[CONTRIBUTION FROM UNIVERSAL OIL PRODUCTS CO. RESEARCH LABORATORIES]

Hydrogenation of Aromatic Compounds at Temperatures Close to their Decomposition in the Presence of Catalysts

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The hydrogenation of aromatic compounds in the presence of mixed catalysts at temperatures close to their decomposition points was first studied by Ipatieff and Klukvin in 1924.[1]

The results of this work led to conclusions which were later confirmed by Ipatieff and Orlow[2] and Kling and Florentin.[3]

However, the work done up to this point did not explain the main problems of destructive hydrogenation in the presence of catalysts. The first question which remained unanswered concerned the hydrogenation of aromatic compounds in the presence of molybdenum oxide catalysts. It is not yet known whether monocyclic aromatic compounds can be hydrogenated under high pressure with other catalysts than nickel or nickel oxide. The first experiments, therefore, concerned the hydrogenation of benzene and xylene under pressure at high temperature (450°F.) in the presence of molybdenum oxide catalysts (MoO_3). It was found that neither benzene nor xylene hydrogenated in the presence of a molybdenum catalyst, while xylene decomposed under these conditions to benzene and toluene.

A second series of experiments dealt with the hydrogenation of naphthalene in the presence of NiO, CuO, Fe_2O_3 and MoO_3 catalysts as well as in their absence, the iron walls of the autoclave acting catalytically.

Since preliminary experiments with fluorene and phenanthrene also resulted in hydrogenation at high temperature in the presence of a molybdenum catalyst, it was concluded that polycyclic aromatic compounds differ from monocyclic compounds under these conditions of hydrogenation.

In the case of naphthalene, it is possible to explain why hydrogenation occurs under the influence of weak catalysts. Naphthalene has two carbon atoms, common to both rings, which differ from the others. One can assume that a molecule of hydrogen is first added to the common carbon atoms (I); the product is immediately isomerized into 1,4-dihydronaphthalene, forming an ordinary double bond in the ring, (II). This compound is easily hydrogenated further to give 1,2,3,4-tetrahydronaphthalene (III).

This assumption is supported by the fact that sodium amalgam causes the hydrogenation of naphthalene to 1,4-dihydronaphthalene (II), which may be transformed into 3,4-dihydronaphthalene with sodium ethoxide.

If the temperature of naphthalene hydrogenation does not exceed 450° tetrahydronaphthalene is obtained almost exclusively. Above 450° the

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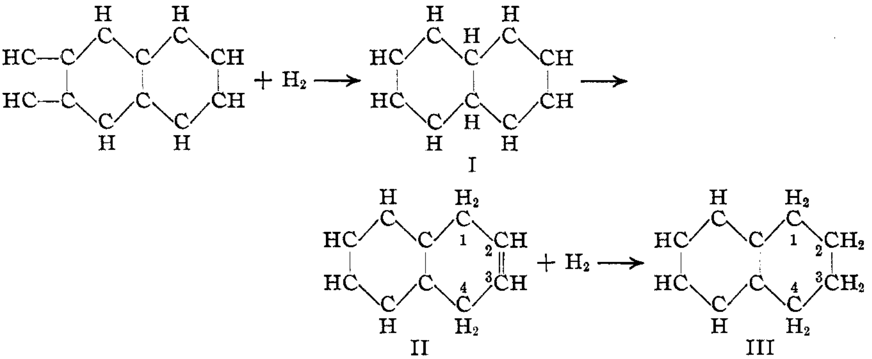
(1) Ipatieff and Klukvin, *Proc. Acad. Sci. Russia*, Leningrad, 1924, **A185**; *Ber.*, **58**, 103 (1925).

(2) Ipatieff and Orlow, *ibid.*, **60**, 1963 (1927); **62**, 719 and 1226 (1929).

(3) Kling and Florentin, *Compt rend.*, **182**, 526 (1926).



tetrahydronaphthalene formed decomposes into benzene hydrocarbons. It must be noted that decomposition of the tetrahydronaphthalene into benzene hydrocarbons causes the occurrence of naphthenes in all fractions of the product only when using a nickel catalyst. This shows that some molecules of the monocyclic aromatic compounds are hydrogenated during this decomposition.

Another series of experiments was concerned with the hydrogenation of phenol at high temperature in the presence of various catalysts. The investigations of Tropsch,[4] Orlow[2] and Kling and Florentin[3] showed that several hydrocarbons can be obtained under such conditions. Our experiments indicated that at high temperature and pressure (with NiO or MoO_3), hydrogenation of the aromatic ring also occurs, yielding cyclohexane in amounts depending upon the nature of the catalyst used.

The possible hydrogenation of the aromatic ring under such conditions can be explained in the same way as it was in 1905[5] when the hydrogenation of phenol under pressure in the presence of nickel oxide was carried out for the first time. The reaction was explained on the basis of the two *tautomeric forms* of phenol: "true" phenol (enol) and *keto* form. During hydrogenation, "true" phenol is reduced to benzene, with the separation of water. The reaction proceeds at high temperatures without catalysts, under the influence of the iron walls of an autoclave. If a strong hydrogenation catalyst, such as nickel oxide, is present, much cyclohexane is obtained. It should be noted that, at 450–490° under high pressure, cyclohexane is isomerized to methylcyclopentane.[6]

When the hydrogenation of phenol is carried out with MoO_3, Fe_2O_3 or CuO, 10 to 30% cyclohexane is always obtained. Its formation, then, is caused more easily by hydrogenation of the second tautomeric form of phenol—the ketone form—for which a less active catalyst is needed.

My investigations[7] showed that alumina, when not very highly heated

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(4) Tropsch, Third International Conference of Bituminous Coal, Pittsburgh, November, 1931.

(5) V. Ipatieff, *J. Russ. Phys.-Chem. Soc.*, **38**, 89 (1906); *Chem. Abstracts*, **1**, 1538 (1907).

(6) Ipatieff and Dovgelewitch, *Ber.*, **44**, 2987 (1911).

(7) Ipatieff, *ibid.*, **37**, 2986 (1904).

and therefore containing water of hydration, is an active dehydrating catalyst. This fact has been contradicted by the work of Kling and Florentin,[8] who state that alumina prepared at 750° gives high yields of benzene in the hydrogenation of phenol at 490° under high pressure. I can explain this fact that alumina does not act as promoter, but as a porous substance.

Special experiments were made on the hydrogenation of aromatic hydrocarbons in the presence of active catalysts poisoned by thiophene. It was found that although one-ring aromatic hydrocarbons are not hydrogenated at high temperature, naphthalene can be hydrogenated in the presence of thiophene, as well as in its absence. Phenol is hydrogenated in the presence of thiophene, but the action is accompanied by the formation of high-boiling products, presumably esters, etc. Thiophene decomposes completely under these conditions.

Experimental Part

The Hydrogenation of Monocyclic Aromatic Hydrocarbons.—The hydrogenation was carried out in a rotating bomb of the type described by Ipatieff, at 450°, in the presence of catalysts. The data are summarized in Table I.

TABLE I

Expt.	Subs.	Catalyst	Time, hours	Temp., °C.	Pressure, atm. start	Pressure, atm. end	Anal. of gas	Index of ref.	Prod. of reaction
4	Benzene	MoO_3	3	430	100	99	H_2	1.5036/17	Benzene
6	Benzene	MoO_3 50% Al_2O_3 50%	3	400	65	65	H_2	1.5030/18	Benzene
7	Benzene	MoO_3 50% Al_2O_3 50%	3	450	65	64	H_2	1.5029/18	Benzene
9	Xylene	MoO_3	3	450	90	75	H_2 95% Par. 5	....	Benzene Toluene Xylene
19	Xylene	MoO_3 50% Al_2O_3 50%	3	450	100	80	....	....	Benzene Toluene Xylene

As shown in Expts. 4, 6 and 7, benzene cannot be hydrogenated in the presence of molybdenum catalysts. Xylene also fails to hydrogenate under these conditions in the presence of molybdenum catalysts, but decomposes to benzene and toluene (Expts. 9 and 19). The product of reaction dissolves entirely in fuming sulfuric acid and distils at 80–140°. It was separated into: (1) fraction boiling at 80–81° which solidified at 0°, and (2) fraction boiling at 108–112° (with nitric acid forms dinitrotoluene).

The Hydrogenation of Naphthalene.—The experiments on the hydrogenation of naphthalene in the presence of different catalysts were carried out in the rotating autoclave at 450–475°. The data obtained are shown in Table II.

Catalyst MoO_3 was precipitated from solution of ammonium molybdate by addition of nitric acid, and dried for thirty-six hours at 210°. $MoO_3Al_2O_3$ consists of a mechanical mixture of the precipitated MoO_3 and Al_2O_3.

$Fe_2O_3Al_2O_3$ and $CuOAl_2O_3$ were precipitated from a solution of mixed nitrate salts of these metals by addition of ammonium hydroxide and dried at 250°.

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(8) Kling and Florentin, International Congress on Bituminous Coal, Pittsburg, November, 1931.

TABLE II

Expt.	Catalyst	Time, hrs.	Temp., °C.	Press., atm. init.	Press., atm. end	% of HC	Analysis of hydrocarbon fractions: Distillation I	Distillation II	Index of refraction 26° I	Index of refraction 26° II	Specific gravity 26° I	Specific gravity 26° II
7	NiO, 50% Al_2O_3, 50%	25	400	80	20	95	77–83	...	1.4441	....	....	....
8		2	450	64	20	93	75–78	78–81	....	....	....	....
12	MoO_3, 50% Al_2O_3, 50%	2	425	65	35	88	70–77	77–82	1.4642	1.4789	0.8125	0.8291
13		2	450	65	35	92	70–78	78–82	1.4671	1.4679	.8155	....
10		3	475	65	35	95	70–78	78–82	1.4679	1.4840	....	....
16	MoO_3	2	450	65	31	83	69–81	81–88	....	1.4650	....	....
17	MoO_3	2	450	65	35	..	70–79	79–83	....	....	....	....
22	Fe_2O_3, 50% Al_2O_3, 50%	2	450	65	55	22	75–82	82–84	1.4815	1.4362	....	....
23		2	450	65	57	..	70–72	72–81	1.4430	1.4750	.8337	....
20	Without catalyst	2	450	65	52	25	75–81	81–84	1.4730	1.4935	.8454	....
21		2	450	65	53	..	...	...	....	....	....	....
25	Al_2O_3	2	450	65	57	10	70–84	...	1.4755	....	....	....
27	Al_2O_3	2	450	65	58	8	...	...	....	....	....	....

Phenol (100 g.)

Expt.	Analysis of hydrocarbon fractions after treatment I and II fractions with fuming H_2SO_4 (20%): Distillation 1	Distillation 2	Index of refraction 26° 1	Index of refraction 26° 2	Specific gravity 26° 1	Specific gravity 26° 2	Product of destr. hydrogenation contained, %: Benz. HC	Cyclohexane	Analysis of gas, %: H_2	C_nH_{2n+2}
7	75–84	...	1.4248	....	....	....	10	90	96	1.6
8	75–84	...	1.4246	....	....	....	12	88	96	1.8
12	75–77	...	1.4163	....	....	....	88	12	...	...
13	74–77	81–83	1.4140	1.4244	0.7583	....	84	16	94.6	1.2
10	74–77	81–83	1.4230	....	....	....	85	15	..	...
16	75–76	79–80	1.4189	1.4240	.7504	0.7620	70	30	..	...
17	...	79–80	....	1.4215	.7326	....	80	20	93.8	1.8
22	75–82	...	1.4230	....	....	....	84	16	94.3	4.0
23	75–82	...	1.4283	....	....	....	84	16	...	...
20	77–79	79–81	1.4249	1.4270	.7634	....	80	20	94.4	3.9
21	...	...	....	....	....	....	..	..	..	...
25	75–82	...	1.4186	....	....	....	88	12	..	...
27	...	...	....	....	....	....	..	..	..	...

$NiOAl_2O_3$.—The precipitation (nitrate salts) was made by addition of ammonium carbonate, the product dried for seventeen hours at 210° and in a stream of air for five hours at 400°. All catalysts were used in amount of 10% of the substance.

From Table II one can see that $NiOAl_2O_3$ catalyst (Expt. 21) gave 38% of the fraction boiling at 196–208°. The analysis and properties prove the presence of *tetralin*. Found: C, 90.76; H, 8.78. Other products were identical with those obtained by Klukvin and myself, *i. e.*, consist of aromatic hydrocarbons—benzene, toluene, etc. In order to ascertain whether other hydrocarbons are present in the aromatic fractions they were treated with 15% fuming sulfuric acid. The hydrocarbons insoluble in sulfuric acid are *naphthenes;* they did not react with the nitrating mixture and analysis gave: boiling point 76–104°, d_4^0 0.7630; n_D^{26} 1.4215; C, 85.82; H, 14.78.

Contacting with MoO_3 as catalyst for a short time, the yield of tetralin increased to 76% (Expt. 24). In this case benzene hydrocarbons are obtained in small amount. When hydrogenation is carried out for a long time the first fraction (80–120°) contains about 10% of naphthenes (after treatment with fuming sulfuric acid), confirmed by analysis: boiling point 72–78°, d_4^0 0.7547, n_D^{26} 1.4070; C, 85.25; H, 14.78.

Analysis showed that methylcyclopentane had been formed by isomerization of cyclohexane.

Experiments 17, 25, 8, 9 and 23 showed that the same results were reached when catalysts MoO_3 or $MoO_3Al_2O_3$ were used and when the time of hydrogenation was extended. At 475° very little tetralin remained; the aromatic hydrocarbon fractions do not contain other hydrocarbons.

Experiments 12 and 13 (catalyst $CuOAl_2O_3$) and Experiments 9, 10 and 11 (catalyst $Fe_2O_3Al_2O_3$) showed that the formation of tetralin also takes place and aromatic hydrocarbons are obtained. Analysis of different fractions (catalyst $Fe_2O_3Al_2O_3$) gave: Fraction 80–110°, C, 91.03; H, 8.76; corresponding to C_7H_8. Fraction 125–150°, C, 90.61; H, 8.83; corresponding to C_8H_{10}. Fraction 175–190°, C, 89.63; H, 8.63; corresponding to C_9H_{12}.

Experiment 26 shows that at 475° in the absence of a catalyst we have the same picture of hydrogenation.

The Influence of Thiophene upon the Hydrogenation of Naphthalene.—It was found that, at high temperatures of hydrogenation, the thiophene does not affect the reaction appreciably. Thus in the hydrogenation of naphthalene ($NiOAl_2O_3$) 38% of tetralin was obtained whereas in the presence of thiophene 33% was obtained.

The Hydrogenation of Phenol.—The hydrogenation of phenol proceeded under the conditions as described in the case of naphthalene. The data are summarized in Table II. Experiment 8 showed the reaction with $NiOAl_2O_3$ proceeded within two hours only when the temperature was 400°. After-treatment of hydrocarbons (95%) with 15% fuming sulfuric acid yielded 90% cycloparaffins—cyclohexane and methylcyclopentane.

Experiments 12, 13, 16 and 17 showed the hydrogenation of phenol in the presence of catalysts $MoO_3Al_2O_3$ and MoO_3; MoO_3 is a more active catalyst and the amount of naphthenes obtained increased slightly.

Analysis of fractions (Experiment 13) after treatment with sulfuric acid proves that we have naphthenes: Fraction 74–77°, C, 85.37; H, 14.30. Fraction 81–83°, C, 84.94; H, 14.60. Calcd. for C_nH_{2n}: C, 85.62; H, 14.38.

Analysis of fractions (Experiment 16) after treatment with sulfuric acid gave: Fraction 73–76°, C, 85.05; H, 14.70. Fraction 79–80°, C, 84.87; H, 14.56.

Experiments 22 and 23 (catalyst $Fe_2O_3Al_2O_3$) showed that the amount of phenol decomposed is considerably smaller (about 25%).

If phenol is hydrogenated *without a catalyst*, almost the same result is obtained as when iron oxide was used. After treatment of the fractions (Expt. 20) boiling 75–81° and 81–84° with 15% sulfuric acid, a hydrocarbon was obtained which did not react with the nitrating mixture. Its analysis showed that it was cyclohexane: C, 84.92; H, 14.61.

Experiments 25 and 27 Catalyst Al_2O_3.—The formation of an unsaturated hydrocarbon becomes noticeable, since the hydrocarbons obtained decolorize permanganate solution. After treatment with fuming sulfuric acid (15%) a hydrocarbon is obtained which does not react with the nitrating mixture and is a mixture of cyclohexane and methylcyclopentane.

The Hydrogenation of Phenol in the Presence of Thiophene.—If the hydrogenation of phenol is carried out in the presence of MoO_3 and 1% thiophene, the same results are obtained. From 200 g. of phenol at 450° for two hours, 160 g. of a product was obtained which contained only 12 g. of unchanged phenol, and hydrocarbons distilled at 69–84°; 26% hydrocarbons remained. They distil at 77–81°, n_D^{26} 1.4215. The hydrocarbons do not react with the nitrating mixture and must be cyclohexane with a small amount of methylcyclopentane. With catalyst $NiOAl_2O_3$ and addition of 1% thiophene the hydrogenation of phenol also takes place but the yield of hydrocarbons decreases to 50%. The rest consisted of unchanged phenol and a small amount of high boiling products. It may be supposed that they consist of phenyl ether and cyclohexylcyclohexanol.

Summary

1. The hydrogenation of monocyclic benzene hydrocarbons cannot take place in the presence of molybdenum catalysts prepared by precipitation in the usual way.

2. During destructive hydrogenation with catalysts, the combination of hydrogen with aromatic compounds occurs first, followed by the decomposition of the hydrogenated product.
3. Active catalysts may hydrogenate the benzylene ring, at the time of its formation, and during the decomposition of a hydrogenated product.
4. The destructive hydrogenation of phenol is due to its tautomeric form.
5. The presence of thiophene does not change the rate of destructive hydrogenation of naphthalene.
6. Thiophene decreases the yield of hydrocarbons during the hydrogenation of phenol.

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The Oxidation of Sym-Triiodophenol[1]

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The present research upon the oxidation of *sym*-triiodophenol was undertaken for the purpose of ascertaining further facts concerning the nature and relative stability of triiodo Type A and diiodo Type B radicals.

A preliminary qualitative survey was made of the oxidation of *sym*-triiodophenol in non-aqueous or in aqueous media by several oxidizing agents.

The oxidation of *sym*-triiodophenol in alkaline solution by potassium ferricyanide was then chosen for further study. The products of this reaction were a large quantity of Lautemann's Red, a small quantity of the dinuclear quinone, 2,6,2′,6′-tetraiododiphenoquinone,[2] and an unstable compound which was not isolated. No phenoxyquinones were found.

Experiments were also carried out for the purpose of showing the relative oxidizing power of the crude oxidation products obtained from the respective oxidations of *sym*-trichloro-, tribromo-, and triiodophenols in glacial acetic acid by a large excess of chromium trioxide. The crude oxidation from the trichlorophenol showed the presence of about 97% of the mononuclear dichloroquinone, which has long been known to be the chief oxidation product formed under these conditions, whereas the crude

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(1) The work described in this paper formed a part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Mary L. Morse in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1929. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. SMITH.

(2) Kammerer and Benzinger [*Ber.*, **11**, 557 (1878)] assigned this formula to a substance which they obtained by the action of potassium tri-iodide solution on a boiling solution of phenol in sodium carbonate. However, the work of Hunter and Woollett indicated that the material obtained by Kammerer and Benzinger was Lautemann's Red. In this case, 2,6,2′,6′-tetraiododiphenoquinone is a new compound.