	Compound	Formula	M. p., °C.	Analyses, %			
				Calcd.		Found	
				C	H	C	H
I	4-Hydroxyphenylxanthane	$C_{19}H_{14}O_2$	150	83.19	5.15	83.63	5.80
	(a) Methyl ether	$C_{20}H_{16}O_2$	112–113	83.28	5.56	83.15	5.64
	(b) Benzoate	$C_{25}H_{18}O_3$	183–184	82.51	4.79	82.17	4.32
II	5-Chloro-2-hydroxyphenylxanthane	$C_{19}H_{13}O_2Cl$	132	73.89	4.24	74.38	4.42
III	2-Hydroxy-5-acetylphenylxanthane	$C_{21}H_{16}O_3$	189	79.71	5.09	79.77	5.03
IV	α-Hydroxy-*x*-xanthylnaphthalene	$C_{23}H_{16}O_2$	195	85.15	4.97	84.91	5.10
V	1-Methoxy-2-xanthyl-4-(2′-phenyl)-butylbenzene	$C_{30}H_{28}O_2$	210	85.66	6.71	85.19	6.95
VI	1-Methoxy-2-xanthyl-4-(3′-methyl-2′-phenyl)-butylbenzene	$C_{31}H_{30}O_2$	202	85.71	6.91	85.95	7.05

The same phenolic condensation products were obtained when using sulfuric acid as the condensing agent. In this case 0.02 mole of sulfuric acid was added to 0.02 mole of xanthydrol and 0.04 mole of phenol. The initial condensation was carried out at 0° and was worked up as described above. Anhydrous aluminum chloride was also employed as a condensing agent; in this instance benzene was used as inert solvent and the reaction mixture was refluxed for eight hours.

Summary

A number of new monohydroxyphenylxanthanes were prepared by simple condensation methods. The physical, chemical and some physiological properties of these crystalline condensation products have been described.

NEW YORK, N. Y. RECEIVED FEBRUARY 23, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

"Hydro-polymerization"[1]

BY V. N. IPATIEFF[2] AND V. I. KOMAREWSKY[2]

In our study of catalytic hydrogenation, it was of great importance to investigate whether olefinic hydrocarbons could be hydrogenated by hydrogen *in statu nascendi,* obtained by decomposing water with iron in the presence of different salts as promoters.[3] For this purpose amylene and isobutene were heated (300°) in a rotating autoclave in the presence of water, reduced iron and magnesium chloride. The results were negative, although a sufficient amount of hydrogen was formed under this condition. In order to see whether magnesium chloride may act as a poison for amylene hydrogenation, a usual hydrogenation of amylene was made with hydrogen, using iron as catalyst in the presence of magnesium chloride. The hydrogenation took place,[4] but an additional new phenomenon was observed, namely, simultaneous polymerization and hydrogenation which produced *decane.* Therefore, investigation was made of other polymerization agents, such as aluminum chloride, zinc chloride and phosphoric acid,[5] in combination with different hydrogenating catalysts (Fe-NiO). In the presence of such mixed catalyst two reactions were found to take place simultaneously: (1) polymerization of the olefin hydrocarbon; (2) hydrogenation of the polymer formed. It is suggested that this reaction be called "hydro-polymerization."

As is evident from the experiments, magnesium chloride and zinc chloride alone do not act as polymerizing agents under the conditions mentioned. However, in the presence of hydrogenating catalysts, polymerization takes place. It is possible that the energy given off during hydrogenation is sufficient to cause the polymerization of olefins by the weak polymerizing catalyst.

(1) Thus, amylene and isobutene, when treated at 300° and under 80 atm. hydrogen pressure in the presence of reduced iron as catalyst, produced pure pentane and isobutane.

(2) Amylene, under the same conditions, in the presence of magnesium chloride alone did not polymerize.

(3) Amylene and isobutene, under the same conditions, in the presence of a mixed catalyst iron and magnesium chloride containing water, produced decanes and octanes.

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(1) Presented before the Division of Organic Chemistry at the 92nd Meeting of the American Chemical Society in Pittsburgh, Pa., September 7–11, 1936.

(2) Research and Development Laboratories, Universal Oil Products Co., Riverside, Illinois.

(3) Benzene, under similar conditions, could not be hydrogenated (Ipatieff, unpublished results).

(4) V. Ipatieff and A. V. Grosse showed the possibility of hydrogenating the olefins in the presence of aluminum chloride (unpublished work).

(5) V. Ipatieff and V. Komarewsky, unpublished work.

Additional evidence that the reaction of hydro-polymerization is a real simultaneous reaction was given by the fact that when the experiments were conducted under conditions not favorable to the hydrogenation in a glass liner placed in the autoclave, the hydrogenation did not take place even in the presence of a hydrogenation catalyst, and at the same time *no polymerization occurred.*

This paper describes the "hydro-polymerization" of amylene and of isobutene in the presence of the hydrogenating catalysts, reduced iron and nickel oxide, together with the polymerizing agents magnesium, zinc and aluminum chlorides.

Experimental Part

Apparatus and Procedure.—All the experiments were carried out in an electrically heated rotating autoclave of the Ipatieff type (800-cc. capacity). The gaseous products of the reaction were analyzed. The liquid products were fractionated by means of a Podbielniak column.

Experiments with Amylene.—(Trimethylethylene containing methylethylethylene, b. p. 35–37°.)

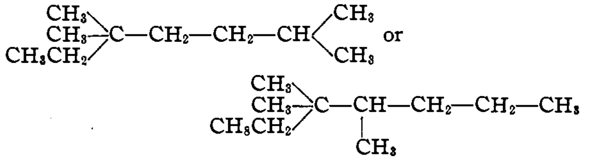
EXPERIMENT 1.—Amylene 40.0 g., reduced iron 10.0 g., hydrogen 80 kg./sq. cm., produced at 300° during four hours 32.0 g. of completely saturated (permanganate test) liquid, insoluble in 96% sulfuric acid; b. p. 35°, that of pure isopentane. Gas remaining at the end of the reaction was pure hydrogen.

EXPERIMENT 2.—Amylene 40.0 g., reduced iron 10.0 g., magnesium chloride ($MgCl_2 \cdot 6H_2O$) 2.0 g., hydrogen 80 kg./sq. cm., produced at 300° during four hours 30.0 g. of liquid with b. p. 35–173°. The liquid contained only 5% of unsaturated hydrocarbons (96% sulfuric acid treatment). By fractionation of the liquid 10.0 g. of product was obtained which boiled at 170–173° and was completely stable toward permanganate and sulfuric acid.

Anal. Calcd. for $C_{10}H_{22}$: C, 84.51; H, 15.49. Found: C, 84.35; H, 15.63; mol. wt., 140; $n^{25}D$ 1.4130.

These data show that pure decane was present. Its formation can be explained as the polymerization of two molecules of amylene to its dimer with simultaneous hydrogenation to decane, $2C_5H_{10} + H_2 = C_{10}H_{22}$.

On the basis of the established facts[6] of the polymerization of olefins, we can ascribe to the obtained isodecane the constitution



The gas remaining after the reaction contained H, 84%; C_2H_4, 5.1%; C_3H_8, 2%; C_4H_4, 1.0%; CH_4, 8.0%.

EXPERIMENT 3.—Forty grams of amylene and 2.0 g. of magnesium chloride heated at 300° during four hours remained unchanged.

EXPERIMENT 4.—Amylene (40.0 g.) was unchanged after heating during four hours at 300° with 62.0 g. of reduced iron, 24.6 g. of water and 2.0 g. of magnesium chloride.

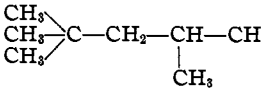
Experiments with Isobutene

EXPERIMENT 5.—At 250° under 80 kg./sq. cm. hydrogen pressure in the presence of reduced iron, isobutene hydrogenated to pure isobutane during four hours.

EXPERIMENT 6.—Fifty grams of pure isobutene (obtained by dehydration of isobutyl alcohol over activated alumina), 12.5 g. of reduced iron, 2.5 g. of magnesium chloride under 80 kg./sq. cm. of hydrogen produced at 250° during eight hours, 23.0 g. of liquid, b. p. 50–210°, which contained 10% of unsaturated hydrocarbons (sulfuric acid treatment). After the treatment with sulfuric acid (96%) the remaining liquid hydrocarbon was completely stable toward permanganate solution and nitrating mixture. By distillation two fractions were separated: (1) 100–110° and (2) 170–180°. The first fraction had the following properties: $n^{25}D$ 1.3990; d^{20}_4 0.6970; mol. wt., 110, and octane number, 100.

Anal. Calcd. for C_8H_{18}: C, 84.21; H, 15.79. Found: C, 84.17; H, 15.8.

On the basis of these data the first fraction consisted mainly of isooctane, 2,2,4-trimethylpentane.



The second fraction (b. p. 170–180°) had properties and analysis corresponding to those of an isododecane. The condensable gas (21.5 g.) from the reaction contained 65% of unreacted isobutene and 31.2% of isobutane. The uncondensable gas was pure hydrogen. It is evident that pyrolysis did not take place.

EXPERIMENT 7.—The isobutene treated under the same conditions as above but in the presence of magnesium chloride alone did not undergo change.

EXPERIMENT 8.—One hundred thirty-five grams of isobutene, 12.5 g. of reduced iron, 5.0 g. of nickel oxide, 5.0 g. of zinc chloride under 80 kg./sq. cm. of hydrogen at 275° during eight hours yielded 109.0 g. of liquid boiling at 32–175° and containing traces of unsaturated hydrocarbons.

Fractionation of this liquid gave 46.5 g. boiling from 100–120° with $n^{25}D$ 1.3976; d^{20}_4 0.6960; mol. wt., 112.

Anal. Calcd. for C_8H_{18}: C, 84.21; H, 15.79. Found: C, 84.15; H, 15.84.

The gas remaining from the reaction consisted of 92.8% hydrogen and 7.2% isobutane.

EXPERIMENT 9.—Isobutene treated under the same conditions but with zinc chloride alone remained unchanged.

EXPERIMENT 10.—One hundred and thirty-three grams of isobutene, 10.0 g. of reduced iron, 5.0 g. of nickel oxide and 2.5 g. of aluminum chloride under 80 kg./sq. cm. of hydrogen produced at 275° during twelve hours 115.0 g. of a liquid (b. p. 40–350°) from which 30.0 g. of isoöctane fraction was fractionated which boiled at 100–110°; $n^{25}D$ 1.4040; d^{20}_4 0.7050; mol. wt., 110.

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(6) V. N. Ipatieff, *Ind. Eng. Chem.*, **27**, 1067 (1935). In this case we have as the catalyst Cl—Mg—OH which forms the ester Cl—Mg—O—C_5H_{11}; and V. N. Ipatieff, "Catalytic Reactions at High Temperatures and Pressures," The Macmillan Co., New York, 1936.

Anal. Calcd. for C_8H_{18}: C, 84.21; H, 15.79. Found: C, 84.10; H, 15.87.

The product isolated was completely stable toward permanganate and nitrating mixture. The yield of isooctane, 2,2,4-trimethylpentane, was less than in some of the other experiments because aluminum chloride is a very strong polymerizing catalyst.

EXPERIMENT 11.—Aluminum chloride alone completely polymerized isobutene under the conditions of the experiments and produced a viscous oil.

Summary

1. A new simultaneous reaction of hydropolymerization was discovered and studied in the case of amylene and isobutene.

RIVERSIDE, ILLINOIS RECEIVED SEPTEMBER 24, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 568]

The Hydration of Unsaturated Compounds. V. The Rate of Hydration of Acetylene in Aqueous Solution of Sulfuric Acid and Mercuric Sulfate[1]

BY R. H. FRIEMAN,[2] E. R. KENNEDY AND H. J. LUCAS

In the usual commercial process of hydrating acetylene to acetaldehyde in the presence of mercuric sulfate and sulfuric acid, there is present an insoluble or slightly soluble amorphous substance, a mercury organic compound or compounds. It is probable that the composition of these precipitates varies with conditions, as pointed out by Whitmore.[3] As to whether these precipitates are intermediates in the hydration process, the evidence is conflicting. Whitmore points out that the hydration of the triple bond may merely be catalyzed by mercuric ions in acid solution, as in the case of piperonylacetylene.[4] It has been postulated that organo-mercury compounds are intermediates.[5]

The Analytical Method.—The procedure finally developed for the analysis of acetylene in aqueous solution, based upon the methods of Davis, Crandall and Higbee[6] and of Eberz and Lucas[7] follows. Into a 300-ml. conical flask having a ground glass stopper with sealed-in stopcock, is pipetted 25.00 ml. of 0.0500 *N* potassium bromate–bromide solution and the flask is evacuated to about 25 mm. with a water aspirator. Then 5 ml. of 6 *N* sulfuric acid is added, the mixture is allowed to stand for two to three minutes, and then in order are pipetted in, 10 ml. of 0.2 *M* mercuric sulfate, 25 ml. of water, and finally 2 to 10 ml. of the sample to be analyzed, a dilute aqueous solution of acetylene. The last is thoroughly rinsed into the flask from a special pipet of the type described by Eberz and Lucas[7] and the flask, still under vacuum and wrapped in a black cloth to exclude light, is shaken mechanically for five to seven minutes. At this time, 5 ml. of 2.0 *N* sodium chloride and 10 ml. of a freshly prepared 20% potassium iodide solution are added. The shaking is continued for another five to seven minutes, the black cloth is removed, the vacuum is then broken, 50 to 100 ml. of water is added to dilute the solution, and titration is made with 0.03 *N* sodium thiosulfate solution. A blank is run at the same time, omitting only the sample.

Discussion of the Analytical Method.—The simple bromate–bromide method of determining unsaturation is not satisfactory for the triple bond, as pointed out by Davis, Crandall and Higbee[6] in the case of acetylene, because of the interference due to oxygen, and by Mulliken and Wakeman[8] in the case of liquid alkynes, for which the analytical results were low. The former authors showed that aluminum, nickel and mercury salts are an aid in the quantitative determination of acetylene. In the present work it has been found that the bromination of acetylene proceeds rapidly and smoothly if the molal ratio of mercuric sulfate to the total halide present is greater than unity, but under these conditions the iodine end-point with starch is uncertain. The addition of sodium chloride overcomes this difficulty, making reproducible results possible.

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(1) For the preceding paper in this series, see Eberz, Welge, Yost and Lucas, THIS JOURNAL, **59**, 45 (1937).

(2) Mr. Frieman died suddenly of a heart attack on January 13, 1935.

(3) Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., N. Y., 1921, p. 118, cites numerous references.

(4) Manchot and Hass, *Ann.*, **399**, 150 (1913).

(5) Vogt and Nieuwland, THIS JOURNAL, **43**, 2071 (1921); Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **1**, 159 (1936).

(6) Davis, Crandall and Higbee, *Ind. Eng. Chem., Anal. Ed.*, **3**, 108 (1931).

(7) (a) Eberz and Lucas, THIS JOURNAL, **56**, 1232 (1934); (b) Lucas and Eberz, *ibid.*, **56**, 460 (1934).

(8) Mulliken and Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **7**, 59 (1935).