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CATALYSIS

Isomerization of Alkenes in the Presence of $Pd(acac)_2$–BF_3OEt_2 Catalytic System

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Abstract—Positional isomerization of alkenes was studied in the presence of $Pd(acac)_2$ + $20BF_3OEt_2$ catalytic system. The reactivity of alkenes decreases in the following order: 1-hexene > 1-heptene > 2-methyl-1-pentene > 4-methyl-2-pentene (*cis* + *trans*).

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Systems containing bis(acetylacetonato)palladium $Pd(acac)_2$ and trifluoroboron etherate are efficient catalysts of dimerization of vinylaromatic hydrocarbons, e.g., selective dimerization of styrene [1, 2], telomerization of diene hydrocarbons with secondary amines [3, 4], and di- and oligomerization of ethylene and propylene [5–7]. These systems exhibit relatively high catalytic activity in positional isomerization of 1-hexene [8]. Isomerization of alkenes in the presence of Pd(II) complexes as catalysts has been extensively studied. Different isomerization mechanisms were proposed. The following processes are believed to be key steps of isomerization: (a) oxidative addition of alkene to Pd(II) to form allylpalladium(IV) hydride [9], (b) formation of carbenium ion by reaction of Pd(II) with alkene coordinated to the transition metal [10], (c) reversible addition of olefin to Pd(II) hydrides without a change in the Pd oxidation state [11]. Akenes like 1-hexene play a critical role in formation of Pd–H bonds in reactive complexes (RC) formed in the presence of $Pd(acac)_2$–BF_3OEt_2 catalytic system. Probably, the composition of these square-planar complexes is $HPd(L,L')BF_4$, where L is unsaturated hydrocarbon and L' = L or PR_3 [12].

Here we experimentally studied isomerization of alkenes in the presence of $Pd(acac)_2$–BF_3OEt_2 catalytic system, as influenced by various factors including the composition of the catalyst, preparation conditions of RC, and the solvent. With the positional isomerization of alkenes as an example, we intended to gain insight into the mechanism of transformation of unsaturated hydrocarbons including alkenes and vinylaromatic and diene hydrocarbons in the presence of bis(acetylacetonato)palladium–boron trifluoride etherate catalytic system.

EXPERIMENTAL

Isomerization of alkenes was performed under argon in a glass reactor equipped with a magnetic stirrer. A solution of appropriate alkene and $Pd(acac)_2$ was allowed to stand at 10°C for 15 min. The isomerization was initiated by addition of BF_3OEt_2. An aliquot (1 ml) of the reaction mixture was taken at regular intervals and placed into a test tube containing 3% aqueous hydrochloric acid to decompose the catalyst. The organic layer was separated and dried over calcium chloride. The isomerization products in the sample were analyzed by gas–liquid chromatography (GLC) on Tsvet-100M and Chrom-42M chromatographs equipped with a flame-ionization detector and a 100-m copper column with an internal diameter of 0.5 mm. We used vacuum oil as the stationary phase. The inlet pressure of the carrier gas was 0.6×10^5 Pa. The column temperature was 45°C.

Synthesis of $Pd(acac)_2$. To a solution of KOH (0.7310 g, 13.028×10^{-3} mol) in 15 ml of H_2O in a beaker was added acacH (1.2423 g, 12.408×10^{-3} mol). The mixture was heated at 45 ± 5°C. A transparent solution of acacK was obtained.

To an aqueous solution (50 ml) of KCl (0.8830 g, 11.844×10^{-3} mol) in another beaker was added $PdCl_2$ (1.0000 g, 5.64×10^{-3} mol). The mixture was heated at 45 ± 5°C with stirring until the brown precipitate completely dissolved to form a brown solution. The solution was filtered while hot.

The solutions were mixed at 45 ± 5°C. The yellow precipitate was filtered off on a Büchner funnel, washed 5–7 times with 100-ml portions of H_2O, and dried at 50°C. $Pd(acac)_2$ was recrystallized from ace-

Table 1. Time dependence of the composition of 1-hexene isomerization products formed in benzene in the presence of $Pd(acac)_2$ + $20BF_3OEt_2$ catalytic system prepared and kept under Ar without the substrate for 30 min. 283 K, $c_{Pd} = 1.47 \times 10^{-3}$ M, $c_{1\text{-hexene}} = 0.941$ M

Time, min	Composition of isomerization products, wt %			
	1-hexene	2-hexene (*trans*)	2-hexene (*cis*)	3-hexene (*cis* + *trans*)
1	91.6	7.9	0.5	–
2	78.8	20.9	0.5	–
3	42.6	54.2	3.2	–
5	–	94.5	5.5	–
8	–	79.3	12.4	8.3
15	–	78.7	8.5	12.8

tone by heating on a water bath. The precipitate was filtered off on a Büchner funnel and dried at 50°C (P = 10 mm Hg). Yield 83%.

Found (%): Pd 34.85, C 39.49, H 4.59.
$Pd(acac)_2$.
Calculated (%): Pd 34.87, C 39.47, H 4.61.

The solvents were treated by the standard procedures used in oranometallic chemistry [13].

The kinetic curves of 1-hexene isomerization in the presence of $Pd(acac)_2$ + $20BF_3OEt_2$ catalytic system are shown in Fig. 1. Curves *2* and *3* corresponding to fractions of *trans*-2-hexene and *cis*-1-hexene, respectively, do not pass through the origin when extrapolated. This can be due to a short induction period of the first step of 1-hexene isomerization, when 1-hexene is involved in formation of catalytically active palladium complexes. Under the experimental conditions (Fig. 1), the 1-hexene conversion into the isomerization products in 10–12 min is more than 15000 mol per mole of $Pd(acac)_2$. The major isomerization product (up to 62%) is *trans*-2-hexene.

When $Pd(acac)_2$ and BF_3OEt_2 react for 30 min in the absence of 1-hexene, i.e., when the conditions of formation of AC change, the rate of 1-hexene isomerization decreases by a factor of approximately 3. However, in this case the selectivity of isomerization into *trans*-2-hexene increases to 94.7% (Table 1).

The study of kinetic features of 1-hexene isomerization in the presence of $Pd(acac)_2$ + $20BF_3OEt_2$ system [8] showed that this process is of the first and zero order with respect to the catalysts and 1-hexene, respectively.

In the presence of PPh_3 (P/Pd = 1), the reaction is of the first and third order with respect to 1-hexene and the catalyst, respectively. Introduction of trivalent phosphorus compounds into the $Pd(acac)_2$ + $20BF_3OEt_2$ catalytic system decelerates isomerization

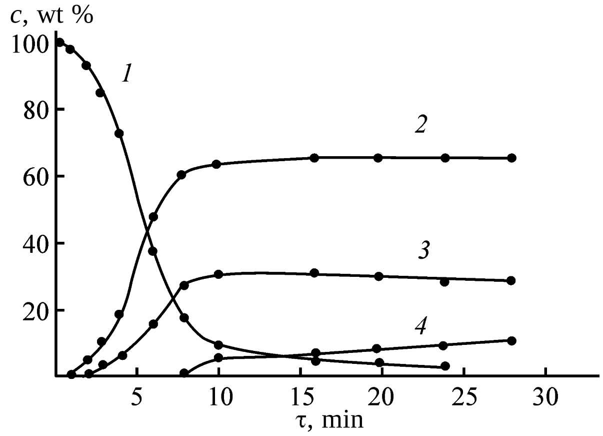

Fig. 1. Composition of 1-hexene isomerization products formed in benzene in the presence of $Pd(acac)_2$ + $20BF_3OEt_2$ at 293 K as a function of time τ: (*1*) 1-hexene, (*2*) *trans*-2-hexene, (*3*) *cis*-2-hexene, and (*4*) 3-hexene. $c_{Pd} = 2.74 \times 10^{-3}$ M, $c_{1\text{-hexene}} = 4.113$ M.

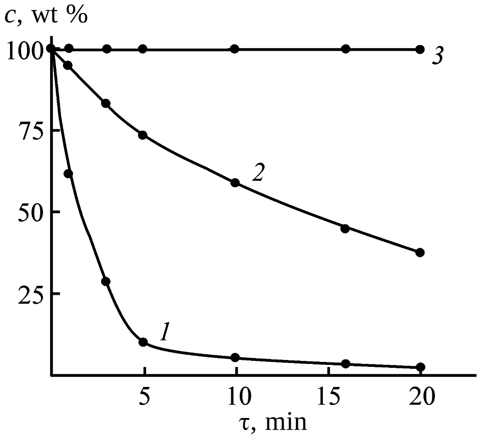

Fig. 2. Concentration of 1-hexene in benzene at 288 K in the presence of $Pd(acac)_2$ + PPh_3 + $20BF_3OEt_2$ catalytic system as a function of time τ. P/Pd: (*1*) 1, (*2*) 1.5, and (*3*) 2. $c_{Pd} = 1.47 \times 10^{-3}$ M, $c_{1\text{-hexene}} = 0.941$ M.

Table 2. Composition of the products of 1-hexene isomerization performed for 10 min in the presence of $Pd(acac)_2$ + $20BF_3OEt_2$ catalytic system containing different phosphines PR_3

Time, min	Composition of isomerization products, wt %			
	1-hexene	2-hexene (*trans*)	2-hexene (*cis*)	3-hexene (*cis* + *trans*)
PPh_3	–	60.8	29.3	9.9
$P(n\text{-}Bu)_3$	–	55.6	34.3	10.1
$P(Cy)_3$	–	53.5	33.7	12.8

Table 3. Composition of the products of 1-hexene isomerization in the presence of $Pd(acac)_2$ + PPh_3 + $20BF_3OEt_2$ catalytic system at different reaction times and different initial concentration of 1-hexene

Time, min	Composition of isomerization products, wt %							
	1-hexene		2-hexene (*trans*)		2-hexene (*cis*)		3-hexene (*cis* + *trans*)	
	1*	2*	1	2	1	2	1	2
1	93.0	100.0	7.0	–	–	–	–	–
2	68.5	78.2	20.5	16.5	11.0	5.3	–	–
3	53.0	75.4	28.8	19.3	18.2	5.3	–	–
5	36.9	47.4	44.1	26.2	19.0	26.4	–	–
10	12.7	16.6	61.4	42.6	22.6	37.4	3.4	–
20	–	–	69.1	48.2	24.4	44.4	6.5	7.4

* $c_{1\text{-hexene}}$: (*1*) 1.89 and (*2*) 0.236 M.

of 1-hexene. The palladium catalyst is completely deactivated when the P/Pd atomic ratio increases to 2 (Fig. 2).

The structure type of trivalent phosphorous compounds has virtually no effect on the selectivity of 1-hexene isomerization (Table 2).

However, in the presence of PR_3, the ratio of *cis* and *trans* isomers of 2-hexene substantially depends on the initial concentration of 1-hexene (Table 3).

When the 1-hexene : palladium ratio changes from 1286 to 160, the ratio of *trans* and *cis* isomers of 2-hexene decreases approximately from 3 to 1.

The catalytic activity of the examined system strongly depends on the solvent. The catalytic activity increases with an increase in the polarity of the solvent in the following series: heptane + benzene (1 : 1 vol : vol) < benzene < toluene < isopropylbenzene. The catalytic activity of $Pd(acac)_2$ + PPh_3 + $20BF_3OEt_2$ system in isomerization of 1-hexene in toluene is slightly higher than that in more polar isopropylbenzene (Fig. 3). This can be due to competitive coordination of 1-hexene and the solvent to RC of palladium.

The isomerization rate decreases when the length of the hydrocarbon chain and the number of substituents at the double bond increase in the series 1-hexene, 1-heptene, 2-methyl-1-pentene, *cis* + *trans*-4-methyl-2-pentene (Fig. 4). This is typical for coordination isomerization of alkenes in the presence of transition metal complexes.

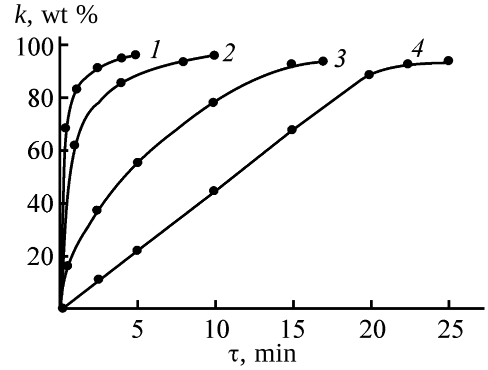

Fig. 3. Conversion of 1-hexene *k* into its isomers in the presence of $Pd(acac)_2$ + PPh_3 + $20BF_3OEt_2$ catalytic system at 283 K in (*1*) toluene, (*2*) isopropylbenzene, (*3*) benzene, and (*4*) benzene + heptane (1 : 1 vol/vol), $c_{Pd} = 1.47 \times 10^{-3}$ M, $c_{1\text{-hexene}} = 0.471$ M.

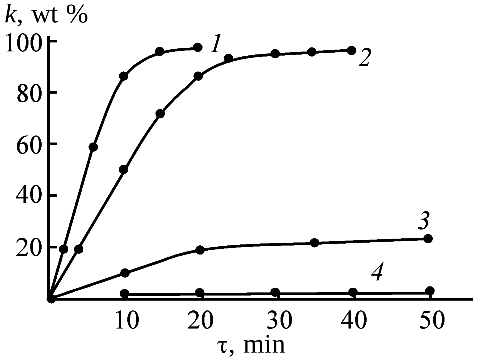

Fig. 4. Conversion *k* of (*1*) 1-hexene, (*2*) 1-heptene, (*3*) 2-methyl-1-pentene, and (*4*) *cis* + *trans*-4-methyl-2-pentene into their isomers in the presence of $Pd(acac)_2 + PPh_3 + 20BF_3OEt_2$ catalytic system at 283 K in benzene. $c_{Pd} = 1.47 \times 10^{-3}$ M, $c_{olefin} = 0.941$ M.

CONCLUSIONS

(1) The $Pd(acac)_2–BF_3OEt_2$ system shows high catalytic activity in positional isomerization of α-alkenes. The conversion of 1-hexene into the isomerization products under the optimal conditions (B/Pd = 20/1, $c_{Pd} = 1.47 \times 10^{-3}$ M, T = 293 K, benzene) within 10–12 min is 15000 mol g-at.$^{-1}$ of Pd. The *trans*-2-hexene content in the isomerization products is up to 62 %.

(2) The catalytic activity of the system decreases when its components are allowed to react with each other for 30 min in the absence of 1-hexene. In this case, however, the selectivity of 1-hexene isomerization into *trans*-2-hexene can be as high as 94.5%.

(3) In the presence of trivalent phosphorus compounds, the rate of α-alkene isomerization decreases, reaching zero value for 1-hexene at P/Pd = 2. The inhibiting effect can be due to blocking of the coordination vacancies of Pd in the RC. The BF_4 ligand should occupy the fourth coordination site in the AC to form $Pd–F \cdot BF_3$ bond. The composition of the resulting charge-transfer complex is $HPd(L_2)FBF_3$, where L is alkene.

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