FORMATION OF SULFUR COMPOUNDS IN THE HYDRODENITROGENATION OF PIPERIDINE, PYRIDINE, 1-PENTYLAMINE AND 1-PENT-4-ENYLAMINE ON A NICKEL–TUNGSTEN CATALYST IN THE PRESENCE OF HYDROGEN SULFIDE

Mirko ČERNÝ

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

Received September 23rd, 1981

Hydrogenations of piperidine, pyridine, 1-pentylamine, and 1-pent-4-enylamine were carried out in an autoclave at 300°C on a sulfidized nickel–tungsten catalyst using either pure hydrogen or a mixture of hydrogen with hydrogen sulfide. Hydrogen sulfide was found to raise the degree of conversion of the starting substances and accelerate the hydrodenitrogenation by formation of sulfur compounds; 1-pentanethiol, di(1-pentyl)sulfide, 2-methylthiacyclopentane, thiacyclohexane and other sulfur compounds were detected in the reaction mixtures in the presence of hydrogen sulfide. A reaction pathway is suggested of the hydrodenitrogenation of piperidine in the presence of hydrogen sulfide, accounting for the favourable effect of the latter on the hydrodenitrogenation of nitrogen compounds.

Hydrodenitrogenation (HDN) of pyridine[1–4], quinoline[5–7], and other heterocyclic nitrogen compounds in the presence of hydrogen sulfide or sulfur-containing compounds on sulfided catalysts was extensively studied in the past years. A tight relation has been established between hydrodenitrogenation and hydrodesulfuration. Increasing the degree of hydrogenolysis of piperidine or tetrahydroquinoline, which is a decisive factor in the HDN, hydrogen sulfide enhances the overall degree of conversion of the starting nitrogen compounds. The way in which hydrogen sulfide improves this hydrogenolysis activity is unknown[2]. Several more or less substantiated hypotheses have been set forth concerning the favourable effect of hydrogen sulfide on the reactions leading to the opening of the piperidine ring, hence to C—N bond scission: *1)* Hydrogen sulfide maintains the catalyst in a completely sulfided state which has a better activity[2–4]; while in the presence of hydrogen alone the catalyst loses sulfur, in the presence of sufficient hydrogen sulfide the catalyst remains fully sulfided. *2)* The effect of hydrogen sulfide may be due to its acidity: *a)* it may assist in the enhancement through its ability to improve the surface acidity of the catalyst itself[4,6,7], *b)* it may aid in reducing the absorptivity of basic nitrogen compounds on the catalyst surface[2], *c)* it may draw the metal from the catalyst to the surface of the support[6], *d)* it may form active transient intermediate complexes, which in its absence are unstable and decompose rapidly[2,4]. The centres catalyzing the C—N bond scission may involve a Brønsted acid site and a transition metal ion[6]. *3)* Formation of unstable, further hydrogenolyzing compounds containing the sulfhydryl group is suggested on HDN of 1,2,3,4-tetrahydroquinoline[5].

As this overview documents, the favourable effect of hydrogen sulfide on HDN is largely supposed to consist in an enhancement of the catalyst activity with respect to the C—N bond scission, resulting in the opening of the piperidine ring.

In the preceding work[8], dealing with HDN of pyridine in the presence of ethanethiol, propanethiol, thiophene, and hydrogen sulfide, the composition of the reaction mixtures from the HDN of pyridine was found different in the absence and in the presence of these sulfur compounds.

Based on the observed presence of a number of new nonbasic compounds it has been suggested that hydrogen sulfide not only acts as a catalyst in the piperidine HDN, but takes an active part in the reaction processes. In fact, pentylamine and other basic nitrogen compounds, intermediates in HDN of piperidine, can react with hydrogen sulfide, either added to the reaction mixture in the pure state or formed by hydrodesulfuration of organic sulfur compounds.

In the present work, attention has been therefore paid to this aspect of hydrorefining processes; the main objective was to analyze the neutral and acidic fractions from the HDN of pyridine and piperidine on a nickel–tungsten catalyst in the presence of hydrogen sulfide. Reasonable results could be obtained thanks to the fact that the HDN was conducted in an autoclave using pure compounds rather than their solutions in xylene, paraffin oil, or other solvents conventionally employed in hydrodenitrogenation studies; in fact, it is very difficult or even impossible to determine gas chromatographically the small quantities of the neutral compounds formed, if these solvents are present. The combined gas chromatography/mass spectrometry technique was also employed for the identification of some compounds in the neutral or acidic fractions. A drawback of the hydrodenitrogenation study carried out in the autoclave as outlined above was the fact that the amount of the hydrogen sulfide added could not be determined accurately enough, because it reacted instantly with piperidine, 1-pentylamine, or 1-pent-4-enylamine and the amount of the absorbed gas was proportional to the feeding period.

EXPERIMENTAL

Chemicals

Pyridine for UV spectroscopy was used after rectification.

Piperidine after rectification was transformed into picrate, which was triply recrystallized from ethanol. The released base was rectified and the fraction with the b.p. 105·5°C was used for the hydrogenation. The pyridine content was 0·093%.

1-Pentylamine was synthesized by reduction of valeronitrile with lithium aluminium hydride (71%, b.p. 103—104°C).

1-Pent-4-enylamine was obtained as follows: Allylmagnesium bromide was reacted with paraformaldehyde in ether to give 3-butenol (39%, b.p. 114·0—114·5°C), which by reaction with phosphorus tribromide in pyridine was transformed into 4-bromo-1-butene (80% p.b., 96·0 to 96·5°C). The latter was allowed to react with KCN in glycol to give allylacetonitrile (78%, b.p. 143—144°C), which then was reduced with lithium aluminium hydride to 1-pent-4-envlamine (71%, b.p. 105·0°C).

The preparation of the catalyst and the hydrogenation procedures have been described[8]. The reaction mixture was analyzed on a gas chromatograph with flame ionization detection using packings of 4% polyethylene glycol 1500 + 3% KOH on Chromosorb and 10% methylphenylsilicone oil on Chromosorb W. The column length was 3 m.

The gas chromatography/mass spectrometry analyses were performed by Dr K. Ubik (Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague) on a combined GC/MS instrument (Pye 104, Model 64, MS 902) using a Watson-Biemann separator. The ion source temperature was 120°C, electron energy 70 eV. The preparation of model sulfur compounds for the identification of the substances detected in the reaction mixture will be described in a forthcoming paper.

Hydrogenolysis of Pyridine in the Presence of Hydrogen Sulfide

20·0 g of pyridine and 0·50 g of catalyst were placed in an autoclave, which after flushing with hydrogen was filled with hydrogen sulfide from a pressure vessel to a pressure of 1·85 MPa and then with hydrogen to a total pressure of 6 MPa. The pyridine-to-hydrogen sulfide molar ratio was 1 : 0·23. The autoclave was heated at 300°C for 5 h; the maximum pressure during the heating was 15·5 MPa. The reaction mixture was allowed to cool down, diluted with 15 ml of ether, and neutralized with dilute hydrochloric acid under cooling with ice/water and stirring. The ether layer was dried with calcium chloride. The ether was distilled off to give 0·80 g of a distillate, b.p. 131—134°C, in which fifteen compounds were revealed by gas chromatography. The chromatogram was identical with that obtained after hydrogenolysis of piperidine in the presence of hydrogen sulfide. In the chromatographic treatment of the starting mixture, attempts were made to prior trap the basic substances on a $CuCl_2$ column[9]. Pyridine, piperidine, and other basic substances were trapped perfectly, but only five neutral substances were detected; the remaining neutral substances, present in trace quantities, could not be trapped.

Hydrogenolysis of Piperidine

20·0 g of piperidine and 0·50 g of catalyst were heated at 300°C for 5 h. The initial pressure of hydrogen, 6 MPa, reached 16 MPa during the heating, and after the cooling down was 5·6 MPa. Samples were taken from the autoclave 1, 3 and 5 h after attaining the temperature 295°C. The fractions of the major components in the reaction mixture were as follows: pentane + pentenes 0·03, 0·05, and 0·10%; 1-methylpiperidine 0·04, 0·05, and 0·05%; piperidine 96·9, 90·8, and 83·8%; pyridine 0·39, 0·24, and 0·20%; 1-pentylpiperidine 0·21, 0·36, and 0·73%; higher-boiling substances 2·42, 8·51, and 15·12%. The reaction mixture was diluted with 10 ml of water and 5 ml of ether, and neutralized with dilute hydrochloric acid under cooling with ice/water and stirring; methyl red was used as indicator. The ether extract was distilled from a Hickmann flask. After distilling off the ether up to b.p. 36°C, the bath temperature was raised again to 220°C. About 0·1 g was obtained of a distillate containing substances which were also present in the ether fraction. Mass spectrometry revealed the presence of the following major compounds: 4-methylnonane-($M^{+\cdot} = 142$), 1-methyl-Z-4-isopropylcyclohexane ($M^{+\cdot} = 140$), 1-methyl-E-4-isopropylcyclohexane ($M^{+\cdot} = 140$), methylisopropylcyclohexene ($M^{+\cdot} = 138$), and methylisopropylcyclohexene ($M^{+\cdot} = 138$), probably 2-menthene. As a blank experiment, isolation of the neutral fraction from the starting piperidine was attempted, but no neutral compounds were present in the ether extract.

Hydrogenolysis of Piperidine in the Presence of Hydrogen Sulfide

20·0 g of piperidine and 0·50 g of catalyst were placed in the autoclave, which after flushing with hydrogen was filled with hydrogen sulfide to the pressure of 1·8 MPa and subsequently with hydrogen to the total pressure 3·5 MPa. The autoclave was heated at 300°C for 5 h and no samples were taken. The maximum pressure during the heating was 14 MPa, which dropped to 1 MPa after cooling

down. The contents of the autoclave (solid crystalline fraction) were taken up in 20 ml of water and 30 ml of ether, and the stirred and cooled mixture was neutralized with concentrated hydrochloric acid using methyl red as indicator. The ether extract was washed with acidified water and pure water and dried with sodium sulfate. Distillation from a Hickmann flask afforded 3·5 g of a neutral fraction, boiling predominantly in the region of 130—140°C at normal pressure. The remainder of the distillate was obtained at a reduced pressure of 1·3 Pa. The acidic aqueous solution was alkalized and extracted with ether to give a basic fraction, which was distilled to afford 7·1 g of distillate, b.p. predominantly about 100°C. The remainder was again obtained by distillation at a reduced pressure of 1·3 Pa. The chromatogram revealed that the basic fraction contained 1-methylpiperidine (0·40%), 1-ethylpiperidine, piperidine (60·4%), pyridine (0·59%), 1-pentylpiperidine (3·59%), higher-boiling compounds, and diethyl ether.

The neutral fraction was subjected to chromatographic separation on a column with a methylphenylsilicon oil packing and on polyethylene glycol + KOH packing. A total of fifteen compounds were detected. The chromatogram was identical with that of the neutral fraction from the hydrogenolysis of pyridine in the presence of hydrogen sulfide. Four compounds were identified as the major components, constituting about 98% of the neutral fraction: 1-pentanethiol, 2-methylthiacyclopentane ($M^{+\cdot} = 102$), thiacyclohexane ($M^{+\cdot} = 102$), and di(1-pentyl)sulfide. The neutral fraction contained in addition small quantities of eleven compounds identified by way of synthesis of the expected model compounds and by spectrometry.

Hydrogenolysis of 1-Pentylamine

20·0 g of 1-pentylamine and 0·50 g of catalyst were heated in the autoclave at 300°C for 5 h. The hydrogen pressure, initially 4 MPa, rose during the reaction to 10·9 MPa. Samples were taken 1, 3, and 5 h after the beginning of the heating. After cooling down the autoclave, the contents were collected and regarded as a sample taken after 6 h. Gas chromatographic analysis afforded the following data: pentane 0·3, 1·0, 1·6, and 3·0%; 1-pentylamine 94·4, 82·5, 70·2, and 68·4%; di(1-pentyl)amine 4·1, 13·0, 22·8, and 23·0%; and higher-boiling substances calculated as the difference to 100% (1·2, 3·5, 5·4, and 5·6%). A portion of the main fraction (6·9 g), diluted with 10 ml of ether and 5 ml of water and stirred and cooled with ice/water, was acidified with concentrated hydrochloric acid using methyl red as indicator. The ether layer was drawn off, washed with a small volume of water, and dried with calcium chloride. The ether was distilled off to give approximately 20 mg of the distillation residue, in which no less than ten compounds were detected gas chromatographically; they were not amenable to a detailed investigation. The aqueous solution of the base hydrochlorides was alkalized with concentrated KOH. Distillation afforded 5·1 g of distillate, boiling in the region of 78 to 200°C, which in addition to a small amount of ether only contained 1-pentylamine, di(1-pentyl)amine, and tri(1-pentyl)amine.

Hydrogenolysis of 1-Pentylamine in the Presence of Hydrogen Sulfide

The autoclave containing 20·0 g of 1-pentylamine and 0·50 g of catalyst was triply flushed with hydrogen, and hydrogen sulfide was introduced up to the total pressure 1·8 MPa. The reaction mixture warmed spontaneously to up 80°C. The hydrogen sulfide dosing was inaccurate, as the gas obviously reacted with 1-pentylamine and the amount of the introduced hydrogen sulfide was dependent on the feeding period. After disconnecting the hydrogen sulfide inlet, hydrogen was let in up to the pressure 3·5 MPa, and the system was heated at 300°C for 5 h. The maximum pressure was 16·0 MPa. After cooling down, the reaction mixture contained 3·2% pentane, 30·7% 1-pentylamine, and 2·3% di(1-pentyl)amine. A sample portion (6·9 g) was diluted with ether; two layers formed: the upper ether layer contained the neutral fraction and free bases, the bottom

layer, 1-pentylamine hydrosulfide. The mixture was diluted with 5 ml of water, and under cooling with ice/water, acidified with concentrated hydrochloric acid using methyl red as indicator. The ether extract was washed with water, dried with calcium chloride, and distilled to give 1·05 g of a neutral fraction, consisting mainly of 1-pentanethiol and small quantities of di(1-pentyl) sulfide and of an unidentified compound. The basic fraction was isolated in the usual fashion. 3·75 g of distillate was obtained containing 1-pentylamine and di(1-pentyl)amine as the major constituents.

Hydrogenolysis of 1-Pent-4-enylamine

20·0 g of the amine and 0·50 g of catalyst were heated under hydrogen at 300°C for 5 h. The initial hydrogen pressure, 4·4 MPa, rose to 9·2 MPa. Samples were taken 1, 3, and 5 h after reaching the temperature 300°C. After cooling down, a sample was taken and regarded as one after 6 h. The samples contained pentane + pentene (5·1, 5·6, 7·7, and 16·1%), 1-pentylamine (13·1, 10·4, 12·1, and 13·8%), the starting substance (19·1, 8·8, 7·2, and 6·4%), and di(1-pentyl)amine (1·7, 2·3, 2·6, and 2·4%). Two additional compounds were present which could not be identified with certainty, but which according to their retention times were probably (1-pent-4-enyl) (1-pentyl)amine and di(1-pent-4-enyl)amine; their contents were 1·7, 2·5, 2·4, and 2·1% and 2·4, 2·8, 2·7, and 2·2%, respectively.

Hydrogenolysis of 1-Pent-4-enylamine in the Presence of Hydrogen Sulfide

Hydrogen sulfide was introduced into the autoclave containing 18·3 g of the amine and 0·457 g of catalyst and flushed with hydrogen, and the reaction mixture warmed spontaneously up to 80°C. The hydrogen sulfide dosing was inaccurate as the two components reacted. Hydrogen was then fed in up to the pressure 4 MPa, and the reaction mixture was heated at 300°C for 5 h. After cooling down the reaction mixture was worked up to give 5·5 g of distillate, b.p. from 50 to 150°C (distillation residue was 1·1 g), the basic fraction afforded 4·1 g of distillate, b.p. from 50 to 210°C (distillation residue 1·0 g). A total of nineteen compounds were detected gas chromatographically in the neutral fraction. Identified were 1-pentanethiol, 1-pent-4-enethiol, 2-methylthiacyclopentane, thiacyclohexane, and di(1-pentyl) sulfide. The basic fraction contained a total of fifteen compounds, no more subjected to a detailed investigation.

RESULTS AND DISCUSSION

The results of the HDN of pyridine and piperidine, carried out both with the pure compounds and in the presence of hydrogen sulfide, lead unambiguously to the conclusion that hydrogen sulfide increases the degree of hydrodenitrogenation also by directly taking part in the chemical reactions. Thus the effect consists not only in the influence of hydrogen sulfide on the catalyst, outlined in the introduction, but primarily in its role as a reacting component.

In the previous study[8], hydrogen sulfide present in the reaction mixture during the HDN of pyridine on a sulfided nickel-tungsten catalyst induced an increase in the pyridine conversion after 5 hours' hydrogenolysis at 300°C from 14% to 20%; the content of C_5 hydrocarbons (pentane and pentenes) rose from 0·25% to 0·66%.

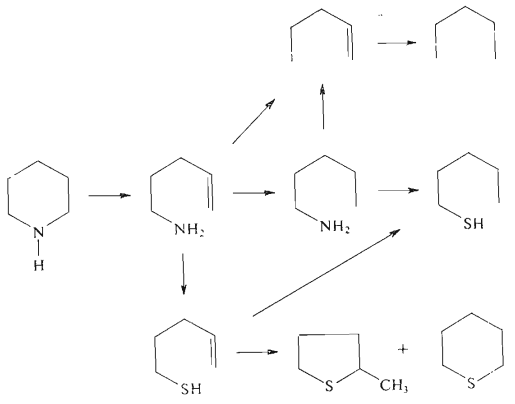
In the present wotk, attention was focussed on the HDN of piperidine. In the absence of hydrogen sulfide, the reaction mixture contained only small quantities of pentane, 1-pentene, and neutral substances predominantly of terpenic nature (0·5% wt. with respect to the starting piperidine) as the nonbasic fraction. In the presence of hydrogen sulfide, on the other hand, the proportion of neutral substances was considerably greater (17·5%), but these were not the final products of the hydrogenolysis of piperidine, hence C_5 and C_{10} hydrocarbons, but new compounds containing sulfur. The degree of piperidine conversion, calculated from the loss of piperidine from the reaction mixture, was higher. It would be similarly higher if it were calculated on the basis of the amount of ammonia formed on the scission of the C—N bonds or of the percentage content of nitrogen in the liquid moiety; both ways of expressing the degree of conversion of nitrogen compounds are currently used for determining the degree of HDN. However, in the reaction conditions applied the C—N bond scission was followed by the formation of new C—S bonds. Of these compounds, which so far have not been reported to be present in reaction mixtures from HDN of nitrogen compounds in the presence of hydrogen sulfide or sulfur compounds, 1-pentanethiol, 2-methylthiacyclopentane, thiacyclohexane, and di(1-pentyl)sulfide were identified with certainty. The occurrence of the two cyclic compounds, 2-methylthiacyclopentane and thiacyclohexane, is of interest, as they are formed by cyclization from 1-pent-4-enethiol. This implies that the latter compound must be an intermediate product of the HDN of piperidine in the presence of hydrogen sulfide. Its occurrence can be explained in terms of a substitution reaction of 1-pent-4-enylamine.

For verifying this assumption, 1-pent-4-enylamine was synthesized and subjected to HDN under the same conditions as used in the HDN of pyridine and piperidine, hence both in the absence and in the presence of hydrogen sulfide. The same applied also to 1-pentylamine. The experiments gave evidence that in the presence of hydrogen sulfide, new sulfur-containing compounds were formed and the degree of conversion of the starting amines increased. This was apparent particularly in the case of 1-pentylamine: while the work-up of the reaction mixture (6·9 g) in the absence of hydrogen sulfide led to 0·02 g of neutral substances and 5·05 g of basic substances, in the presence of hydrogen sulfide the neutral fraction (from the same reaction mixture quantity) was as high as 1·05 g and the basic fraction dropped to 3·75 g. The effect of hydrogen sulfide on the HDN of 1-pentylamine consisted also in a suppression of the disproportionation of the primary amine into secondary and tertiary amines: in the presence of hydrogen sulfide the reaction mixture contained 4·5 times less 1-pentylamine, 24 times less di(1-pentyl)amine, and no tri(1-pentyl)amine as compared with the HDN of pure 1-pentylamine. The amount of C_5 hydrocarbons was approximately the same (3·0 and 3·2%, respectively).

The fact that while 1-pentanethiol and di(1-pentyl) sulfide were found in the reaction mixture from HDN of 1-pentylamine, 2-methylthiacyclopentane and thiacyclohexane were not detected, indicates that no 1-pent-4-enethiol, which could afford the

above two compounds, was formed. This is borne out also by the results of HDN of 1-pent-4-enylamine without and with hydrogen sulfide. In this case, too, the proportion of neutral substances was appreciably higher if hydrogen sulfide was present. Of great importance is here the fact that 2-methylthiacyclopentane and thiacyclohexane were identified in the reaction mixture, confirming thus the presence of 1-pent-4-enethiol, which could form from 1-pent-4-enylamine only through a substitution reaction. The effect of the double bond in 1-pent-4-enylamine as compared with 1-pentylamine showed up also in the easier formation of C_5 hydrocarbons, hence easier C—N bond scission. This is apparent from the content of C_5 hydrocarbons in the product of the HDN of 1-pentylamine.

Based on the results obtained, a reaction pathway is suggested for the HDN of piperidine in the presence of hydrogen sulfide as shown in Scheme 1.



SCHEME 1

The piperidine ring is opened as a result of C—N bond scission, giving rise to 1-pent-4-enylamine. A minor part of this compound is hydrogenated to 1-pentylamine, a major part undergoes a substitution reaction with hydrogen sulfide to give 1-pent-4-enethiol. The latter then cyclizes to 2-methylthiacyclopentane and thiacyclohexane, hydrogenates to 1-pentanethiol, or further undergoes polymerization and condensation reactions. 1-Pentylamine releases ammonia to give pentene and reacts with hydrogen sulfide to afford 1-pentanethiol. Pentane and pentene are formed by hydrogenolysis of 1-pent-4-enylamine and 1-pentylamine; it is also conceivable that

they appear as a result of hydrodesulfuration of 1-pent-4-enethiol and 1-pentanethiol. In addition to these principal reactions there occur also addition reactions of hydrogen sulfide to the double bonds, disproportionations of the R—NH_2 and R′—NH_2 primary amines (R = 1-pentyl, R′ = 1-pent-4-enyl) to the R_2NH, R'_2NH, and RR′NH secondary amines, formation of R_2S, R'_2S, and RR′S sulfides, and formation of neutral and basic higher-boiling fractions and non-distillable condensation and polymerization products. The pentene formed also isomerizes to paraffinic hydrocarbons and C_{10} terpenic hydrocarbons.

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Translated by P. Adámek.