[CONTRIBUTION FROM THE DIVISION OF FUEL TECHNOLOGY AT THE PENNSYLVANIA STATE COLLEGE]

The Hydrogenolysis of Carbazole[1,2]

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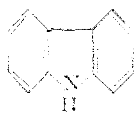
The hydrogenolysis of pure compounds is one of several possible approaches by which the chemical mechanism of coal and tar hydrogenolysis may be investigated. Using this technique, the behavior of several hydrocarbons and oxygen-, sulfur- and nitrogen-containing compounds has already been studied. The hydrocarbons include benzene,[3] indene,[4] naphthalene,[5] and their homologs. The oxygen-containing compounds include phenol,[6] the cresols and dihydric phenols,[7] α- and β-naphthol,[8] benzoic acid,[9] abietic acid,[10] and diphenylene oxide,[11] and some related structures. The sulfur-containing compounds include carbon disulphide, phenyl mercaptan and thiophene,[12] and the nitrogen-containing compounds include quinoline.[13,14]

The present investigation is concerned with the hydrogenolysis of carbazole, I



the structure of which is such that information may be secured concerning the hydrogenation of heterocyclic and benzenoid rings and the extent to which heterocyclic nitrogen, believed to be present in coal,[15] is removed in the hydrogenolysis process as well as the possible mechanism by which it is removed.

Hydrogenolyses were conducted in the absence of an added catalyst at a temperature of 450° with initial hydrogen pressures of 1880 to 1920 p.s.i. for different lengths of time. The partial pressure of hydrogen, calculated from product composition at the end of the reaction periods, varied from 4720 to 4980 p.s.i. at 450°. Experiments were conducted by heating the retort to 450° (referred to as 0 hours) and by holding it at 450° for two and for three hours of continuous operation and for two two-hour periods of intermittent operation. During the intermittent operation the reaction gases were removed after the first two hours and fresh hydrogen added for the second two-hour period.

Discussion

The catalytic hydrogenation of carbazole at relatively low temperatures,[16,17] has resulted in the formation of mixtures of the various hydrogenated carbazoles. Using controlled conditions, the different degrees of saturation ranging from 1,2,3,4-tetrahydro- to dodecahydrocarbazole were obtained. The first evidence of pyrolysis accompanying the hydrogenation of carbazole was obtained[18] by the isolation of dimethylindole from reaction for 12–18 hours under the rather mild conditions of 200–220° and 8–10 atmospheres. In contradiction to this, however, it has been stated,[11,19] that carbazole was unusually stable to hydrogenation-cracking reactions, but no experimental evidence was reported.

Before discussing the present work it must be pointed out that even though no catalyst was added, the wall of the retort and the thermocouple casing in all probability exert a catalytic effect.

The extent to which the heterocyclic nitrogen in carbazole is released as gaseous products is shown in Fig. 1 together with moles of hydrogen consumed and moles of methane formed per mole of carbazole destroyed.

It is evident that the heterocyclic nitrogen is quite stable to the conditions of the reaction. Under the most severe conditions, two two-hour periods, only 5% of the available nitrogen appeared in the gaseous products. For the 0 hour reaction, this nitrogen appeared only as NH_3, but with increasing reaction time free N_2 appeared and the N_2/NH_3 ratio increased slightly with the time of reaction. This suggests that the free nitrogen is formed by the thermal decomposition of ammonia as would be expected from equilibrium data considerations.

The small amount of nitrogen removed, the appearance of ammonia and free nitrogen in the gaseous products, and the constant increase in the removal of nitrogen with time of hydrogenolysis are all in agreement with the removal of nitrogen during the hydrogenolysis of coal.[20] This close similarity supports the view that at

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[2] Presented before the Gas and Fuel Division, A. C. S., 116th National Meeting, Sept. 18-23, 1949, Atlantic City, N. J.

[3] Hall, *J. Soc. Chem. Ind.*, (Trans.), **57**, 347 (1938).

[4] Hall and Cawley, *J. Soc. Chem. Ind.*, (Trans.) **54**, 208 (1935).

[5] Hall, *Fuel*, **12**, 76 (1933).

[6] Cawley, *ibid.*, **11**, 217 (1932).

[7] Cawley, *ibid.*, **12**, 29 (1933).

[8] Hall, *ibid.*, **12**, 419 (1933).

[9] Cawley, *ibid.*, **12**, 366 (1933).

[10] Charmbury and Wright, THIS JOURNAL, **66**, 526 (1944).

[11] Hall and Cawley, *J. Soc. Chem. Ind.*, (Trans.) **58**, 7 (1939).

[12] Cawley and Hall, *ibid.*, (Trans.) **62**, 116 (1943).

[13] Rapoport, *J. Appl. Chem.* (*USSR*), **9**, 1456 (1936).

[14] Yamazuchi, *Bull. Chem. Soc. Japan*, **9**, 303 (1934).

[15] Lowry, "Chemistry of Coal Utilization," John Wiley and Sons, Inc., New York, N. Y., 1945, p. 450-484.

[16] Adkins and Coonradt, THIS JOURNAL, **63**, 1563 (1941).

[17] Kosaka and Kayamari, *J. Soc. Chem. Ind. Japan*, **44**, No. I, Suppl. Bind., 23 (1941). *C. A.*, **35**, 5108 (1941).

[18] Padoa and Chiaves, *Lincei*, **16**, [2] 762 (1907); *Chem. Centr.*, **79**, I, 649 (1908).

[19] British Fuel Res. Board Rept. for year ending Mar. 31, 1937, p. 126.

[20] Fischer and Eisner, *Ind. Eng. Chem.*, **29**, 1371 (1937).

least a part of the nitrogen in coal may be present as heterocyclic nitrogen.

The exact mechanism for the formation of the small quantity of ammonia could not be definitely established. The isolation of benzene and aniline indicate that destruction occurs at the heterocyclic ring. The formation of alkylated pyrroles and hydrocarbon gases indicate that destruction occurs at the aromatic ring. In any event, neither type of destruction occurs to any appreciable extent as evidenced by the small quantities of these substances in comparison to the large amount of carbazole destroyed. The primary reaction is unknown also, but the evidence suggests pyrolysis of the carbazole to form unidentifiable reactive fragments which polymerize into undistillable, ether soluble, nitrogen-containing substances. The same type of reaction has been suggested[21] as the primary reaction for the hydrogenolysis of coal and asphalt in the absence of a catalyst.

Experimental

Apparatus and Procedure.—The hydrogenolyses were conducted in an alloy steel rotary type retort previously described.[22]

The experimental procedure was the same as that used in the hydrogenolysis of abietic acid[10] with the following exceptions: (1) all experiments were conducted at 450°, (2) a 0.1 *N* H_2SO_4 trap was inserted in the absorption train between the traps immersed in ice water and dry ice-acetone mixture, and (3) the ascarite anhydrone trap was eliminated.

Experimental Results.—A general summary of the hydrogen consumed and the gaseous products formed is shown in Fig. 1. The amounts of hydrogen consumed and methane and nitrogen formed were obtained from the gas analyses before and after the hydrogenolysis. Only in one case, three hours of continuous operation, was any material obtained in the liquid air trap. This consisted of a small amount of methane (0.17 g.), and ethane (0.75 g.), both of which were obtained by the low temperature distillation. The amount of ammonia was obtained by titrating the excess acid in the sulfuric acid trap with 0.1 *N* NaOH, as there was no evidence of any volatile amines being present in the reaction gases.

TABLE I

SUMMARY OF THE LIQUID AND SOLID REACTION PRODUCTS, (G. PER 100 G. OF CARBAZOLE)

Temperature, 450°; initial pressure 1880–1920 p.s.i.

	Continuous		Intermittent	
	0 hours	2 hours	3 hours	2–2 hours
Ice-water trap (tar-like material)	0.11	0.92	1.30	1.76
Dry Ice–acetone trap (benzene)	0.25	1.10	1.59	2.25
Ether insoluble retort products (carbazole)	77.5	59.0	55.5	52.4
Ether soluble basic retort products (aniline + unidentified material)	0.2	4.2	6.6	6.5
Ether soluble neutral retort products (liquids and solids)	19.5	31.9	33.0	34.6

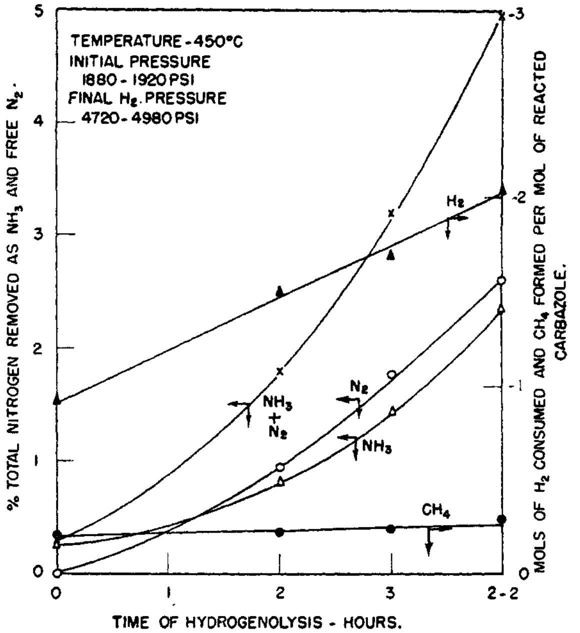

Fig. 1.—The gaseous products of hydrogenolysis.

A summary of the yields of liquid and solid products is presented in Table I.

The amount of tar-like material collected in the trap immersed in ice water was insufficient for further investigation.

The material obtained in the trap immersed in Dry Ice–acetone was a colorless solid at the low temperature and a colorless liquid at room temperature. This material was mostly benzene (boiling point of 80–81°, refractive index of 1.5000; and nitration gave a 1,3-dinitrobenzene, m. p. 89–89.5; no depression with authentic material).

The ether insoluble material was mostly unreacted carbazole (m. p. 242–244°; produced no m. p. depression with the original material; a "carbazole blue" reaction; and the picrate of carbazole, m. p. 181–183°).

The ether soluble basic material was mostly aniline (boiling range 181–183°; refractive index range of 1.5812–1.5896; produced a bleaching powder color test; and formed an acetyl derivative m. p. 114–115°).

Identification of the neutral ether soluble retort products could not be definitely established due to the difficulties involved in separating and purifying the various constituents, in obtaining a sufficient amount of the purified material, and in finding consistent physical properties in the literature for similar products. Nevertheless, the results did indicate possible structures. The neutral retort products obtained from the various operations were all solids with melting points in the range of 200–210°. These solids were combined and subjected to distillation at reduced pressure from which several fractions amounting to only 10% of the material were obtained before decomposition occurred in the still pot. The first fraction had a distillation range of 148–163° at 38 mm. pressure. On standing, part of this fraction solidified. After recrystallization, the solid fraction had a melting point of 63–65°. This compares reasonably well with 2-ethyl-3-methylindole reported to have a melting point of 66°. The picrate of the liquid had a melting point of 171–172° which compares with the melting point of the picrate of 1,2-diethylindole. The second fraction from the distillation had a boiling range of 163–183° at 38 mm. pressure and the picrate from this fraction had a melting point of 167–169°. The picrate of dodecahydrocarbazole melts at 167–168°. The third fraction from the distillation had a boiling range of 183–190° at 20 mm. pressure and the picrate of this fraction melted at 150–151°, the same as the

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[21] Weller, Clark and Pelipetz, *Ind. Eng. Chem.*, **42**, 334 (1950).

[22] Wright and Gauger, The Pennsylvania State College, Mineral Industries Experiment Station Technical Paper No. 31 (1936).

picrate of 2-ethyl-3-methylindole. The yields of all these fractions were too small for further investigation.

Summary

The non-catalytic hydrogenolysis of carbazole for different lengths of time at 450° and at cold hydrogen pressures of about 1900 p.s.i. has shown the following:

1. The carbazole is quite resistant to reaction and is only decomposed to the extent of 48% under the most severe conditions.
2. The primary reaction is, in all probability, the formation of unidentifiable reactive fragments which polymerize into undistillable ether-soluble products.
3. The heterocyclic nitrogen is quite resistant to removal since 5% is the maximum amount found in the reaction gases.
4. The nitrogen in the gaseous products increases slowly with an increase in the time of hydrogenolysis and appears initially as ammonia.
5. Benzene, aniline, methane and ethane are minor products of the hydrogenolysis.

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[Contribution from the Research Laboratories, K-25 Plant, Carbide and Carbon Chemicals Division Union Carbide and Carbon Corporation]

Reactions of Polyfluoro Olefins. III.[1] Preparation of Polyfluoro Ethers[2]

By John T. Barr, Karl E. Rapp, Roy L. Pruett, Carl T. Bahner, J. Donald Gibson and Robert H. Lafferty, Jr.

Saturated polyfluoroalkyl ethers have been prepared by the base-catalyzed addition of alcohols to polyfluoro olefins.[3,4,5] Saturated and unsaturated aryl polyfluoroalkyl ethers have been prepared by the action of alkali metal aryloxides on polychloropolyfluoroethanes and propanes.[6] Park, Sharrah and Lacher[7] have obtained 1,2-dialkoxy-3,3,4,4-tetrafluorocyclobutenes by what they regard as a metathetical reaction of metal alkoxides and hexafluorocyclobutene.

This paper describes the preparation of several of these previously reported polyfluoro ethers and several unreported ones, and a study of the mechanism of the reaction between hexafluorocyclobutene and alcohols.

Chlorotrifluoroethyl ethers were prepared by the method of Park, *et al.*[5] The yields and physical constants are shown in Table I. Analytical results for all new compounds are given in Table III. Samples were prepared for analysis and for the determination of physical properties by careful fractionation.

The finding of Park, Sharrah and Lacher[7] that only the dialkoxy cyclobutenes were formed by the reaction of alcohols and hexafluorocyclobutene in the presence of potassium hydroxide in the bubble tube has been substantiated. However, when potassium hydroxide was the catalyst for the reaction in a closed system a large proportion of the product was the monoalkoxy butene, even in the presence of a large excess of alcohol. Benzyltrimethylammonium hydroxide catalyst gave predominantly the monoether in either the bubble tube or a closed system. In contrast to the instability during storage which was reported[7] and found for the dialkoxy butenes, these monoalkoxy compounds were relatively stable. The reaction of phenolic compounds with hexafluorocyclobutene in ether solution, using tertiary amines as catalysts, gave only the monoaryloxy butenes.

Because of their failure to obtain saturated ethers from the reaction of metal alkoxides and hexafluorocyclobutene, Park and associates[7] have proposed a vinylic substitution mechanism for this reaction, supported by an extrapolation from thermodynamic data which they had obtained. It has been proposed,[1,8] however, that the reactions of thiols and amines with hexafluorocyclobutene proceed by an addition mechanism analogous to the reactions of other polyfluoro olefins. A saturated bis-(butylthio)-pentafluorocyclobutane of the structure to be expected from an addition mechanism has been reported. The more stable unsaturated products were thought to have been formed by the loss of hydrogen fluoride from the saturated addition products.

During this work the presence of hydrogen fluoride was noted many times during the purification of the products, and an effort was made to isolate a corresponding saturated mono- or dialkoxy substituted cyclobutane. In every case decomposition occurred before the material could be obtained in a pure state. Quantities of hydrogen fluoride were formed by this spontaneous decomposition of the products within a few hours after their formation. It was found repeatedly,

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[1] The previous paper in this series is: Pruett, Barr, Rapp, Bahner, Gibson and Lafferty, This Journal, **72**, 3646 (1950).

[2] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation.

[3] Hanford and Rigby, U. S. Patent 2,409,274 (1946); *cf.* E. I. du Pont de Nemours and Company, British Patent 583,874 (1947).

[4] Miller, Fager and Griswold, This Journal, **70**, 431 (1948).

[5] Park, Vail, Lea and Lacher, *ibid.*, **70**, 1550 (1948).

[6] McBee and Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

[7] Park, Sharrah and Lacher, This Journal, **71**, 2337 (1949).

[8] Rapp, Pruett, Barr, Bahner, Gibson and Lafferty, *ibid.*, **72**, 3642 (1950).