quinone is given according to the electronic theory of acids and bases.

An alternative mechanism is proposed, but it is shown that the application of the Lewis theory is equally valid for both mechanisms considered.

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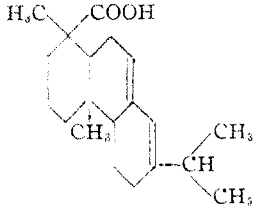
[CONTRIBUTION FROM THE DEPARTMENT OF FUEL TECHNOLOGY OF THE PENNSYLVANIA STATE COLLEGE]

The Hydrogenolysis of Abietic Acid[1]

BY H. B. CHARMBURY AND C. C. WRIGHT

Although many investigations on the hydrogenolysis of coal are reported in the literature, interpretation of the results has been hindered because of the lack of information concerning the mechanism of the reaction. One method of attack upon this problem has been through hydrogenolysis of pure organic compounds, several of which, such as benzene, indene, naphthalene, naphthols, phenol, cresols and carboxylic acids[2] have already been studied. The complexity of the compounds has been gradually increased with the ultimate goal of hydrogenating polynuclear structures as closely related to the so-called "coal molecule" as possible. The present work is concerned with the hydrogenolysis of abietic acid, I,



I

the structure of which is such that information may be secured concerning oxygen removal from the carboxyl group, alkyl severance of the two different alkyl groups, alicyclic decomposition due to the breakdown of the hydrophenanthrene structure and hydrogen consumption due to saturation of the double bonds and to hydrogenation cracking reactions.

Hydrogenolyses were conducted for two hours at temperatures ranging from 325 to 450°, with initial hydrogen pressures of 1900 to 1975 P. s. i. (133.6–138.9 kg./sq. cm.). Because the results of these experiments indicated that 400° is the critical temperature for oxygen removal, alkyl severance and hydrogen consumption, experiments were also conducted at this temperature, using the same initial hydrogen pressure, for 1, 2 and 3 one-hour periods. The reaction gases were removed and the retort charged with fresh hydrogen at the end of each one-hour period.

Oxygen Removal.—Using temperatures and pressures in the range of 300–500° and 1000–3000 P. s. i. several investigators[3,4,5,6] have shown that much of the oxygen present in coal is removed rapidly and in the early stages of hydrogenation and that the remaining oxygen is removed at a slow but rather constant rate. Boomer[7] has suggested a theory that coals contain at least two types of oxygen: oxygen as carboxyl which is removed rapidly, and oxygen as hydroxyl which is more resistant. Fisher[8] also supports this theory and shows that using a Pittsburgh coal 60% of the oxygen is eliminated much more rapidly than the remaining 40% and that most of the oxygen which is removed in the early stages appears in the products as water. Storch[9] has studied the oxygen removal of the anthraxylon fraction of various coals and found that the oxygen is removed as carbon dioxide and water in the early stages and that the oxygen removal increases with decreasing rank of the coal. An extended study by Storch[10] revealed that upon hydrogenation the low rank coals high in oxygen lose 10–20% of their oxygen as carbon dioxide whereas the higher rank coals lose only 3 to 6% in this form.

Cawley[11] has studied the removal of oxygen from the carboxyl linkage by hydrogenating benzoic acid (or ferrous benzoate) at 450° and 100 atmospheres pressure and reported 24% benzene and 41% toluene in the reaction products along with a relatively large amount of water. The presence of toluene and water indicates a removal of oxygen by a reduction of the carboxyl group.

The data of Fig. 1 show, however, that the removal of oxygen from abietic acid takes place for the most part as a straight decarboxylation with the formation of carbon dioxide, and that the total percentage of oxygen removed is directly proportional to the temperature of hydrogenolysis. At 450° the elimination of oxygen is virtually complete.

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(1) From the thesis of H. B. Charmbury presented to the faculty of The Pennsylvania State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) The hydrogenolysis of these compounds has been studied by the British Fuel Research Board and their results will be found in the Board reports from 1931 to 1938 inclusive.

(3) Bakes, *Dept. Sci. Ind. Research Tech. Paper*, **37**, 214 (1933).

(4) Boomer and Saddington, *Can. J. Research*, **12**, 825 (1935).

(5) Graham and Skinner, *J. Soc. Chem. Ind.*, **48**, 129T (1929).

(6) Horton, King and Williams, *J. Inst. Fuel*, **7**, 85 (1933).

(7) Boomer, Saddington and Edwards, *Can. J. Research*, **13B**, 11 (1935).

(8) Fisher and Eisner, *Ind. Eng. Chem.*, **29**, 1371 (1937).

(9) Storch, *et al.*, *Fuel*, **19**, 13 (1940).

(10) Storch, *et al.*, *ibid.*, **20**, 5 (1941).

(11) Cawley, *ibid.*, **12**, 366 (1933).

The data of Table I for intermittent operation substantiate the results obtained for two hour hydrogenolyses with respect to the formation of carbon dioxide and indicate relatively rapid oxygen removal as carbon dioxide. This supports Boomer's[7] interpretation of coal hydrogenation data.

TABLE I

REMOVAL OF OXYGEN AS CARBON DIOXIDE, CARBON MONOXIDE AND WATER FOR INTERMITTENT HYDROGENOLYSES

	% Oxygen removed as				
During	CO_2	CO	CO_2 + CO	H_2O	CO_2 + CO + H_2O
1st hr.	61.1	12.0	73.1	5.8	78.9
2nd hr.	0.0	3.0	3.0	4.9	7.9
3rd hr.	.0	0.0[a]	0.0[a]	0.3[a]	0.3[a]

[a] These values are corrected for the amount of CO and H_2O formed as a result of the decomposition of 0.22 g. of CO_2 present as impurities in the original hydrogen gas, assuming the decomposition takes place as $CO_2 + H_2 \rightarrow CO + H_2O$.

The carbon monoxide obtained in both the continuous and intermittent hydrogenolyses may result from the partial reduction of the carboxyl group to form the aldehyde followed by its decomposition, or from the reduction of carbon dioxide. Since the presence of aldehydes and alcohols was not detected in the reaction products and since the amount of carbon dioxide decreases above 400° with an increase in the amount of carbon monoxide, it appears that the carbon monoxide results from the reduction of the carbon dioxide. This is further substantiated by the fact that during the third hour of intermittent operation not all of the carbon dioxide present as an impurity in the original hydrogen gas could be accounted for, but small amounts of carbon monoxide and water were found. This can only be explained by a reduction of the carbon dioxide at this temperature and pressure to form the other gases. Such a reduction has been suggested by Storch[12] to take place in the gaseous products resulting from coal hydrogenation.

The water formation may result from the reduction of the oxides of carbon, from the reduction of the carboxyl group, or as LaLande[13] suggests from the pyrolysis of abietic acid by the formation of the anhydride.

It is believed that the same type of reduction of the carboxyl linkage does not occur with abietic acid as Cawley[11] observed with benzoic acid because of the presence of the stable methyl group attached to the same carbon as the carboxyl and or because of the fact that the carboxyl group is attached to a tertiary alicylic carbon atom and not an aromatic structure. The present work as well as that of Cawley[11] substantiates Boomer's theory[7] in regard to carboxyl oxygen removal and both may be used to explain Storch's[10] results, since it is generally known[14] that the aromaticity of coals increases with increasing rank.

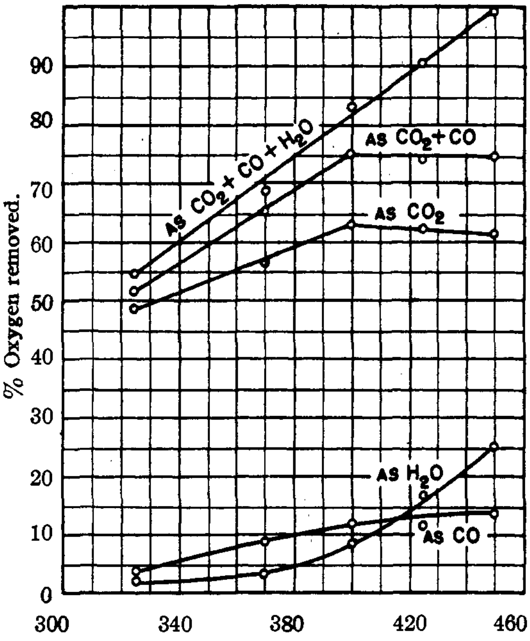

Fig. 1.—Oxygen removal for two-hour hydrogenolyses.

Alkyl Severance.—The British Fuel Research Board[15] has carried out the destructive hydrogenation of such compounds as 1- and 2-methyl- and 2,6-dimethylnaphthalene and found that the methyl groups are stable up to rather high temperatures. For example, at 450° these compounds are only demethylated to the extent of about 3%, but at 500° almost complete demethylation takes place. The 2,6-dimethyl compound is demethylated in stages yielding methylnaphthalene as an intermediate product.

At the present time, the authors do not know of any literature concerning the higher hydrocarbon gases which are obtained as a result of coal hydrogenation because all the data presented in the technical literature are in terms of Orsat analyses and thus the saturated gases are reported only as methane and ethane.

Some idea concerning the amount of alkyl severance which occurs during the hydrogenolysis of abietic acid may be obtained by examining Fig. 2. This figure shows the grams of methane, ethane and propane formed from 100 g. of the acid as a function of the hydrogenolysis temperature. From the amount of propane formed it may be seen that depropylation does not occur to any appreciable extent up to a temperature of about 380°, but that above this temperature it increases rather rapidly. The theoretical yield of propane from 100 g. of abietic acid by the removal of the isopropyl group alone is 14.6 g. and if the ethane

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[12] Storch, *et al.*, U. S. Bur. Mines, Reports Investigations, 3498.

[13] LaLande, *Ind. Eng. Chem.*, **26**, 678 (1934).

[14] Bone and Himus, "Coal, Its Constitution and Uses," Longmans, Green and Co., New York, N. Y., 1936.

[15] British Fuel Research Board Report P-75 (1934).

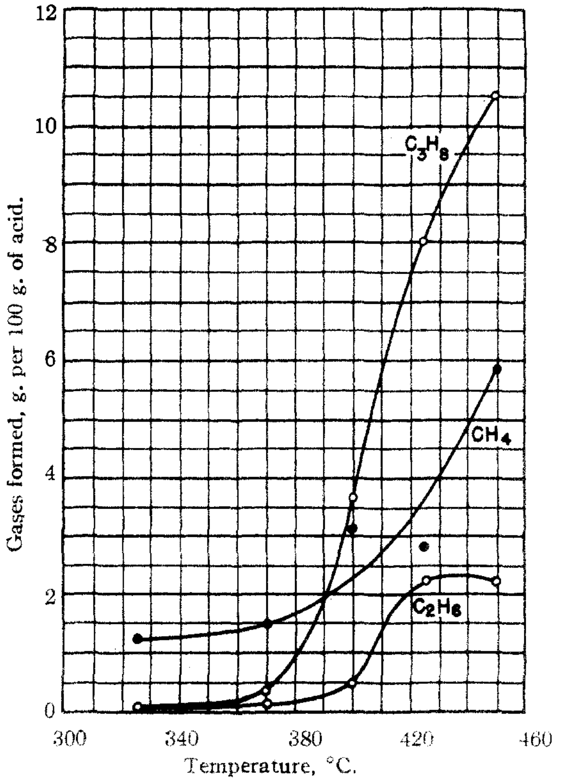

Fig. 2.—Alkyl severance for two-hour hydrogenolyses.

present is considered as resulting from the cracking of propane the total amount formed at 450° is 13.6 g.

The amount of propane formed on one hour of hydrogenolysis was only 0.98 g. as compared with 3.12 g. for two hours of continuous operation. During the second and third hours of operation only 0.53 g. and 0.37 g. were formed. Thus, after three hours of intermittent operation the total amount of propane was only 1.88 g. These data indicate that the amount of depropylation is a function of hydrogen concentration or partial pressure. Although the exact partial pressure of hydrogen cannot be calculated because of the unknown vapor pressure of the various liquid products at reaction conditions, it is, nevertheless, possible to obtain a general idea of the relative values by considering the concentration of hydrogen in the non-condensable gases at the completion of the reaction. These values are respectively 90.39% after two hours continuous operation and 92.59, 97.25 and 97.53% after the first, second and third hour of intermittent operation.

Further evidence of depropylation may be found in the liquid products resulting from the second and third hours of hydrogenolyses. Although these products were not definitely identified, the ultimate analyses definitely indicate a removal of the isopropyl group. Table IV lists the ultimate analyses of these compounds and the possibilities are 1,12-dimethyl- and 1-methyldodecahydrophenanthrene.

Because no ethane was detected in the gaseous products from the intermittent operations as compared to 0.47 g. from the two hour continuous hydrogenolysis, the experiments establish definitely that the ethane results from the cracking of propane during the second hour of continuous treatment. This again can be attributed to the lower partial pressure of hydrogen.

The mechanism of methane formation is more complex for it may result from demethylation, from the reduction of carbon monoxide, from the cracking of higher hydrocarbon gases and from alicyclic decomposition. The relatively large amount of methane at the low temperatures appears to be due to demethylation, probably of the methyl group in the number 12 position since all of the dehydrogenation experiments[16,17,18] show this group to be far less stable than the group in the number 1 position. This may occur as a straight dealkylation or as the severance of the methyl group with an adjacent hydrogen. At the higher temperatures methane is believed to result from all four possible methods.

The hydrogenolysis of the abietic acid for one, two and three hours resulted in the formation of approximately 2 g. of methane during the first hour, 1 g. during the second and 1 g. during the third. This compares with 3.69 g. for two hours of continuous operation and indicates that the methane formation is a function of time as well as hydrogen concentration. It is believed that at 400° for different lengths of time practically all the methane formation results from demethylation since there is very little evidence of alicyclic decomposition and only a small amount of carbon monoxide available for reduction.

Alicyclic Decomposition.—The present data concerning alicyclic decomposition are rather limited due to the fact that none of the hydronaphthalenes or the two-ring intermediate compounds have been definitely identified even though data are available on the three-ring structures, as well as on the final single-ring products of this type of decomposition. At 370° there is evidence of hydrogen addition either as a saturation of one of the two double bonds or as a 1,4 addition to the conjugated system. At the higher temperatures, however, dehydrogenation takes place as indicated by the presence of two and three double bonds in the liquid products. Since this type of dehydrogenation occurs, there is less tendency for alicyclic decomposition.

From the two hour hydrogenolyses the amounts of the two-ring intermediate products have been estimated in terms of the total products from the distillation curves to be about 3, 17, 20 and 25% at temperatures of 370, 400, 425 and 450°, respectively, and 10, 2 and 1% during the first, second

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(16) Diels and Karstens, *Ber.*, **60**, 2323 (1927).

(17) Ruzicka and Waldmann, *Helv. Chim. Acta*, **16**, 842 (1933).

(18) Fieser, "Chemistry of Natural Products Related to Phenanthrene," A. C. S. Monograph No. 70, Reinhold Publishing Corp., New York, N. Y., 1936.

and third hour of intermittent hydrogenolysis. Thus, even after three hours, the amount was appreciably less than that obtained for two hours of continuous operation. These data indicate that at 400° the extent of alicyclic decomposition is a function of the hydrogen concentration and emphasizes the fact that very misleading conclusions may be obtained from coal hydrogenolysis experiments when the hydrogen concentration is not considered in interpreting the results.

The specific dispersion, refractive index and boiling point data show that these intermediate compounds are related to the alkyl hydronaphthalenes although no particular compound has been definitely identified. This would indicate splitting of one of the three rings with the formation of a hydronaphthalene ring structure and an alkyl side chain. Biggs[19] has shown that the oils resulting from the hydrogenation of Pittsburgh coal are chiefly polyhydroaromatic hydrocarbons and LeClaire[20] has found the same results for other coals. LeClaire's data indicate that the distillation fractions of such oils have refractive indices ranging from 1.4823 to 1.5710, densities ranging from 0.888 to 1.038, and specific dispersions ranging from 97.9 to 174.4.

The final products of alicyclic decomposition did not amount to more than approximately 10% of the total products even at the highest temperature of hydrogenolysis. However, the physical properties of some of the fractions of the products indicated that the following compounds were present: *trans*-1,2-dimethylcyclohexane, methylcyclohexane, 1,3-dimethylcyclopentane, ethylcyclohexane and 3,5-dimethylcyclohexene-1. Since there were no five-numbered rings in the original material, the presence of 1,3-dimethylcyclopentane indicates that isomerization must have taken place. Such an isomerization was described by independent workers[21,22] who hydrogenated benzene and cyclohexane under similar conditions and identified methylcyclopentane in the products. The presence of methyl and ethyl cyclohexane indicate agreement with the theory of Hall[23] concerning the alicyclic decomposition of hydronaphthalene.

Hydrogen Consumption.—Figure 3 shows the grams of hydrogen consumed as a function of hydrogenolysis temperature. The rather low hydrogen consumption at the lower temperatures is due principally to the saturation of one of the double bonds, to demethylation and to depropylation. The higher consumption of hydrogen at the higher temperatures is due to the alkyl and alicyclic decomposition and also to the reduction of the oxides of carbon.

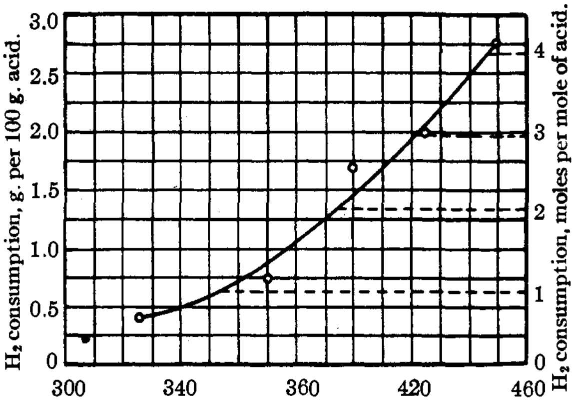

Fig. 3.—Hydrogen consumption for two-hour hydrogenolyses.

The intermittent hydrogenolyses show that only 0.48 g. of hydrogen is consumed during the first hour and 0.44 g. of this can be accounted for in the formation of methane and propane and the reduction of carbon dioxide. During the second and third hours of intermittent operation virtually no hydrogen consumption occurred. In fact, during the third hour, slightly more hydrogen was recovered than was available at the beginning of the third hour of treatment. These data compare with a hydrogen consumption of 1.67 g. during the two-hour continuous hydrogenolysis at the same temperature. Despite the relatively low consumption of hydrogen the carbon and hydrogen analyses of the products isolated indicate that one of the two possible ethylenic linkages had been saturated and thus show the probable dehydrogenation of some of the unidentified products.

The foregoing data may be interpreted as evidence that hydrogen consumption under the conditions investigated is primarily due to cracking reactions and that little, if any, hydrogen is consumed in the saturation of ethylenic linkages. Storch,[9,10,24,25] on the other hand, has shown that after the first hour the hydrogen consumption upon hydrogenolysis of a Pittsburgh seam coal at 1000 p. s. i. and 400° is a straight line function of the reaction time up to fifteen hours of treatment, and that the straight line relationship is likewise true, irrespective of the rank or oxygen content of the coals studied. From 20 to 25% of the hydrogen consumed in this manner may have been utilized in the removal of non-carboxyl oxygen according to data for oxygen removal, but the marked difference between the results for coal and abietic acid requires further explanation. In part, the difference may be due to the more aromatic structure and greater ease of saturation of ethylenic linkages in coal, because of the presence of the hydrogen carrier, tetralin, and the 1% stannous sulfide, or as has been shown in previous sections

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[19] Biggs, THIS JOURNAL, 58, 1020 (1936); Biggs and Weiler, *ibid.*, 59, 369 (1937).

[20] LeClaire, *ibid.*, 63, 343 (1941).

[21] Ando, *J. Soc. Chem. Ind.* (Japan), 42, 391 (1939); *C. A.*, 34, 2339 (1940).

[22] British Fuel Research Board Report, pp. 172–181 (1938).

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

[24] Storch, Fisher, Eisner and Clarke, *Ind. Eng. Chem.*, 32, 346 (1940).

[25] Storch, Hawk and O'Neill, THIS JOURNAL, 64, 230–236 (1942).

TABLE II

WT. OF HYDROGEN CONSUMED AND GASEOUS PRODUCTS FORMED G./100 G. OF ABIETIC ACID

	Time of hydrogenolysis, 2 hours					Temperature of hydrogenolysis, 400°		
Products[a] formed	325°	370°	400°	425°	450°	During 1st hr.	During 2nd hr.	During 3rd hr.
H_2 consumed[b]	0.40	0.73	1.67	1.99	2.76	0.48	0.00	−0.02
CO	.65	1.66	2.18	2.09	2.47	2.22	.56	.19
CO_2	7.04	8.17	9.17	9.10	8.91	8.90	.03	− .22
H_2O	0.3	0.4	1.0	2.0	3.0	0.81	.63	.14
CH_4	1.27	1.50	3.69	2.82	5.83	2.20	1.03	1.03
C_2H_6	0.00	0.17	0.47	2.24	2.17	0.00	0.00	0.00
C_3H_8	.02	.30	3.12	8.02	10.50	.98	.53	.37
i-C_4H_{10}	.00	.00	1.69	2.55	6.82	1.37	1.38	.32
n-C_4H_{10}	.00	.00	0.73	0.61	1.09			

[a] Values are corrected for impurities in original hydrogen. [b] Percentage composition of original gas: CO_2, 0.15; O_2, 0.35; CO, 0.00; H_2, 98.40; CH_4, 0.30 and N_2, 0.80.

of the paper due to cracking reactions which appear to be favored at lower partial pressure of hydrogen.

Experimental

Procedure and Apparatus.—The acid used in the experiments was obtained by recrystallization of commercial abietic acid using LaLande's[13] modification of Steele's[26] method. At least three recrystallizations were used for each batch of crystals after which they were dried at reduced pressure over anhydrous calcium chloride at 65° for a period of three hours, weighed and placed immediately into the hydrogenation retort under an atmosphere of hydrogen. The melting point of the acid was 158° and did not vary more than ±1° for the various batches. The analyses of the various batches of acid varied within 0.1% of the theoretical values for C and H.

The hydrogenations were conducted in an alloy steel rotary type retort previously described.[27] One hundred grams of the recrystallized acid was placed in the retort together with the alloy steel stirrer, the retort flushed several times with hydrogen, and hydrogen introduced to a pressure of 1900 to 1975 p. s. i. (133.6–138.9 kg./sq. cm.). After checking the retort for leaks, it was placed in the hot furnace and heated to the reaction temperature in eighty to one hundred and thirty minutes, depending upon the temperature desired. Hydrogenolyses were conducted for one hundred and twenty minutes at 325, 370, 400, 425 and 450° and also at 400° for one, two and three sixty-minute periods with the reaction gases being removed and the retort charged with fresh hydrogen after each hour. After each of the reaction periods the retort was cooled rapidly to 150° and the gaseous products removed at this temperature.

The reaction gases were passed through a series of traps to separate and isolate the various components. The first trap was immersed in ice water, the second in a dry ice-acetone mixture, the third trap was a tube packed with ascarite and anhydrone, and the fourth trap was immersed in liquid air. The non-condensable gases then passed through a sampling bottle and a Sargent wet test meter.

The non-condensable gases were analyzed using the U. S. Steel Chemist Procedure with a Burrell Delux Model H apparatus. The gaseous products trapped in liquid air were identified by their boiling points as determined on a low temperature Podbielniak fractional distillation apparatus, Standard Precision Model J. The higher boiling gases collected in the first two traps as well as the Podbielniak residue were separated using a Penn State semi-micro distillation column and where a sufficient quantity of any one component was available it was identified by its physical constants.

After removal of the gaseous products the retort was cooled to room temperature and the remaining products removed by solution in ether and separated into basic, acidic and neutral fractions by extraction with 5% hydrochloric acid and 5% sodium hydroxide. The neutral fractions were separated by distillation at reduced pressure, and where a sufficient quantity of any one fraction was available it was purified by semi-micro distillation at reduced pressure and the probable structure determined by interpretation of the physical constants according to Thorpe and Larson,[28] and the quantitative elementary analysis.

Experimental Results.—The results for the hydrogen consumed and the gaseous products formed are listed in Table II.

The residues from the Podbielniak distillations of products resulting from the two-hour hydrogenolyses at 400, 425 and 450° were of sufficient amounts to warrant further investigation. Each individual residue was separated by semi-micro distillation. The refractive index, n^{20}D, of the various fractions from the 400° hydrogenolysis varied from 1.3980 to 1.4492. From this distillation there was about 0.5 g. which had a *n* of 1.4275, a boiling point of 119° at 732 mm., and a density of 0.773 at 20°/4°. These values agree with those for *trans*-1,2-dimethylcyclohexane.[29] The residue from the hydrogenolysis at 425° had a *n* ranging from 1.3691 to 1.4155 and a boiling point ranging from 40 to 92° but did not yield enough of any one fraction to be identified. The *n* range of the distilled residue from the hydrogenolysis at 450° varied from 1.3690 to 1.4426, the main portion of which had a *n* of 1.4240, a boiling point at 732 mm. of 97°, and a density at 20°/4° of 0.768. These values agree with those of Egloff[30] for methylcyclohexane.

The weight of condensable material obtained in traps 1 and 2 from the two-hour hydrogenolyses at 325, 370 and 400° was not sufficient to warrant further investigation. However, in each case there was obtained two immiscible layers in trap 1, the bottom layer of which was identified as

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(26) L. L. Steele, THIS JOURNAL, **44**, 1333 (1922).

(27) C. C. Wright and A. W. Gauger, The Pennsylvania State College, Mineral Industries Experiment Station Technical Paper No. 31.

(28) R. E. Thorpe and R. G. Larson, *Ind. Eng. Chem.*, **34**, 853 (1942).

(29) A. P. I. Hydrocarbon Research Project at Ohio State Univ., 1941.

(30) Egloff, "Physical Constants of Hydrocarbons." Reinhold Publishing Corp., New York, N. Y., 1940.

TABLE III

LIQUID PRODUCTS OF HYDROGENOLYSIS G./100 G. ABIETIC ACID

	Time of hydrogenolysis 2 hours					Temperature of hydrogenolysis, 400°		
	325°	370°	400°	425°	450°	During 1st hr.	During 2nd hr.	During 3rd hr.
Ether insoluble	5.1	None	None	None	None	None	None	None
Extract by acid	3.2	1.1	0.1	0.4	Trace	0.3	Trace	Trace
by alkali	17.5	14.1	2.7	1.6	0.8	3.4	0.8	0.8
Neutral material	62.8	67.6	68.9	59.4	47.7	80.4	76.6	75.3

water. The top layer, as well as the material in trap 2, could be identified only as a hydrocarbon. There was also obtained in trap 1 in each case a very small amount of red brown solid material which was identified as iron oxide. This resulted from the decomposition of an iron salt of abietic acid which will be described later.

After removal of the water layer the combined condensable material obtained in traps 1 and 2 from the two hour hydrogenolyses at 425 and 450° was dried and fractionated by semi-micro distillation. The *n* of the various fractions from the hydrogenolysis at 425° ranged from 1.4113 to 1.4520. Of these fractions it was possible to identify two different constituents. The first had a *n* of 1.4113, a boiling point of 90 to 91° at 729 mm. and a density at 20°/4° of 0.743. These values agree with those presented by Evans[31] for 1,3-dimethylcyclopentane. The second constituent had a *n* of 1.4356, a boiling point of 128° at 731 mm. and a density of 20°/4° of 0.783. These values agree with those of Levina[32] for ethylcyclohexane. The *n* of the fractions from hydrogenolysis at 450° ranged from 1.4110 to 1.4630. The main portion had a boiling point of 128° at 732 mm., a density at 20°/4° of 0.792 and a *n* of 1.4430. These values agree with those presented by Knoevenagel[33] for 3,5-dimethylcyclohexene-1.

The products obtained in traps 1 and 2 minus the water, from any one run of the intermittent hydrogenolyses were insufficient for further investigation. They were all combined, however, and distilled using the semi-micro column. The refractive indices and distillation temperatures of the various fractions ranged from 1.3781 to 1.4490 and from 38 to 124°, but there was not enough of any one fraction to be definitely identified.

The results of separating the products remaining in the retort into acid soluble, alkali soluble and neutral fractions are shown in Table III.

Examination of the products of hydrogenolysis at 325° which remained in the retort after the gaseous products had been removed, showed one which appeared to be ether insoluble but which upon closer examination was found to be very slightly soluble in ether. It was a light gray amorphous solid with a characteristic odor and a decomposition range of 230 to 232°. On ignition it decomposed into a black solid which burst into a bright flame and left a dark red residue. The amorphous solid was identified as an iron salt of abietic acid by tests with KCNS and $K_4Fe(CN)_6$ and by mixed melting point determinations on the recrystallized alkali soluble portion of the compound with freshly prepared abietic acid.

When the acid extracted material shown in Table III was made alkaline with 5% sodium hydroxide, ferric hydroxide precipitated. This indicated the presence of an iron salt of abietic acid in the ether soluble fraction.

The alkali extracts were acidified with 5% hydrochloric acid and extracted with ether. The ether solutions were dried over anhydrous sodium sulfate and stripped of ether over a steam-bath. On standing overnight a white crystalline material separated from the liquid fractions obtained from the hydrogenolyses at the three lowest temperatures. These crystals, representing approximately 90% of the total amount present, were identified by mixed melting points as unreacted abietic acid. The identity of the remaining liquid acidic material was not definitely established but it had a *n* of 1.524 and an ultimate analysis of 80.65 to 80.76% C, 10.53 to 10.80% H, and 8.55 to 8.71% O. These liquid acids also gave a negative test for unsaturation which indicated that they may be the tetrahydroabietic acid about which the existing literature is rather confusing.

Distillation of the neutral products from the hydrogenolysis at 325° under reduced pressure yielded water as a distillate and left a wax-like residue. A portion of this residue was soluble in hot acetone and crystallized from the acetone upon cooling. The crystals were separated by filtration but upon exposure to air they turned into a wet amorphous mass. Filtration of the crystals in a desiccator over phosphoric anhydride was successful, but in attempting to determine the melting point the same type of transformation again occurred. The residue from the acetone extraction was identified as a sodium salt of abietic acid.

The neutral products from each hydrogenolysis were distilled under reduced pressure and in each case, small fractions collected and their refractive indices measured at 15°. Where various fractions showed the same refractive index they were combined and redistilled using the semi-micro column. On redistillation only the middle 60% of the fraction was used for obtaining the physical constants. Table IV shows the probable products from the hydrogenolyses based on their elementary analyses and specific dispersions. Since, to

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(31) Evans, *J. Inst. Petroleum Tech.*, **24**, 321 (1938).

(32) Levina, *J. Gen. Chem.* (U. S. S. R.), **8**, 1776 (1938).

(33) Knoevenagel, *Ann.*, **297**, 113 (1879).

TABLE IV

PROBABLE PRODUCTS OF HYDROGENOLYSIS OF ABIETIC ACID

Temp. of hydrogenolysis, °C.	Time of hydrogenolysis, hr.	% of neutral prdts.	B. p. °C.	B. p. Mm.	n_{20}	d^{20}_4	Probable product	Analyses, %[a] Carbon Calcd.	Analyses, %[a] Carbon Found	Analyses, %[a] Hydrogen Calcd.	Analyses, %[a] Hydrogen Found	Sp. disp. Calcd.	Sp. disp. Found
370	2 contin.	48	139–142	4	1.5165	0.943	12-Me-Δ9,14-dodecahydroretene[b]	87.61	87.71	12.39	12.13	107.9	107.1
400	2 contin.	18	122–125	4	1.5312	.946	1,12-DiMe-Δ9,14; 7,8 decahydrophenanthrene[b]	88.81	88.68	11.19	11.14	144.6	144.0
400	2 contin.	27	143–146	5.5	1.5252	.943	12-Me-decahydroretene[c]	88.29	88.16	11.71	11.76	137.4[e]	137.4
400	1st	21	122–128	4	1.5242	.942	2 Structural isomers of decahydroretene	88.44	88.31	11.56	11.42	142.7 118.7	129.9
400	1st	24	127–130	3	1.5191	.938	1,12-DiMe-dodecahydrophenanthrene	87.99	87.92	12.01	12.05	109.8	128.8
400	2nd	15	127–131	2	1.5222	.943	1-Me-dodecahydrophenanthrene	88.15	88.00	11.84	11.75	110.4	124.4
400	3rd	25	146–155	5	1.5238	.942	1-Me-dodecahydrophenanthrene	88.15	87.98	11.84	11.80	110.4	134.0
425	2 contin.	30	118–120	3	1.5329	.946	1-Me-Δ7,8; 9,14 decahydrophenanthrene[d]	89.03	88.93	10.97	10.91	147.8	148.2
450	2 contin.	10	112–116	4	1.5476	.951	1-Me-octahydrophenanthrene	89.92	89.69	10.08	10.09	[f]	179.9

[a] Data given are the mean of duplicate analyses agreeing within 0.1%. [b] Colorless liquid with a characteristic odor. Gave positive unsaturation tests with Br_2 and $KMnO_4$. [c] Green liquid with a characteristic odor. Unsaturation test with $KMnO_4$ required heat. [d] Colorless liquid with a kerosene-like odor. Unsaturation tests positive. Assuming double bonds to be in conjugated position but not in the 7, 8 position, the latter giving a sp. disp. of 140.5. [f] Various calculated figures for sp. disp. depending on location of double bonds are: Δ9, 14; 5, 13; 7,8: 172.8; Δ9, 14; 7, 8; 12, 13: 185.3; Δ9, 14; 7, 8; 10, 11: 185.3; Δ9, 14; 10, 11; 12, 13:149.9.

the authors' knowledge, the physical constants of these products are not presented in the technical literature no comparison could be made.

Summary

The hydrogenolysis of abietic acid for two hours at temperatures ranging from 325 to 450° and initial hydrogen pressure of 1900 to 1975 P. s. i. and also at 400° for one, two and three hours at the same pressure has shown that:

1. The amount of unconverted acidic material is quite appreciable at 325° but decreases to practically zero as the temperature is increased to 450°.
2. The removal of oxygen takes place, for the most part, as a straight decarboxylation with the formation of carbon dioxide in the early stages of hydrogenolysis.
3. The total percentage of oxygen removed is directly proportional to the temperature of hydrogenolysis and is virtually complete at 450°.
4. The formation of carbon monoxide results at least in part from the reduction of the carbon dioxide.
5. Depropylation does not occur to any appreciable extent up to a temperature of about 380° but increases rapidly above this temperature.
6. Depropylation is also a function of hydrogen concentration or partial pressure of hydrogen.
7. Part of the ethane results from the cracking of propane.
8. Severance of one of the methyl groups occurs to an appreciable extent even at the lower temperatures of hydrogenolysis and is also a function of time and hydrogen concentration.
9. Alicyclic decomposition does not occur to any appreciable extent up to a temperature of 425°, but increases rapidly above this temperature and is a function of hydrogen concentration.
10. The hydrogen consumption at the lower temperatures is due principally to the partial saturation of the ethylenic linkages and at the higher temperatures to the alkyl and alicyclic decomposition as well as to the reduction of the oxides of carbon.

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