Catalytic Hydrogenation of Indole in Furnace Oil

Separation and Identification of Reaction Products

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THE IMPORTANCE of the effects which nitrogen-containing compounds have on catalytic processes is becoming increasingly apparent (*14, 19, 24*). Virtually all of the acid-catalyzed reactions, which include many of those now practiced in the petroleum industry, are affected adversely by nitrogen compounds in the stream being processed. Nitrogen compounds, which in many cases are basic in character, interact with the acidic catalysts to diminish activity. For this reason, it proves advantageous in many instances to remove or destroy the nitrogen-containing compounds present in reactant fractions prior to processing over acid catalysts (*6*).

Hydrogenation appears to be a very effective means for removing nitrogen from petroleum (*15*). The reaction is actually one of hydrogenolysis in which the carbon-to-nitrogen bonds are broken, and the nitrogen is freed as ammonia. Hydrogenation is the most selective means for nitrogen removal, since the remainder of the nitrogen compound is converted to a pure hydrocarbon remaining in the product. To obtain a more thorough understanding of the hydrogenolysis reaction, various nitrogen compound types have been blended with an aliphatic middle distillate of low nitrogen content and hydrogenated. This article presents the results obtained from the hydrogenolysis of indole, a compound type found in petroleum fractions. Only partial destruction of the indole has been sought, and the resulting nitrogen compounds in the product have been isolated in order to study the nature of these reaction intermediates.

EXPERIMENTAL

Hydrogenation. The indole–middle distillate blend was made up to contain 5000 p.p.m. of nitrogen. The indole was reagent grade, and the middle distillate a straight-run furnace oil having the following properties:

°API (gravity)	30.2	Aromatics	25.2 vol. %
Nitrogen, total	18 p.p.m.	Olefins	3.8 vol. %
Nitrogen, basic	13 p.p.m.	Saturates	71.0 vol. %

The blend was hydrogenated in a continuous flow, fixed catalyst bed reaction system of conventional design employing a catalyst of the supported sulfactive type. The hydrogenolysis of indole proceeded under relatively mild conditions giving a series of nitrogen-containing reaction products. The reaction conditions used were 300 p.s.i.g., 315° C. (600° F.), and 4.0 LHSV (liquid hourly space velocity). These conditions led to a hydrogenated product containing 4300 p.p.m. of nitrogen, 739 p.p.m. of which were basic and 3561 p.p.m. nonbasic nitrogen.

Isolation of Nitrogen Compounds. The steps involved in the isolation and separation of nitrogen compounds formed by catalytic hydrogenation of indole in a furnace oil are shown in Figure 1. For the isolation of the basic nitrogen compounds, 50 ml. of oil was extracted three times with 50 ml. of 1*N* HCl. The aqueous acidic phase was then extracted three times with 50 ml. of chloroform to remove entrained oil. After this treatment, the aqueous phase was made basic, and the liberated nitrogen bases were extracted from the aqueous medium with four 50-ml. portions of chloroform. The organic phases were combined and dried with sodium sulfate, and the chloroform was removed in a stream of nitrogen. This concentrate was reserved for further study.

After removal of the basic nitrogen compounds, the remaining oil containing the nonbasic nitrogen compounds was passed through a column of activated aluminum oxide (Alcoa, grade F-20; 50 cm. long, 1.9 cm. i.d.). The column was washed with 200 ml. of isohexane to remove the oil, followed by desorption of the nonbasic nitrogen compounds with 500 ml. of methanol (Spectrograde). The solvent was removed with nitrogen, and the resulting concentrate containing the nonbasic nitrogen compounds reserved.

Separation of Nitrogen Compounds. For further separation,

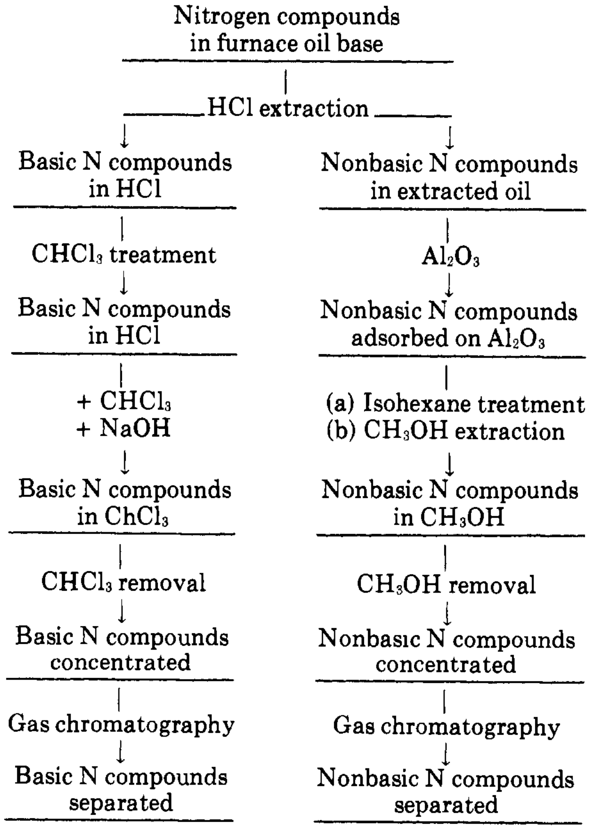

Figure 1. Separation scheme

the basic and nonbasic nitrogen concentrates were chromatographed on an intermediate temperature range gas chromatographic unit and the cuts collected.

Approximately 18 mg. of the basic nitrogen concentrate was chromatographed on a stainless steel column (5 feet long, ¼ inch i.d.) with 10% (by weight) Flexol 8N8 on 42 to 60-mesh firebrick as packing material. The column was maintained at a constant temperature of 150° C. in a stirred air bath. A Gow-Mac thermal conductivity cell served as the detector. Helium was used as carrier gas at a flow rate of 109 ml. per minute. The temperature of the flash chamber was 200° C. and that of the outlet of the column 210° C. Water cooled test tubes, 10 ml. in capacity, were used as receivers for the separated compounds and changed in accordance with the peaks on the chromatogram. The fractions collected in this manner were used for the indentification work.

Figure 2 shows a chromatogram obtained from the separation of the basic nitrogen compounds. The identified compounds are: *N*-ethylcyclohexylamine, *n*-octylamine, *β*-cyclohexylethylamine, *β*-phenylethylamine, *o*-ethylaniline, indoline, quinoline, a dimethylquinoline, 1,2,3,4-tetrahydroquinoline, and indole.

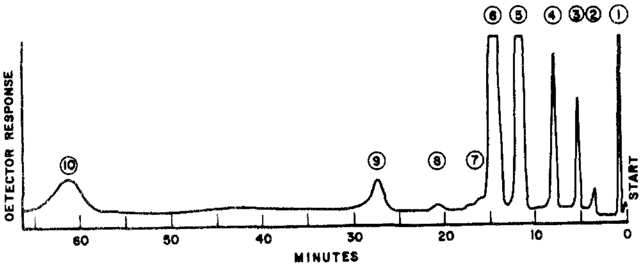

Figure 2. Gas chromatographic separation on Flexol 8N8

Compounds are given in Table I

The separation of the nonbasic nitrogen compounds was possible in the gas chromatographic unit using a 25% (by weight) Craig polyester succinate on 35- to 80-mesh firebrick as packing material. The temperature of the air bath was 226° C. The flow rate of helium was 120 ml. per minute. The temperature of the flash chamber was 250° C., that of the outlet 265° C. Figure 3 shows a chromatogram of the nonbasic nitrogen compounds. Peak 3 corresponds to indole and constitutes the greatest portion of the nonbasic nitrogen compounds found.

Methods of Identification. The methods used for the identification of the separated nitrogen compounds were ultraviolet and infrared spectroscopy, melting points of picrates, and gas chromatography retention times.

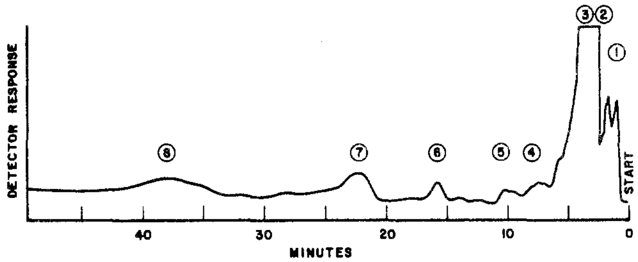

Figure 3. Gas chromatographic separation on Craig polyester succinate

Compounds are given in Table II

All fractions from the gas chromatographic separation were investigated by ultraviolet absorption spectroscopy in a Cary recording spectrophotometer. Methanol was used as solvent for each fraction.

To obtain the most intense infrared spectra possible, it was necessary to concentrate the methanol solutions of the gas chromatographic cuts on sodium chloride plates. This was easily done by transferring the methanol solution to a small glass dish on the Kofler hot stage and stripping off the solvent at 70° C. A sodium chloride plate (1.5 × 1.5 × 0.2 cm.) was placed over the glass dish and the temperature of the stage raised until the nitrogen compound condensed on the underside of the plate. The condensation was observed with a microscope. The thin layer of condensate was covered with another sodium chloride plate, and the two plates were inserted into the cell compartment. The spectra were obtained with a Perkin-Elmer Model 21 instrument.

To prepare the picrates, several drops of each methanol solution were transferred to separate cover glasses. A drop of alcoholic picric acid solution was then added and mixed to permit the formation of the picrate. The melting points of the picrates were determined on a Kofler hot stage using a microscope and were compared with those obtained with pure nitrogen compounds or with literature values.

To confirm the results obtained by the previous methods, gas chromatography retention times were compared with those of known materials (Table I). For this particular group of basic compounds and column packing the retention times increase with the boiling points. This is significant because it provided a means for predicting the presence of possible compounds and was used as an aid in completing their identification.

Basic Nitrogen Compounds. The weight per cent distribution shown in Table I for the individual compounds resulted from an area determination of the gas chromatographic peaks after calibrations were made for each compound. The total weight of the identified compounds

Table I. Nitrogen Compounds Separated by Gas Chromatography on Flexol 8N8 and Their Identification

Peak[a]	Compounds	M.P. of Picrate, ° C. Found	M.P. of Picrate, ° C. Reference	Retention Time, Min.	B.P., B.P., ° C.	Weight %
1	*N*-Ethylcyclohexylamine	133	133	0.6	164	4.8
2	*n*-Octylamine	114	112	3.3	179.6	1.0
3	*β*-Cyclohexylethylamine	154	155	5.0	188.0	4.2
4	*β*-Phenylethylamine	166	174	7.5	195.0	8.1
5	*o*-Ethylaniline	195	195	10.7	215.6	24.7
6	Indoline	172	174	13.0	230.0	37.9
7	Quinoline	203	203	15.5	237.7	1.1
8	Dimethylquinoline	230	230[b]	19.8	. . .	0.7
9	1,2,3,4-Tetrahydroquinoline	140	141	25.7	251.0	6.9
10	Indole (from indole polymer)	(52)[c]	(52)[c]	57.5	254.0	10.6

[a] Ultraviolet spectra of peaks 4 to 10 and infrared spectra of peaks 5, 6, 9, 10 are identical with reference spectra. [b] M.P. of several isomeric dimethylquinoline picrates. [c] M.P. of indole.

separated on Flexol (fractions 1 through 10 in Figure 2) represented approximately 25% of the total basic nitrogen compounds. The remaining basic nitrogen compounds showed much higher retention times and were only partly identified. Figure 4 shows the infrared spectra of the isolated *o*-ethylaniline, indoline, and 1,2,3,4-tetrahydroquinoline compared with the authentic compounds. The spectra of indoline and 1,2,3,4-tetrahydroquinoline are very similar to those of *o*-alkylanilines (*3*). None of the identified compounds were found in the original furnace oil base. This information was obtained by treating the base oil in a manner identical with that of the indole blended oil. Hence it seemed unnecessary to identify the nitrogen compounds in the original oil base.

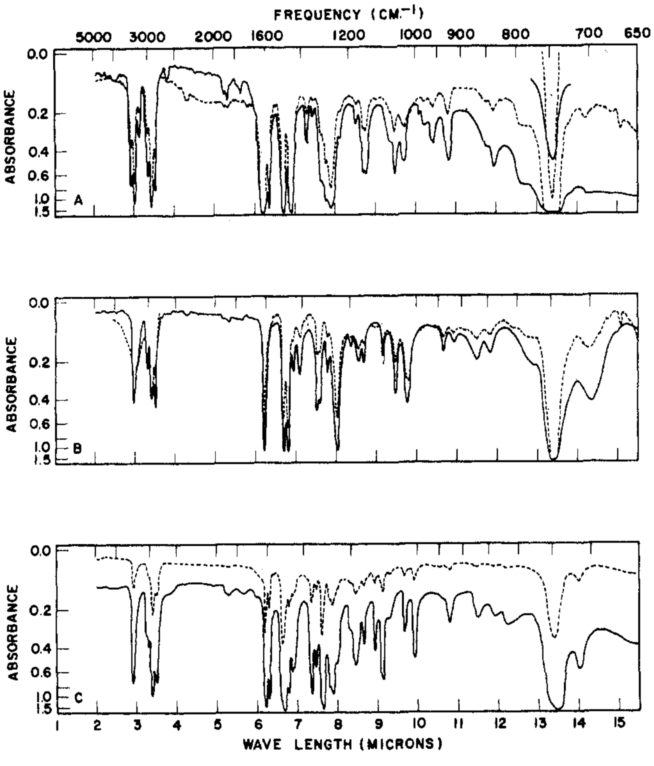

Figure 4. Infrared spectra

A o-Ethylaniline *B* Indoline *C* 1,2,3,4-Tetrahydroquinoline

The presence of indole among the basic nitrogen compounds separated by gas chromatography was explained by the isolation of triindole hydrochloride along with an unidentified basic indole polymer and the amine hydrochlorides. The triindole hydrochloride was identified by comparison of its ultraviolet and infrared spectra and melting point with those of known material (*10, 12, 18, 21-23, 28*). Both polymers decomposed thermally on the gas chromatographic column and formed indole. This was shown by charging solutions of isolated indole polymer and triindole hydrochloride in methanol to the column. In both cases peaks appearing on the chromatogram had the same retention times as indole. To determine if triindole was formed during the process of hydrocracking or in the extraction procedure with hydrochloric acid, 3 grams of indole was dissolved in 50 ml. of oil, and the oil extracted with three 50-ml. portions of 1*N* HCl. After addition of sodium hydroxide and chloroform to the aqueous phase, a white precipitate was formed which could be separated. After recrystallization from methanol-acetone solution, about 0.5 gram of triindole hydrochloride was obtained. The analytical data suggested the formation of triindole hydrochloride ($C_{24}H_{22}N_3Cl$, 387.92). Calculated: C, 74.31; H, 5.72; N. 10.83; Cl, 9.14. Found: C, 73.39; H, 6.08; N, 11.00; Cl 7.94. Thus, the triindole hydrochloride could also be formed in the extraction procedure with HCl and not only in the hydrogenation process.

Nonbasic Nitrogen Compounds. The investigation concerned with the nonbasic nitrogen compounds revealed that several substituted indoles were formed during the hydrogenolysis. Figure 5 shows the ultraviolet spectra of fractions obtained from the separation by gas chromatography on Craig polyester succinate. The analytical data obtained for the individual fractions are listed in Table II.

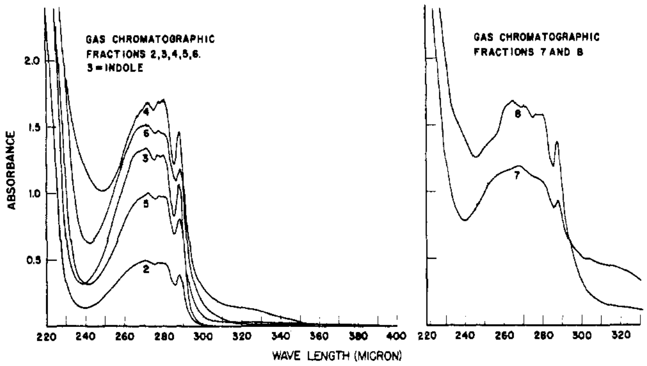

Figure 5. Ultraviolet spectra of indoles separated on Craig polyester succinate

Table II. Nitrogen Compounds Separated by Gas Chromatography on Craig Polyester Succinate and Their Identification

Peak	Compd. (Proposed)	Ultraviolet $\lambda_{max.}$, Mμ	M.P. of Picrate, ° C. Found	Ref.	Retention Time, Min.
1	Not identified	. . .	. . .	. . .	0.7
2	3-Isopropylindole	271, 281, 288	102	102	1.5
3	Indole	272, 280, 288	(52)[a]	(52)[a]	2.4
4	1,3-Dimethyl-2-ethylindole	273, 280, 288	88	88	6.5
5	3-Propylindole	272, 281, 288	113	114	9.0
6	1-Ethylindole	272, 277, 288	105	105	15.0
7	2-*tert*-Butylindole	268, 280, 288	133	133	20.5
8	Indole type	265, 271, 277, 280, 288	114	. . .	34.0
. . .	Carbazole type	238, 248, 260, 296, 320, 336	106	106[b]	255

[a] M.P. of indole. [b] M.P. of *N*-benzylcarbazole.

The compounds that may be present include 3-isopropylindole, indole, 1,3-dimethyl-2-ethylindole, 3-propylindole, 1-ethylindole, 2-*tert*-butylindole, another indole type compound, and a carbazole type compound. The ultraviolet spectrum of the substituted carbazole is shown in Figure 6 together with the spectrum of pure carbazole.

Undoubtedly, substituted indoles constitute a major portion of the compounds that are retained on Flexol. These substances are very likely derived from the thermal decomposition of several alkylated basic indole polymers on the gas chromatographic column. The indole polymers were probably formed by reaction with hydrochloric acid as explained for triindole hydrochloride.

DISCUSSION

Since hydrogenation conditions were chosen to avoid a complete hydrogenolysis of the indole, it was possible to obtain several intermediates. The isolation of nine basic nitrogen compounds, which constitute 25% of the total basic material, and of several nonbasic nitrogen compounds

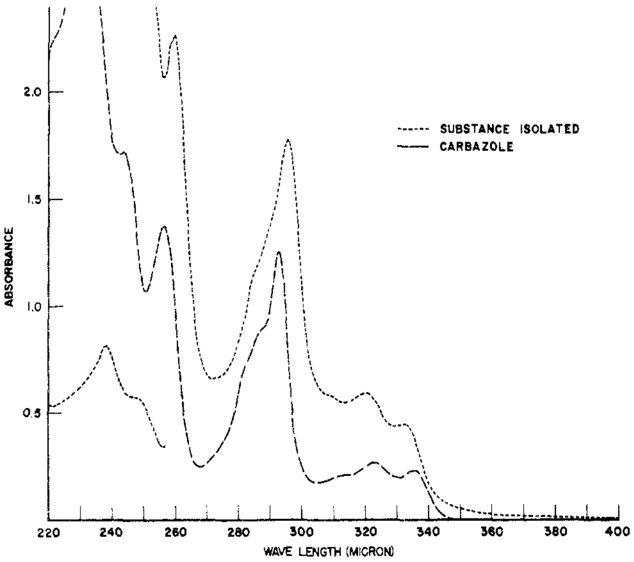

Figure 6. Ultraviolet spectra of carbazoles

illustrates the variety of reactions involved in this process.

The catalytic hydrogenation of indole has been the subject of many investigations (*1, 2, 8, 11, 13, 26, 27*) which have yielded fundamental knowledge of this reaction. The formation of indoline and several other compounds, including anilines, formed by hydrogenolysis of the pyrrole ring or of both rings in the indole molecule, was observed in several of these investigations and, therefore, expected under the conditions of this investigation. The presence of anilines is apparently peculiar to catalytically cracked stocks because they have not been found in straight-run or thermally cracked products (*17*). The formation of 2-ethylcyclohexylamine and of perhydroindole was expected, but the actual presence of these compounds among the reaction products could not be proved. The formation of *n*-octylamine, quinolines, 1,2,3,4-tetrahydroquinoline, alkylated indoles, and carbazoles, however, was not anticipated. Their presence indicated that, along with the hydrogenolysis of indole, a reaction of indole with the hydrocarbon medium resulted in alkyl indoles. Apparently, the formation of an alkyl ion from a hydrocarbon of the oil is the first step in this reaction.

The formation of quinoline by heating 2-methylindole is a well known reaction (*20*) and possibly explains the occurrence of quinolines among the basic reaction products. A 3-alkylindole cation appears to be the first intermediate in a reaction which starts with the opening of the pyrrole ring in the alkylated indole and forms 1,2-dihydroquinolines by dehydrocyclization (*9*). The compound, 1,2-dihydroquinoline, is unstable and disproportionates to form quinoline and 1,2,3,4-tetrahydroquinoline, both of which were actually isolated as reaction products. However, if the nitrogen in 1,2-dihydroquinoline is replaced by an alkyl group, no disproportionation is possible; therefore, *N*-alkyl-1,2-dihydroquinolines are stable (*16*). Some ultraviolet spectra indicated the formation of such products. Indoline, 1,2,3,4-tetrahydroquinoline, and alkylated tetrahdroquinolines have been suggested as antiknock additives for gasolines (*5*). In another investigation (*25*) it was found that the addition of controlled amounts of nonbasic nitrogen compounds to hydrocarbons before catalytic cracking improved the antiknock properties of the resulting products. From the present work, it can be assumed that indoline, 1,2,3,4-tetrahydroquinoline, or similar compounds were probably formed in the catalytic cracking process, which in turn improved the antiknock properties of the distillate. Bratton and Bailey (*4*) also have observed the thermal transformation of nonbasic nitrogen compounds existing naturally in petroleum into basic compounds, especially into alkylquinolines.

The hydrogenolysis of indole—e.g., to *n*-octylamine,—can be achieved easily compared with the hydrogenolysis of alkylindoles. In fact, the more the pyrrole ring in indole is alkylated and the closer the substituents are to the nitrogen atom, the more difficult is the hydrogenolysis of the alkylindoles. The present study indicated that no alkylamines with a longer carbon chain than *n*-octylamine were formed; therefore, alkylindoles were not hydrogenated completely. The hydrogenolysis of carbazoles requires even more severe conditions. It was not investigated whether the formation of the alkylcarbazole, which was isolated in this investigation, resulted from interaction of two alkylated anilines to a biphenyl system followed by liberation of ammonia at high temperatures (*7*), or from the condensation of partially hydrogenated indoles. Whatever the mechanism might be, an elimination of aromatic hydrogen was evidently possible under the conditions of this catalytic hydrogenation and resulted in the connection of two aromatic rings.

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