Metathesis of 1,5-Cyclooctadiene over Supported Rhenium Oxide Catalysts

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The metathesis of 1,5-cyclooctadiene (COD) was investigated over supported rhenium oxide catalysts in terms of carrier effects, acid properties of the catalysts, product distributions, and the reversibility of the reaction. Only alumina plays an effective role as a support. The reaction of COD over rhenium oxide–alumina catalyst yields oligomers, C_{8n}, sesqui-oligomers, C_{8n+4}, and polymers. The important results are as follows: 1) The product distribution in terms of the carbon number of the products shows a decay curve with maxima around C_{12}, C_{16}, and C_{20}. 2) The reaction of oligomers gives COD and some products similar to those of COD. 3) The reactivity of 1,5,9-cyclododecatriene (CDT) was low compared with COD, 1,5,9,13-cyclohexadecatetraene (CHT), and 1,5,9,13,17-cycloeicosapentaene (CEP). 4) A reaction of a mixture of macrocyclic polyenes and polymers gave appreciable amounts of CDT, CHT, and CEP, whereas no COD was obtained. On the basis of the results, we conclude that the products, oligomers, sesqui-oligomers, and polymers, are formed independently from the active intermediary polymers which are formed from COD.

The metathesis of acyclic alkenes has been investigated extensively both in homogeneous and heterogeneous systems. It is known that the effective catalysts for this reaction include compounds or complexes of Mo, W, and Re.[1–3)]

One of the characteristics in the metathesis reaction of cyclic alkenes is to form two kinds of homologues, cyclic oligomers and polyalkenes,[4,5)] which are not obtained in the disproportionation of acyclic alkenes. Though some studies on the polyalkenenes have been reported[6)] and put into practical applications in high polymer industries because of their high selectivity for ring-opening polymerization,[6)] less attention has been paid to the formation of cyclic oligomers.

1,5-Cyclooctadiene (COD) was reportedly catalyzed by homogeneous metal complexes to yield not only cyclic oligomers and poly(octadiene) but "sesqui-oligomers."[5–8)] In a previous paper,[8)] we briefly reported a heterogeneous catalytic metathesis of COD on Re_2O_7–Al_2O_3, yielding oligomers and sesqui-oligomers, in which the distribution of C_{12}—C_{32} cyclopolyenes was different from that in homogeneous catalyst system.

It will also be quite interesting to investigate how the sesqui-oligomers (C_{8n+4}) are formed from COD (eight membered ring diene) and what kind of reaction path is dominant and will give the three types of products: poly(octadiene) (polymers), cyclic oligomers (oligomers), and sesqui-oligomers.

In this study, supported rhenium oxides were used in the metathesis of COD; their catalytic activities and selectivities are compared with surface properties. The reactivity of 1,5,9-cyclododecatriene (CDT, C_{12}), 1,5,9,13-cyclohexadecatetraene (CHT, C_{16}), and 1,5,9,13,17-cycloeicosapentaene (CEP, C_{20}), and the reversibility of the reaction are discussed and a probable reaction path is proposed.

Experimental

Materials. *Catalyst Preparation*: Supported molybdenum and rhenium oxide catalysts were prepared by impregnating various metal oxide supports with aqueous solutions of ammonium heptamolybdate (Wako Pure Chemical Ind., Ltd., GR) and ammonium perrhenate (Engelhard), respectively, followed by drying and calcining at desired temperatures in air for more than two hours. The supports tested here were SiO_2–Al_2O_3, Al_2O_3, MgO, TiO_2, ZnO, ZrO_2, SnO_2, La_2O_3, ThO_2, WO_3, and MgO–ZnO. SiO_2–Al_2O_3 was obtained from Nikki Chemical Co., and contained 15 wt% of Al_2O_3. Magnesium oxide was the GR grade of Kanto Chemical Co. Aluminas were "an activated alumina" from Nishio Industry Co., Ltd, N611 from Nikki Chemical Co., A022 and TK13R from Tokai Konetsu Kogyo, Neobead MSC from Mizusawa Chemical Co., Ltd., and Albes FE and FF from Showa Tansan Kaisha, Ltd. An alumina was prepared by neutral hydrolysis of aluminum triisopropoxide (Wako Pure Chemical Ind. Ltd.). Titanium dioxide, ZnO, ZrO_2, SnO_2, and La_2O_3 were prepared by hydrolysis of titanium tetrachloride (Wako, GR), zinc nitrate (Nakarai Chemicals, Ltd., GR), zirconium(IV) dichloride oxide (Wako, GR), tin(IV) chloride (Wako, GR), and lanthanum nitrate (Nakarai Chemicals, Ltd., extra pure) with aqueous ammonia, respectively, followed by washing, drying, and calcining in air at 500 °C for 3 h. Thorium oxide and WO_3 were obtained by thermal decomposition of thorium nitrate (Wako, GR) at 550 °C for 1 h and of ammonium dodecatungstate (Wako, GR) at 550 °C for 10 h, respectively. A mixed oxide MgO–ZnO (1:9 in molar ratio) was provided by hydrolysis of aqueous mixture of $Zn(NO_3)_2$ and $MgCl_2$ with 28% aqueous ammonia, followed by washing, drying, and calcining in air at 500 °C for 3 h.

6.5 wt% of Re_2O_7 was mounted on all carriers except Al_2O_3, on which the amount of Re_2O_7 was varied from 0.5 to 10 wt%. The amount of MoO_3 supported was 5.1 wt%.

Reactants and Solvents: COD (Shell) was distilled under atmospheric pressure without using any drying reagents.

CDT, CHT, and CEP were obtained by fractional distillation from the reaction mixture of COD. Polymers which contain the open-chain polymers and macrocyclics higher than C_{56} were also prepared from COD products by distillation.

Solvent purifications are as follows. Benzene and cyclohexane (Wako, GR) were distilled over metallic sodium. 1,2-Dichloroethane (Wako, GR) was distilled over phosphorus pentaoxide. Heptane and ethyl alcohol (Wako, GR) were dried over molecular sieves; carbon tetrachloride (Wako, Pure Grade) was dried over calcium chloride. Hexane, ethyl acetate (Wako, GR), and dioxane (Kanto, GR) were used without further purifications.

Procedure. The reactions were carried out at 0 to

80 °C with continuous stirring in a round bottom flask which contained 0.5 ml of COD with 5 ml of solvent and 0.2 g of catalyst. Small amounts of samples for analysis were taken out from the reaction mixture at appropriate time intervals.

The reaction products were analyzed by three sets of gas chromatographs: (A) equipped with a 3 m column of Silicone DC 200 at 200 °C for lower molecular weights macrocyclics (C_8—C_{20}) analysis. (B) equipped with a 1 m column of SE-30 with temperature programming for the analysis of an internal standard and C_8—C_{28} macrocyclics. (C) equipped with a 1 m column of Dexsil 300 GC (3%) with temperature programming for C_{16}—C_{56} macrocyclics analysis.

Products were identified by gas chromatography, IR, and mass spectra, in comparison with their authentic samples. Quantitative analyses were made by using an absolute calibration curve.

Measurement of Surface Acidity. Acidic properties of the catalysts were examined by the butylamine titration method using Hammett indicators.

Definition of Terms. The term "the conversion of COD" was defined as a percentage ratio of the converted COD to the initial amount of COD. The term "the amount of polymers" was defined as the difference between the amount of COD converted and the total amount of the products which can be analyzed by gas chromatography. "Catalytic activity" and "selectivity" were defined as the ratio of the total amount of macrocyclics to the initial amount of COD and the ratio of macrocyclics to the converted COD, respectively.

$$\text{Conversion} = \frac{\text{Converted COD}}{\text{Initial COD}} \times 100\%$$

$$\text{Amount of Polymers} = (\text{Converted COD}) - (\text{Total Product})$$

$$\text{Catalytic Activity} = \frac{\text{Total Macrocyclics}}{\text{Initial COD}}$$

$$\text{Selectivity} = \frac{\text{Macrocyclics Individual}}{\text{Converted COD}}$$

Results and Discussion

Effect of Carriers on Catalytic Activity. The reactions were carried out over single or impregnated oxides. Only Re_2O_7–Al_2O_3 showed an activity for the formation of macrocyclic polyenes and polymers; the following catalysts were completely inactive: MoO_3, WO_3, Re_2O_7, Al_2O_3, Re_2O_7–MgO, Re_2O_7–TiO_2, Re_2O_7–ZnO, Re_2O_7–ZrO_2, Re_2O_7–SnO_2, Re_2O_7–La_2O_3, Re_2O_7–ThO_2, Re_2O_7–MgO–ZnO, and Re_2O_7–$SiO_2 \cdot Al_2O_3$ or MoO_3–Al_2O_3. The high catalytic activity of Re_2O_7–Al_2O_3 implies that only alumina plays a special role in the formation of the active sites. Such a specific role of Al_2O_3 is also reported in the disproportionation of propylene over MoO_3–Al_2O_3[9] and Re_2O_7–Al_2O_3.[10] Various aluminas, which were supplied by different industries, were examined to investigate the role of Al_2O_3. Table 1 lists the names of these aluminas, their crystal forms, and their surface areas. The numbers correspond to that of Fig. 1. As Fig. 1 shows, catalytic activities are well correlated with the surface area of supports and do not depend on crystal forms (α, γ, *etc.*). Therefore, in the following studies, the alumina which had the largest surface area was used as the carrier of rhenium oxide.

Table 1. List of Alumina Used

No.	Name	Crystal form	Surface area $/\text{m}^2\,\text{g}^{-1}$
1	Albes-FF	(fibrillar)	330
2	TK-13R	γ-	230
3	Albes-FE	(fibrillar)	110
4	N-611	γ-	200
5	Neobead M6C	γ-	210
6	A-022	α-	1

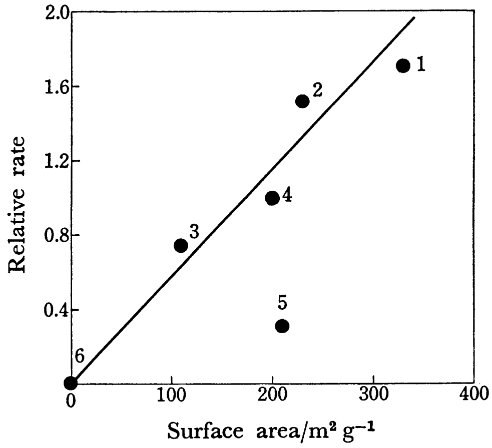


Fig. 1. Correlation between surface area and relative rate. Numbers correspond to those in Table 1.

The amount of Re_2O_7 supported was varied from 0.5 to 10 wt% to Al_2O_3. The catalytic activity increased up to 3 wt% and became constant above this range.

Optimum and reproducible activity was obtained by calcining the catalyst at 600 °C in air for more than 2 h.

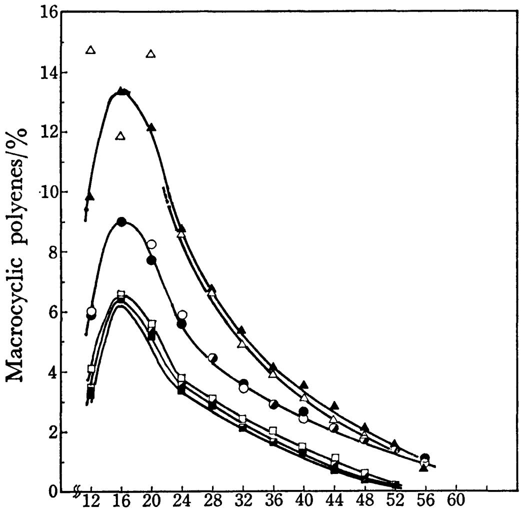
Catalytic Activities and Acid-Base Properties of Catalysts. Since some relationships were suggested between the acidic properties of catalysts and the catalytic activities for the metathesis of alkenes,[11–15] the acidic strength and the acidity (number of acid sites) of the catalytically active Re_2O_7–Al_2O_3 and the inactive MoO_3–Al_2O_3 were compared. These catalysts have strong acid sites ($\text{p}K_a = -5.6$) which were not found on the component oxides themselves, *i.e.*, the strong acid sites were created by the combination of those oxides. Though both catalysts have fairly large amounts of acid sites, one of the catalysts, MoO_3–Al_2O_3, does not show any catalytic activity. However, the activity of Re_2O_7–Al_2O_3 was decreased with the increase of the amount of NaOH added and completely lost by the addition of 1.24 mmol/g NaOH. These results seem to indicate that the acidic property does not directly dominate the catalytic activity, but is one of the important factors which control the activity.

Effect of Solvent on Catalytic Activity. It is known that some particular solvents are favorable for a high conversion or a high selectivity in metathesis.[16,17] The solvents used in this study are listed in Table 2, together with the conversion of COD, the catalytic

Table 2. Effect of solvents[a)]

Solvent	Reaction time min	Conversion %	Activity %	Selectivity %
Benzene	80	37	11	30
Carbon tetrachloride[b)]	75	38	8	21
Cyclohexane[b)]	60	24	7	29
Hexane[b)]	60	23	4	17
1,2-Dichloroethane	60	20	0.8	4
Dioxane	120	0	0	—
Ethyl acetate	120	0	0	—
Ethyl alcohol	120	0	0	—

a) Reaction conditions: temp=40 °C, solvent=5.0 ml, COD=0.5 ml. b) White polymer was found on glass wall.



Carbon number of macrocyclics

Fig. 2. Product distributions in terms of the carbon number of the products.
■, ◪, □: after 5, 10, and 15 min reaction, respectively, of 2 wt% solution of COD in heptane. △, ▲: After 0.5 and 9 h reaction, respectively, of 5 wt% solution of COD in benzene. ○, ●: After 4 and 51 h reaction, respectively, of 10 wt% of COD in heptane.

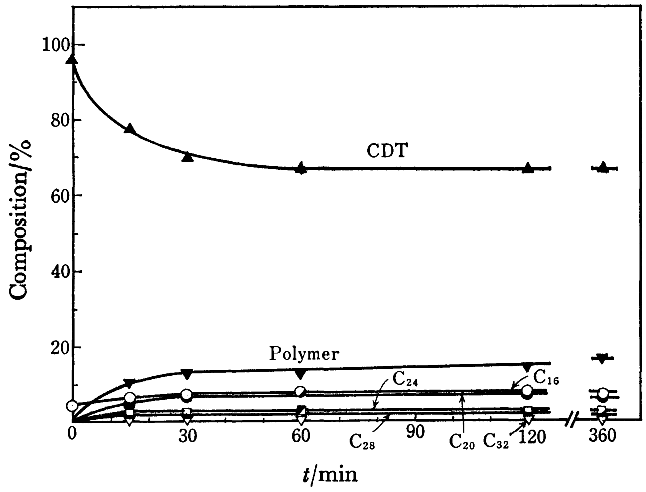


Fig. 3. Reaction of CDT ▲: CDT, ▼: polymer, ○: C_{16}, ●: C_{20}, □: C_{24}, ■: C_{28}, ▽: C_{32}.

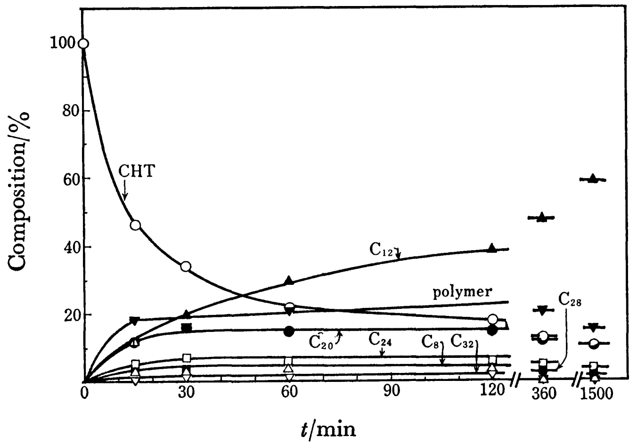


Fig. 4. Reaction of CHT ○: CHT, ▲: C_{12}, ▼: polymer, ○: C_{20}, □: C_{24}, △: C_8, ■: C_{28}, ▽: C_{32}.

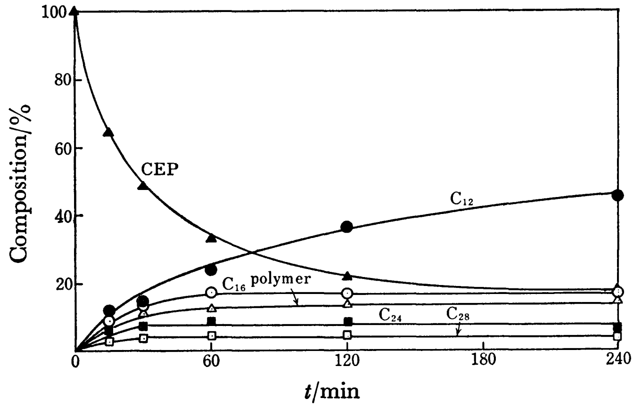


Fig. 5. Reaction of CEP ▲: CEP, ●: C_{12}, ○: C_{16}, △: polymer, ■: C_{24}, □: C_{28}.

activity, and the selectivity. Besides benzene and cyclohexane, which are known as suitable solvents in homogeneous systems, carbon tetrachloride is also a good solvent for obtaining high conversion, activity, and selectivity. On the other hand, in ethyl alcohol, dioxane, and ethyl acetate, no product was obtained. Product distributions did not depend on the solvents used. Though the effective solvents seem to be good for polymers as well as oligomers, further studies should be done to clarify the role of solvents.

Product Distributions. As in the case of homogeneous systems, the metathesis of COD over Re_2O_7–Al_2O_3 yields oligomers, C_{8n}, sesqui-oligomers, C_{8n+4}, and polymers. Figure 2 shows the dependency of the product distribution in terms of the carbon number of macrocyclics. The spectrum seems to be a decay curve over C_{20} product, with an ambiguous maximum around the first three products: CDT, CHT, and CEP. The product distributions were essentially unchanged through the entire reaction period, until most of the COD was consumed. These results suggest that oligomers and sesqui-oligomers are formed by parallel paths but not by a consecutive reaction path.

The Reaction of Oligomers and Sesqui-oligomers. The results of the individual reactions of CDT, CHT,

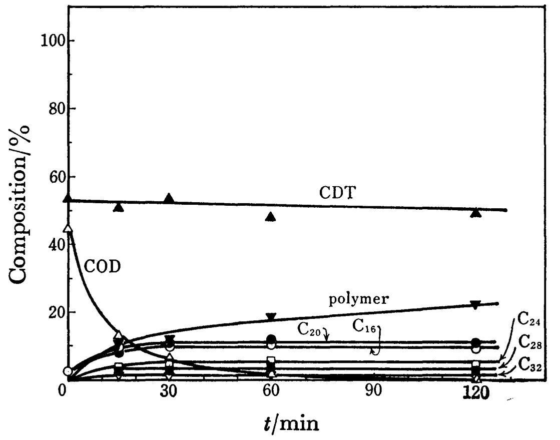


Fig. 6. Competition reaction of COD and CDT ▲: CDT, △: COD, ▽: polymer, ●: C_{20}, ○: C_{16}, □: C_{24}, ■: C_{28}, ▽: C_{32}.
Reaction mixture contains 0.4% of COD, 0.5% of CDT, and benzene as solvent.

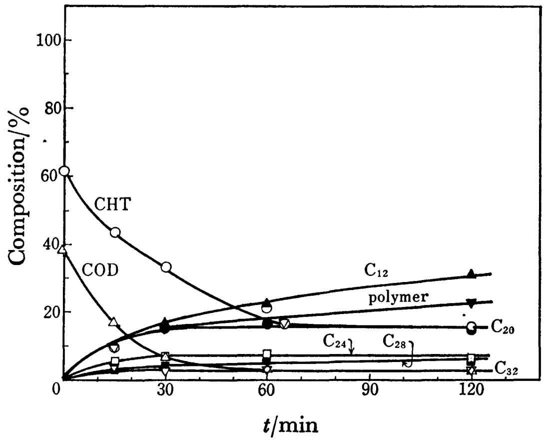


Fig. 7. Competition reaction of COD and CHT ○: CHT, △: COD, ▲: C_{12}, ▼: polymer, ●: C_{20}, □: C_{24}, ■: C_{28}, ▽: C_{32}.

and CEP are shown in Figs. 3, 4, and 5, respectively. Sesqui-oligomers react and give similar products to those of oligomers, except there is no production of COD. Such results are consistent with the results shown in Fig. 2, which indicate that the product distributions of both oligomers and sesqui-oligomers produced by the metathesis of COD are on the same line.

If we assume that those products were formed by a consecutive oligomerization reaction, it is expected that the product distribution may be different in reactions in which CDT, CHT, or CEP is used as a reactant, since they are supposed to be the intermediate reaction products in the consecutive reaction. Thus, the data which suggest similar product distributions (Figs. 3, 4, and 5) lead us to conclude that each product, CDT, CHT, or CEP, is formed independently and not by a consecutive step.

In the competitive reaction of CDT or CHT with COD, the product distributions hardly differed from those in the reaction of individual materials, as shown in Figs. 6 and 7. This reveals that the competitive reaction is the simple superposition of two independent reactions of COD and other cyclic polyenes.

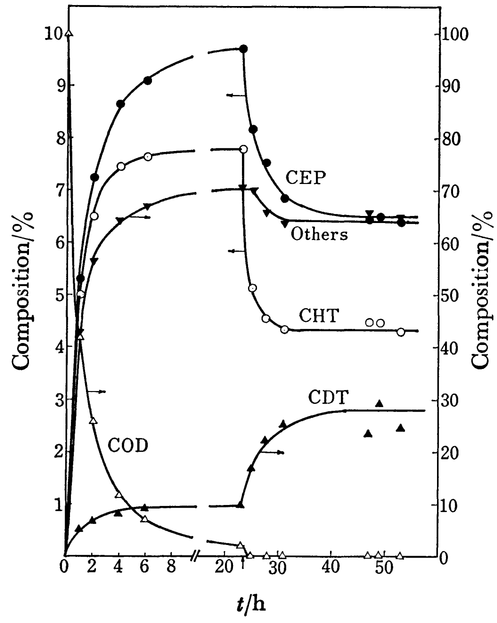


Fig. 8. Reaction of COD △: COD, ▲: CDT, ○: CHT, ●: CEP, ▼: polymer. An arrow on the time scale indicates the addition of a new catalyst.

The reactivity of macrocyclics can be estimated from the competitive reactions and the individual ones. COD is the most reactive and is followed by CHT and CEP. The low reactivity of CDT is indicated by the following observations. (1) the reaction seems to stop at about 30% conversion within 1 h, when CDT is used as the reactant, while CHT and CEP react over 70% within 1 h and keep converting to the products. (2) CDT is continuously formed as the product during the reaction, while the additional formation of other products such as C_{20}, C_{24}, and C_{28} was not observed after 1 h. (3) in a competitive reaction of COD and CDT, only COD was a reactive component.

Though CHT gives a small amount of COD (about 3%), CDT and CEP do not give any. No production of COD in the latter case may be due to the absence of a reverse reaction or to the rapid disappearance of the COD formed. Since the reactivity and the distribution of the products from CHT do not differ markedly from that of CEP or CDT, it will be reasonable to conclude that no reverse reaction takes place from CDT or CEP to COD. The formation of COD from oligomers, such as CHT, will be a simple deoligomerization. The difficulty in the formation of COD from sesqui-oligomers will be understood by considering that such a reaction must accompany the C_4 fragments.

Depolymerization and Equilibrium. A depolymerization of macrocyclic polyenes and polymers was examined to elucidate the reversibility of the reaction; a 1 wt% mixture containing 75.5 wt% of C_{24}—C_{52} macrocyclics and 24.5 wt% of polymers was used at 40 °C. The composition of the mixture after 4 h reaction was as follows: 13.5% of CDT, 8.5% of CHT, 12% of CEP, 35% of macrocyclics, and 31% of polymers. No COD was obtained. These results are coincident with those which have been obtained in homogeneous catalyst systems. Scott *et al.* found the formation of C_{12}—C_{32} materials in the reaction of a diluted solution of the "extracted high molecular weight COD polymers" by using the system WCl_6–$EtAlCl_2$–EtOH.⁷⁾

Figure 8 shows the result of the prolonged reaction of COD. When the amount of COD is sufficient (more than 5%), the ratios of the first three products, CDT, CHT, and CEP, are held almost constant at about 9.5:8:9.5, and the reaction seems to reach equilibrium. However, after the amount of COD decreased below 5%, an addition of a fresh catalyst leads a remarkable change in the ratio of the first three products. The amount of CDT increases abruptly and the amounts of CHT and CEP decrease rapidly, while the amount of the higher molecular weight products becomes a little smaller. After a long period, COD disappeared completely from the reaction mixture and the reaction seems to reach equilibrium again, where the composition of the products is CDT=25, CHT=4.5, CEP=6.5, and others=64.

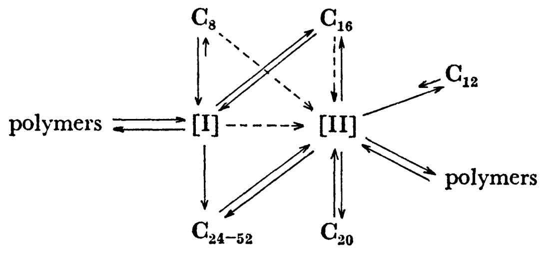
Reaction Route. Before presenting a probable reaction route, it will be convenient to summarize the important findings.

a) COD is formed by a degradation of the oligomers (dimer, trimer, tetramer, *etc.*) but not from the sesqui-oligomers.

b) Some oligomers and sesqui-oligomers are formed by the back reaction of the polymers which contain chained species of high molecular weight and large ring-size polyenes.

c) The consecutive reaction is unlikely.

The following reaction scheme interprets the observations.



I and II represent active intermediary polymers (AIP). An assumption of two intermediates is based on the observations that CDT and CEP did not give any COD. Arrows with different lengths between C_8 and I and between C_{12} and II mean that, for instance, the rate of formation of I from C_8 is faster than that of C_8 from I. The dotted arrows indicate that it is uncertain whether II is formed directly from C_8 and C_{16} or indirectly *via* II.

Formation of Polymers. The polymers will be formed either as the desorption products of one part of the "active intermediary polymers" (AIP) or as the product of the ring-opening polymerization of COD with the AIP. A sufficient amount of COD will give a large amount of polymers by the latter reaction. The polymers produced may readsorb on the sites to form the AIP and may give the oligomers. A large amount of polymers produced may inhibit the reaction by covering the active sites.¹⁸⁾

Formation of Oligomers and Sesqui-oligomers. Oligomers will be formed by an intramolecular disproportionation of the AIP. COD does not participate in this reaction process. The oligomers produced can be reconverted to the AIP and give polymers or other oligomers with a new product distribution. The AIP from the oligomers can produce COD by an intramolecular reaction of the AIP, while the AIP from the sesqui-oligomers does not. Presumably, the latter AIP is different from the others.

The oligomers and the sesqui-oligomers will be formed by the intramolecular reaction process, *i.e.*, by the "pinch off" process proposed by Scott *et al.*⁷⁾ As already shown in Fig. 2, the distribution of the reaction products shows a decay curve, as the ring-size of the products increases. Especially, the distribution of the products which have larger ring-size than C_{20} is expressed very well by a single curve. This indicates that the product distribution will dominantly depend on the "pinch off" probability of the intramolecular reaction in the formation of the individual products, where the production of the smaller polyenes is much higher than that of the higher ones. The deviation of the product distribution of the three products, C_{12}, C_{16}, and C_{20}, from this plot will be brought about from the following reactions: CDT (C_{12}), which is the product of the intramolecular reaction of polyenes, reacts with COD (C_8) to form CEP (C_{20}) or dimerizes to give C_{24} species. The former reaction ($C_{12}+C_8$) will take place more easily than the latter ($C_{12}+C_{12}$), because COD is more reactive than CDT (C_{12}). Dimerization of COD to form CHT (C_{16}) should also be taken into consideration.

Formation of AIP. Though the AIP are supposed to be the macrocyclic polyenes¹⁹⁾ or open-chain polymers which are adsorbed on the catalyst at multiple points, it is not clear how the AIP forms from COD. One possible way is to assume a chain reaction, as Chauvin has proposed,²⁰⁾ in which a carbene intermediate mechanism was proposed for the polymerization of cycloolefins. Considering the reaction time-course, the AIP is supposed to be formed at a very early stage of the reaction.

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