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Role of Homogeneous Steps in the Heterogeneous Catalytic Hydrogenation of Substituted 2-Nitroazobenzenes

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Abstract—The homogeneous reactions of nitrohydrazo derivatives contribute substantially to the benzotriazole selectivity of the hydrogenation of substituted 2-hydroxynitroazobenzene. The rate of the homogeneous steps is governed by the solvent composition rather than by the substituent in the starting nitroazobenzene. An increase in pH in both aqueous and aqueous-alcohol solutions increases the rate constants of the homogeneous reactions of various substituted nitrohydrazo derivatives and considerably enhances the selectivity of the reaction with respect to the compounds containing a triazole ring. A kinetic model has been suggested to qualitatively describe the influence of the pH value of the medium on the rate of the cyclization of substituted 2'-hydroxy-5'-hydrazobenzenes into the corresponding benzotriazole N-oxides.

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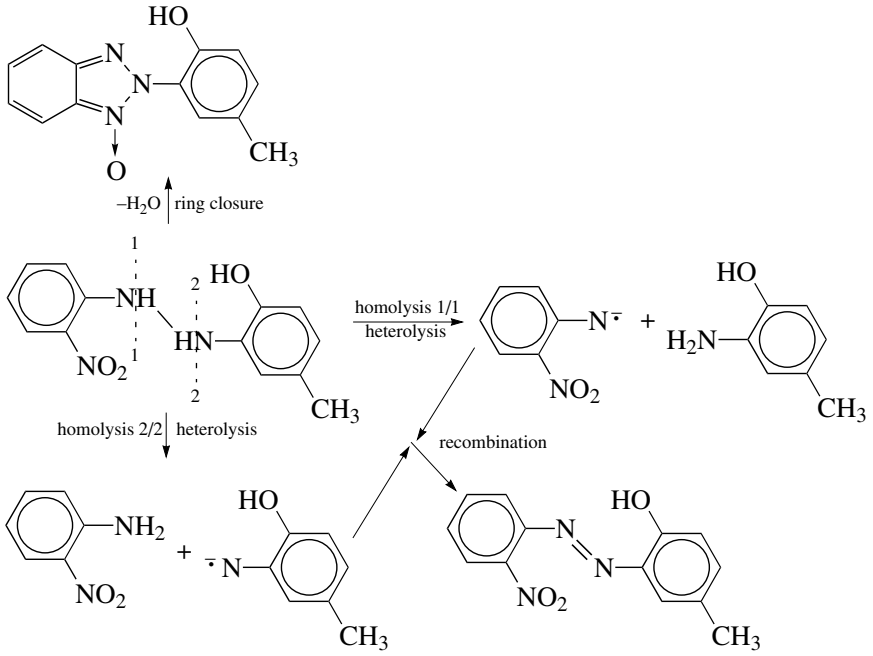
INTRODUCTION

One of the intermediate products of the heterogeneous catalytic hydrogenation of a substituted 2-nitro-2'-hydroxyazobenzene (NAB) in aqueous-alcohol media is the corresponding nitrohydrazobenzene (NHB) [1], which can further be hydrogenated to an aromatic amine. We found that NHB can also react in the solution bulk via a homogeneous catalytic mechanism of the acid–base type [1, 2]. This finding is in agreement with data reported by other researchers [3]. The possible homogeneous steps of 2-nitro-2'-hydroxy-5'-methylhydrazobenzene (NHBM) conversion are shown in Scheme 1.

The possibility of the homogeneous conversion of substituted NHBs into products containing a triazole ring, including substituted benzotriazole N-oxides (N-O), is



Scheme 1. Mechanism of the homogeneous conversion of 2-nitro-2'-hydroxy-5'-methylhydrazobenzene [1, 2].

Rate constants of the steps of the homogeneous conversion of substituted nitrohydrazobenzenes in a water-propanol-2 mixture ($x_1 = 0.66$) as a function of pH at 275 K

pH	NHB	σ*	$k_{conv} \times 10^3$, s^{-1}	$k_{rc} \times 10^3$, s^{-1}
8.56	NHBM	–0.10	0.35 ± 0.05	0.25 ± 0.05
	NHBTB	–0.14		
	NHBC	+0.46		
14.08	NHBM	–0.10	15 ± 1	13 ± 1
	NHBTB	–0.14	26 ± 2	22 ± 2
	NHBC	+0.46	22 ± 2	19 ± 2
4.93	NHBM	–0.10	0.15 ± 0.02	0.10 ± 0.02
	NHBTB	–0.14		
	NHBC	+0.46		

* Quoted from [11].

due to the *ortho*-conjugation of the nitro and hydrazo groups in the molecule of the starting compound [4]. The hydroxyl group in an *ortho*-position with respect to the azo group enhances the ring-closure ability of NHB due to a change in the parameters of intramolecular bonds [5, 6]. The formation of amines and substituted NAB is likely due to the radical mechanism of NHB conversion [7]. The effect of the nature of the substituents in the NHB molecule on the rate of homogeneous NHB conversion in aqueous-alcohol media with various pH values remains to be elucidated.

The purpose of the present study is to analyze the homogeneous steps of the liquid-phase heterogeneous catalytic hydrogenation of NAB with electron-donor and electron-withdrawing substituents and to develop a formal kinetic model for the NHB ring closure step yielding an N-oxide.

EXPERIMENTAL

Substituted NABs (1 g) were hydrogenated on a skeletal nickel catalyst (0.3 g) using the static method under atmospheric pressure in a temperature-controlled reactor at 275 K with vigorous stirring of the liquid phase (100 cm^3). Skeletal nickel was prepared by treating a nickel–aluminum alloy with 6 M NaOH. The compounds to be hydrogenated were 2-nitro-2'-hydroxy-5'-carboxyazobenzene (NABC), 2-nitro-2'-hydroxy-5'-*tert*-butylazobenzene (NABTB), and 2-nitro-2'-hydroxy-5'-methylazobenzene (NABM). Hydrogenation was carried out in a water–propanol-2 solvent ($x_2 = 0.66$) and in aqueous solutions with various pH values. In aqueous-alcohol media, the acetic acid concentration was 0.17 mol/l and the sodium hydroxide concentration was 0.0125 mol/l. The volume of absorbed hydrogen was measured during the reaction, from which the specific hydrogenation rate was derived. After 1 mol of H_2 per mole of NAB was absorbed, the process in an acidic or neutral medium was terminated and samples (20 cm^3) of the reaction mixture were taken, which were kept in the absence of a hydrogenation catalyst under flowing hydrogen in the dark. TLC data indicated the absence of other hydrogenation products capable of transforming by a homogeneous reaction into benzotriazole derivatives, in particular, nitrosoazo compounds [1, 2]. A sodium hydroxide solution was added to the samples hydrogenated in a neutral solvent to estimate the rate of homogeneous reactions in an alkaline medium. The changes in the concentrations of NHB and its conversion products were monitored by a method combining TLC and spectrophotometry [2]. The overall NHB conversion via the routes shown in Scheme 1 was characterized by the apparent rate constant k_{conv}, and the step of NHB conversion to N-O was characterized by the ring closure rate constant k_{rc}. The constants k_{conv} and k_{rc} were derived from the time dependences of the NHB and N-O concentrations using a first-order rate equation.

We have already discussed the specific features of NHBM reactions in aqueous and aqueous-alcohol media with various pH values [1, 2]. It has been found by TLC that the homogeneous conversion of NHBM in the light at room temperature in air yields NABM, 3-amino-4-hydroxytoluene (A), 2-nitroaniline (NA), and 2'-hydroxy-5'-methylphenylbenzotriazole N-oxide. In an acid-containing aqueous-alcohol medium, NHBM is mainly converted into NABM, NA, and A. The introduction of sodium hydroxide into the solvent results in a nearly complete conversion of NHBM into the corresponding N-oxide [1, 2].

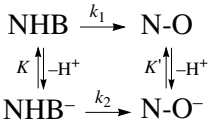
The overall conversion and ring closure rate constants for intermediates in aqueous-alcohol media and the Hammett constants for the substituents in the NHB molecules [8] are given in the table. The results obtained suggest that NHB is converted slowly under these conditions, but via the same mechanism as in the light at room temperature. In neutral and acidic media, NHB is simultaneously converted via all routes presented in Scheme 1, as is indicated by the difference between k_{conv} and k_{rc} being as large as 25–40%. The low rate of the formation of NA, NAB, and amines from NHB in the dark confirms that the reaction proceeds via a free-radical mechanism [7].

For all of the NHBs examined, the rate constants of the homogeneous steps in the alkaline medium are two orders of magnitude higher than the rate constants in an acid or neutral medium. For the alkaline medium, k_{conv} and k_{rc} differ by at most 15%, indicating a considerable increase in the contribution from the route leading to N-O. Thus, the introduction of sodium hydroxide into a neutral solvent accelerates the formation of the triazole ring and enhances the selectivity of hydrogenation with respect to substituted benzotriazoles (BT), which result from the reduction of N-O in ~100% yield [9]. An analysis of kinetic data for the steps of the conversion of methyl-, *tert*-butyl-, and carboxyl-substituted nitrohydrazobenzenes (NHBM, NABTB, and NHBC, respec-

tively) in the alkaline medium has demonstrated that the determining factor in ring closure is the solvent composition rather than the substituent.

A substantial role in ring formation is played by *ortho*-localization, which causes the perturbation of the π-electron system of the molecule upon attack on the *ortho*-position with respect to the substituent [5, 6]. Probably, as in the formation of other rings, the rearrangement of NHB is favored by the shift of the equilibrium to the tautomer that readily forms a ring [6]. For NHB derivatives containing a hydroxyl group, ionization enhances the reactivity of the resulting ion toward electrophiles and increases the complanarity of the molecule, resulting in an increase in the ring closure rate. That is why, in a solvent containing sodium hydroxide, the ring closure rate is much higher and the electron-donor effects of substituents are equalized to a considerable extent [5, 7, 10–12].

The rate constants of ring closure reactions are known to depend on the pH of the solvent [3, 11], including the case of homogeneous NHB conversion [1, 2]. NHB cyclization yielding N-O can be illustrated by Scheme 2. It is accepted that the ionizations of NHB and N-O are reversible reactions, whose stoichiometric equations are given in Scheme 3.



Scheme 2.

$$\mathrm{NHB} + \mathrm{OH^-} \overset{K}{\rightleftharpoons} \mathrm{NHB^-} + \mathrm{H_2O}$$

$$\mathrm{N\text{-}O} + \mathrm{OH^-} \overset{K'}{\rightleftharpoons} \mathrm{N\text{-}O^-} + \mathrm{H_2O}$$

Scheme 3.

In Schemes 2 and 3, NHB and NHB^- are the nonionized and ionized forms of substituted nitrohydrazobenzenes, N-O and $N\text{-}O^-$ are those of benzotriazole N-oxides, k_1 and k_2 are the rate constants of the ring closure steps yielding N-O for the nonionized and ionized forms of NHB, and K and K' are the equilibrium constants of the ionization steps.

The concentration equilibrium constants can be expressed as follows:

$$K = \frac{[\mathrm{NHB^-}][\mathrm{H_2O}]}{[\mathrm{NHB}][\mathrm{OH^-}]} = \frac{[\mathrm{NHB^-}][\mathrm{H_2O}][\mathrm{H_3O^+}]}{[\mathrm{NHB}]K_\mathrm{w}};$$

$$K' = \frac{[\mathrm{N\text{-}O}][\mathrm{H_2O}]}{[\mathrm{N\text{-}O}][\mathrm{OH^-}]} = \frac{[\mathrm{N\text{-}O^-}][\mathrm{H_2O}][\mathrm{H_3O^+}]}{[\mathrm{N\text{-}O}]K_\mathrm{w}}.$$

The overall rate of NHB ring closure is determined by the rate equation

$$r_\mathrm{rc} = k_1[\mathrm{NHB}] + k_2[\mathrm{NHB^-}], \quad (1)$$

where [NHB] and $[NHB^-]$ are the equilibrium concentrations of the nonionized and ionized forms of NHB during the reaction.

Kinetic analysis of the above schemes together with the balance equations relating the total NHB concentration in the reaction system to the concentrations of the ionized and nonionized forms of the reactants leads to the rate equation

$$r_\mathrm{rc} = k_\mathrm{app}[\mathrm{NHB}], \quad (2)$$

where k_app is the apparent rate constant of NHB ring closure with N-O formation

$$k_\mathrm{app} = \frac{k_1 + k_2\dfrac{KK_\mathrm{w}}{[\mathrm{H_2O}][\mathrm{H_3O^+}]}}{1 + \dfrac{KK_\mathrm{w}}{[\mathrm{H_2O}][\mathrm{H_3O^+}]}}. \quad (3)$$

According to Eq. (2), the dependences of the ring closure rate on the NHB concentration are described by a first-order rate equation and the apparent rate constant depends on the pH of the solution, in good agreement with the experimental data presented here and with the results of earlier studies [1, 2]. At low pH,

$$k_1 \gg k_2\frac{KK_\mathrm{w}}{[\mathrm{H_2O}][\mathrm{H_3O^+}]}; \quad \frac{KK_\mathrm{w}}{[\mathrm{H_2O}][\mathrm{H_3O^+}]} \ll 1,$$

and the rate equation (2) appears as

$$r_\mathrm{rc} = k_1[\mathrm{NHB}]; \quad (4)$$

at high pH,

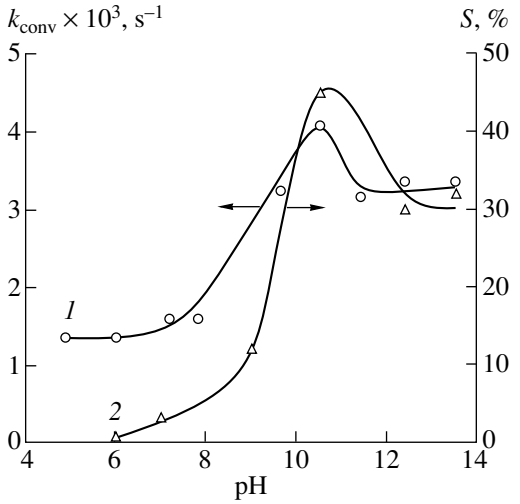
$$k_1 \ll k_2\frac{KK_\mathrm{w}}{[\mathrm{H_2O}][\mathrm{H_3O^+}]}; \quad \frac{KK_\mathrm{w}}{[\mathrm{H_2O}][\mathrm{H_3O^+}]} \gg 1,$$

and the rate equation (2) is written as

$$r_\mathrm{rc} = k_2[\mathrm{NHB}]. \quad (5)$$

The above kinetic model qualitatively describes the pH effect on the NHBM ring closure rate. The experimental data illustrating the dependences of k_conv for NHBM and the N-O selectivity (S) of NABM hydrogenation on the pH of the aqueous solution are shown in the figure. For aqueous media, the selectivity and NHBM conversion rate constant peaks coincide within ±0.5 pH units. Therefore, above pH 9.5, the ratio of the rates of the homogeneous and heterogeneous steps of the catalytic reaction ensures the most complete ring closure in substituted NHB derivatives with the formation of N-O. An increase in pH both in aqueous solutions and in the water–propanol-2 mixture increases the selectivity of the reaction with respect to the compounds containing a benzotriazole ring. This confirms the earlier assumption that the ionization of the reacting molecules plays the determining role in the homogeneous NHB ring closure and that the latter makes a considerable contribution to the N-O selectivity of the reaction.

Thus, the homogeneous reactions of the nitrohydrazo derivatives contribute substantially to the selec-



(*1*) NHBM conversion rate constant (k_{conv}) and (*2*) the N–O selectivity of NHBM hydrogenation (*S*) versus the pH of the aqueous solution.

tivity of the hydrogenation of substituted 2-hydroxynitroazobenzenes with respect to the corresponding benzotriazoles, which are used as efficient UV absorbents in polymers [13]. The simultaneous occurrence of homogeneous and heterogeneous catalytic steps is a distinctive feature of the liquid-phase hydrogenation of substituted 2-hydroxynitroazobenzenes.

REFERENCES

1. Lefedova, O.V., Nemtseva, M.P., and Nikolaev, V.N., *Zh. Fiz. Khim.*, 2003, vol. 77, no. 7, p. 1183 [*Russ. J. Phys. Chem.* (Engl. Transl.), vol. 77, no. 7, p. 1059].
2. Zuenko, M.A., Nemtseva, M.P., Lefedova, O.V., and Nikolaev, V.N., *Zh. Fiz. Khim.*, 2004, vol. 78, no. 6, p. 1015 [*Russ. J. Phys. Chem.* (Engl. Transl.), vol. 78, no. 6, p. 877].
3. *Sbornik voprosov i zadach po analiticheskoi khimii* (Collection of Questions and Problems on Analytical Chemistry), Vasil'ev, V.P., Ed., Moscow: Vysshaya Shkola, 1976.
4. Dzhoul', D. and Smit, G., *Heterocyclic Chemistry*, London: Van Nostrand Reinhold, 1972.
5. Temnikova, T.I. and Semenova, S.N., *Molekulyarnye peregruppirovki v organicheskoi khimii* (Molecular Rearrangements in Organic Chemistry), Leningrad: Khimiya, 1983.
6. Ivanskii, V.I., *Khimiya geterotsiklicheskikh soedinenii* (Chemistry of Heterocyclic Compounds), Moscow: Vysshaya Shkola, 1978.
7. *Chemical Reactivity and Reaction Paths*, Klopmann, G., Ed., New York: Wiley, 1974.
8. Pal'm, V.A., *Osnovy kolichestvennoi teorii organicheskikh reaktsii* (Fundamentals of the Quantitative Theory of Organic Reactions), Leningrad: Khimiya, 1967.
9. Gostikin, V.P., Lefedova, O.V., and Ulitin, M.V., *Kinet. Katal.*, 1987, vol. 28, no. 2, p. 347.
10. Gornostaev, L.M., *Soros. Obraz. Zh.*, 1996, no. 4, p. 33.
11. Poltorak, O.M. and Chukhrai, E.S., *Fiziko-khimicheskie osnovy fermentativnogo kataliza* (Physicochemical Foundations of Enzymatic Catalysis), Moscow: Vysshaya Shkola, 1971.
12. Mann, P., *Doctoral (Chem.) Dissertation*, Ivanovo: Ivanovo Inst. of Chemical Engineering, 1990.
13. Noukakis, D. and Suppan, P., *J. Photochem. Photobiol., A*, 1991, vol. 58, no. 3, p. 393.