SOME FEATURES OF THE ISOMERIZATION OF α -OLEFINS IN THE PRESENCE OF HETEROGENIZED NICKEL COMPLEXES

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The dimerization of ethylene which proceeds very efficiently in the presence of carbonyltriphenylphosphine -nickel complex heterogenized on Al_2O_3 and π -CH₃H₅NiX/Al₂O₃ (X = Cl and Br) is accompanied by the isomerization of α -olefins to β -olefins [1, 2]. In contrast to homogeneous catalyst systems [3], there is only fragmentary data on double bond migration in the presence of heterogenized nickel complexes.

In the present work, we studied some features of the isomerization of α -olefins relative to the structure of the starting hydrocarbon and reaction conditions in the presence of these catalysts obtained by complexation on the support surface.

EXPERIMENTAL

The carbonyltriphenylphosphine – nickel complex supported on Al_2O_3 (Ct-1) was prepared by analogy to our previous method [4]. The IR spectra of the samples contained characteristic bands for Ni (CO)₂ (Ph₃P)₂ [4]. Samples of π -C₃H₅NiCl/Al₂O₃ (Ct-2 with 2% Ni) and π -C₃H₅NiBr/Al₂O₃ (Ct-3 with 2% Ni) were prepared and identified as in our previous work [4]. The nickel content in the Ni (CO)₂ (Ph₃P)₂/Al₂O₃ samples was determined on a Perkin-Elmer 330 atomic-absorption spectrophotometer according to our previous procedure [1, 2].

The sample of Ni (CO)₂ (Ph₃P)₂ was prepared according to Rose and Stathan [5]. The IR spectra of this complex corresponded to that described by Tolman [6]. The starting olefins were dried immediately before use. The purity as determined by gas-liquid chromatography was 99.1% for 1-hexene, 99.4% for 1-heptene, 91.2% for 4-methyl-1-pentene, and 99.5% for 2-methyl-1-pentene.

The organoaluminum compounds (AlEt₃, AlCl₂Et, AlClEt₂, and Al₂Et₃Cl₃) were used as solutions obtained from the pure compounds.

The olefin isomerization was carried out in a glass reactor with a constant-temperature jacket equipped with a thermometer and magnetic stirrer. A sample of 40 ml dry heptane, the catalyst batch, and 0.5-2.0 ml olefin were added to the reactor in an argon atmosphere and the reactor was brought to a constant temperature. The required amount of organoaluminum compound was added; this addition was considered the onset of the reaction.

RESULTS AND DISCUSSION

A study of the effect of different reaction conditions and of the substrate structure on the extent of conversion and selectivity of the isomerization of α -olefins in the presence of Ct-1, Ct-2, and Ct-3 revealed several features of the catalytic action of these complexes in addition to the general relationships described for homogeneous and heterogeneous analogs. The activating role of the base has been reported for catalysts obtained by the grafting of previously synthesized π -allylic and dicarbonylditriphenylphosphine—nickel complexes to the support [7, 8]. In our catalyst samples, for which heterogenization occurs upon complexation in the reaction of Ni(CO)₄ and the corresponding ligands on the support surface, an analogous effect was not found. As in the case of ethylene oligomerization [1, 2], the isomerization of 1-hexene (1-H) proceeds very rapidly only upon activation of the catalysts by organoaluminum activators.

The extent of conversion depends on the nature of the ligands: In the case of π -allylnickel halides, it hardly changes by replacing Cl with Br but sharply increases in going to Ct-1 which contains PPh₃ as the

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Fig. 1. Effect of the nature of the ligands on the activity of heterogenized nickel complexes activated by $Et_3Al_2Cl_3$: 1) π -C₃H₅NiBr/Al₂O₃, 2) π -C₃H₅NiCl/Al₂O₃, 3) Ct-1, $[1-H]_0 = 0.380$ mole/liter, 20°C, Al/Ni = 10, Ni = 9.8 $\cdot 10^{-5}$ g-atom.

Fig. 2. Effect of the Al : Ni ratio on the activity of the $Ct-1 - Et_3Al_2Cl_3$ catalyst system in the isomerization of 1-H: 1) 0.5:1, 2) 1:1, 3) 2:1, 4) 10:1, $[1-H]_0 = 0.19$ mole/liter.

TABLE 1. Isomerization of 1-Hexane in the Presence of Ct-1 and Ni (CO)₂ (Ph₃P)₂ – Et₃Al₂Cl₃ in Heptane Solvent at 20 °C ([Ni] = 0.00212 mole/liter, [1-hexene]₀ = 0.38 mole/liter)

Time, min	Content in reaction mixture, %									
	1-H		trans-2-H		cis-2-H		3-H		cis/trans-3-H	
	I*	II *	I	11	I	11	I	п	I	11
1 3 5 10 30 60	52 11 8 6 3 2	77 42 35 20 10 9	$\begin{array}{c} 33 \\ 55 \\ 59 \\ 61 \\ 64 \\ 64 \\ 64 \end{array}$	14 29 34 41 44 47	15 33 30 31 30 29	13 29 31 39 45 41	-1 3 2 3 5	- - - 1 3	0,45 0,60 0,51 0,51 0,47 0,45	0,93 1,00 0,91 0,95 1,02 0,87

*I and II) Ct-1 and Ni (CO)₂ (Ph_3P)₂, respectively.

ligand (Fig. 1). A similar promoting effect of the phosphine group on isomerization was previously found for platinum and iridium complexes [9, 10].

An increase in the Al : Ni ratio gives an increase in catalytic activity with an increase in the excess organoaluminum component (Fig. 2) which is typical for nickel systems. However, high activity of our complexes is achieved even for Al : Ni =2 (see Fig. 2, curve 3), while the isomerization of olefins in the presence of nickel salts proceeds actively only with a significantly greater excess of the alkylaluminum halides (\geq 50) [3]. These data may be explained assuming that deactivation of active hydride species (bimolecular interaction with the formation of colloidal nickel with subsequent coagulation to form the metal), which proceeds rapidly in a homogeneous system [11], is hindered in the case of complexes attached to a support. Indeed, supported π -allylnickel halides are significantly more stable than the soluble complex [1, 4]. In the case of Ct-1, stabilization of nickel in an anomalously low oxidation state is a result not only of the action of the base but also, to a considerable extent, of the effect of the donor-acceptor ligands, which produces some levelling of the activities of the homogeneous and heterogeneous catalysts in the case of high Al : Ni ratio (10) (Table 1). The stabilizing role of the support is even more evident for a slight excess of Et₃Al₂Cl₃. Thus, for Ni (CO)₂ · (PPh₃)₂ + Et₃Al₂Cl₃ with Al : N=2, the system almost completely loses its activity after only 10 min with 60% conversion of 1-H, while, under the same conditions, the supported complex remains active for 1 h (Fig. 3).

A feature of Ct-1 discovered in the isomerization of 1-H was its sensitivity to the type of organoaluminum activator. A high reaction rate was found only for $Et_3Al_2Cl_3$. The catalyst had low activity not only with Et_3Al but even with Et_2AlCl and $EtAlCl_2$ which have similar reducing and acid properties; variation of the Al : Ni ratio from 2 to 10 does not lead to a significant change in the activity of the catalytic system (Table 2).

This finding is interesting but not unexpected in light of the complexity of the reaction of Ni (0) complexes with organoaluminum compounds including a series of oxidation-reduction reactions Ni (0) \neq Ni (I) \neq Ni (II) and exchange reactions [12]. The efficiency of Et₃Al₂Cl₃ as the activator is apparently related to the optimal ratio of reducing and acid properties of this compound for the given nickel complex. TABLE 2. Effect of the Nature of the Organoaluminum Activator on the Activity of Ct-1 in the Isomerization of 1-Hexene at 20°C in Heptane Solvent, $([Ni]=0.00212 \text{ mole/liter}, [1-hexene]_0=0.095 \text{ mole/}$ liter)



Fig. 3. Effect of the support on the activity and stabilization of Ni $(CO)_2$ · $(PPh_3)_2$ activated by $Et_3Al_2Cl_3$: 1) Ct-1, 2) Ni $(CO)_2(PPh_3)_2$. [Ni]=2.12 mmoles/liter, Al/Ni=2, $[1-H]_0=0.38$ mole/liter.

Fig. 4. Temperature effect on the activity of $Ct-1-Et_3Al_2Cl_3$ in the isomerization of 1-H, $[1-H]_0=0.095$ mole/liter, [Ni]=0.09 mmoles, Al : Ni=2.



Fig. 5. Dependence of the conversion of α -olefins on their structure in the presence of Ct-1-Et₃Al₂Cl₃: 1) 1-hexane, 2) 4-methyl-1-pentene, 3) 1-heptene, 4) 2-methyl-1-pentene.

Fig. 6. Change in the composition of the reaction mixture during the isomerization of 1-hexene in the presence of the $Ct-1-Et_3Al_2Cl_3$ catalytic system: 1) 1-hexene, 2) trans-2-hexene, 3) cis-2-hexene, 4) 3-hexene (cis and trans).

Study of the temperature effect on the rate of 1-H isomerization revealed a relatively narrow range for Ct-1 activity (Fig. 4). This is apparently related primarily to a change in the ratio of the rates of formation and decomposition of the active species in the range studied from -20° to $+50^{\circ}$ C.

Since the effect of temperature and of the amount and nature of the organoaluminum compound is qualitatively analogous to most homogeneous Ziegler – Natta systems, we may presume similarity in the mechanism for the catalytic isomerization of α -olefins. The effects of the structure and chain lengths of the olefins on their reactivity are in accord with this hypothesis. In particular, in the presence of Ct-1, behavior typical of homogeneous coordination isomerization was found, in which the olefin reactivity is determined, as a rule, by steric hindrance to coordination. Normal olefins with a terminal double bond isomerize with the greatest rate and 1-hexene isomerizes more rapidly than 1-heptane. The isomerization rate for 4-methyl-1-pentene is practically the same as for 1-hexene (Fig. 5). However, the alkene reactivity decreases with increasing number of alkyl groups at the unsaturated carbon atoms. This is clearly evident by comparison of the isomerization data for 4- and 2-methyl-1-pentenes and the rates of the transformations of 1-H to 2-hexene and of 2hexene to 3-hexene, respectively (see Fig. 6).

Analysis of the isomerization data for 1-H (see Table 1) and 2-H shows that the cis-2-H/trans-2-H ratio for Ct-1 is one-half that for the homogeneous system and, in both cases, it is significantly greater than the thermodynamic equilibrium value (~0.30) [13]. This finding indicates the effect of the support in Ct-1 on this reaction. A similar effect was seen previously for the isomerization of 1-heptene on supported palladium salts [13]. The kinetic curves given in Fig. 6 which characterize the change in the composition of the reaction mixture over time indicate that the major source of 3-H is cis-2-H formed in the conversion of 1-H to a mixture of isomeric 2-H.

These results, especially the data on the effect of the structure of the starting olefin on the isomerization rate, are in good accord with the hydride mechanism for double bond migration usually accepted for homogeneous systems. The π -complexation of the substrate with the coordinatively unsaturated nickel hydride complex, the conversion of the π -complex to a σ -complex, and the subsequent elimination of hydrogen from the carbon atom are crucial for this mechanism. An increase in steric hindrance and decrease in thermodynamic stability of the π -complex formed [13] give the following series for reactivity: 1-hexene \approx 4-M-1-P > 1-hep-tene \approx cis-2-hexene > trans-2-hexene \approx 2-M-1-P.

Thus, in addition to the olefin double bond migration features, which are common with homogeneous analogs such as the effect of the Al : Ni ratio, amount and nature of the organoaluminum compound, ligand environment of nickel, and structure of the starting olefin on the reaction rate, several specific features are found for heterogenized complexes due to the effect of the support.

CONCLUSIONS

1. The reactivity of hydrocarbons in the presence of dicarbonyl-bis(triphenylphosphine)nickel (0) heterogenized on Al_2O_3 decreases in the order: 1-hexene \approx 4-methyl-1-pentene > 1-heptene > 2-methyl-1-pentene.

2. The Ni (CO)₂ (PPh₃)₂/Al₂O₃ – $Et_3Al_2Cl_3$ catalytic system displays high isomerization activity in a relatively narrow temperature range.

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