

SPeculiarities of the Kinetics of Hydrogenation Reaction of 2-nitro-2' Hydroxy-5'-methylazobenzene in Aliphatic Alcohols on Skeleton Nickel

Atef S. Alzaydien

Department of Chemistry, Mutah University, P. O. Box 7, Jordan

Abstract: The kinetic regularities of the reaction of liquid phase hydrogenation of 2-nitro-2'-hydroxy-5'-methylazobenzene on skeleton nickel in aliphatic alcohols have been studied. The study of the kinetics of hydrogenation reaction NAB was carried out by a static method in a thermostatic reactor with intensive stirring of a liquid phase at two different temperatures 275 ± 2 K and 303 K. The measurement of the rate of hydrogen absorption was done by volumetric method. The quantitative control of the main reaction products was carried out with the use of the following methods: spectrophotometry, polarography and thin layer chromatography. The effect of water and sodium hydroxide additions in solvent composition on the reaction selectivity with respect to the desired product 2,2'-hydroxy-5'-methylphenylbenzotriazole (BT) has been investigated. It is established that the main intermediate reaction products are 2,2'-hydroxy-5'-methylphenylbenzotriazole (NO) and a nitrohydroazoderivative which is cyclized homogeneously into NO. It is shown that homogeneous stages of the process play an important role in the selectivity of the reaction with respect to substituted benzotriazole.

Key words: Aliphatic alcohols · Skeleton nickel · Rate · N-oxide · BT · Selectivity · Cyclization

INTRODUCTION

It is well known that substituted benzotriazoles have high chemical affinity to the polymers and do not possess cancerogeneous properties [1-4]. 2H-benzotriazoles are used for photo-stabilization of polyethylene, polystyrene and for preparation of contact lenses and printed plates. The main method of obtaining benzotriazoles is the reduction of substituted 2-nitroazobenzenes which is carried out by chemical, electrochemical and catalytic methods [5-7]. For the production of 2,2'-hydroxy-5'-methylphenylbenzotriazole (BT) the 2-nitro-2'-hydroxy-5'-methylazobenzene (NAB) is used as a starting compound. Irrespective of the method of NAB reduction the reaction is characterized by the formation of a large number of side products which influence greatly the selectivity of the process with respect to the desired product - BT [7,8].

The kinetic investigations carried out and the literature data are supporting the fact that liquid phase hydrogenation of NAB proceeds according to the multi-route parallel-consecutive scheme and the rate and selectivity of the reaction are greatly influenced by the nature and the composition of a solvent [7-9]. The aim of the research is to study the kinetic regularities of

hydrogenation reaction of NAB on the skeleton nickel catalyst in aliphatic alcohols at different operating conditions.

MATERIALS AND METHODS

A skeleton nickel obtained by the treatment of nickel-aluminum alloy of the composition Ni: Al: Fe = 46.3: 53.6: 0.1 mass % with 25 % aqueous solution of sodium hydroxide was used as a catalyst. An active catalyst had specific gravity equal to 90 ± 5 m²/g Ni, the porosity was equal to 0.5 [10]. Methanol, ethanol, propan-2-ol, butan-2-ol without and with the additions of water and sodium hydroxide were used as solvents. The study of the kinetics of hydrogenation reaction NAB was carried out by a static method in a thermostatic reactor with intensive stirring of a liquid phase at two different temperatures 275 ± 2 K and 303 K. The measurement of the rate of hydrogen absorption was done by volumetric method [11].

The quantitative control of the main reaction products was carried out with the use of the following methods: spectrophotometry, polarography and thin layer chromatography. The qualitative analysis of the

hydrogenisate composition was done by the method of a thin layer chromatography on Silufoll plates with the use of toluene-ethylacetate binary solvent in the volumetric ratio 10: 1 as an identifying agent. After dividing the sample in a thin layer of adsorbent chromatographic spots characterizing single compounds were washed by well-known volumes of propan-2-ol and then the solutions were analyzed spectrophotometrically. The determination of the concentration of the substances under study was done by measuring the optical densities of hydrogenisate samples in propan-2-ol at the wavelengths corresponding to the maximum absorption in ultraviolet spectra of pure substances.

The integral index calculated as the relation of BT mass to the mass of all reaction products was used as a reaction selectivity parameter (S_{BT} , %) for BT. BT was separated from hydrogenisate at pH equal 10.5 and the content of the main substance was determined spectrophotometrically.

As the main kinetic reaction characteristics, the values of reaction rates at low degrees of NAB conversion were used. In this case the initial reaction rates (r_H^0) are directly related to the reaction ability of an organic reagent and hydrogen and they depend only upon the quantity of an original hydrogenated reagent. Side products due to their low concentration do not affect significantly the numerical values of initial reaction rates. Thus the initial rate of hydrogen absorption is considered to be an objective kinetic characteristic of NAB hydrogenation reaction.

RESULTS AND DISCUSSION

The results of the previous kinetic researchers are evidence of the fact that the form of the curves which characterize the dependencies of the observed reaction rate upon the amount of hydrogen absorbed in the reaction changed slightly in passing from methanol to 2-butanol. Irrespective of the nature of an aliphatic alcohol used as solvent for each mole of NAB hydrogenated 3.3 ± 0.2 mole of hydrogen gas was absorbed and the reaction selectivity with respect to BT remained practically constant and was $35 \pm 2\%$.

The constancy of initial hydrogen absorption rate and the amount of BT in passing from methanol to 2-butanol can be considered as an evidence of close reaction ability of an original compound in relation to hydrogen and of similar character of intermediate products which are formed during the course of the reaction in all aliphatic alcohols. The main kinetic characteristics of the process are present in Table 1.

Fig. 1 shows the dependencies of NAB, N-oxide 2,2'-hydroxy-5'-methylphenylbenzotriazole (NO), intermediate reaction product 2-nitro-2'-hydroxy-5'-methylhydroazobenzene (NHB), aromatic amines-2-phenyldiamine (FDA), 3-amino-4-hydroxytoluene (AHT), 2-amino-2'-hydroxy-5'-aminoazobenzene (AAB) and non-identified compound X, which is a presumably a tautomeric form of NHB [12] upon the time of NAB hydrogenation reaction on skeleton nickel in propan-2-ol at 275 ± 2 K. From the kinetic curves presented in Fig. 1 it follows that in the initial phase of the reaction the concentration of NAB rapidly decreased which was attended by the formation of NO, NHB and X and the concentrations of NO and NHB exceeded significantly the concentration of X. Further NO was converted into BT and the hydrogenation of NHB and X proceeded at significantly higher rates than NO. It was attended with the formation of AAB, FDA, AHT. The qualitative view of the curves shown in Fig. 1 corresponds to kinetic curves which characterize the changes of the concentrations of original and intermediate products in consecutive-parallel reactions [13].

The analysis of similar dependencies of the concentrations of substances which take part in the reaction upon the time in propan-2-ol-water binary solvent with 0.68 mol fraction of alcohol and in the same solvent with the addition of 0.0125 M of sodium hydroxide is supporting the fact that the introduction of water and sodium hydroxide into a solvent led to a sharp decrease in FDA, AHB and NHB concentrations. In mixed solvents AAB concentration during the course of the reaction decreased but the concentration of the products having in its composition benzotriazole cycle-NO and BT sharply increased. The quick conversion of NHB into X in the presence of water and sodium hydroxide may be due to the increase of the rates of heterogeneous stages of a

Table 1: The characteristics of hydrogenation reaction of 2-nitro-2'-hydroxy-methylazobenzene on skeleton nickel in aliphatic alcohols at 303 K.

Solvent	M.M g mol ⁻¹	$r_H^0 \times 10^4$, mole.min ⁻¹	V_{H_2} , mole NAB. min ⁻¹	S_{BT} , %
Methanol	32	22±2	3.3±0.1	32±2
Ethanol	46	19±2	3.1±0.1	37±3
Propan-2-ol	60	18±2	3.2±0.1	35±3
Butanol	74	20±2	3.3±0.1	36±4

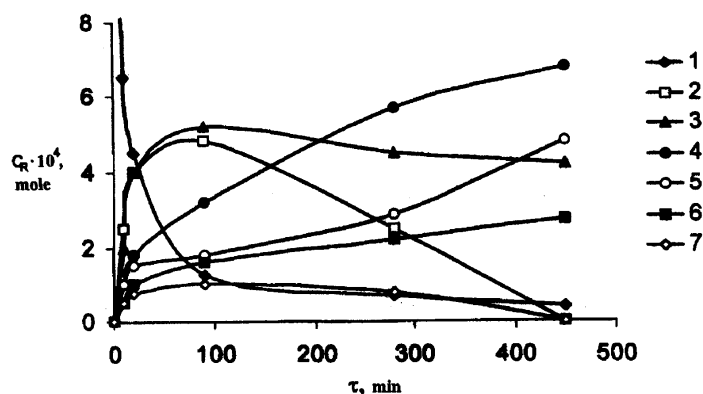


Fig. 1: The dependencies of concentrations of the substances participating in a liquid phase hydrogenation reactions of NAB on skeleton nickel in propan-2-ol (C_R) upon the reaction time (t). Temperature is 275 ± 2 K, $g_{cat} = 0.625$ g volume of a liquid phase = 100 cm^3 , $C_R = (18.5 \pm 0.5) \cdot 10^{-4}$ mole I-NAB; 2-NHB; 3-NO; 4-AHB; 5-FDA; 6-AAB; 7-X

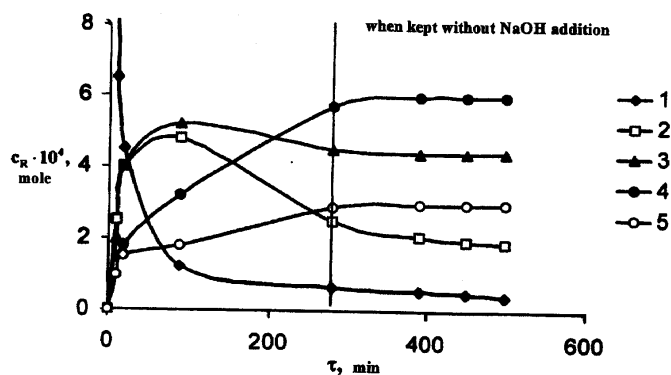


Fig. 2: The dependencies upon the time t of concentrations of substances participating in the reaction of liquid phase hydrogenation of NAB on skeleton nickel in propan-2-ol- C_R with the exclusion of the heterogeneous-catalytic reactions and without additions of sodium hydroxide Temperature is 275 ± 2 K, $g_{cat} = 0.625$ g the volume of a liquid phase is 100 cm^3 , $C_R = (18.5 \pm 0.5) \cdot 10^{-4}$ mole I-NAB; 2-NHB; 3-NO; 4-AHB; 5-FDA.

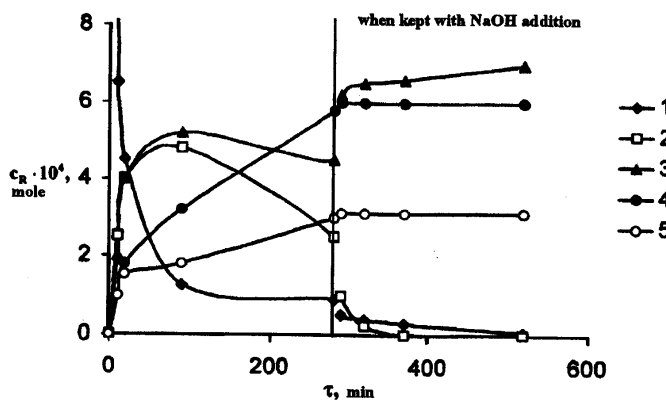


Fig. 3: The dependencies upon time of the concentrations of substances participating in the reaction of liquid phase hydrogenation of NAB on skeleton nickel in propan-2-ol- C_R including the exclusion of the heterogeneous-catalytic reactions and with the addition of sodium hydroxide Temperature 275 ± 2 K; $g_{cat} = 0.625$ g the volume of a liquid phase 100 cm^3 , $C_R = (18.5 \pm 0.5) \cdot 10^{-4}$ mole I-NAB. 2-NHB. 3-NO. 4-AHB. 5-FDA .

catalytic process and also to the growth of the rates of homogeneous reactions particularly the cyclization of NHB in a solution [12].

To evaluate the reasons of the influence of homogeneous rearrangement stages of reaction intermediates on the rates of formation of the compounds which contain NO and BT triazole cycle the following method was used: at a definite reaction moment the contribution of heterogeneous-catalytic reactions of converting the intermediate products was excluded. The mixing up was switched off in the reactor, the reaction medium was separated from the catalyst and the concentrations of substances which participate in the reaction at definite time moments of the homogeneous process were measured. The time of switching off the mixing process corresponded to the time during which 1 ± 0.1 mole of hydrogen per one mole of NAB was absorbed. The given time moment corresponds to maximum concentrations of NO and NHB in a catalytic reaction. The experiments were carried out in a closed system in hydrogen atmosphere which excluded the effect of outer factors: light, oxygen of the air, etc. on the kinetic regularities of homogeneous conversions proceeding in the volume of a solution with the participation of a reaction products.

To evaluate the role of adding sodium hydroxide in some experiments carbonate free solution of sodium hydroxide was introduced into the reaction medium either at the beginning or at the moment of excluding heterogeneous catalytic stages of the hydrogenation reaction which corresponded to the stopping of mixing. The analytical methods of the control of the composition of the reaction medium did not differ from the methods of analysis used in other kinetic experiments. The examples of dependencies of NAB, NO, NHB, FDA, ANT in the process of a liquid phase hydrogenation and homogeneous processes after switching the mixing off upon the time are given in Fig. 2 and Fig. 3. From the kinetic curves shown in Fig. 2, Fig. 3 and the results of other similar experiments it follows that after retarding the catalytic reaction in the absence as well as in the presence of sodium hydroxide the concentration of NAB remained constant. The concentrations of AAB, FDA and AHT after retarding the reaction irrespective of the nature of a

reaction medium in the limits of the experimental error did not change upon the time as well and that was an evidence of the fact that heterogeneous-catalytic stages of the process did not proceed. On the contrary, the concentrations of NHB and X after retarding the catalytic reaction in 2-propanol was decreased in time and simultaneously there was observed some growth in NO concentrations. The introduction of the sodium hydroxide additions into the solvent caused sharp decrease more than two times of the concentrations of NHB and X, attended by the sharp increase in NO concentration. It should be underlined that NHB in the process of keeping in the alkaline media completely disappeared from the solution and converting into NO and the growth of the concentration of the later completely ceased after the disappearance of NHB.

CONCLUSIONS

The results of the experiments on the reaction kinetics proceeding with the exclusion of heterogeneous-catalytic stages of liquid phase hydrogenation of NAB with the participation of the intermediate products show that the formation of the compounds containing a triazole cycle NO and BT proceeds as a result of homogeneous conversions of NHB and X. The growth of the rate of homogeneous stages under the influence of sodium hydroxide additions proves that triazole rearrangement proceeds according to the mechanism of homogeneous catalytic reactions of acid-basic type with the participation of hydroxide ions. This problem was discussed earlier in [12, 14]. One of the probable reasons of changing the selectivity of hydrogenation reaction of NAB with respect to NO and BT is the presence of homogeneous stages in the general scheme of conversions of NAB and the change of homogeneous reaction rates under the influence of a solvent. The introduction of water of sodium hydroxide into the aliphatic alcohol results in the great yield of NO and BT. It is illustrated by the data presented in Table 2. Thus the modification of a catalytic system by changing its homogeneous constituent - a solvent is the effective way of regulating the selectivity of hydrogenation reaction of NAB with respect to NO and BT.

Table 2: The characteristics of hydrogenation reaction of 2-nitro-2'-hydroxy-5'-methylazobenzene on skeleton nickel in mixed solvents at 303 K.

Solvent	$r_H \times 10^4$, mole.min ⁻¹	V_{H_2} , mole NAB. min ⁻¹	S_{BT} , %
Methanol-water	30±2	29±0.2	37±2
Methanol-water-NaOH	32±2	2.4±0.2	72±4
Propan-2-ol-water	25±2	2.8±0.2	40±2
Propan-2-ol-water-NaOH	28±2	2.3±0.2	73±2

List of Abbreviations:

NAB : 2-nitro-2'-hydroxy-5'-methylazobenzene
NO : N-oxide 2,2'-hydroxy-5'-methylphenylbenzotriazole
NHB : 2-nitro-2'-hydroxy-5'-methylhydroazobenzene.
FDA : 2-phenylendiamine.
AHT : 3-amino-4-hydroxytoluene.
AAB : 2-amino-2'-hydroxy-5'-aminoazobenzene.
M.M : Molar Mass.
SBT : Yield of benzotriazole.
 r_H° : Initial reaction rate by absorbed Hydrogen.
 C_R° : Initial concentration of reagent-NAB
 g_{cat} : Weight of catalyst.

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