Fukui, T. Asuda, and S. Onoyi, *Polym. J.*, **3**, 100 (1972).
(35) Y. Uemura and R. S. Stein, *J. Polym. Sci.*, in press.
(36) T. Oda and R. S. Stein, *J. Polym. Sci., B*, **9**, 543 (1971); *J. Polym. Sci, A2*, in press.
(37) R. S. Stein, T. Oda, R. Finkelstein, and Y. Vemura, *Bull. Amer. Phys. Soc., Ser. II*, **17**, 361 (1972).

The Olefin Metathesis Reaction

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Olefin metathesis is a catalytically induced reaction wherein olefins undergo bond reorganization, resulting in a redistribution of alkylidene moieties (eq 1).[1]

All metathesis catalysts are derived from transition metal compounds. It is convenient to classify these catalysts into two main groups: (a) heterogeneous catalysts—transition metal oxides or carbonyls de-

posited on high-surface-area supports,[3] (b) homoge-

(1) "Olefin disproportionation" is the name first selected by the authors of ref 2 to describe the *overall* process of the [metathesis + isomerization] of acyclic olefins using heterogeneous metal oxide catalysts. At the outset of the discovery of homogeneous catalysts capable of inducing a "clean" metathesis reaction, it became evident that the term "olefin disproportionation" was inadequate to properly describe the nature and scope of the reaction, and was even misleading in certain cases. Since the basic process on hand is an alkylidene interchange, it was decided to adopt the name "olefin metathesis," as this name properly conveys the nature and scope of the reaction. In its specific applications (as shown throughout the present Account) it can be utilized to: (a) disproportionate olefins; (b) polymerize cycloolefins; (c) prepare catenanes and other macrocyclics; (d) synthesize dienes and trienes. Hence, olefin disproportionation is to be considered a special case of the more general olefin metathesis reaction.

(2) R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 170 (1964).

(3) For a detailed review see G. C. Bailey, *Catal. Rev.*, **3**, 37 (1969).

After completing his undergraduate education and earning the M.Sc. degree at the Hebrew University of Jerusalem, Israel, Nissim Calderon came to the United States and enrolled in the then newly created Ph.D. program in Polymer Science at the University of Akron. His research in Jerusalem and Akron involved synthesis of organometallics and their application as polymerization catalysts. After earning his Ph.D. in 1962, he joined the Synthetic Rubbers department of the Goodyear Tire & Rubber Comyany, where his main activity has been research in the area of transition metal–olefin chemistry. In 1967 he was appointed Section Head in the Basic Polymer Research Department in charge of new elastomers.
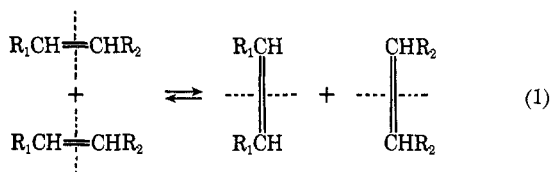
$$R_1CH\!=\!CHR_2 \quad R_1CH \quad CHR_2$$
$$+ \quad \rightleftharpoons \quad \| \quad + \quad \| \tag{1}$$
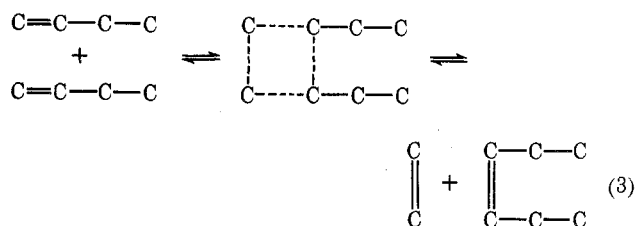$$R_1CH\!=\!CHR_2 \quad R_1CH \quad CHR_2$$

neous catalysts—transition metal salts or coordination compounds in combinations with selected organometallic derivatives or Lewis acids.[4,5]

The first to report processes involving olefin metathesis were Eleuterio, who described the ring-opening polymerization of cycloolefins[6] by a MoO_3–Al_2O_3 catalyst, and Banks and Bailey,[2] who employed various heterogeneous catalysts for the disproportionation of olefins at high temperatures. In 1963 and subsequently, Natta, et al.,[7-9] reported the use of homogeneous catalysts derived from $MoCl_5$ or WCl_6 and organoaluminum derivatives for the ring-opening polymerization of cycloolefins.

$$CH\!=\!CH \longrightarrow [-(CH_2)_nCH\!=\!CH-]_n \tag{2}$$
$$(CH_2)_n$$
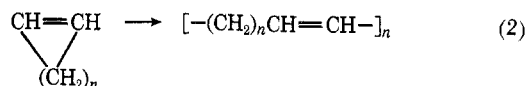
These early literature citations do not indicate that the respective workers recognized the fact that the basic chemistry involved in the cycloolefin polymerization by ring opening, and in the seemingly unrelated olefin disproportionation reaction, is actually the same.

In a U. S. patent application filed in 1966, Calderon and Chen[10] reported that W/Al homogeneous catalyst combinations are highly effective in promoting the olefin metathesis reaction. The products from metathesis of a mixture of 2-butene and 2-butene-d_8 showed that the redistribution process proceeds via an interchange of alkylidene moieties as depicted in eq 1. A detailed discussion of this aspect of the reaction was later presented in formal publications.[4,5] Shortly thereafter, Bradshaw and coworkers,[11] who studied the metathesis reaction over heterogeneous catalyst systems, concluded that their results supported a "quasicyclobutane" intermediate (eq 3). Critical experi-

$$C\!=\!C\!-\!C\!-\!C \quad C\text{----}C\!-\!C\!-\!C$$
$$+ \quad \rightleftharpoons \quad \rightleftharpoons$$
$$C\!=\!C\!-\!C\!-\!C \quad C\text{----}C\!-\!C\!-\!C$$

$$\quad\quad C \quad C\!-\!C\!-\!C$$
$$\quad\quad \| \quad + \quad \| \tag{3}$$
$$\quad\quad C \quad C\!-\!C\!-\!C$$

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

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

(6) H. S. Eleuterio, U. S. Patent 3,074,918 (1963).

(7) G. Natta, G. Dall'Asta, G. Mazzanti, and G. Mortoni, Makromol. Chem., 69, 163 (1963).

(8) G. Natta, G. Dall'Asta, and G. Mazzanti, Angew. Chem., 76, 765 (1964).

(9) G. Natta, G. Dall'Asta, I. W. Bassi, and G. Carella, Makromol. Chem., 91, 87 (1966).

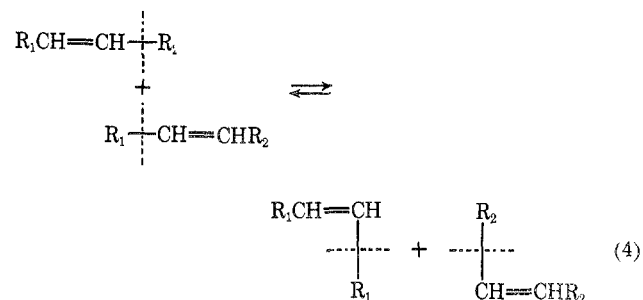(10) N. Calderon and H. Y. Chen, U. S. Patent 3,535,401 (1970).

(11) C. P. C. Bradshaw, E. J. Howman, and L. Turner, J. Catal., 7, 269 (1967).

ments to substantiate the quasi-cyclobutane structure were not offered.

The present Account is intended to describe: (a) the salient features of the metathesis reaction by homogeneous catalysts; (b) suggested mechanistic schemes; and (c) useful applications.

Salient Features

Redistribution by Transalkylidenation. Mass spectral studies[5] show that olefin metathesis does not proceed by transalkylation as depicted in eq 4. Rather

$$R_1CH\!=\!CH\!-\!R_4$$
$$+ \quad \rightleftharpoons$$
$$R_1\!-\!CH\!=\!CHR_2$$

$$R_1CH\!=\!CH \quad R_2$$
$$\text{----} \quad + \quad \text{----} \tag{4}$$
$$R_1 \quad CH\!=\!CHR_2$$

the data are consistent with transalkylidenation according to eq 1. A further confirmation of the transalkylidenation mechanism was provided by Mol, et al.,[12] who carried out metathesis experiments involving [2-^{14}C]propylene over supported metal oxide catalysts. Analysis of the metathesis products obtained from [1-^{14}C]propylene and [3-^{14}C]propylene excluded formation of any π-allyl intermediates during the redistribution process.[13]

Random Distribution of Alkylidene Groups. Olefin metathesis is a process wherein bond energy values do not differ substantially between the various equilibrating components in the system; hence, entropy considerations should dominate this essentially thermoneutral reaction[14] and thus afford a statistical distribution of products when carried to equilibrium. A series of metathesis experiments on various mixtures of 2-pentene and 6-dodecene, in which the relative concentrations of the [$CH_3CH\!=\!$], [$C_2H_5CH\!=\!$], and [$C_5H_{11}CH\!=\!$] were varied, demonstrated that the concentrations of the anticipated reaction components are in excellent agreement with those predicted for a random scrambling of constituents (see Figure 1).

Macrocyclization of Cycloolefins. Metathesis of cycloolefins should result in the formation of high molecular weight polymeric rings; in other words, the ring-opening polymerization of cycloolefins by tungsten-based catalysts can be considered a special case of the olefin metathesis reaction.[15] Earlier proposals that cycloolefin polymerizations, catalyzed by tungsten, proceed by cleavage of carbon–carbon single bonds α to the double bond[8] would not appear to be valid.

(12) J. C. Mol, J. A. Moulijn, and C. Boelhouwer, Chem. Commun., 633 (1968).

(13) A. Clark and C. Cook, J. Catal., 15, 420 (1969).

(14) G. Calingaert and H. A. Beatty, J. Amer. Chem. Soc., 61, 2748 (1939).

(15) K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; see also Advan. Chem. Ser., No. 91, 399 (1969).
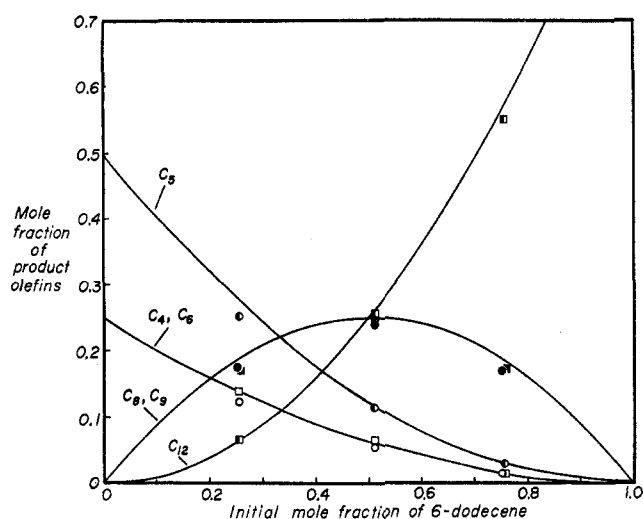
Figure 1. Metathesis of 2-pentene with 6-dodecene. solid lines represent theory for ideal random composition: (O) C_4, 2-butene; (●) C_5, 2-pentene; (□) C_6, 3-hexene; (●) C_8, 2-octene; (■) C_9, 3-nonene; (◫) C_{12}, 6-dodecene.

The following important implications, which bear directly on the nature of cycloolefin polymerization, follow from the features discussed in the preceding paragraphs. (a) Ring-opening polymerization should possess the basic features of equilibrium polymerization. (b) Macrocyclic species should be present in the polymerization mixture at equilibrium, according to eq 5. (c) In the absence of side reactions the applica-

$$\tag{5}$$
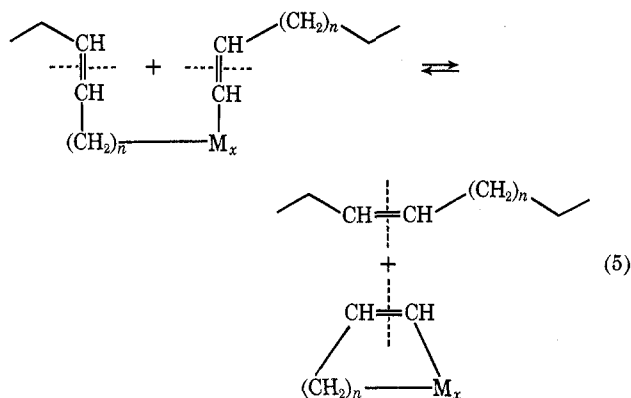
M_x represents x repeated units

tion of the olefin metathesis reaction to cycloolefins should yield only macrocyclic species. (d) Acyclic vinylenic compounds should lead to ring scission, resulting in open-chain polymer molecules. (e) Ring-chain equilibrium occurs when a, b, and d are operative.

Cis–Trans Equilibria. The intimate relationship between the olefin metathesis reaction and cis–trans interconversions is apparent from the early metathesis work involving both homogeneous and heterogeneous catalysts. Metathesis experiments on pure cis- and trans-2-pentene with the catalyst systems $C_2H_5AlCl_2$–WCl_6–C_2H_5OH and $C_2H_5AlCl_2$–$py_2Mo(NO)_2Cl_2$ demonstrated[5,16] that, at equilibrium, a thermodynamically favored cis/trans composition for the respective 2-butenes, 2-pentenes, and 3-hexenes is obtained.
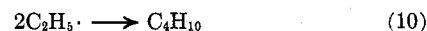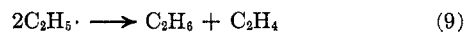
(16) W. B. Hughes, Chem. Commun., 431 (1969).

Mechanistic Schemes

A scheme proposed for the olefin metathesis reaction consists of three main processes.[5] The first is bis-olefin–metal complex formation as depicted in eq 6.

$$WCl_6 + C_2H_5OH + C_2H_5AlCl_2 + 2RCH\!=\!CHR' \longrightarrow$$

$$\tag{6}$$
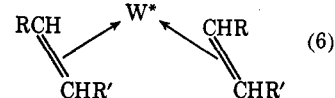
Experimentally, WCl_6 and C_2H_5OH are combined prior to addition of the $C_2H_5AlCl_2$. During this step, which presumably affords $WCl_5OC_2H_5$, a distinct color change from dark blue to red burgundy is observed. It is accompanied by the evolution of a stoichiometric amount of HCl.[17] The moderately stable $WCl_5OC_2H_5$ slowly decomposes into C_2H_5Cl[18] and an orange crystalline precipitate, presumably $WOCl_4$.

When the organoaluminum compound comes into contact with the tungsten component, an active catalyst is formed instantaneously. The activity of this catalyst prepared in the absence of olefin decays at a moderate rate.[19] By analogy to classical Ziegler–Natta catalysts,[20] one postulates the following sequence of reactions.

$$WCl_6 + C_2H_5AlCl_2 \longrightarrow C_2H_5WCl_5 + AlCl_3 \tag{7}$$

$$C_2H_5WCl_5 \longrightarrow WCl_5 + C_2H_5\cdot \tag{8}$$

$$2C_2H_5\cdot \longrightarrow C_2H_6 + C_2H_4 \tag{9}$$

$$2C_2H_5\cdot \longrightarrow C_4H_{10} \tag{10}$$

The formation of ethane and ethylene (in addition to ethyl chloride) during the reaction of $WCl_5OC_2H_5$ and $C_2H_5AlCl_2$ has been confirmed experimentally.[21] By a sequence similar to eq 7–10, WCl_5 may undergo further reduction to WCl_4. Moreover, pentavalent tungsten may undergo disproportionation, as depicted in eq 11. The presence of $AlCl_3$, formed during the re-

$$2WCl_5 \rightleftharpoons WCl_6 + WCl_4 \tag{11}$$
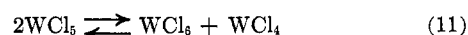
duction of W(VI), may give rise to associations via μ-chloride bonding (eq 12) and acid–base type equilibria (eq 13).

$$\tag{12}$$

$$WCl_x + AlCl_3 \rightleftharpoons WCl_{x-1}^+ + AlCl_4^- \tag{13}$$
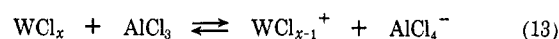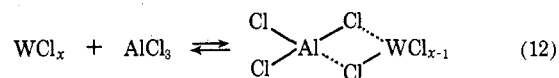
It is suspected that $AlCl_3$, whenever present, does play an active role in the metathesis catalyst. Indirect evidence points to this contention. (a) The activity of the binary C_4H_9Li–WCl_6 catalyst system[22] can be increased by at least 100-fold if an equimolar

(17) K. F. Castner, private communication.
(18) E. A. Ofstead, private communication.
(19) N. Calderon and D. D. Bates, unpublished results.
(20) See a review chapter by D. O. Jordan in "The Stereochemistry of Macromolecules," Vol. 1, A. D. Ketely, Ed., Marcel Dekker, New York, N. Y., 1967, Chapter 1, pp 1–45.
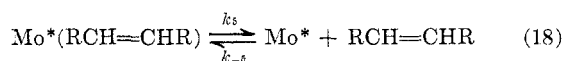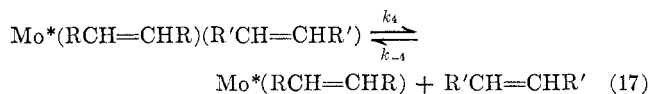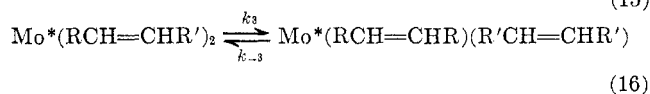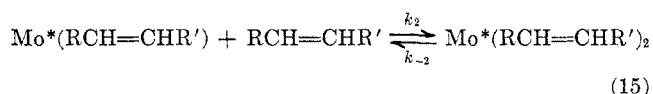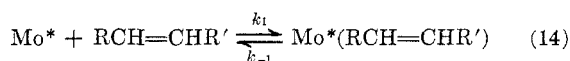(21) W. A. Judy, unpublished results.
(22) J. L. Wang and H. R. Menapace, J. Org. Chem., **33**, 3794 (1968).

amount of $AlCl_3$ is added to the reaction[21] (Li:W:Al molar ratio of 2:1:1). (b) WCl_4 obtained by reduction of WCl_6 with H_2 at high temperatures is an inactive metathesis catalyst; however, in combination with $AlCl_3$ (Al:W molar ratio of 2–4:1), a highly active catalyst, free of any organometallic component, is obtained.[21] (c) An active metathesis catalyst is also obtainable from $AlCl_3$–WCl_6 or $AlBr_3$–WCl_6 combinations[21,23] (Al:W molar ratio of 2–8:1). Apparently, the aluminum component does not function as a reducing agent.

The fragmentary results available suggest that the formation of active sites involves removal of chloride ligands from the coordination sphere of the tungsten, thus providing coordination sites for the incoming olefinic ligands. This can be accomplished by either a reduction sequence (eq 7–10), or by an acid–base equilibrium (eq 13), or both. In either case the aluminum component appears to play an important role. It may be further speculated that, by association via μ-chloride bonding (eq 12), the aluminum component retards the oligomerization tendencies of reduced tungsten chlorides.

The series of reactions encompassed by eq 6 would terminate with formation of the complex bearing two olefinic ligands in a cis configuration about the tungsten (W*). The complexation process is thought to be a stepwise process. Hughes,[24] who conducted a kinetic study of the metathesis of 2-pentene, interpreted his results in terms of five basic equilibria. The kinetic

$$Mo^* + RCH{=}CHR' \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Mo^*(RCH{=}CHR') \quad (14)$$

$$Mo^*(RCH{=}CHR') + RCH{=}CHR' \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Mo^*(RCH{=}CHR')_2 \quad (15)$$

$$Mo^*(RCH{=}CHR')_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Mo^*(RCH{=}CHR)(R'CH{=}CHR') \quad (16)$$

$$Mo^*(RCH{=}CHR)(R'CH{=}CHR') \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} Mo^*(RCH{=}CHR) + R'CH{=}CHR' \quad (17)$$

$$Mo^*(RCH{=}CHR) \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} Mo^* + RCH{=}CHR \quad (18)$$

results are in agreement with the suggestion that the formation of the monoolefinic complex (eq 14) is more facile than the formation of the bisolefin complex (eq 15).

The Transalkylidenation Step. The mode of bond scission which is observed in the metathesis reaction is suggestive of a concerted reaction pathway proceeding via a four-centered transition state. Equation 19 illustrates the transalkylidenation step using layman's symbols of dotted lines and arrows. The only real contention intended to be conveyed by eq 19 is that, during the concerted process, there is a transition state
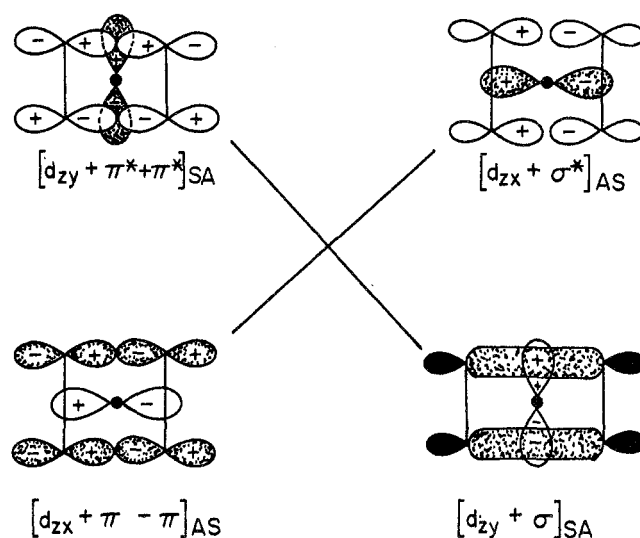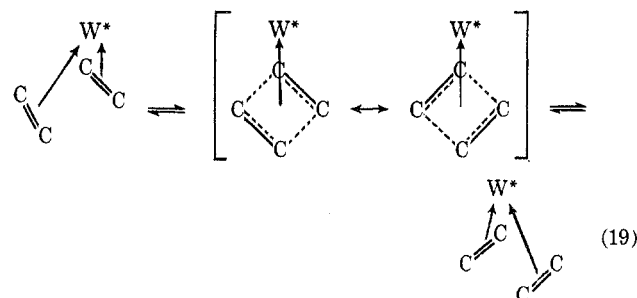
(23) P. R. Marshall and B. J. Ridgewell, *Eur. Polym. J.*, **5**, 29 (1969).
(24) W. B. Hughes, *J. Amer. Chem. Soc.*, **92**, 532 (1970).

Figure 2. The removal of symmetry restrictions through a relocalization of ligand–metal AS and SA electron density (F. Mango, *et al.*, *J. Amer. Chem. Soc.*, **93**, 1123 (1971)).

characterized by having all four carbons equally related to the metal.

If the process described in eq 19 is accepted as being a true concerted one, the formation of the quasi-cyclobutane transition state and its transformation into a bisolefin–metal complex should be viewed as cycloaddition reactions; hence, the principles of orbital symmetry conservation[25] of Woodward and Hoffmann must be considered here.

According to Mango[26,27] a transition metal complex, having atomic d orbitals of the proper symmetries and an available electron pair, can conceivably switch a symmetry-forbidden [$2_s + 2_s$] cycloaddition to a symmetry-allowed transformation; if so, a concerted reaction pathway does exist for the conversion of two olefinic ligands coordinated to a transition metal into a four-membered ring. Figure 2 illustrates Mango's "forbidden-to-allowed" transformation. A simultaneous injection of a pair of electrons from the d_{zy} metal orbital into the $\pi^* + \pi^*$ antibonding combination and withdrawal of a pair of electrons from the bonding π–π combination by the d_{zx} metal orbital can be executed with conservation of orbital symmetry. The net result is a filled SA σ and a vacant AS σ^* orbital.

(25) For a complete presentation see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, Germany, 1970.
(26) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967).
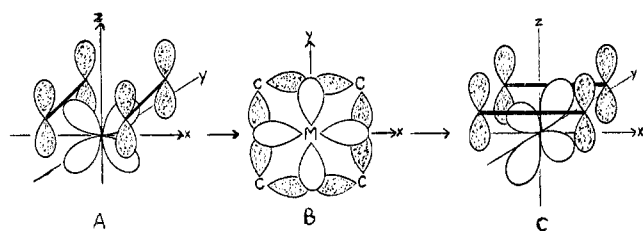(27) F. D. Mango, *Advan. Catal.*, **20**, 291 (1969).

Figure 3. Transalkylidenation *via* tetramethylene–metal transition state.

Should the quasi-cyclobutane transition state (eq 19) be considered a ground-state cyclobutane? Not necessarily. Lewandos and Pettit,[28] in a recent publication, suggested that the transalkylidenation process proceeds *via* a transition state 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." Figure 3 illustrates the transformation *via* the "tetramethylene–metal" transition state as suggested by Lewandos and Pettit.

Arguments concerning the conservation of orbital symmetry, involved with rendering an "allowed" status to the process depicted in Figure 3, are not presented here for the sake of brevity. The important feature of the proposed mechanism is that the transformation of the bisolefin complex into the tetramethylene–metal transition state is accomplished by forward donation of four electrons from filled ligand orbitals to empty metal orbitals and back donation of four electrons from filled metal orbitals to empty ligand orbitals. Consequently, the carbon–carbon σ bonds of the initial olefins are ruptured concurrently with the π bonds, so that no genuine cyclobutane molecule is ever realized along the reaction coordinate.

The Olefin Exchange Step. In order to account for the high rates of reaction which are observed at very low catalyst levels, a rapid olefin exchange (eq 20) that alternates with the transalkylidenation step (eq 19) was proposed.[5] This scheme is somewhat different from the
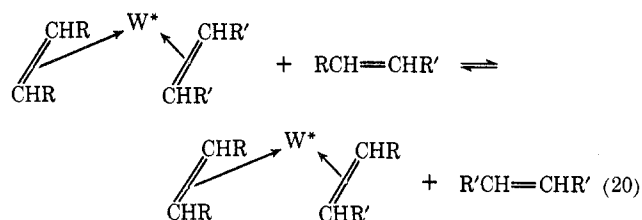

decomplexation equilibria suggested by Hughes[24] (eq 17 and 18), as it implies that ligand exchange occurs through a nucleophilic displacement; that is, the incoming ligand is accommodated within the coordination sphere of the metal prior to the disengagement of the leaving ligand.

A careful analysis of products obtained during the early stages of cycloolefin polymerizations suggests that the olefin exchange step is slower than the transalkylidenation step. The propagation process proposed for the cycloolefin polymerization comprises two steps[15] which represent the application of eq 19 and 20

(28) G. S. Lewandos and R. Pettit, *Tetrahedron Lett.*, 789 (1971).
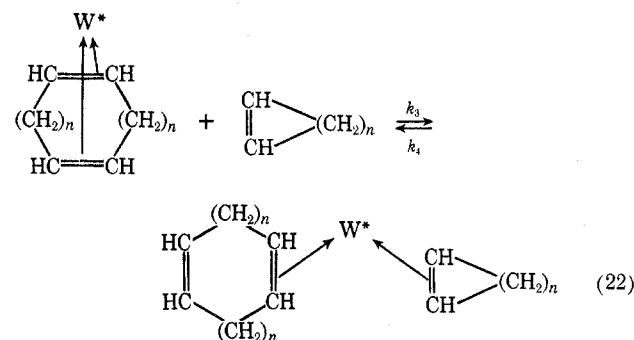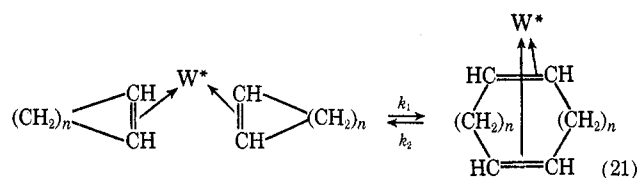
to cycloolefins (eq 21 and 22). Reiteration of these two steps would lead to the formation of macrocyclic polymers. One may also visualize a transfer process involving an olefin-exchange step (eq 23).
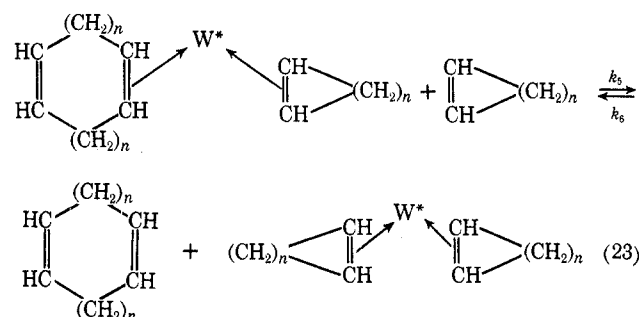
If the exchange step ($k_3 \ldots k_6$) were faster than the transalkylidenation step (k_1, k_2), the transfer-to-monomer process would predominate in the early stages of the reaction. This should result in a preponderance of low molecular weight oligomers, with little or no high molecular weight product formed initially. Under such circumstances, one would expect the number-average molecular weight of the product to remain very low until the final stage of the polymerization.

However, experimental results do not support this scheme. High molecular weight polymer was observed during early stages of the ring-opening polymerization of cyclooctene ($C_2H_5AlCl_2$–WCl_6–C_2H_5OH catalyst[29]). Similar results have been observed in the polymerization of cyclopentene by tungsten-based catalysts.[18,30] These results can be accommodated by assuming that the transalkylidenation step is much faster than the olefin-exchange step—an assumption which is contrary to that of Hughes,[24] who concluded that the rate-determining step is in fact the transalkylidenation step (eq 16). However, this difference may be reconciled by the fact that different catalyst systems were employed in these studies (W *vs.* Mo).

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Synthetic Applications

Olefin Synthesis. The applicability of the olefin metathesis reaction in areas such as enhancing the market value of petrochemical streams is obvious. A process for converting surplus propylene to ethylene and butene has been commercialized.

The effect of substitution on ease of participation in the metathesis reaction is: $[CH_2{=}] > [RCH_2CH{=}] > [(R)_2CHCH{=}] > [(R)_2C{=}]$. In addition, chlorine substitution at vinylic sites deactivates the double bond toward the metathesis reaction.[31]

Polyalkenamers. A homologous series of linear unsaturated polyalkenamers is provided by the application of the olefin metathesis reaction to cycloolefins of the general formula $\overline{[(CH_2)_nCH{=}CH]}$, where $n = 2$, 3, 5, 6 . . . and higher, with the exception of cyclohexene which does not undergo ring-opening polymerization. Unsaturated alicyclic monomers possessing more than one double bond undergo polymerization, provided that the double bonds are not conjugated.[32] Depending on the structure of the repeat units and the configuration of the double bonds, polyalkenamers may possess properties ranging from amorphous elastomeric to crystalline plastics.[33]

Careful analysis of experimental results[34] suggests that the high molecular weight polyalkenamers are essentially linear and not macrocyclic. To accommodate these results the participation of traces of acyclic olefins in metathesis steps during polymerization is suspected.

Macrocyclics and Catenanes. By proper selection of reaction conditions (high dilutions) it was shown that the metathesis of cycloolefins affords relatively high yields of macrocyclic compounds.[35] Of special interest is the cyclic dimer of cyclooctene, 1,9-cyclohexadecadiene, which is convertible to the respective musk-like ketone.[36]

Wolovsky[37] and Ben-Efraim, Batich, and Wasserman[38] carried out concurrent mass spectrometric studies on the macrocyclic species obtained from the metathesis of cyclododecene. Both concluded that interlocking ring systems are present in the mixture. The formation of these exquisite cyclic structures was accounted for[37,38] by assuming an intramolecular
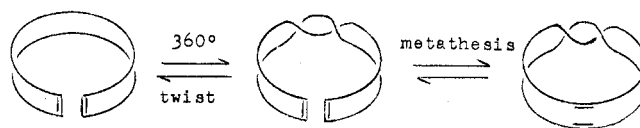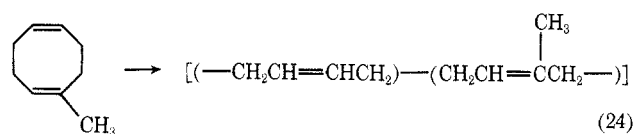

Figure 4. Formation of catenanes.

metathesis of a "strip" twisted by 360°, as illustrated in Figure 4.

Perfectly Alternating Copolymers. Substituted cycloolefins can be polymerized to high molecular weight polymers,[32] thus providing a convenient route for the synthesis of certain perfectly alternating copolymers. For example

$$[(—CH_2CH{=}CHCH_2)—(CH_2CH{=}\overset{\overset{\textstyle CH_3}{|}}{C}CH_2—)] \qquad (24)$$

The preparation of several diene alternating copolymers by this method has been reported by Ofstead.[31]

Liquid Polymers, Dienes, and Triene Syntheses. The cross-metathesis of cycloolefins with acyclic olefins may be utilized as a method for synthesis of liquid polymers, dienes, and trienes.[39,40] Michajlov and Harwood[41] have utilized the process for the characterization of polymer structures. For example, they were able to determine the monomer sequence distribution in a variety of butadiene–styrene copolymers. By employing high 2-butene:copolymer ratios they were able to exhaustively cleave copolymer chains into low molecular weight fragments which were then subjected to analysis by gas chromatography. The various cleavage products were characteristic of specific sequences of the monomers in the parent copolymer.

Conclusion

As with other newly discovered catalytic reactions, the surge in development of useful applications for the olefin metathesis reaction outpaced the elucidation of the reaction mechanism. Undoubtedly, as more researchers focus their attention on this relatively new process, an expansion of the scope of its applications will occur. Concurrently, one hopes that critical experimentation will be conducted that will clarify at least some of the mechanistic aspects proposed to date.

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