Reduction of Ethyl Bromide by Triethylgermane in the Presence of Di(tert-butyl)mercury. A sample of 2.2 g EtBr was mixed with 3.2 g Et_3GeH at 20°C. Gas—liquid chromatographic analysis indicated that there is no reaction under these conditions. A reaction commences at 20°C upon the addition of 3.1 g $t\text{-}Bu_2Hg$ to the reaction mixture. Gas—liquid chromatographic analysis indicated that the sample of Et_3GeH was converted quantitatively into Et_3GeBr.

CONCLUSIONS

A radical chain mechanism was proposed for the reaction of triethylgermane with dialkylmercury compounds.

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CATALYTIC ACTIVITY OF PALLADIUM COMPLEXES SUPPORTED ON SILICA GELS MODIFIED BY TERTIARY AMINES AND QUATERNARY AMMONIUM BASES IN HYDROGENATION REACTIONS

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547.233.3+547.233.4

A palladium complex on silica gel modified by γ-aminopropyl groups catalyzes the hydrogenation of $C{=}C$, $C{\equiv}C$, and $C{=}N$ bonds [1], reduction of NO_2 groups [2], and the hydrohalogenation of thiophene derivatives [3]. We have studied the catalytic properties of new palladium complexes immobilized on the surface of silica gel modified by N-substituted aminomethyl and γ-aminopropyl groups in hydrogenation and the isomerization of allylbenzene (AB).

EXPERIMENTAL

The supports for catalysts C_I–C_{IV} (Table 1) were obtained by treatment of γ-chloropropyl-containing silica gel obtained according to Semikolenov et al. [4] with 15-20% benzene solutions of pyridine (C_I), triethylamine (C_{II}), diethylamine (C_{III}), and piperidine (C_{IV}) for 6-18 h at 80°C. The prepared supports were carefully washed with benzene to remove traces of the amine, dried at 100-100°C, and washed with aqueous ammonia until chloride was no longer detected in the washing. The supports for catalysts C_V and C_{VI} were prepared by treatment of silica gel with aminomethyl- and aminopropyltriethoxysilane with subsequent condensation of the surface amino groups with chloroacetic acid. After washing with water to remove HCL and excess modifier, the samples were dried at 120°C.

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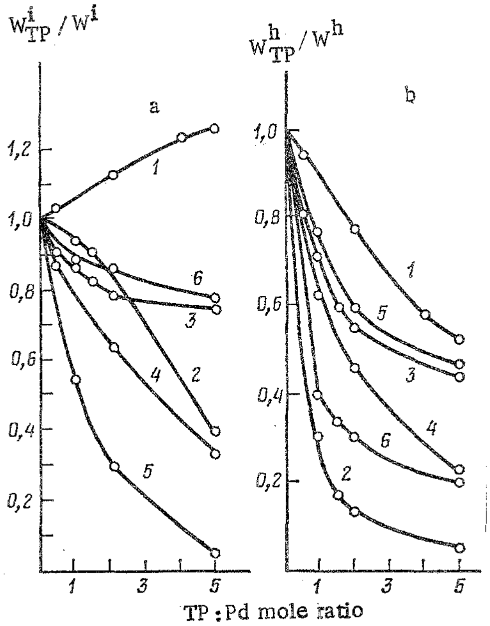


Fig. 1. Effect of added thiophene on the hydrogenation (a) and isomerization (b) of allylbenzene. The number on the curves corresponds to the catalyst indices (See Table 1).

The catalysts, which were chloride complexes of Pd on supports I-VII, were obtained by treatment of these supports with a methanolic solution of $NaPdCl_4$ (1.45 mole/liter) [1]. The catalytic experiments were carried out at 1 atm H_2 at 20°C in a long-necked hydrogenation flask by our previous procedure [1]. The reactions were run with 0.003 mole AB, 0.05 g catalyst, 0.02 g $NaBH_4$, and 20 ml methanol. The hydrogenation of o-nitrochlorobenzene (o-NCB) taken in portions of 0.001 mole was carried out analogously.

The products of the hydrogenation of AB were analyzed on a Biokhrom-21 chromatograph with a 55-m glass capillary column packed with OV-101 at 80°C. The products of the reduction of o-NCB were analyzed on an LKhM-8MD chromatograph with flame ionization detector, nitrogen gas carrier on a 1 m × 3 mm stainless steel column packed with SE-30 on Chromosorb W at 100°C.

The catalyst activity was characterized as the specific initial transformation rate of AB (W, mole/liter•min•mole Pd) in the hydrogenation to give propylbenzene (W^h) and in the isomerization to cis- and trans-propenylbenzenes (W^i) and was determined graphically. The effect of the presence of thiophene (TP) on the course of the reaction was given by the W_{TP}/W ratio, where W_{TP} is the specific initial rate of the reactions in the presence of TP.

RESULTS AND DISCUSSION

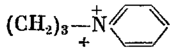
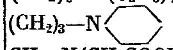
The data in Table 1 indicate that the supported complexes with mono- and bidentate ligands (catalysts C_I-C_{VI}) have high activity in the hydrogenation and isomerization of AB. The specific initial rate for the conversion of AB on C_I-C_V is lower than on the previously studied complex, C_{VII}. However, catalysts C_I and C_{II} displayed somewhat higher activity in hydrogenation than C_{VII}. The activity of the metal complexes with monodentate ligands in the conversion of AB decreases in the series: $C_{II} > C_I > C_{IV} > C_{III}$.

The greatest activity among the complexes with bidentate ligands is found for the palladium complex on silica gel modified by γ-propylaminediacetate groups (C_{VI}): $W = W^h + W^i =$ 400 moles/liter•min•mole Pd.

The ratio of the rates of AB isomerization and hydrogenation (W^i/W^h) ranged from 0.28 for C_I to 0.94 for C_{VI}. This ratio is 2.5 for the palladium complex with aminopropyl groups.

The catalytic activity and stability in the hydrogenation of olefins of palladium benzonitrile complexes increases upon treatment with TP [5]. Experiments on the effect of TP on the rate and direction of AB transformation showed that the action of TP even for TP/Pd = 1.5:1 produces a decrease in the activity of catalysts C_I-C_{VI} relative to double bond hydrogenation (Fig. 1). In the presence of large amounts of TP, the hydrogenation rate varies only slightly. The deactivating effect of TP depends on the nature of the complex and falls off in the following series: $C_{II} > C_{VI} > C_{III} > C_V > C_I$.

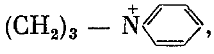
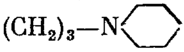
TABLE 1. Catalytic Activity of Palladium Complexes on Modified Silica Gel in the Hydrogenation and Isomerization of Allylbenzene

Catalyst	Modifying group	Pd content, mass %	Initial rate, moles/liter·min·mole Pd		W^i/W^h
			isomerization W^i	hydrogenation W^h	
C_I		2	200	700	0,28
C_{II}	$(CH_2)_3-\overset{+}{N}(C_2H_5)_3$	0,3	335	625	0,54
C_{III}	$(CH_2)_3-N(C_2H_5)_2$	0,8	220	170	1,29
C_{IV}		0,3	260	290	0,90
C_V	$CH_2-N(CH_2COOH)_2$	0,6	240	365	0,66
C_{VI}	$(CH_2)_3-N(CH_2COOH)_2$	1,2	2675	1380	1,94
C_{VII}	$(CH_2)_3-NH_2$	3,0	1510	595	2,54

Somewhat different behavior is noted for double bond displacement. The isomerizing activity of catalysts C_{IV} and C_V decreases significantly in the presence of TP. For example, W^i on catalyst C_V is reduced by a factor of about 30 for PT/Pd = 5:1. On the other hand, the effect of TP on the rate of AB isomerization is only slight on catalysts C_{III} and C_{VI}, while the catalyst activity is somewhat enhanced in the case of C_I. The observed effect of TP on the rate and direction of AB transformation is apparently due to partial bonding of Pd in a complex with TP, leading to a reduction in its capacity to activate H_2 and, thus, to an inhibition of hydrogenation.

We studied the reduction of o-NCB in order to clarify the nature of the catalysts prepared. The reaction proceeds in the presence of C_I–C_{VI} (in the absence of an HCl acceptor) only through the formation of nitrobenzene. Chloroaniline was not detected in the reaction medium. These findings indicate that our catalytic systems are metal complexes [3, 6].

CONCLUSIONS

1. Palladium complexes supported on silica gel modified by , $(CH_2)_3-\overset{+}{N}(C_2H_5)_3$, $(CH_2)_3-N(C_2H_5)_2$, , $(CH_2)_3-N(CH_2COOH)_2$, and $CH_2-N(CH_2COOH)_2$ groups catalyze the hydrogen and isomerization of the double bond in allylbenzene.

2. Going from a monodentate ligand to completely substituted ligands leads to a decrease in the activity of the palladium complexes supported on silica gel.

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