CATALYTIC HYDROGENATION OF DISUBSTITUTED BENZENES AND CONFIGURATIONAL ISOMERIZATION OF CORRESPONDING CYCLOHEXANES

COMMUNICATION 1. STEREOSELECTIVITY OF HYDROGENATION OF ISOMERIC ALKYLANILINES ON Ru–C AND Rh–C CATALYSTS UNDER PRESSURE

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The stereochemistry of the reaction for the reduction of disubstituted benzenes was studied mainly on the example of xylenes, phthalic acid derivatives and diamines [1,2]. The hydrogenation of benzene derivatives with two different substituents was studied to a lesser degree [3,4]. In the present paper we studied the rate and the stereoselectivity of the reaction for the hydrogenation of the isomeric toluidines and ethylanilines as functions of their structure and the process conditions.

EXPERIMENTAL METHOD

The hydrogenation was run under static conditions at constant pressure. The pressure was maintained with an accuracy of ± 1%, and the temperature with an accuracy of ± 1°. The rate of the process was judged by the H_2 absorption, which was recorded automatically.

A 100-ml stainless steel autoclave served as the reactor, which was equipped with a stirrer (2600 rpm), a manometer, and valves for purging the system and for taking samples during reaction.

The 5% catalysts were prepared as follows: the Ru–C catalyst by deposition (from aqueous solution) of the salt $Ru(OH)Cl_3$, while the Rh–C catalyst was prepared by the deposition of $RhCl_3$ on OUB active carbon (granule size 0.05-0.1 mm^3) and subsequent reduction with hydrogen at 250-300°C for 3 h. For reaction we took 5 g of the alkylaniline and 0.75 g of catalyst, while the volume of the solution was 50 ml.

Based on the GLC data, the purity of the starting toluidines and ethylanilines was 98-99%. The composition of the catalyzates was determined by GLC. Here we used and 8 m × 2 mm column that was filled with 10% Silicone DS-710 deposited on Celite 545, a katharometer as the detector, helium as the carrier gas, and a temperature of 90-120° [5].

TABLE 1. Initial Hydrogenation Rate of Toluidines (M/liter · min · 10^{-4}) on Rhodium and Ruthenium Catalysts (Temperature 85°C, 80 atm)

Solvent	Ru—C			Rh—C		
	p-toluidine	o-toluidine	m-toluidine	p-toluidine	o-toluidine	m-toluidine
Ethanol	100	68	58	62	32	23
Ethanol – 15% CH_3COOH (1 : 1)	146	120	68	185	—	151
Ethanol – diethylamine	23	8	12	—	—	—
Cyclohexane	33	21	18	23	23	18

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TABLE 2. Amount of cis-Isomer (in mixture of isomers) in Catalyzate during the Hydrogenation of p-Toluidine on Ruthenium Catalyst in Ethanol

T., °C	cis-Isomer, %	Pressure, atm	cis-Isomer, %	dV/dt·10^{-4}, M/liter·min
at a constant pressure of 80 atm		at a constant temperature of 85°		
42	74	20	71	25
60	74	50	73	65
70	74	80	73	100
85	73	100	72	120
93	73	120	71	137

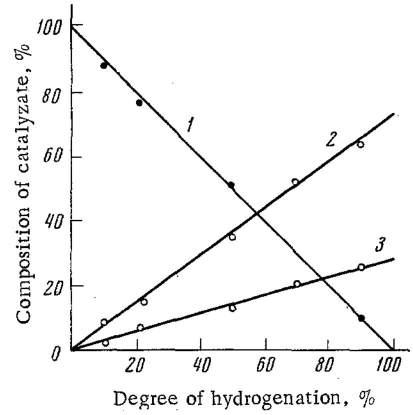

Fig. 1. Hydrogenation of p-toluidine on Ru–C catalyst in ethanol at 85° and 80 atm: 1) p-toluidine; 2) cis-1, 4-methylcyclohexylamine; 3) trans-1, 4-methylcyclohexylamine.

DISCUSSION OF EXPERIMENTAL RESULTS

The principal characteristics of the progress of the process and the effect of the conditions were studied on the example of the hydrogenation of p-toluidine in the presence of ruthenium. Under the selected conditions the hydrogenation proceeds in the kinetic region: when the speed of the stirrer is increased from 2000 to 2600 rpm the reaction rate remains constant and increases linearly with increase in the amount of catalyst.

The reaction is zero order in the compound being hydrogenated: the initial rate of H_2 absorption is independent of the p-toluidine concentration in solution (in the range 0.18-1.0 M/liter). Some of the p-toluidine is apparently caused by a partial poisoning of the catalyst. This is in agreement with the fact that the initial rate of hydrogen absorption decreased when several portions of the toluidine were hydrogenated in succession on the same catalyst sample. The initial reaction rate increased linearly from 26 × 10^{-4} to 100 × 10^{-4} M/liter · min when the hydrogen pressure was increased from 20 to 80 atm (gauge atmosphere).

A change in the composition of the solvent leads to a change in the initial rate of the process. The addition of CH_3COOH to alcohol accelerates the reaction, while the addition of either diethylamine or alkali to the solution retards the reaction. The addition of hydrochloric acid lowered the reaction rate, probably due to poisoning of the catalyst by chloride ion. The reduction proceeded most slowly in cyclohexane medium. On both catalysts and in all of the solvents the hydrogenation rate of the isomeric toluidines decreases in the order: $p \geq o > m$ (Table 1). This order is not observed only for the ethanol–diethylamine system.

An analysis of the composition of the catalyzate in the experiments where samples were removed reveals that when the hydrogenation is run in alcohol solution the ratio of the geometric isomers of the formed

TABLE 3. Amount (%) of cis-Isomer of Alkylcyclohexylamine (in mixture of isomers) during the Hydrogenation of Alkylanilines (Degree of conversion = 60-70%) on Rhodium and Ruthenium Catalysts (Temperature 86°, 80 atm)

Solvent	Hydrogenated alkylanilines									
	Ru—C					Rh—C				
	o-toluidine	m-toluidine	p-toluidine	o-ethylaniline	p-ethylaniline	o-toluidine	m-toluidine	p-toluidine	o-ethylaniline	p-ethylaniline
Ethanol	73	73	73	71	68	77	69	76	76	68
Ethanol – 15% CH_3COOH	83	76	75	77	68	79	69	76	75	70
Ethanol – diethylamine (1:1)	67	71	67	—	62	72	61	73	—	—
Cyclohexane	69	75	67	69	67	76	65	76	64	74

methylcyclohexylamines is retained constant until the starting toluidine is converted completely (Fig. 1). From this it follows that under the selected conditions the secondary process for the conversion of the formed cis-isomer to the trans-form fails to take place, and the observed ratio of the isomers in the catalyzate is determined by the direction of the primary hydrogenation reaction.

It is known that the trans-isomers (e, e) should be more stable in the series of the 1,2- and 1,4-disubstituted cyclohexanes, while the cis-isomers should be more stable in the case of the 1,3-disubstituted derivatives. As can be seen from the obtained results, the composition of the formed isomers is not related to their thermodynamic stability, and apparently is determined by the orientation of the substituents relative to the surface of the catalyst during the adsorption of the alkylanilines.

As was shown for the Ru catalyst (Table 2), the ratio of the formed isomers of the cis- and trans-1, 4-methylcyclohexylamines is independent of the pressure (in the range 20-120 atm) and the temperature (42-93°). The ratio in the formation rates of the cis- and trans-isomers of 1,4-methylcyclohexylamine is only slightly dependent on the composition of the solvent. However, it can be mentioned that the maximum yield of the cis-isomer (75%) is observed in the same solvent ($C_2H_5OH-CH_3COOH$) in which the reaction proceeds at the fastest rate, while the minimum yield (67%) was obtained in either the alcohol–diethylamine solvent or in cyclohexane, in which solvents the hydrogenation rate is slowest.

Analogous results were obtained when the other isomeric methyl- and ethylanilines were hydrogenated on the Ru–C and Rh–C catalysts in different solvents (Table 3). A somewhat higher yield of the alkylcyclohexylamines is obtained in an alcohol medium containing CH_3COOH. On both catalysts the amount of the cis-isomer in the mixture of isomers is practically independent of the position of the alkyl substituent in the aromatic ring. In contrast to this, when the xylenes are hydrogenated on PtO_2, Pt/C or Pd/C catalysts the formation of the cis-dimethylcyclohexanes decreases in the order: $o > m > p$ [6].

CONCLUSIONS

1. The initial hydrogenation rate of the methyl- and ethylanilines on Ru–C catalyst is independent of the concentration of the hydrogenated compound and increases linearly with increase in the hydrogen pressure in the range 20-80 atm.

2. The hydrogenation rate of the isomeric toluidines in ethanol on Ru–C and Rh–C catalysts decreases in the order: $p \geq o > m$. The reaction is accelerated when acids are added and is retarded in alkaline solutions.

3. The cis-isomer of the alkylcyclohexylamine is formed predominantly on both Ru–C and Rh–C catalysts. The ratio of the cis–trans isomers (during hydrogenation on Ru–C) is independent of the pressure (20-120 atm) and the temperature (42-93°).

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