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NOTES

A Study of *cis–trans* Isomerization During Metathesis of *cis*-2-Pentene with the Catalytic System: $W(CO)_5P(C_6H_5)_3 + C_2H_5AlCl_2 + O_2$

Homogeneous olefin disproportionation always gives a mixture of the geometric isomers of the starting olefin and of the products (*1–2*). However, with catalytic systems which exhibit a high activity, the final isomer composition always corresponds to the thermodynamic ratio of the geometric isomers. A few studies have already been devoted to the steric course of metathesis in its early stages. Many catalytic systems have been used for metathesis of *cis*-2-pentene and each showed individual characteristics. With (WCl_6 + C_2H_5OH + $C_2H_5AlCl_2$), Calderon *et al.* (*1*) found the reaction to be selective in favor of the *cis* isomer of the products (2-butene and 3-hexene) regardless of the isomeric nature of the initial 2-pentene. Many considerations led the authors to the conclusion that disproportionation is the principal mode of geometric isomerization. When *n*-butyl lithium was used as cocatalyst of WCl_6 (*3*), different stereochemical results were obtained with 2-pentene, since at 40% conversion the *trans/cis* ratio of 2-butene was 0.8 instead of the thermodynamic equilibruim observed with $C_2H_5AlCl_2$. Moreover, Wang, Menapace and Brown (*4*) found that $AlCl_3$ increased the rate of metathesis of the system WCl_6, *n*-butyl lithium but also favored the formation of more *trans* isomers in the products (2-butene and 3-hexene) and the remaining 2-pentene. They explained this result by assuming a more extensive isomerization by cationic aluminum species. We report here our results concerning the stereochemistry of *cis*-2-pentene metathesis with the catalytic system [$W(CO)_5P(C_6H_5)_3 + C_2H_5AlCl_2 + O_2$] and try to explain the results on kinetic grounds.

The equipment used to perform kinetic experiments has already been described (*5*). The catalyst system consisted of $W(CO)_5P(C_6H_5)_3$ (denoted W) + $C_2H_5AlCl_2$ (Al) + O_2; each component was necessary for catalytic activity. For example, in a typical experiment at room temperature no catalytic activity was observed for metathesis of *cis*-2-pentene in chlorobenzene with W + Al (Al:W = 4 and olefin:W = 100). The activity was observed only when molecular oxygen was introduced in the system (O_2:Al = 1.5).

We will report here only the *cis–trans* composition of 2-butenes and 2-pentenes, the results obtained with 3-hexenes being similar to those of 2-butenes. When disproportionation of *cis*-2-pentene was performed with [$W(CO)_5P\phi_3 + EtAlCl_2 + O_2$], the metathesis equilibrium was reached in 20 min and the *cis–trans* composition corresponded to thermodynamic equilibrium for 2-butenes and 2-pentenes. However, in the early stages of the reaction, *cis*-2-butene was produced in much higher amount as already observed by various authors with many catalytic systems. The very high activity encountered in the first minutes is a real obstacle to the study of *cis–trans* isomerization. For this reason, we were led to use a catalyst which exhibited a weak activity. We have already observed that upon introducing O_2 to the catalytic system [$W(CO)_5P\phi_3$ + $EtAlCl_2$] CO is slowly given off and the rate of metathesis is greatly lowered as CO is evolved. It is therefore possible to decrease the rate of reaction by a known factor upon introduction of the olefin at various stages of CO evolution (*5*). A typical result is given in Fig. 1 where *cis*-2-pentene is introduced after 1 CO per W has been evolved. In this case, the catalyst exhibits a very low activity since disproportionation equilibrium is reached in about 200 min. A significant result concerns the variation of the concentration of 2-butenes with time (Fig. 1). In the first minutes, the *cis*-2-butene concentration increases, goes through a maximum and then decreases, whereas the *trans*-2-butene concentration always increases. This indicates the presence of a secondary geometric isomerization of *cis*-2-butene to the *trans* isomer. For a catalyst of low activity metathesis of *cis*-2-pentene would produce *cis*-2-butene and *trans*-2-butene with a certain ratio *trans/cis* (in favor of the *cis* isomer) and then a subsequent isomerization of *cis*-2-butene to *trans*-2-butene (probably by a metathetic process as shown below).

In order to determine the limit ratio *trans/cis* of 2-butene at low conversion, we made the following experiments: metathesis of *cis*-2-pentene was performed at various stages of CO evolution, so that it was possible to determine the ratio *trans/cis* of butene for various conversions taken 4 min after olefin introduction. The results are plotted in Fig. 2, together with data of Wang and Menapace (*3*) obtained with (WCl_6 + *n*-butyl lithium). Extrapolation to zero conversion gave a value of 0.6 ± 0.1 for the *trans/cis* ratio of 0.66 at the very beginning of metathesis with the catalytic system (WCl_6 + C_2H_5OH + $C_2H_5AlCl_2$).

The good agreement observed between various precursor catalysts is very unexpected if we consider the major differences in the oxidation number of W and in the nature of the cocatalyst. It could suggest a common intermediate active form of tungsten although it is not in itself a sufficient proof. It is interesting to note that both in homogeneous and heterogeneous systems, tungsten catalysts exhibit a lower stereoselectivity than molybdenum catalysts for which ratios of 0.2 are observed at very low conversion (*6*, *7*).

In order to determine the more likely mechanism (cationic or metathetic) for the *cis–trans* isomerization of 2-butene, we made the following experiment. *cis*-2-Butene was introduced to [$W(CO)_5P\phi_3$ + $EtAlCl_2$] (without O_2) ($Al/W = 4$, $C_4/W = 20$): *cis–trans* isomerization and double bond shift were observed in very minor amount. But when O_2 was introduced [in such case, the system becomes very efficient

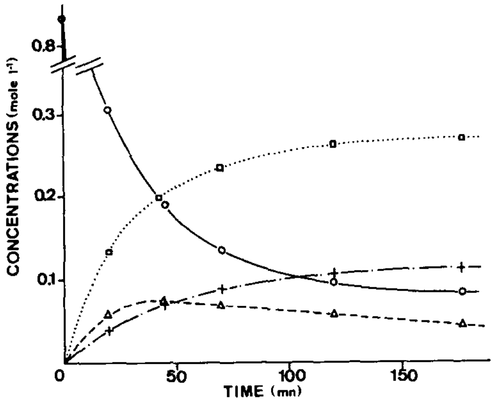


FIG. 1. Variation of concentration of the reactants with time during methathesis of *cis*-2-pentene. 3-Hexenes have been omitted for the clarity of the figure. (○) *cis*-2-pentene, (△) *cis*-2-butene, (+) *trans*-2-butene, (□) *trans*-2-pentene.

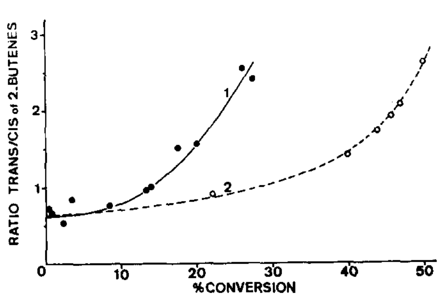


FIG. 2. Influence of conversion on the ratio *trans/cis* of 2-butene. (1) Present results obtained with $W(CO)_5P\phi_3$, $EtAlCl_2$, O_2; (2) results from Ref. (*4*).

for olefin metathesis and 2-butenes undergo metathesis with themselves (*1*)], instantaneously *cis*-2-butene was converted to the thermodynamic *cis–trans* equilibrium with no butene-1 or its disproportionation products. This reaction was followed by an oligomerization reaction of the two isomers. If O_2 was introduced to $EtAlCl_2$ alone in the presence of *cis*-2-butene, no *cis–trans* isomerization occurred, but a fast oligomerization of the *cis* isomer was observed. It must be pointed out here that the oligomerization was observed only when the ratio olefin:$EtAlCl_2$ was lower than ca. 10. This oligomerization observed after O_2 interaction with $EtAlCl_2$ is believed to be a cationic secondary reaction (*8*) but this does not seem to be the case for the *cis–trans* isomerization which occurs only in the presence of a metathetic catalytic system ($W + Al + O_2$), and not with the system ($Al + O_2$). It seems therefore that *cis–trans* isomerization of 2-butene occurs here according to a metathetic mechanism.

The initial rate of *cis–trans* isomerization of *cis*-2-pentene has also been measured at various stages of CO evolution and compared with the rate of metathesis (defined as the rate of formation of 2-butene). Results are given in Fig. 3: the *cis–trans* isomerization of 2-pentene shows the same behavior as the metathesis reaction when CO is evolved, suggesting probably a metathesis process for *cis–trans* isomerization of the starting olefin.

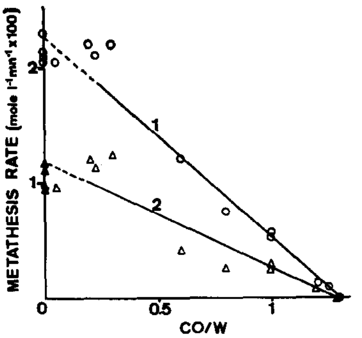


Fig. 3. Catalytic activity for *cis–trans* isomerization of *cis*-2-pentene (2) and for metathesis of *cis*-2-pentene (1), at various stages of CO evolution.

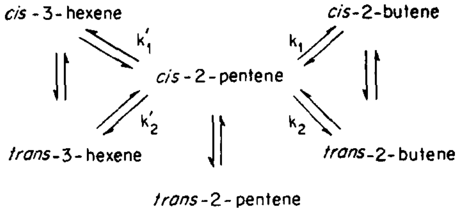
The following conclusions can be drawn from our results:

1. *cis–trans* isomerization of *cis*-2-butene is a secondary reaction of the disproportionation reaction of *cis*-2-pentene.

2. the metathesis of *cis*-2-pentene gives a mixture of *trans* and *cis*-2-butene with a ratio *trans/cis* = 0.6 at very low conversion and this apparently occurs for many catalytic systems which include W as transition metal. *Cis–trans* isomerization of *cis*-2-butene then proceeds probably by a metathetic mechanism which progressively leads to thermodynamic equilibrium.

3. It is possible that metathesis of *cis*-2-pentene gives also *trans*-2-pentene by a metathetic mechanism.

These conclusions show the complexity of studying the kinetics of metathesis. In order to characterize the activity of a given complex for this reaction, one has to take into account the following parallel and consecutive reactions:



where $k_2/k_1 = 0.6$, $k'_2/k'_1 = 0.86$, and $k_1 + k_2 = k'_1 + k'_2$.

This explains why different steric behavior is observed with various precursor complexes. This *cis–trans* composition depends mainly on the concentration and the lifetime of the active form of the catalyst: a *trans/cis* ratio close to the thermodynamic equilibrium indicates in fact a high metathesis activity and not a secondary cationic isomerization (*4*).

It is interesting to note that *cis–trans* isomerization of polyalkenamer is also a secondary reaction during polymerization of cyclopentene (*9*), a result which shows the strong parallelism between metathesis of acyclic and cyclic olefins.

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