FORMATION OF SULPHUR COMPOUNDS DURING THE HYDRODENITROGENATION OF ANILINE, CYCLOHEXYLAMINE, BENZYLAMINE, AND 2-PHENYLETHYLAMINE ON A NICKEL–TUNGSTEN CATALYST IN THE PRESENCE OF HYDROGEN SULPHIDE

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Hydrodenitrogenations of aniline, cyclohexylamine, benzylamine, and 2-phenylethylamine were performed on a sulphided nickel–tungsten catalyst at 300°C in an autoclave filled with hydrogen in the absence and in the presence of hydrogen sulphide. Due to the presence of hydrogen sulphide the degree of conversion increased from 0·9 to 3·6% for aniline and from 72 to 99% for benzylamine, and the fraction of neutral substances increased from 2·4 to 7% for cyclohexylamine and from 5·0 to 8·9% for 2-phenylethylamine. The neutral fractions contained cyclohexanethiol, thiobenzamide, 2-phenylethanethiol, and other sulphur compounds giving evidence that the increased degree of conversion of the amines was due to the hydrogen sulphide taking direct part in the chemical reaction.

The investigation of the hydrodenitrogenation (HDN) of the title compounds is a continuation of the study of the HDN of pyridine, piperidine, 1-pentylamine, 1-(4-pentenyl)amine, quinoline, 1,2,3,4-tetrahydroquinoline, 2-methylpiperidine, and 2-methylquinoline conducted on a sulphided Ni–W catalyst in the presence of hydrogen sulphide[1–3]. The favourable effect of hydrogen sulphide on the HDN of nitrogen-containing heterocyclic substances such as pyridine or quinoline is often explained in terms of its action on the catalyst only. According to Satterfield and coworkers[4], hydrogen sulphide reduces the number of sulphur vacancies, hence, centres responsible for the hydrogenation and dehydrogenation of the heterocyclic ring, and increases reversibly the number of the Brønsted acid centres which catalyze the hydrogenolysis, *i.e.*, the C—N bond scission and ring isomerization. As a result of this action, the hydrogenation of aromatic rings is suppressed and the role of the hydrogenolysis reactions increases. In fact, however, the favourable effect of hydrogen sulphide on the HDN of some nitrogen bases can be explained also in terms of its chemical action[5,6]. Sulphur compounds have been detected in appreciable quantities in the neutral fractions from the HDN of model substances; for instance, thiacyclo-

hexane and 2-methylthiacyclopentane have been found during the HDN of pyridine, piperidine, or 1-(4-pentenyl)amine[1,2], similar cyclic sulphur compounds have been identified in the HDN products of quinoline, 1,2,3,4-tetrahydroquinoline, or 2-methylquinoline[2,3]. In this manner hydrogen sulphide has been proved to raise the degree of conversion of these compounds by participating chemically in the HDN giving rise to sulphur compounds, which on additional hydrodesulphuration reactions furnish mixtures of alkanes, alkenes and hydroaromatics.

The aim of the present work was to examine the effect of hydrogen sulphide on the HDN of additional nitrogen compounds occurring as actual or potential intermediates in the HDN of some model substances, *viz.* aniline, cyclohexylamine, benzylamine, and 2-phenylethylamine. These compounds were subjected to HDN on a sulphided Ni—W catalyst in pure hydrogen or in hydrogen mixed with hydrogen sulphide.

HDNs of aniline have been performed using palladium[7], rhodium[8], or cobalt, nickel, molybdenum and tungsten[9-13] catalysts in their oxidic or sulphide forms. The neutral fractions contained benzene, cyclohexane, or their mixtures in dependence on the reaction conditions. Propylcyclohexane, propylbenzene, and propylcyclohexene were found in the neutral fraction from the HDN of 2-propylaniline on a sulphided Ni–Mo catalyst[14]. The degree of HDN of 2-ethylaniline on this catalyst was reduced by hydrogen sulphide[4], which slowed down the hydrogenation and dehydrogenation and accelerated the hydrogenolysis and isomerization reactions. Cyclohexylamine served as the model substance for HDN during the study of the structure of some basic compounds[9,13]; cyclohexane emerged as the major product on Mo and W catalysts in their oxidic and sulphided forms. With benzylamine the HDN proceeds under considerably milder conditions than with all of the other compounds mentioned. On a Pd catalyst the C–N bond scission took place at temperatures as low as 20°C giving rise to methylcyclohexane[15]. In ethanol, the HDN occurred at 150—160°C (ref.[16]). On $RhCl_3$, toluene formed in a 59% yield on heating with 2,3-dihydroindole in cumene[8] at 180°C. 2-Phenylethylamine gave ethylbenzene in a 39% yield under similar conditions[8], or in a 23% yield in the presence of Raney nickel in ethanol at its boiling temperature[17].

EXPERIMENTAL

The hydrodenitrogenations were conducted in a rocking autoclave of a 97 ml volume, which, accomodating 20 g of the substance of choice and 0·500 g of catalyst, was flushed twice with hydrogen and then filled with hydrogen in an amount such that its pressure in the system heated to the requisite temperature did not exceed 15 MPa. In experiments where hydrogen sulphide was admitted, the autoclave flushed twice with hydrogen was filled with hydrogen sulphide gas to a maximum pressure of 1·7 MPa, and hydrogen was added to a total pressure of 6—7 MPa. The hydrogen used up was replenished during the HDN so that the process occurred under a pressure of 13—15 MPa. All reactions were sustained by heating at 300°C for 6 h. After cooling down, sample was taken and the reaction mixture, which was pasty or even solid, particularly on the reaction in the presence of hydrogen sulphide, was diluted with ether and water, homogenized, and poured off. The constantly cooled mixture then was neutralized with hydrochloric acid, the ethereal extract was drawn off, washed with water, and dried with calcium chloride. The ether was removed by evaporation and the neutral fraction obtained was weighed and analyzed.

Catalyst preparation has been described[18]. The reaction mixtures were analyzed on a gas chromatograph with flame ionization detection, using a packing of 5% OV-17 silicon elastomer on Inerton AW (column length 2·5 m). Gas chromatography/mass spectrometry analyses were performed on an MS 902 instrument (Associated Electric Industries, Manchester) interfaced to a Pye Unicam 104 gas chromatograph via a steel capillary with a Biemann separator. The chromatographic column (glass, length 1·8 m, i.d. 4 mm) was packed with 3% OV-17 silicone elastomer on Gas Chrom Q support. Thiols were observed to undergo dehydrogenation dimerization at higher temperatures, giving rise to the corresponding disulphides.

Starting substances. Benzylamine (Light) was neutralized on ice with concentrated hydrochloric acid, and the hydrochloride was extracted triply with ether. After releasing the base with solid KOH, benzylamine was extracted with ether and rectified under reduced pressure. Aniline (Fluka) and cyclohexylamine were purified likewise. 2-Phenylethylamine was prepared from benzyl cyanide by reduction with $LiAlH_4 + AlCl_3$. The original procedure[19] was adapted so that the neutral fraction was steam distilled off from the acidified solution of the hydrochloride after the reduction, and its residues were removed after cooling, by extraction with ether. Fraction of b.p. 99—102°C/1·3 kPa was used.

HDN of aniline was performed at a pressure of 13·5 MPa. The resulting mixture contained 99·1% aniline. The neutral fraction, 1·3% (m/m) with respect to the initial aniline, contained mainly cyclohexane and cyclohexene (in a mutual ratio of approximately 2—3 : 1) and diphenylamine. The acid aqueous solution was neutralized and extracted with ether to give 96·7% aniline and N-cyclohexylaniline, b.p. 66°C/1·3 kPa.

HDN of aniline in the presence of hydrogen sulphide was conducted at a maximum pressure of 15·5 MPa. The mixture, containing 96·4% aniline, was worked up to give 2·3% (with respect to initial aniline) of neutral fraction which in addition to diphenylamine (1·7%) and aniline (0·03%) contained cyclohexane (0·14%), cyclohexene (0·03%), benzene (0·04%), cyclohexylcyclohexane (0·002%), and also cyclohexanethiol (0·27%) and traces of dicyclohexyl disulphide.

HDN of benzylamine was accomplished at a pressure of 13—13·7 MPa. The product contained 28·3% benzylamine. The insoluble solid (0·1 g) was filtered out, recrystallized from ethanol, and identified as tribenzylamine hydrochloride. The neutral moiety was obtained as fraction I, b.p. up to 108°C (8·95 g), and fraction II, b.p. 108—109°C/1·3 kPa (0·35 g). Fraction I was constituted mainly by toluene, which was also present in fraction II, where the major components were 1,2-diphenylethane, 2-methyldiphenylmethane, 4-methyldiphenylmethane, N-benzylidenebenzylamine, and benzonitrile. Traces of diphenylmethane, 1,1-diphenylethane, benzylcyclohexane, 3-benzylcyclohexene, dicyclohexylmethane, cyclohexylcyclohexane, hexylbenzene, heptylbenzene, 1-phenyl-5-methylhexane, 1,3-diphenylpropane, 1,4-diphenylbutane, and butylcyclohexane were also present. The aqueous acidified solution was concentrated at reduced pressure and the bases were relased with KOH, extracted with ether, dried with solid KOH, and distilled. Benzylamine, b.p. 60—61°C/1·2 kPa (5·0 g), and dibenzylamine, b.p. 149—153°C/1·2 kPa (2·2g), were obtained.

HDN of benzylamine in the presence of hydrogen sulphide was executed at 13—15 MPa. The benzylamine to hydrogen sulphide molar ratio was 1 : 0·30. Benzylamine was found in the product in a fraction of 0·96%. After the ether was removed from the neutral fraction (12·4 g) by distillation, a precipitate separated; this was recrystallized from a toluene–ether mixture to give 2·1 g of thiobenzamide, identified by its mass spectrum and melting point. A fraction boiling at 70—109°C, containing toluene with a small amount of 1,2-diphenylethane, was obtained by distillation; the fraction was not subject to mass spectrometry analysis. Alkalized and extracted with ether, the acid aqueous solution furnished 0·35 g of a basic fraction, the major component of which was benzylamine. No dibenzylamine was detected.

HDN of cyclohexylamine. In contrast to the other HDNs, the autoclave was filled with hydrogen to a pressure of 7 MPa; on heating to 300°C the pressure increased slowly from the maximum of 14·9 MPa to 15·6 MPa, and after cooling down the pressure was again 7 MPa. The reaction mixture was neutralized to give 3·2 g of insoluble dicyclohexylamine hydrochloride. The neutral fraction (0·49 g) contained cyclohexane and cyclohexene as the major components together with traces of cyclohexylcyclohexane and 3-cyclohexylcyclohexene. The basic fraction (14·5 g) consisted of the initial amine.

HDN of cyclohexylamine in the presence of hydrogen sulphide. A solid reaction product was obtained. The neutral fraction (1·4 g, 7%) contained cyclohexanethiol (4·9% with respect to initial amine), cyclohexane (0·6%), cyclohexene (0·3%), dicyclohexyl disulphide (0·8%), dicyclohexyl sulphide (0·04%) and cyclohexylcyclohexane (0·03%). The basic fraction contained unreacted amine (15·4 g).

HDN of 2-phenylethylamine was performed at a maximum pressure of 13·6 MPa. A precipitate of di-(2-phenylethyl)amine was isolated and recrystallized from ethanol (0·95 g). The neutral fraction (0·9 g, 4·95%) was composed of ethylbenzene (4·8%), toluene (0·04%), styrene (0·02%), 1,3-diphenylbutane (0·06%), 1,4-diphenylbutane (0·02%), and 1,3-diphenylpropane (0·01%). The basic fraction (15·8 g), b.p. 79—80°C/1·3 kPa, was the initial amine.

HDN of 2-Phenylethylamine in the presence of hydrogen sulphide. The reaction mixture was semiliquid. The neutral fraction (1·7 g, 8·9%) again contained ethylbenzene (6·65%), toluene (0·07%), styrene (0·03%), 1,3-diphenylbutane, 1,4-diphenylbutane, and 1,3-diphenylpropane (total 0·44%). In addition, 2-phenylethanethiol (1·42%), 1-phenylethanethiol (0·14%), three $C_{16}H_{18}S$ compounds, and a $C_{16}H_{12}S$ compound (total 0·11%) were found. A basic fraction of b.p. 79—81°C/1·3 kPa was isolated in a yield of 16·2 g.

RESULTS AND DISCUSSION

Hydrogen sulphide is found to have a favourable effect on the hydrogenolysis reaction in the HDN of aniline, cyclohexylamine, benzylamine, and 2-phenylethylamine, similarly as in the HDN of some compounds containing heterocyclically bonded nitrogen, where the presence of hydrogen sulphide brought about an increase in the degree of conversion (*e.g.*, from 14 to 20% for pyridine[18]) or in the total neutral fraction (from 0·5 to 17·5% for piperidine[1], from 0·3 to 15% for 1-pentylamine[1], from 2·6 to 7·7% for 1,2,3,4-tetrahydroquinoline[2], or from 25 to 50% for isoquinoline[3]) and where the neutral fraction contained sulphur compounds in appreciable quantities (*e.g.*, 40% of the neutral fraction for 2-methylquinoline or 90% for 2-methylpiperidine[3]).

In the HDN of aniline, the degree of conversion of the starting substance increased from 0·9 to 3·6% owing to the presence of hydrogen sulphide. The neutral fraction from the HDN in the presence of hydrogen sulphide contained the expected compounds such as cyclohexane, cyclohexene, benzene, cyclohexylcyclohexane, cyclohexanethiol, and dicyclohexyl disulphide; their amounts, however, were as low as tenths per cent. The structure of the compounds detected suggests that the first step in the HDN of aniline is the hydrogenation of the benzene ring system. In fact,

benzene has also been found in the reaction mixture; this, however, can be explained in terms of the dehydrogenation of cyclohexene. Cyclohexanethiol was present in an amount of 0·27%. This compound was found in the product of the HDN of cyclohexylamine in the presence of hydrogen sulphide in a yield of 4·9%, together with dicyclohexyl sulphide and dicyclohexyl disulphide. Owing to the presence of hydrogen sulphide in the HDN of cyclohexylamine the total neutral fraction increased from 2·4 to 7%. Hydrogen sulphide also hindered the disproportionation reactions of cyclohexylamine to dicyclohexylamine, which in the absence of hydrogen sulphide was isolated in an amount of 13%.

During the HDN of benzylamine, hydrogen sulphide induced an increase of the amine conversion from 71·7 to 99%. In the absence of hydrogen sulphide the neutral fraction contained toluene as the major component, together with benzonitrile and compounds derived from more or less hydrogenated diphenylalkanes, of which 1,2-diphenylethane, 2-methyldiphenylmethane, and 4-methyldiphenylmethane were of interest from the point of view of the hydrogenolysis mechanism. In the presence of hydrogen sulphide, the neutral fraction contained 10·5% thiobenzamide, the formation of which can be explained in terms of the dehydrogenation of benzylamine to benzonitrile which in turn reacts with hydrogen sulphide in the usual manner. Hydrogen sulphide also suppressed the disproportionation of benzylamine to di- and tribenzylamine.

Present during the HDN of 2-phenylethylamine, hydrogen sulphide induced an increase in the neutral fraction from 5·0% to 8·9%; in addition to ethylbenzene as the major product, this fraction contained toluene, styrene, and diphenylalkanes. 2-Phenylethanethiol and other sulphur compounds were also obtained, and the disproportionation of the amine to a secondary amine was suppressed.

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