

Mechanism of Formation of N-oxide Substituted Benzotriazols in the Reaction of Liquid Phase Catalytic Hydrogenation of 2-Nitro-2'-Hydroxy-5'-Methylazobenzene

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Abstract: the Kinetic of the liquid phase hydrogenation reaction of 2-nitro-2'-hydroxy-5' methylazobenzene on skeleton nickel in aliphatic alcohol with the addition of water and sodium hydroxide at different initial concentration of an original compound has been studied. It is established that one of the intermediate reaction products along with N-oxide 2-2'-hydroxy-5'-methylphenylbenzotriazol is 2-nitro-2'-hydroxy-5'-methylhydroazobenzene which in the presence of sodium hydroxide in the volume of the solution is cyclized into N-oxide. High selectivity on 2-2'-hydroxy-5'-methylphenylbenzotriazol can be achieved at high concentration of NAB-H₂ adsorption complexes and high cyclization of 2-nitro-2'-hydroxy-5'-methylhydroazobenzene into N-oxide 2-2'-hydroxy-5'-methylphenylbenzotriazol that is due to the presence of catalytic amount of sodium hydroxide in the volume of the solution.

Key words: Skeleton nickel, N-oxide, adsorption complex, cyclization

INTRODUCTION

It is known that the main intermediate reaction product of the liquid phase catalytic hydrogenation of 2-nitro-2'-hydroxy-5'-methylhydroazobenzene (NAB) is N-oxide 2-nitro-2'-hydroxy-5'-methylphenylbenzotriazol (NO)^[1-4].

Earlier in^[2-5] the mechanism of NAB hydrogenation which leads to the formation of NO due to the deoxidation of nitro group and formation of 2-nitro-2'-hydroxy-5'-methylazobenzene (NZ) was proposed. It was established experimentally^[3,4] that NZ is formed in small amount in the process of NAB with skeleton nickel only in the interaction absence of hydrogen on the surface of a catalyst. The formation of NZ during the interaction with NZ with skeleton nickel was proved by the qualitative reaction on hydrogenated samples with hydrochloric solution of resorcinol and data of I.R. spectrum of the product extracted from the surface of a catalyst. While keeping the sample of the hydrogenate containing NZ in the presence of sodium hydroxide at 333 K there was observed the increase of NO concentration with the rate equal $(1.5 \pm 0.5) \cdot 10^{-6}$ mole/s probably due to NZ cyclization of nitroazocompounds into N-oxide in the presence of base was underlined in^[7].

In the conditions of liquid phase NAB hydrogenation in the presence of absorbed hydrogen NZ is not observed in solution. It is connected with small probability of deoxidation in the conditions of hydrogenation^[6] thus it

cannot be the only source of NO formation another predecessor of NO formation as it was supposed in^[2,5] can be the adsorption complex NAB-H₂, but the question about the reaction groups of combining hydrogen and about the formation of products during the destruction of adsorption complex is not discussed. The aim of the research is to clear out the stoichiometric mechanism of NAB catalytic hydrogenation, evaluation of reasons which explain the effect of the solvent and initial concentration of an original reagent on the rate and the selectivity of the reaction in relation to NO and BT.

MATERIALS AND METHODS

To find the intermediate a complex study of Kinetic regularities of the reaction at the temperature equal 274 ± 0.5 K was done which made possible low rate of hydrogenation stages of the catalytic process.

NAB hydrogenation was carried out a static method in a thermostatic reactor with intensive mixing up a liquid phase. The rates of hydrogen adsorption were measured in the reaction according to known method^[8].

As the main kinetic characteristics of NAB hydrogenation reaction average values of the hydrogenation rates were used, the degree of NAB conversion being not more than 25% the time from the beginning of the reaction is 1 ± 2 min. The selectivity of the reaction for the substances containing, benzotriazole cycle was determined in terms of the total yield of NO and BT

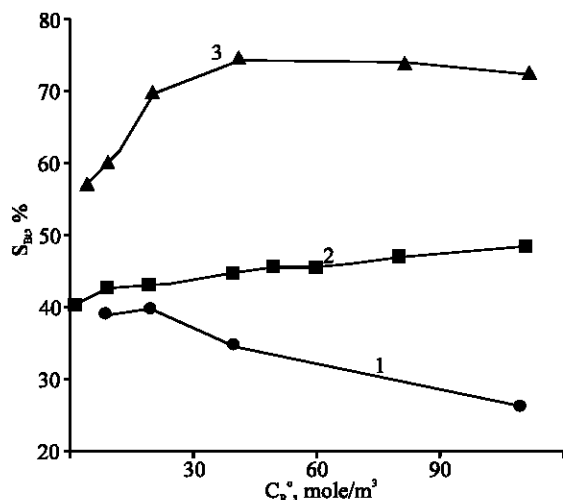


Fig. 1: The dependence of hydrogenation selectivity of NAB S_{BT} on a skeleton nickel in 2-propanol-1, binary solvent 2-propanol-water with $x_2 = 0.68$ -2 and in the same solvent with the addition of 0.012 M of sodium hydroxide-3 on the initial concentration NAB C_N^0 at 333 K and $P_{H_2} = 0.55$, $g_{cat} = 0.625$ g, the volume of the solvent = 100 cm³

List of abbreviation

NAB: 2-nitro-2'-hydroxy-5'-methylazobenzene

NZ: 2-nitrozo-2'-hydroxyl-5'-methylazobenzene

NO: N-Oxide 2, 2'-hydroxy-5'-methylphenylbenztriazol

BT: 2,2'-hydroxy-5'-methylphenylbenztriazol

NHB: 2-nitro-2'-hydroxy-5'-methylhydroazobenzene

mf: Molar fraction

g_{cat} : Weight of catalyst

P_{H_2} : Pressure of hydrogen

which was calculate from the mass of the products evolved from the reaction medium at PH=3.

A skeleton nickel obtained by leaching with 25% aqueous solution of sodium hydroxide nickel-aluminium alloy Ni : Al : Fe (46.3 : 53.6 : 0.1 mass % composition was used as a catalyst). An active catalyst has specific gravity equal 90 ± 5 m²/g Ni, porosity was 0.5^[9].

2-propanol as well as binary mixtures 2-propanol-water with 0.66 m.f. alcohol and 2-propanol-water with addition of 0.0125 M sodium hydroxide were used as solvents.

The qualitative analysis of the composition of the reaction mixture and the division of intermediate products of liquid phase hydrogenation NAB was carried out using thin layer chromatography according to the method^[10].

After dividing the mixture of the components in a thin layer adsorbents the chromatograph spots corresponding to the R_f values of single compounds were washed with calibrated volumes of 2-propanol and spectrophotometric analysis was done to determine the concentration of the intermediate products.

RESULTS AND DISCUSSION

In the research it was experimentally proved that during the catalytic hydrogenation of NAB along with NO with high rate another intermediate product which was identified as 2-nitro-2'-hydroxy-5'-methylhydroazobenzene (NHB) was formed which in the volume of NHB liquid phase can be cyclized NO^[11] the homogeneous cyclization of NHB and NO can proceed as result of the previous transfer of a proton from a hydroazogroup to a nitrogroup^[12]. Similar formation of NO seems to take place during the reduction cyclization of NAB by sulphur containing reagents in strongly alkaline media^[13]. As the carriers of a proton hydroxide ions and in their absence-water molecules but less effectively can be used^[12].

With the growth of initial NAB concentration the possibility of displacing intermediate NHB including is increased and the relationship of the rates of heterogeneous and homogeneous stages can be greatly changed. from this view point the data on the influence of NAB on BT yield should be considered^[14]. The effect of initial concentration of NAB on the yield of NO and BT in 2-propanol and its mixture with water and sodium hydroxide are given in Fig.1.

The data shown in Fig.1. prove that at low concentrations of NAB the yield of BT dose not exceed 35-40% in 2-propanol as well as in mixed solvents with the addition of water and sodium hydroxide when NAB in 2-propanol is increased (curve 3) the yield of BT is decreased and in 2-propanol-water solvent it is increased.(curve 2).

In aliphatic alcohols relatively high yield of BT is observed only at low initial concentration of NAB to 0.5×10^{-4} mole (curve 1) and further it is decreased. It can be due to the formation of adsorption complex NAB with hydrogen which at the moment of splitting out from it a water molecule even in a chemisorption layer is cyclized into NO with high rate. The adsorption complex-(NAB-H₂) can be formed as a result of a previous coordination of a molecule on nitrogen and oxygen molecule similarly to the complex considered in^[15,16] but in this case with simultaneous activation of azogroup of NAB molecule^[11].

Table 1: The effect of water and sodium hydroxide on the hydrogenation rate of NAB and the rate of homogeneous converting NHB into NO at 274±1K

| Solvent | Average rate of hydrogenation of NAB, 10 ⁷ , mole s ⁻¹ | The rate of converting NHB, 10 ⁷ , mole s ⁻¹ |
|-----------------------|--|--|
| 2-propanol | 10±1 | 0.045±0.005 |
| 2-propanol-water | 25±5 | 0.065±0.005 |
| 2-propanol-water-NaOH | 40±5 | 2.5±1 |

Table 2: The effect of a solvent on hydrogen adsorption heats of ΔH_{ads} by skeleton nickel in solvents: I-methanol ; II-methanol-water (0.78 ÷ 0.48 m.f. methanol); III-methanol-water-sodium hydroxide (0.78÷ 0.48 m.f. methanol, 0.0125 M of NaOH)

| Solvent | I | II | III |
|--|------|------|-------|
| - ΔH_{ads} , kJ.mole ⁻¹ | 60±5 | 70±5 | 90±10 |

Table 3: The effect of a solvent on accumulation rate of NO and NHB, the relations of the directions of associative and dissociative adsorption mechanism of NAB, the values of maximum yields of NO and NHB at 274± 1K

| Solvent | Accumulation rate, 10 ⁷ , mole s ⁻¹ | | | Maximum yield, % | |
|-----------------------|---|---------|----------|------------------|-----|
| | NO | NHB | ξ | NO | NHB |
| 2-propanol | 2.1±0.1 | 3±0.3 | 1 : 1.45 | 46 | 16 |
| 2-propanol-water | 5.5±0.5 | 2.5±0.5 | 1 : 1.45 | 65 | 10 |
| 2-propanol-water-NaOH | 17±2 | =0.1 | 1: 0.01 | 98 | > 2 |

Caption for the Figure of the article by Atef S. AL Zaydien
Mechanism of Forming N-Oxide Substituted Benztrizol in the Reaction of Liquid Phase Catalytic Hydrogenation of 2-nitro-2'-hydroxy-5'-methylazobenzene

The dissociative adsorption mechanism of NAB should be connected with adsorption of azogroup at the expense of donation transfer of a metal into azogroup and hydrogen attack on nitrogen atoms which result in the formation of NAB. This compound is intensively displaced into the solution by original NAB it confirmed by the result of thin layer chromatography. The rate of homogeneous cyclization of NHB into NO in neutral media is low (Table 1) thus with the increase of initial concentration of NAB in aliphatic alcohols the rate different of heterogeneous and homogeneous stages is increased and consequently the yield of NO and BT is decreased with the growth of initial concentration of NAB.

After the introduction of water into an aliphatic alcohol the decrease of NO and BT yield with the growth of initial concentration is retarded (curve 2). This fact is connected with the change of relationship of heterogeneous and homogeneous stages of the process and the increase of the rate homogeneous cyclization of NHB and NO (Table 1).

The significant growth of BT yield is observed in 2-propanol-water with the addition of sodium hydroxide.(curve 3) The yield with the increase of NAB concentration is connected with the fact that during the displacement of intermediate substance from the surface of a catalyst their cyclization in the volume of a solution

proceeded with high rate especially in the presence of sodium hydroxide^[12].

The researches carried out show that on adding water into the aliphatic alcohol increased two times and became comparable with rates of hydrogenation stage (Table 1).

Sharp increase of cyclization rate of NAB in the presence of sodium hydroxide into a binary solvent of 2-propanol-water can be connected with shifting the equilibrium to a tautomeric from NHB which is cyclized into NO with high rate, the ionization of molecules favours the increase of cyclization rate^[12].

It is known that introduction of sodium hydroxide into aqueous or aqueous alcohol solvent results in the increase of hydrogen adsorption forms which are characterized by greater values of adsorption of a catalyst adsorption heats. The data of the calorimetric studies given in Table-2 show that the heats of hydrogen adsorption increase while passing from pure alcohol solvents containing water the addition of sodium hydroxide.

And thus one can consider that in the presence of sodium hydroxide the conversion of NAB can proceed predominantly according to the adsorption of the bonds rearrangements rates in the adsorption complex and favours the formation of NO in a chemisorption layer as compared with NHB formation with rate while passing from pure aliphatic alcohol to mixed solvents. The appearance of NO must lead the accumulation of NHB in the volume of a solution. The effect of a solvent on hydrogen adsorption in methanol with the addition of water and sodium hydroxide were discussed in^[17].

Table 3 shows the rates of accumulation NO and NHB in the solvents under investigation. The evaluation of the contribution of different directions reflecting the direct conversion of NAB into NO and NHB- ξ has been done and the values of maximum yields of NO and NHB in the solvents under investigation were presented.

On the base of experimental data obtained one can give the following possible reasons of a solvent effect on the rate and selectivity of NAB hydrogenation. The solvent changes the relationship of directions resulting in the formation of an adsorption complex which quickly rearranges into NO and intermediate product of incomplete hydration of azogroup-NHB capable to be cyclized into NO but only in the presence of sodium hydroxide. High NO and BT yield in liquid phase catalytic hydrogenation of NAB can be achieved only in the case when NAB hydrogenation proceeds predominantly through the formation of an adsorption complex during the activation of both reaction groups and in the case when the components of a solvent are the catalysts of homogeneous cyclization stages of NHB and NO.

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