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Abstract

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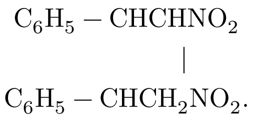
STUDY OF THE STEPWISE MECHANISM OF THE REDUCTION OF β-NITROSTYRENE IN AN ACIDIC MEDIUM ON Pd BLACK

(Presented by Academician A. A. Balandin on 26 XII 1963)

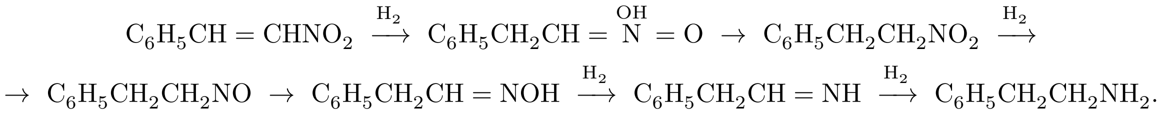
The molecule of β-nitrostyrene is a conjugated system (^{1}) containing three groups capable of being hydrogenated. It is natural to expect that the reduction of such compounds may proceed through a series of intermediate stages.

In works devoted to the catalytic hydrogenation of β-nitrostyrene, it was shown that the process proceeds in a complex manner and that its direction is determined primarily by the character of the medium (^{2}, ^{3}). In an alcoholic medium in the presence of palladium and platinum, hydrogenation leads predominantly to the formation of a dimeric product, to which the structure of 1,4-dinitro-2,3-diphenylbutane was assigned



$$\begin{array}{l} C_6H_5-CHCHNO_2 \\ \qquad\qquad\quad | \\ C_6H_5-CHCH_2NO_2. \end{array}$$

In glacial acetic acid, the oxime of phenylacetaldehyde is also formed. Under these conditions the amine is not obtained. Similar results were obtained by Kohler and Drake (^{4}) on various metallic catalysts. The authors suggested that, in the reduction of β-nitrostyrene to the amine, the process may proceed according to the scheme:



$$C_6H_5CH=CHNO_2 \xrightarrow{H_2} C_6H_5CH_2CH=\overset{OH}{N}=O \rightarrow C_6H_5CH_2CH_2NO_2 \xrightarrow{H_2}$$
$$\rightarrow C_6H_5CH_2CH_2NO \rightarrow C_6H_5CH_2CH=NOH \xrightarrow{H_2} C_6H_5CH_2CH=NH \xrightarrow{H_2} C_6H_5CH_2CH_2NH_2.$$

The reduction of β-nitrostyrene to β-phenethylamine was successfully carried out when a mixture of glacial acetic and concentrated sulfuric acids was used

Fig. 1. Kinetic curve of the hydrogenation of β-nitrostyrene (Pd black—1 g, 0.02 mole of nitrostyrene)

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Fig. 2. Dependence of the composition of the catalyst on the amount of hydrogen absorbed (1 g Pd black) in the reduction of β-nitrostyrene

Figure 2: Fig. 2. Dependence of the composition of the catalyst on the amount of hydrogen absorbed (1 g Pd black) in the reduction of β-nitrostyrene

as the solvent (^{5}). However, the stepwise mechanism proposed in (^{4}) was not confirmed experimentally.

In the present work the stepwise mechanism of the reduction of β-nitrostyrene in the presence of Pd black in an acidic medium was investigated. The composition of the catalyst was determined by polarographic and chromatographic methods of analysis developed by us.

The catalytic reduction of arylnitroalkenes—derivatives of β-nitrostyrene—is of interest as a convenient method for the synthesis of physiologically active amines and a number of other nitrogen-containing compounds.

Nitrostyrene was synthesized according to (^{6}), m.p. 58-58.2° (literature data: m.p. 59°). Phenylacetaldehyde oxime was prepared according to (^{7}), m.p. 98-98.6°. 1-Phenyl-2-nitroethane was obtained from β-nitrostyrene by reduction with $LiAlH_4$ at −45° (^{8}); b.p. 100-104°/3 mm Hg, n_D^{20} 1.5305 (literature data: b.p. 73-74.6°/0.5 mm Hg, n_D^{20} 1.5275). β-Phenethylamine was obtained according to (^{9}), b.p. 197.6°, hydrochloride m.p. 217° (literature data: b.p. 198°, hydrochloride m.p. 217-218°). $\beta\beta'$-[Diphenylethyl]amine was obtained according to (^{10}), hydrochloride m.p. 272° (literature data: 274.5°).

Hydrogenation of β-nitrostyrene was carried out at 25° in a thermostated duck-shaped vessel with vigorous stirring (700 oscillations/min). Pd black was prepared from palladium chloride by reduction with formalin in an alkaline medium (^{11}). As solvent, a mixture of glacial CH_3COOH and concent-

sulfuric acid (15 : 1 by volume). During the course of hydrogenation, catalyst samples of ~ 0.2 ml were taken for analysis.

The phenylacetaldehyde oxime and β-nitrostyrene formed in the process were determined polarographically. The content of β-nitrostyrene in the catalyst was calculated from the limiting current of its first wave ($E_{1/2}$ I = −0.220 V),

Fig. 1. Kinetic curve of the hydrogenation of β-nitrostyrene (Pd black—1 g, 0.02 mole of nitrostyrene)

Fig. 2. Dependence of the composition of the catalyst on the amount of absorbed hydrogen (1 g Pd black) in the reduction of β-nitrostyrene

and the total content of β-nitrostyrene and oxime from the current of the second wave ($E_{1/2}$ II $= -0.710$ V). The amount of oxime was found by difference. The sensitivity of the method made it possible to determine down to 1% β-nitrostyrene and 2% oxime (relative).

1-Phenyl-2-nitroethane and β-nitrostyrene give two diffusion waves whose potentials differ by 0.45 V. In a mixture, a 0.1 mM concentration of 1-phenyl-2-nitroethane can be determined.

The amines were analyzed by gas-liquid chromatography. The sensitivity of the method made it possible to determine down to 0.1% of the amines theoretically formed.

The reduction of β-nitrostyrene in a mixture of acetic and sulfuric acids on Pd black proceeds with the absorption of four moles of hydrogen. The kinetic curve of the process (Fig. 1) consists of two regions: absorption of the first two moles proceeds at a constant rate; with further hydrogenation the reaction rate continuously decreases. Analysis of the catalyst in each of these regions shows (Fig. 2) that the shape of the kinetic curve corresponds to two stages of the reaction. In the first stage, β-nitrostyrene is reduced with a high degree of selectivity (84%, calculated from the ratio of the oxime formed to the nitrostyrene that reacted) to phenylacetaldehyde oxime. By the time two moles of hydrogen have been absorbed, the catalyst contains 75% oxime, 11% unreacted β-nitrostyrene, and about 5% β-phenylethylamine. The constancy of the rate of hydrogen absorption in this region indicates a zero order of the reaction with respect to β-nitrostyrene. The same reaction order was found by Schmidt et al. (12) for the reduction of β-nitrostyrene with hydrogen under pressure on PtO_2 in acetic acid.

In the second stage of the reaction, the phenylacetaldehyde oxime formed is hydrogenated.

After absorption of four moles of hydrogen, the yield of β-phenylethylamine is 91.6%; the remaining 8% is resin (Table 1).

In the Kohler and Drake scheme (4), formation of 1-phenyl-2-nitroethane is assumed as an intermediate product. In a binary mixture, 1-phenyl-2-nitroethane is hydrogenated considerably more slowly than β-nitrostyrene (Fig. 3).

Therefore, in the case of formation of 1-phenyl-2-nitroethane as an intermediate product during the hydrogenation of β-nitrostyrene, it should have accumulated in the catalyst. The methods we used made it possible to determine 0.5% of 1-phenyl-2-nitroethane of the theoretically formed amount; however, this compound was not detected in the catalyst.

Table 1

Composition of the catalyst deposit as a function of the amount of hydrogen absorbed

(Conditions: 1 g Pd black, 0.02 mole β-nitrostyrene, 80 ml CH_3COOH–H_2SO_4 (15:1))

Absorbed H_2, moles	Degree of conversion of nitrostyrene, mole %	Catalyst-deposit composition, mole %: oxime	Catalyst-deposit composition, mole %: amine	Catalyst-deposit composition, mole %: residue
0	0	–	–	–
0.5	24	24	–	–
1.0	48	46	traces	2
1.5	70	65	traces	5
2.0	88	76	5	7
2.5	94	61	22	11
3.0	100	42	40	18
3.5	100	25	56	19
4.0	100	–	92	8

Table 2

Dependence of the reaction rate and direction on the amount of catalyst

Pd black, g	Stage I: dV/dt, ml/min	Stage I: oxime yield from theoretical, %	Stage II: dV/dt, ml/min	Stage II: primary amine yield from theoretical, %	Stage II: secondary amine yield from theoretical, %
0.10	31.0	76	0.20	32	–
0.21	61.4	76	0.75	34	51
0.38	107.2	76	20.0	61	–
1.01	356.0	75	264.0	92	traces

It should be noted that in the second stage of the process there is some discrepancy between the degree of hydrogenation of the oxime and the amount of amine formed (Fig. 2, Table 1). The maximum deficiency in the product balance at the moment when 3.5 moles of H_2 have been absorbed is 19%, which is probably explained by the formation of an intermediate product (as well as resinous substances). This is confirmed by the fact that, after ether extraction from the acidic solution of the oxime formed and of the unreacted β-nitrostyrene, upon alkalization a hydrochloride separated as an oily, readily fusible precipitate. The latter rapidly resinified in air, which prevented its purification and identification.

Fig. 3. Change in the content in the catalyst of 1-phenyl-2-nitroethane (a) and β-nitrostyrene (b) as a function of the amount of hydrogen absorbed during hydrogenation of their binary mixture (1:1)

Figure 3: Fig. 3. Change in the content in the catalyst of 1-phenyl-2-nitroethane (a) and β-nitrostyrene (b) as a function of the amount of hydrogen absorbed during hydrogenation of their binary mixture (1:1)

It may be assumed that this is β-phenylethylhydroxylamine, not described in the literature. The possibility of hydroxylamine formation under similar conditions is confirmed by data on the catalytic hydrogenation of acetophenone oxime ([13]).

Fig. 3. Change in the content in the catalyst of 1-phenyl-2-nitroethane (*a*) and β-nitrostyrene (*b*) as a function of the amount of hydrogen absorbed during hydrogenation of their binary mixture (1:1).

It is interesting that the dependence of the rate of the first and second stages of the process on the amount of catalyst (0.1–1 g) proved to be different (Table 2). The rate of hydrogenation of β-nitrostyrene to the oxime is proportional to the amount of catalyst. In the second stage the rate changes disproportionately: when the amount of catalyst is decreased by a factor of 10, the rate decreases by a factor of 130. A disproportionate decrease in the hydrogenation rate on going to small amounts of catalyst had also previously been observed in other processes ([14]).

During successive hydrogenation of several portions of β-nitrostyrene on one and the same portion of catalyst, the activity of the latter decreases almost tenfold, and the reaction does not go to completion.

The cause of catalyst poisoning may be either the profound dehydrogenating action of β-nitrostyrene or the poisoning influence of the reaction products. Although β-nitrostyrene extracts about 120 ml of hydrogen from 1 g of Pd black, under hydrogenation conditions the latter is rapidly regenerated.

This is confirmed by the correspondence between the amount of hydrogen absorbed in stage I and the degree of hydrogenation of β-nitrostyrene. The addition of large amounts of phenylacetaldehyde oxime does not reduce the initial rate of hydrogenation of β-nitrostyrene and, consequently, poisoning of the catalyst is not associated with formation of the oxime.

Hydrogenation with small amounts of catalyst is characterized not only by a decrease in rate, but also by a change in the direction of the process in the second stage (Table 2). In this case the yield of the primary amine decreases to 33.6%, and after absorption of 4 moles of hydrogen the catalyst contains 50.8% secondary $\beta\beta'$-[diphenylethyl]amine, about 3% β-cyclohexylethylamine, 6% unreacted oxime, and about 1% other amines (probably $\beta\beta'$-[dicyclohexylethyl]amine and β-[cyclohexyl-β'-phenylethyl]amine).

Thus, the process of formation of the primary amine is complicated by a number of side reactions, the rates of which become commensurate with the rate of hydrogenation of the oxime. In this connection it becomes clear why, in order to obtain primary amines from arylnitroalkenes, it has been recommended to carry out the reduction with large amounts of catalyst—1 g per 0.02 mole of nitro compound [15]. From the data obtained, certain conclusions may be drawn concerning the pathways of reduction of β-nitrostyrene in an acidic medium. In the first stage β-nitrostyrene is reduced to phenylacetaldehyde oxime without intermediate formation of 1-phenyl-2-nitroethane. In the second stage the hydrogenation of the oxime proceeds in two directions (I and II), possibly through the intermediate formation of the aldimine and phenylethylhydroxylamine (A and B):

$$\begin{array}{llll} & \xrightarrow{\text{II}} C_6H_5CH_2CH{=}NH & \longrightarrow & (C_6H_5CH_2CH_2)_2NH \\ & \qquad A\uparrow & & \quad\nearrow \\ C_6H_5CH_2CH{=}NOH & & \text{I} & \\ & \qquad B\downarrow & & \quad\searrow \\ & \longrightarrow C_6H_5CH_2CH_2NHOH & & C_6H_5CH_2CH_2NH_2. \end{array}$$

The ratio of these directions depends on the amount of catalyst: in the presence of large amounts of catalyst only traces of the secondary amine are detected; with small amounts of catalyst, up to 51% secondary amine is formed, while the yield of the primary amine decreases from 92 to 34%.

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