FORMATION OF SULPHUR COMPOUNDS IN THE HYDRODENITROGENATION OF 2-METHYLQUINOLINE, 2-METHYLPIPERIDINE, INDOLE, AND ISOQUINOLINE ON A NICKEL–TUNGSTEN CATALYST IN THE PRESENCE OF HYDROGEN SULPHIDE

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2-Methylquinoline, 2-methylpiperidine, indole, and isoquinoline were subjected to hydrodenitrogenation (HDN) on a sulphidized nickel–tungsten catalyst in an autoclave at 300 and 350°C using pure hydrogen or a hydrogen–hydrogen sulphide mixture. The neutral fraction from the HDN of 2-methylquinoline and 2-methylpiperidine contained 40 and 90% sulphur compounds, respectively. The presence of hydrogen sulphide in the HDN of isoquinoline resulted in an enhanced fraction of the neutral moiety. A reaction mechanism is suggested for the HDN of 2-methylquinoline and 2-methylpiperidine in the presence of hydrogen sulphide, in which the latter contributes to the higher degree of conversion due to the formation of corresponding sulphur compounds.

This hydrodenitrogenation (HDN) study of the title compounds is a continuation of the investigation of the HDN of pyridine, piperidine, 1-pent-4-enylamine, and quinoline on a sulphidized Ni–W catalyst in the presence of hydrogen sulphide[1,2], in which the latter was found to raise the degree of conversion by taking part in the chemical reactions; compounds involving sulphur atoms were identified in the reaction mixture, which gave evidence that hydrogen sulphide affects the HDN of the compounds under study by formation of sulphur compounds. These entered then hydrodesulphurization reactions to give a mixture of the corresponding alkanes, alkenes, and aromatics.

In the present work, the HDN is studied of other compounds containing a heterocyclically bonded nitrogen that are present in crude oil and its fractions. Particular attention is paid to the neutral fractions, containing hydrocarbons and sulphur compounds. In the past, the reaction mixtures from the HDN using pure hydrogen were analyzed for indole[3–8], isoquinolin[9], 2-methylquinoline[10,11], 2-methylpiperidine[12], and 2-methylpyridine[13]. No sulphur-containing compounds have been reported to arise from the HDN of indole in the presence of hydrogen sulphide[14]. Other authors dealing with the HDN of pyridine and quinoline bases in the presence of hydrogen sulphide explain the favourable effect of the latter in terms of an increased activity of

the catalyst employed. In the present paper it is shown that a way in which hydrogen sulphide can raise the degree of conversion of nitrogen substances is by formation of sulphur compounds.

EXPERIMENTAL

Chemicals and apparatus. 2-Methylquinoline (Cambrian Chemicals) and isoquinoline (Fluka) were distilled prior to use; their purity was checked gas chromatographically. 2-Methylpiperidine was obtained by reduction of 2-methylpyridine with sodium in butanol (yield 86%) and double crystallization of picrate. B.p. after rectification was 116–117°C. Indole (Fluka) *puriss.* was used with no pretreatment.

The catalyst was prepared as reported previously[15]. The reaction mixtures were analyzed on a gas chromatograph with flame ionization detection using a 2·5 m column packed with 5% OV-17 silicone elastomer on Inerton AW. The gas chromatography-mass spectrometry analyses were performed on an AEI MS 902 mass spectrometer (Associated Electric Industries, Manchester, England) interfaced to a Pye Unicam 104 gas chromatograph equipped with a stainless steel capillary and a Biemann separator. A chromatographic glass column 1·8 m long, i.d. 4 mm, was used; the packing was 3% OV-17 silicone elastomer on Gas Chrom Q. At higher temperatures, thiols were found to undergo dehydrogenation dimerization giving rise to the corresponding disulphides.

Hydrogenolysis of 2-methylquinoline in the presence of hydrogen sulphide. 2-Methylquinoline (20 g) with catalyst (1 g) was placed in a 97 ml autoclave, which was then flushed with hydrogen and filled with hydrogen sulphide to a pressure of 1·7 MPa; the reactant and hydrogen sulphide were in the molar ratio of 1 : 0·39. After admitting hydrogen up to a pressure of 6 MPa in cold, the hydrogenation was conducted at 350°C for 5 h, admitting additional hydrogen up to a pressure of 12–14 MPa. After cooling down, the reaction mixture was diluted with water and ether and acidified with dilute hydrochloric acid. The ether layer was separated and dried with calcium chloride, and the solvent was distilled off at a bath temperature of 100°C to give 3·2 g of a neutral fraction, consisting of 60% hydrocarbons and 40% sulphur compounds. The following hydrocarbons were indentified: butylcyclohexane and 1-methyl-2-ethylbenzene (32% in total), decahydronaphthalene (11%), 1-methyl-2-propylbenzene (6%), 1-methyl-4-isopropylcyclohexane (1%), propylcyclohexane (1%), 1-methyl-4-ethylcyclohexane (1%), ethylcyclohexane (0·5%), methylcyclohexane (0·5%) and butylbenzene (0·5%). The remaining 6·5% was constituted by C_7H_{14}, $C_{10}H_{16}$, $C_{10}H_{16}$, and $C_{10}H_{20}$ hydrocarbons and by substances with $M^+ = 128, 128, 130, 130, 130, 132, 132,$ and 138, the structure of which could not be elucidated unambiguously. Among the sulphur-containing substances, octahydro-2-methyl-2*H*-1-benzothiopyran and octahydro-2-ethyl-benzo(*b*) thiophene were the major components; three $C_{10}H_{18}S$ compounds (stereoisomers of the two above substances) and substances with $M^+ = 132$ and 184 were also present.

Hydrogenolysis of 2-methylpiperidine in the presence of hydrogen sulphide. 2-Metylpiperidine (19·5 g) and catalyst (1 g) were placed in the autoclave, the latter was flushed twice with hydrogen, hydrogen sulphide was admitted up to a pressure of 1·7 MPa, and hydrogen was added to a pressure of 4·7 MPa; the 2-methylpiperidine to hydrogen sulphide molar ratio was 1 : 0·28. The autoclave was heated at 300°C for 6 h. The reaction mixture, which became solid on cooling, was diluted with water (15 ml) and ether (15 ml) and made acidic with dilute hydrochloric acid under cooling. The ether layer was separated and dried with calcium chloride; ether was then removed by evaporation at a bath temperature of 100°C. A total of 2·4 g of a neutral fraction was obtained. The major constituent was 2-methylthiacyclohexane (54%); additional components

(besides a small amount of ether) were 1-hexene and 3-hexene (10%), 2-hexanethiol and 2,5-dimethylthiacyclopentane (17%), 2-ethylthiacyclopentane (4%), two $C_6H_{12}S$ compounds (probably 2-hex-5-enethiol and 1-hex-4-enethiol), $C_6H_{14}S$ (probably 1-hexanethiol), two $C_{12}H_{24}S$ compounds, $C_{12}H_{26}S$, $C_{12}H_{24}S_2$, and $C_{12}H_{26}S_2$. The acid aqueous solution was made alkaline to release basic compounds, which were extracted with ether and dried with solid KOH. The total amount was 14·7 g. In additon to 2-methylpiperidine as the highly predominating component, 2-hexylamine and 1-hexylamine were also found gas chromatographically to be present in a ratio of approximately 2·4 : 1. 1-(1-Hexyl)-2-methylpiperidine and 1-(2-hexyl)-2-methylpiperidine were also detected besides other substances that were not subject to examination.

Hydrogenolysis of isoquinoline in the absence of hydrogen sulphide. Isoquinoline (20 g) was heated with catalyst (0·5 g) in the 97 ml autoclave for 8 h at a temperature of 350°C and a pressure of 9—11 MPa. The mixture was cooled, and 17·4 g was neutralized with dilute hydrochloric acid under cooling with ice-cool water and extracted with ether. The extract was dried with calcium chloride and the solvent was evaporated to give 4·4 g (25%) of a fraction boiling at 60°C/100 kPa to 152°C/1·3 kPa. The basic fraction was isolated by alkalizing the aqueous solution and extracting with ether. The extract was dried with solid KOH and distilled to afford 4·5 g (26%) of a fraction boiling at 104—115°C/1·5 kPa. By composition the two fractions resembled closely those obtained from the HDN of isoquinoline in the presence of hydrogen sulphide.

Hydrogenolysis of isoquinoline in the presence of hydrogen sulphide. Isoquinoline (16·1 g) and catalyst (0·5 g) were placed in the autoclave, which was flushed with hydrogen and then filled with hydrogen sulphide to a pressure of 1·7 MPa and with hydrogen to a total pressure of 6 MPa; the isoquinoline to hydrogen sulphide molar ratio was 1 : 0·46. The autoclave was heated at 350°C and 12·5—14 MPa for 8 h. After sampling (0·5 g) the reaction mixture furnished 7·8 g (50%) of a neutral fraction boiling at 62°C/100 kPa—164°C/1·5 kPa, and 2·4 g (16%) of a basic fraction boiling at 108—114°C/1·5 kPa. In the neutral fraction, 1-methyl-2-ethylbenzene (85%), *o*-xylene (9%), 1,2-diethylbenzene (4%), methylindane (0·3%, the methyl group position was not identified), *cis* + *trans* 1-methyl-4-ethylcyclohexane (0·2H), ethylbenzene (0·2%), *cis* + *trans* 1-methyl-2-ethylcyclohexane (0·2%) and naphthalene (0·1%) were found. 1,2,3,4-Tetrahydronaphthalene, isoheptane, ethylcyclohexane, toluene, 1,2-diethylcyclohexane, bicyclononane-[0.3.4], 1-methyl-2-isopropylbenzene, xylene (the methyl group positions were not identified), dimethylcyclohexane (the methyl group positions were not identified), and a C_9H_{18} hydrocarbon were present in quantities below 0·1%. Of sulphur compounds, only *cis* + *trans* 2-thiadecahydronaphthalene (0·3%) and methylbenzo(*b*)thiophene (less than 0·1%) (methyl group probably in position 6) were present. In the basic fraction, 1,2,3,4-tetrahydroisoquinoline, isoquinoline, methylisoquinoline (four isomers, in two of them the methyl groups were in positions 1 and 6), and methyl-1,2,3,4-tetrahydroisoquinoline (four isomers, in two of them the methyl groups were in positions 1 and 6) were identified.

Hydrogenation of indole in the presence of hydrogen sulphide. Indole (12 g) with catalyst (0·5 g) was placed in the autoclave, which was flushed twice with hydrogen and filled with hydrogen sulphide to a pressure of 1·7 MPa and with hydrogen to a total pressure of 6 MPa; the indole to hydrogen sulphide molar ratio was 1 : 0·59. The reaction mixture was heated at 300°C for 6 h; the pressure increased to 12—14 MPa. The cooled reaction mixture was diluted with water and ether (10 ml each) and acidified with dilute hydrochloric acid using methyl red as indicator. The insoluble moiety was separated by filtration. From the ether layer containing the neutral fraction, the solvent was removed by evaporation, and two fractions were obtained by distillation: fraction I (0·2 g), boiling at 46—122°C, and fraction II (2·2 g), boiling at 122°C/100 kPa to 130°C/1·6 kPa. Fraction I contained 48% indole and 26% 1-methyl-2-ethylbenzene. Present were also ethylcyclohexane (4%), bicyclo[0.3.4]nonane (2%), ethylbenzene (2%), *o*-xylene (2%), 1-ethyl-

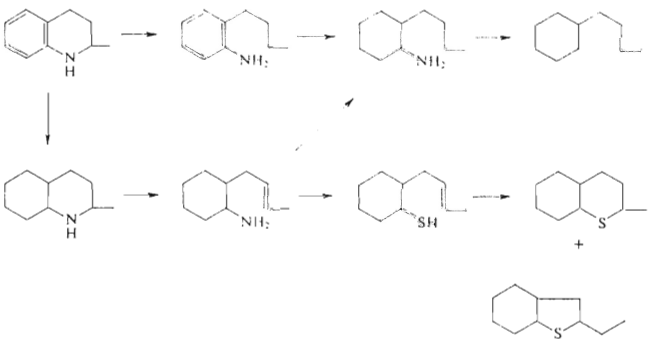
cyclohex-1-ene (2%), 1,1-dimethylcyclopentane, methylcyclohexane, and a $C_{10}H_{14}$ hydrocarbon (all below 1%). Of sulphur compounds, *cis* + *trans* 2-ethylcyclohexanethiol (6%), *cis* + *trans* octahydrobenzo(*b*)thiophene (2% – the isomer ratio was 2 : 1), a $C_7H_{11}S$ compound (2%), 2-methyl-3-ethylthiacyclopentane (1%), and 1,2-dihydrobenzo(*b*)thiophene (1%) were found. The two isomers of 2-ethylcyclohexanethiol were identified based on their chromatographic retention times rather than on the mass spectrometric analysis because during the latter, hydrogen sulphide split off and the mass spectra of 1-ethylcyclohex-1-ene were obtained in both cases. Fraction II contained 99% indole and 0·7% 1-methyl-2-ethylbenzene; in addition, compounds involved in fraction I were present. The total content of sulphur compounds in fractions I and II was 1%. The basic fraction (1·6 g), obtained by alkalization of the aqueous solution, extraction with ether, and drying with solid KOH, boiled at 96–99°C/1·6 kPa and contained 54% 2-ethylaniline, 40% 1,2-dihydroindole, 3% aniline, 1% 2-methylaniline, and traces of quinoline, 1,2,3,4-tetrahydro-2-methylquinoline, and methyl derivatives of quinoline.

RESULTS AND DISCUSSION

The results indicate that similarly as in the HDN of pyridine, piperidine, and quinoline[1,2], hydrogen sulphide participates in the chemical reactions, giving rise to sulphur compounds, also in the HDN of 2-methylpiperidine and 2-methylquinoline. Sulphur components were isolated from the reaction mixtures in surprisingly high quantities; they constituted 40% of the neutral fraction from the HDN of 2-methylquinoline, and even as much as 90% of the neutral fraction from the HDN of 2-methylpiperidine. In this manner the total amount of the neutral fraction of the reaction mixture increased considerably, and consequently the degree of HDN of the initial nitrogen compound rose too. For isoquinoline, the effect of hydrogen sulphide also appeared in an enhanced amount of the neutral fraction in the reaction mixture as comparated with the experiments conducted in the absence of hydrogen sulphide, but sulphur compounds in this fraction were present in a negligible quantity (about 0·3%). In other respects the composition of the two neutral fractions was very similar. This suggests that hydrogen sulphide either merely increased the activity of catalyst for the HDN of isoquinoline, or reacted chemically, but the compounds formed underwent HDS to give approximately the same hydrocarbons as arise from the HDN of isoquinoline in the presence of hydrogen only. After the HDN of indole, the reaction mixture contained the starting substance in predominating amounts, which hampered considerably the isolation and identification of the other compounds in the neutral fraction. Sulphur compounds constituted as little as 1% of the isolated neutral fraction.

The reaction pathway of the cleavage of 2-methylquinoline in the presence of hydrogen sulphide resembles that for the cleavage of quinoline (Scheme 1). The pyridine ring is hydrogenated consecutively to the 1,2,3,4-tetrahydro derivative, followed by hydrogenation to 2-methyldecahydroquinoline. The bond scission takes place between the nitrogen atom and the carbon atom in position 2 giving rise to 2-(but-2-enyl)cyclohexylamine, which enters a substitution reaction with hydrogen sulphide to give 2-(but-2-enyl)cyclohexanethiol. This cyclizes immediately to com-

pounds with a five-membered and a six-membered ring, *viz.* octahydro-2-methyl--2*H*-1-benzothiopyran and octahydro-2-ethyl-benzo(*b*)thiophene (Scheme 1). The two compounds made up 40% of the neutral fraction and 5·4% mol. with respect to

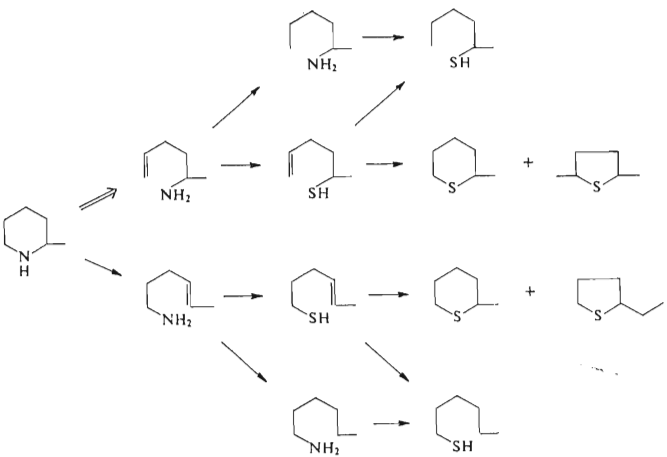


SCHEME 1

the starting 2-methylquinoline. The neutral fraction contained, in addition, butylcyclohexane in a mixture with 1-methyl-2-ethylbenzene (32%), decahydronaphthalene (11%),1-methyl-2-propylbenzene (6%), and in amounts of 1 – 0·5%, propylcyclohexane, ethylcyclohexane, methylcyclohexane, 1-methyl-4-isopropylcyclohexane, 1-methyl-4-ethylcyclohexane, and butylbenzene. Hence, present were compounds that contain, besides the cyclohexane ring, also a benzene ring, thus indicating that one of the intermediate in the HDN of 2-methylquinoline or 1,2,3,4-tetrahydro--2-methylquinoline is 2-butylaniline, the presence of which in the basic fraction from the HDN of 2-methylquinoline has been confirmed[12]. It should also be mentioned that in a microhydrogenolysis of 2-methylquinoline on Ni–Mo and Ru–Rh catalysts, 1-butylcyclohexane was identified[10,11] as the major product in the presence of minor quantities of propylbenzene and methyl-, ethyl-, and propylcyclohexane.

From the results of HDN of 2-methylpiperidine in the presence of hydrogen sulphide it can be inferred that here, too, hydrogen sulphide raises considerably the amount of the neutral fraction due to its reaction with the products giving rise to sulphur--containing compounds; this results in an appreciable increase in the degree of conversion. Sulphur compounds made up 90% of the total isolated neutral moiety. The presence of 2-methylthiacyclohexane, 2-hexanethiol, 2,5-dimethylthiacyclopentane, and 2-ethylthiacyclopentane was established with certainty, the presence of 2-hex-5-

-enethiol, 1-hex-4-enethiol, and 1-hexanethiol is very likely. The structure of the remaining $C_{12}H_{24}S$, $C_{12}H_{26}S$, $C_{12}H_{24}S_2$, and $C_{12}H_{26}S_2$ compounds could not be elucidated unambiguously; it can be, however, assumed that they will be analogous to thise isolated and identified from the HDN of 1-pent-4-enylamine or piperidine on the same catalyst in the presence of hydrogen sulphide[1]. The results give evidence that in 2-methylpiperidine the C–N bond scission takes place primarily between nitrogen and carbon in position 6, where the steric hindrance is weaker. As shown in Scheme 2,



SCHEME 2

2-hex-5-enylamine undergoes a substitution reaction giving rise to 2-hex-5-enethiol, which in part is hydrogenated to 2-hexanethiol and in part cyclizes to 2-methylthiacyclohexane and to 2,5-dimethylthiacyclopentane. To a lesser extent the C–N bond scission concerns also the bond to carbon in position 2, carrying the methyl group. In this case 1-hex-4-enylamine is transformed into 1-hex-4-enethiol, which is hydrogenated to 1-hexanethiol or cyclizes to 2-methylthiacyclohexane and 2-ethylthiacyclopentane.

Another evidence of use in the identification of the position in which the piperidine ring is cleaved is the presence of 2-hexylamine (scission of the 1–6 bond) and 1-hexylamine (scission of the 1–2 bond), and also of tertiary amines resulting from transalkylation reactions of these amines with 2-methylpiperidine; these are 1-(1-hexyl)-2-methylpiperidine and 1-(2-hexyl)-2-methylpiperidine, which were identified to-

gether with a number of other compounds in the basic fraction. It is worth mentioning that 2-methylpiperidine on a sulphidized Co–Mo catalyst in the presence of hydrogen solely was cleaved in the 1 – 6 position[12], and the same was observed during the HDN of 2-methylpyridine on a platinum catalyst using pure hydrogen[13].

The amount and composition of the neutral and the basic fractions from the HDN of isoquinoline were investigated in the absence and in the presence of hydrogen sulphide. While in the former case the neutral moiety isolated by distillation amounted to 25% of the product, in the latter case this proportion increased to 50%. For both, the neutral fraction contained 1-methyl-2-ethylbenzene as the major component (85%), 1,2-diethylbenzene (4%), 1,2-dimethylbenzene (9%), and a number of $C_7 - C_{10}$ hydrocarbons formed by alkylation and dealkylation reactions. As sulphur-containing compounds, the two isomers of 2-thiadecahydronaphthalene and methylbenzo(*b*)-thiophene were found in traces only (0·3%). The basic fraction contained, in addition to a small amount of unreacted isoquinoline, 1,2,3,4-tetrahydroisoquinoline as the predominant component, and various alkyl derivatives of these two compounds. It can be concluded that in the HDN of isoquinoline, hydrogen sulphide affected only the degree of its conversion but not the composition of the neutral and basic fractions.

The neutral fraction from the HDN of indole accomplished in the presence of hydrogen sulphide contained indole as the major component; other substances were present in a quantity as low as 0·2% with respect to the starting compound. As sulphur-containing substances, traces of *cis* + *trans* 2-ethylcyclohexanethiol, *cis* + + *trans* octahydrobenzo(*b*)thiophene, and 2,3-dihydrobenzo(*b*)thiophene were present, hence compounds having the same number of carbon atoms or a similar skeleton as the starting indole. Benzo(*b*)thiophene has been reported[16] to arise in a yield of 2·7% from a pressureless reaction of indole with excess hydrogen sulphide on Al_2O_3 at 600°C.

The results offer a better insight into the HDN of nitrogen compounds in the presence of hydrogen sulphide or sulphur compounds from which hydrogen sulphide can form. The two reactions, hydrodenitrogenation and hydrodesulphurization, appear to be closely related and affect each other. They cannot be investigated separately because they occur concurrently, and the fate of the sulphur compounds formed depends on their stability in the reaction medium; they either persist or undergo desulphurization reactions giving rise to those hydrocarbons, or compounds related to them, that result from the HDN itself in the absence of hydrogen sulphide.

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