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EFFECT OF THE HYDROGEN PRESSURE ON THE KINETICS OF THE LIQUID-PHASE CATALYTIC HYDROGENATION OF AROMATIC NITRO COMPOUNDS

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The published work on liquid-phase hydrogenation at elevated pressures [1-3] has been largely concerned with a determination of the conditions required for obtaining high yields of amino products. There has been essentially no study of the variation of the initial, intermediate, and final products in the course of reaction, attention being directed to the effect on pressure on the rate of uptake of hydrogen and the composition of the products present in the system at various times after initiation of the reaction.

It has been reported [2] that the rate of the hydrogenation reaction increases linearly with an increase in the pressure, but only up to a certain point, beyond which the reaction rate is determined by the nature of the compound being hydrogenated, the nature of the solvent and catalyst, and the working temperature.

The present work was a study of the variation of the initial, intermediate, and final products resulting from the catalytic, liquid-phase hydrogenation of p-chloronitrobenzene (PCNB) at various hydrogen pressures. PCNB was chosen for this work because the kinetics of its hydrogenation have already been described in considerable detail [3-6].

Figure 1 shows the variation of the concentration of the original nitro compound during hydrogenation on a 5% iridium catalyst supported on activated carbon under hydrogen pressures ranging from 0.1 to 0.9 MPa. It can be seen that the hydrogenation of PCNB was a first-order process in the nitro compound, with the apparent rate constant for the process varying linearly with the hydrogen pressure.

Figure 2 shows the variation of the system content of the p-chlorophenylhydroxylamine (PCPhHA) intermediate during hydrogenation at various hydrogen pressures.

In the initial stages of the reaction, the PCPhHA content of the system increased in direct proportion to the partial pressure of the hydrogen, both of the rate constants, the one for PCNB and the other for PCPhHA, being linear functions of the pressure. Once the nitro compound had been completely consumed, the concentration of PCPhHA in the system was no longer affected by a change in the pressure. These observations were consistent with the mechanism of PCPhHA catalytic disproportionation proposed in [5], but not with the scheme of PCPhHA reduction given in [7]. This indicated that a high yield of intermediates might be

TABLE 1. Variation of the PCPhHA Yield with the Conditions of Hydrogenation

Catalyst	T., °C	Pressure, MPa	Maximum PCPhHA content of the reacting system, %	Yield of PCPhHA, relative to PCNB consumed, %
Ir/C (IKhF-5)	20	0.1	77.9	79.9
	20	0.3	80.2	81.6
	20	0.5	85.7	87.8
	20	0.7	87.6	88.5
	20	0.9	95.1	98.0
Pt/C (BPL-2.5)	20	0.1	12.4	13.6
	20	0.7	30.9	31.2
	-10	0.7	63.0	68.8

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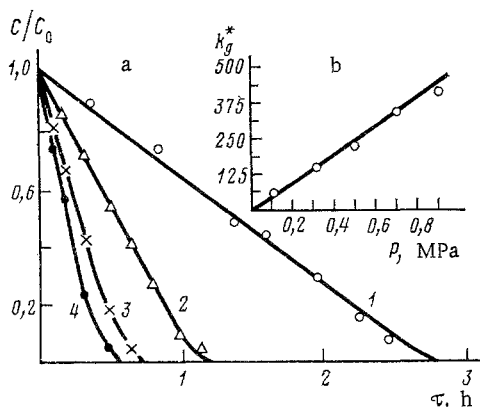


Fig. 1

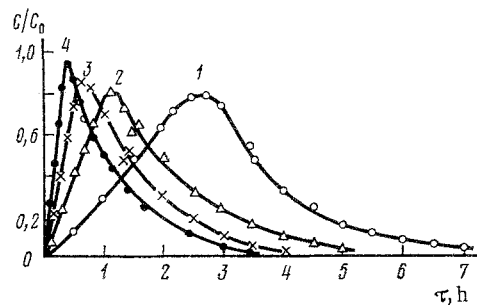


Fig. 2

Fig. 1. The alteration in the relative PCNB content in the course of hydrogenation on an iridium catalyst (a), and the apparent rate constant for hydrogenation, k_g^* , mole/kg·h (b), at the following hydrogen pressures (MPa): 1) 0.1; 2) 0.3; 3) 0.5; 4) 0.5.

Fig. 2. The alteration of the PCPhHA content of the system during hydrogenation on an iridium catalyst at the following hydrogen pressures (MPa): 1) 0.1; 2) 0.3; 3) 0.5; 4) 0.9.

attained by so choosing the conditions that the rate of hydrogenation of the original nitro compound would be high, and the rate of disproportionation of the product phenylhydroxylamine low. Actually, increasing the hydrogen pressure increased the rate of PCPhHA formation without affecting the rate of PCPhHA disproportionation, thus increasing the product yield (Table 1).

The table also summarizes the results of experiments on the hydrogenation of PCNB on BPL-2.5, a catalyst which is highly active in disproportionation reactions. Here the yield of PCPhHA at 20°C and normal pressure was only 13.6%. The PCPhHA yield could be increased to 30.9% by raising the pressure from 0.1 to 0.7 MPa. Since the activation energy was higher for disproportionation than for hydrogenation [5], the yield of PCPhHA could be increased further to 68.8% by lowering the temperature to -10°C.

The content of the amino product in the reacting system altered with the change in the PCNB and PCPhHA concentrations, rising slowly at first, and then increasing quite rapidly once the nitro compound had been completely hydrogenated (Fig. 3). It can be seen from the figure that an increase in the hydrogen pressure increased the length of the period over which the initial hydrogenation rate was low, and this despite the fact that the rate of amino product formation was essentially independent of the pressure, both initially and after exhaustion of the nitro compound.

In order to increase the selectivity for formation of the intermediate aromatic amines in pure form it is well to carry out dehydration under conditions which will assume a high rate of disproportionation of the product phenylhydroxylamine.

EXPERIMENTAL

Experiments were carried out in a jacketed 0.2-liter Vishnevskii autoclave equipped with a stirrer operated at 1440 rpm. Preliminary work having shown that the rate of hydrogenation was not affected by alternation in the stirring rate above 980 rpm, or by varying the amount of catalyst from 0.2 to 2.5 g, it was concluded that component diffusion to the catalyst surface was not the limited step in the hydrogenation process.

The autoclave was loaded with 150 ml of isopropyl alcohol, 5 g of PCNB, and 0.6 g of either the iridium catalyst (IKhF-5, Technical Specification (TU) 6-02-7-44-74), or the platinum catalyst (BPL-2.5, TU 6-02-7-99-78), in the form of particles 80-200 μ m in diameter.

The hydrogen, an All-Union State Standard 3022-72 grade A material containing 99.7% of the basic component, was drawn from a tank. The PCNB, a pure grade, TU-MKhP 2189-49 product, had been twice recrystallized from isopropyl alcohol solution. The isopropyl alcohol was cp TU 6-09-402-75 grade material.

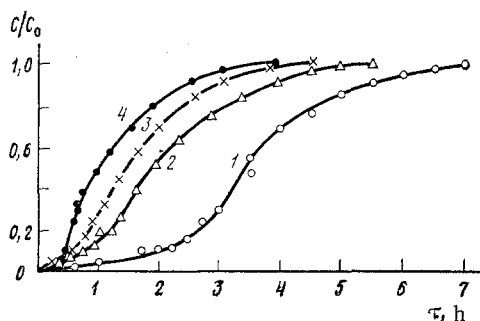


Fig. 3. The alteration in the p-chloroaniline content of the system during the hydrogenation of PCNB on an iridium catalyst at the following hydrogen pressures (MPa): 1) 0.1; 2) 0.3; 3) 0.5; 4) 0.9.

Samples removed from the system in the course of the reaction were analyzed for PCPhHA and p-chloroaniline by potentiometric titration with an 0.2 N NaNO_2 solution [5]. The content of unreacted PCNB remaining in the system was determined by gas-liquid chromatography, working with a Khrom-4 chromatograph equipped with a flame-ionization detector and a 2.5-m \times 3-mm column packed with a 15% solution of polyethylene glycol adipate on Chromaton, with He as the carrier gas.

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CONCLUSIONS

1. The relation between the rate of liquid-phase nitro compound hydrogenation and the hydrogen pressure is complex. Over the pressure range from 0.1 to 0.9 MPa, the concentration of the initial nitro product varies in direct proportion to the hydrogen pressure, and this despite the fact that the rate of conversion of the intermediate phenylhydroxylamine into the amino product is unaffected by an alteration in the pressure. This supports the suggestion that the catalytic hydrogenation of nitro compounds proceeds through disproportionation, rather than reduction, of the phenylhydroxylamines.

2. The possibility of increasing the selectivity of the hydrogenation reaction for p-chlorohydroxylamine formation is discussed, and it is shown that the yield of this product can be increased markedly by working at high pressure and low temperature.

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