The activation energy of the reaction is approximately 25 kcal., some 25 to 40 kcal. less than the energy required to break the carbon-to-carbon bond in oxalic acid; apparently coördination lowers the activation energy by this amount. Thus, the necessity of the intermediate to the specificity is explained.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Reactions of Isopropyl Alcohol in the Presence of Catalysts Containing Magnesium Oxide[1]

BY LEON L. GERSHBEIN, HERMAN PINES AND V. N. IPATIEFF

The effect of metal oxide catalysts, having either dehydration or dehydrogenation properties, upon isopropyl alcohol has been the subject of extensive study by various investigators. Alumina or thoria, which are dehydration catalysts, converted isopropyl alcohol to propene, whereas copper or copper–zinc catalysts caused the dehydrogenation of this alcohol to acetone. The effect of the action of a catalyst composed of a mixture of oxides having dehydrating and dehydrogenating properties has been reported by Krause and Slobodin.[2] These authors did not reveal the composition of their catalysts; they reported, however, that under certain conditions isopropyl alcohol yielded a conjugated methylpentadiene.

Because the study of the action of magnesium oxide upon secondary alcohols has not been reported in the literature, an investigation of the decomposition of isopropyl alcohol in the presence of magnesium oxide has been undertaken.

The magnesia catalysts were prepared from the magnesium nitrate by precipitation of the hydroxide with (a) ammonia at 85–95°, (b) ammonia at 25°, and (c) sodium hydroxide at 25°.

Although magnesia was considered as a dehydrogenation catalyst[3] on the basis of its action upon ethyl alcohol, it was found in this study that this catalyst at 490° caused both dehydration and dehydrogenation of isopropyl alcohol, the latter predominating. The reaction was very slow at a temperature of about 410°. The experiments were made at atmospheric pressure and the isopropyl alcohol was passed over the catalyst at an hourly liquid space velocity of 0.90.

The product obtained from this reaction consisted of a mixture of compounds that contained acetone, propene, liquid hydrocarbons, mesityl oxide, and some higher boiling oxygen-containing compounds. The extent of the formation of the various products obtained depended upon the type of magnesium oxide used; this is evident from the data summarized in Table I.

TABLE 1

DECOMPOSITION OF ISOPROPYL ALCOHOL OVER MAGNESIA

Experiment no.[a]	1	2	3
Mode of preparation	NH_4OH @ 85–95°	NH_4OH @ 25°	NaOH @ 25°
Catalyst charged, g.	29.7	23.9	40.0
% of alcohol recovered	5.9	4.4	17.1
Alcohol passed, g.	347	306	357
Products obtained, mole %[b]			
Propene	11.4	12.3	12.8
Acetone	46.9	43.1	63.9
Liquid hydrocarbons	14.8	10.6	2.6
Mesityl oxide	7.7	8.2	5.0

[a] Duration of experiments was six hours, temperature 490°, liquid hourly space velocity 0.90. [b] Based on isopropyl alcohol reacted.

The compositions of the products given in this and other tables are reproducible within 0.5% in cases where the quantity of the product formed was greater than 5–8%. When the concentration of the various compounds analyzed was small, the error involved was larger.

The liquid hydrocarbons obtained contained 2-methylpentenes, 2-methyl-1,3-pentadiene, the latter amounting to 50–65% of the total liquid hydrocarbons, and a conjugated cyclohexadiene of the formula C_9H_{14}, probably 1,5,5-trimethyl-1,3-cyclohexadiene. The structure of the methylpentadiene was determined by means of its maleic anhydride adduct.[4] The proof of the structure of the C_9H_{14} hydrocarbon (b. p. at 130–135°) was based on the following facts: (a) on catalytic hydrogenation under pressure it absorbed two moles of hydrogen per mole of hydrocarbon to form a cyclic hydrocarbon of the formula C_9H_{18}. (b) It reacted with maleic anhydride, indicating the presence of a conjugated double bond. (c) The C_9H_{18} hydrocarbon did not undergo dehydrogenation at 240° in presence of platinized alumina. At 300°, however, the dehydrogenation proceeded with the formation of hydrogen, methane and *m*-xylene; the latter was identified through its nitro derivatives. The dehydrogenation results indicated the presence of a geminal carbon atom which contained two methyl groups.[5]

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[1] This investigation was supported in part by the Universal Oil Products Company.

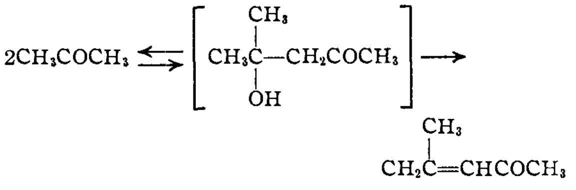
[2] V. P. Krause and Ya. M. Slobodin, *J. Applied Chem.* (*U. S. S. R.*), **9**, 1278 (1936).

[3] Paul Sabatier, "Catalysis in Organic Chemistry," translated by E. Emmet Reid, D. Van Nostrand Company, New York, N. Y., 1923, p. 702.

[4] G. B. Bachman and C. G. Goebel, THIS JOURNAL, **64**, 787 (1942).

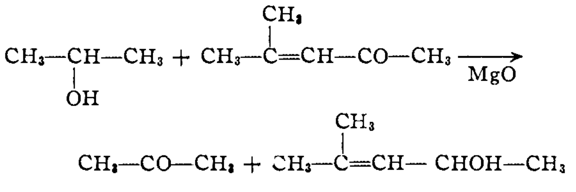
[5] V. N. Ipatieff, H. Pines and R. C. Olberg, *ibid.*, **68**, 1709 (1946).

The various products of the reaction owe their origin to the dehydration of isopropyl alcohol to propene and water, and the dehydrogenation to acetone and hydrogen. Part of the acetone undergoes condensation to form diacetone alcohol. The latter substance is unstable in the presence of the catalyst and undergoes dehydration to mesityl oxide.



$$2CH_3COCH_3 \rightleftarrows \left[CH_3\underset{OH}{\overset{CH_3}{C}}-CH_2COCH_3 \right] \longrightarrow CH_3\overset{CH_3}{C}=CHCOCH_3$$

Further reaction of mesityl oxide with acetone yields isophorone. Magnesia may also act as a hydrogen transfer catalyst, the hydrogen donor being isopropyl alcohol, and the hydrogen acceptor mesityl oxide to effect the changes



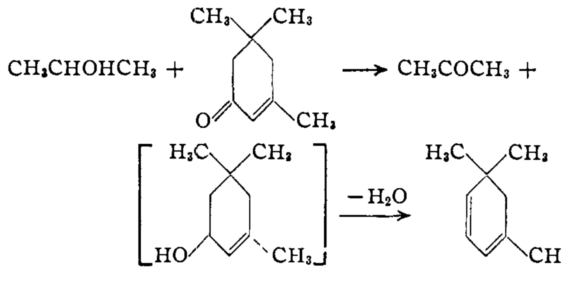
$$CH_3-\underset{OH}{CH}-CH_3 + CH_3-\overset{CH_3}{C}=CH-CO-CH_3 \xrightarrow[MgO]{} CH_3-CO-CH_3 + CH_3-\overset{CH_3}{C}=CH-CHOH-CH_3$$

The alcohol can then undergo dehydration to 2-methylpentadienes.

Alumina has also been found to effect a similar type of a hydrogen transfer reaction involving alcohols and ketones.[6]

The formation of 2-methylpentenes may be explained by (1) a hydrogen transfer reaction occurring between isopropyl alcohol and 2-methylpentadienes or (2) hydrogenation of mesityl oxide by hydrogen transfer to methylisobutylcarbinol; the latter then undergoing dehydration to 2-methylpentenes.

The formation of the cyclic hydrocarbon 1,5,5-trimethyl-1,3-cyclohexadiene can also be interpreted by a hydrogen transfer reaction involving isopropyl alcohol and isophorone as indicated by the equations



The structure assigned to this diolefin is based on the fact that it yields a maleic anhydride adduct and does not undergo dehydrogenation at 240° but does at 300° to form *m*-xylene and methane.

In order to prove the formation of 1,5,5-trimethyl-1,3-cyclohexadiene from isophorone by means of a hydrogen transfer reaction, a solution consisting of 80 mole per cent. of isopropyl alcohol and 20 mole per cent. of isophorone was passed over magnesia. It was found that the yield of 1,5,5-trimethyl-1,3-cyclohexadiene amounted to 38 mole per cent. based on the isophorone reacted or 46 mole per cent. if calculated on the basis of the isopropyl alcohol reacted. The latter yield is considerably higher than that obtained from isopropyl alcohol alone.

In the absence of a hydrogen donor, such as isopropyl alcohol, acetone did not yield unsaturated hydrocarbons when passed over magnesia catalyst; about 3% of the acetone, however, reacted to form condensation products. The introduction of molecular hydrogen did not influence this reaction.

Effect of Dehydration Promoters.—It has been shown that magnesia is primarily a dehydrogenation and a hydrogen transfer catalyst, and only to a smaller extent a dehydration catalyst. It was of interest, therefore, to determine whether the dehydrating properties of magnesia could be increased by adding alumina to it. Accordingly, catalysts promoted by alumina in amounts of 2 to 20% were prepared and the decomposition of isopropyl alcohol over these was investigated. It was found that as the alumina content increased the catalysts assumed greater dehydration properties as evidenced by the increase in propene and decrease in the acetone formed. At the same time the alumina-promoted catalysts caused the formation of saturated ketones such as isobutyl and diisobutyl ketone, which were probably formed by a hydrogen transfer reaction involving the double bonds of mesityl oxide and phorone, respectively. Small amounts of 2,6-dimethyl-3-heptene were also formed, perhaps through a hydrogenation of diisobutyl ketone and phorone to the corresponding saturated alcohols followed by dehydration. The experimental results obtained are summarized in Table II.

TABLE II

DECOMPOSITION OF ISOPROPYL ALCOHOL OVER MAGNESIA CONTAINING ALUMINA PROMOTERS

Experiment no.[a]	1	4	5	6	7
Catalyst charged, g.	29.7	25.7	27.9	38.9	37.0
Alumina, wt. %	0	2[b]	5[b]	10[c]	20[c]
Alcohol passed, g.	347	358	351	335	377
Alcohol recovered, %	5.9	4.3	0	0.9	0
Products obtained, mole %[a]					
Propene	11.4	16.7	30.2	28.3	26.1
Acetone	46.9	34.2	17.0	9.5	8.7
Methylpentenes and methylpentadienes	14.8[e]	13.4[e]	11.4	10.8	9.1
2,6-Dimethylheptenes	....	3.8[f]	1.9	2.7	4.2
Methyl isobutyl ketone	....	10.1	16.4	17.6	13.6
Diisobutyl ketone	....	2.3	4.4	8.3	11.4

[a] Duration of experiments was six hours, temperature 490°, liquid hourly space velocity, 0.90. [b] Impregnated catalyst. [c] Prepared by coprecipitation. [d] Based on isopropyl alcohol reacted. [e] Cyclic hydrocarbons are also present. [f] Mixture of 2,6-dimethylheptenes and mesityl oxide, the latter predominating.

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(6) R. C. Olberg, H. Pines and V. N. Ipatieff, *ibid.*, **66**, 1096 (1944).

The lower boiling liquid hydrocarbons formed in this reaction consisted of methylpentenes and methylpentadienes; methylpentanes were absent. The ratio of monoölefins to dienes formed increased from one to two with the increase of the concentration of alumina from 2 to 20%. Cyclic hydrocarbons corresponding to 1,5,5-trimethyl-1,3-cyclohexadiene occurred in traces except in the experiment that contained 2% of alumina as a promoter.

In order to determine whether saturated ketones and higher boiling olefins could be formed by a hydrogen transfer reaction, a solution consisting of 95 mole per cent. of isopropyl alcohol and 5 mole per cent. of mesityl oxide was passed over a magnesia catalyst promoted by 10% of alumina. Complete conversion of the mesityl oxide occurred; an increase in the yield of methyl isobutyl ketone and diisobutyl ketone was also observed (Table III).

TABLE III

DECOMPOSITION OF ISOPROPYL ALCOHOL–MESITYL OXIDE AND ISOPROPYL ALCOHOL–METHYL ISOBUTYL KETONE OVER MAGENSIA–ALUMINA CATALYST

Experiment no.[a]	6	22	23
Isopropyl alcohol charged, moles	5.58	5.40	4.19
Mesityl oxide charged, moles	...	0.28	...
Methyl isobutyl ketone, moles	...	...	0.75
Product obtained based on isopropyl alcohol charged, mole %			
Propene	28.3	23	13
Acetone	9.5	11	11
Methyl isobutyl ketone	17 6	20	[b]
Diisobutyl ketone	8.3	11	26
2-Methylpentenes and 2-methylpentadienes	10.8	16	15
2,6-Dimethylheptenes	2.7	3.6	11.3

[a] Duration of experiments was six hours, temperature 490°, liquid hourly space velocity was 0.9. The catalyst used consisted of magnesia containing 10% of alumina. [b] Methyl isobutyl ketone recovered, 0.61 mole.

The proportion of diisobutyl ketone and dimethylheptenes formed increased considerably when a mixture composed of 15 mole per cent. of methyl isobutyl ketone and 85 mole per cent. of isopropyl alcohol was introduced over a magnesia catalyst containing 10% of alumina.

Although alumina as such is primarily a dehydrating catalyst this action was not very pronounced when incorporated into magnesia. It was of interest, therefore, to determine the effect of another dehydrating catalyst, namely, thoria upon magnesia. A catalyst containing 5% thoria was found to increase greatly the dehydrating tendency of the catalyst. The data, which are given in Table IV, show that, unlike alumina, thoria causes very little hydrogen transfer to occur.

TABLE IV

COMPARISON OF THORIA AND ALUMINA AS DEHYDRATION PROMOTERS

Experiment no.[a]	5	8
Catalyst charged, g.	27.9	36.5
Promoter	Alumina[b]	Thoria[b]
Alcohol passed, g.	351	354
Alcohol recovered, %	0	1.2
Products obtained, mole %[c]		
Propene	30.2	71.8
Acetone	17.0	18.5
Methyl isobutyl ketone	16.4	0.5
Methylpentenes and methylpentadienes	11.4	4.2
Diisobutyl ketone and methylpentadienes	4.4	0
2,6-Dimethylheptenes	1.9	0

[a] Duration of the experiments was six hours, temperature 490°, liquid hourly space velocity, 0.90. [b] The catalyst consisted of magnesia containing 5% by weight of promoter. The catalyst was prepared by impregnation. [c] Based on isopropyl alcohol reacted.

Effect of Dehydrogenation Promoters.—In order to determine whether the dehydrogenation properties of magnesia can be increased by the addition of various promoters, the oxides of the following metals were added: molybdenum, iron, copper, chromium, manganese and zinc. These catalysts, containing 2 mole per cent. of promoters, were prepared by the method of impregnation. In addition, a catalyst containing 2% of metallic aluminum and 10% of zinc oxide was also tested; the latter catalyst was prepared by coprecipitation (Table V).

It was found that most of the catalysts tested had only a slight dehydrogenating effect upon the decomposition of isopropyl alcohol. It was of interest to note that molybdena, which is usually considered to be a dehydrogenation catalyst, caused an increase in the dehydration of isopropyl alcohol resulting in the formation of propene and propane; the latter was formed from propene through a hydrogen transfer reaction.

In view of the unexpected behavior of molybdena, it was decided to investigate the effect of this promoter more thoroughly. A series of experiments were carried out using molybdena in amounts of 2, 5, 10, 20 and 55% (Table VI). The catalysts were prepared by impregnation. In all cases the alcohol decomposition was complete. In contrast to the experiments with other catalysts, carbon deposits were observed at the end of the runs. The effect of molybdena alone was also studied.

It was found that when the content of molybdena in alumina was increased, the extent of dehydration of isopropyl alcohol increased also as evidenced by the amount of propane and propene formed. Of interest is the marked rise in dehydration when the molybdena content was increased from the 10 to the 20%. It can be seen that catalysts with molybdena in amounts of about 20% and higher did not cause hydrogen transfer. The manner of treating the magnesia–molybdena catalyst was of great importance. For instance, the passage of air over a used catalyst

TABLE V

DECOMPOSITION OF ISOPROPYL ALCOHOL OVER MAGNESIA CONTAINING DEHYDROGENATION PROMOTERS

Experiment no.[a]	1	9	10	11	12	13	14	15	16
Catalyst charged, g.	28.9	35.4	27.6	27.6	25.1	27.1	25.8	25.4	24.4
Promoter, 2 mole %	...	MoO_3	Fe_2O_3	Al[b]	Cu	Cr_2O_3	MnO	ZnO	ZnO[c]
Alcohol charged, g.	347	317	353	336	325	353	343	338	324
Alcohol recovered, mole %[d]	5.9	0	0	8.1	9.4	0	7.4	0	3.4
Products obtained, mole %									
Propene	11.4	29.7[e]	3.7	12.1	7.1	4.3	7.7	6.6	7.1
Acetone	46.9	36.0	58.6	46.2	47.5	46.9	55.4	55.1	50.8
Liquid hydrocarbons	14.8	17.2[f]	6.8	11.8	12.6	3.1	7.4	1.8	8.8
Mesityl oxide	7.7	4.6	13.5	8.1	6.2	17.6	6.4	10.8	9.1

[a] Duration of experiments was six hours, temperature 490°, hourly liquid space velocity, 0.90. [b] Powdered metallic aluminum was added. [c] Coprecipitated catalyst containing 10% zinc oxide. [d] Based on isopropyl alcohol reacted. [e] Contains 50% of propane. [f] 2-Methylpentane was present.

TABLE VI

DECOMPOSITION OF ISOPROPYL ALCOHOL OVER MAGNESIA-CONTAINING-MOLYBDENA PROMOTER

Experiment no.[a]	1	9	17	18	19	20	21
Catalyst charged, g.	28.9	35.4	36.5	34.3	35.0	50.3	90.2
Molybdena, % by wt.	0	2	5	10	20	55	100
Alcohol charged, g.	347	317	276	319	364	290	359
Products obtained. mole %[b, c]							
Propene	11.4	14.8	17.3	36.5	80.2	80.0	87.4
Propane	...	14.9	11.7	13.8	8.05	5.0	3.7
Acetone	46.9	36.0	30.1	23.3	6.3	3.5	Trace
Mesityl oxide	7.7	4.6	3.4	1.8	...	...	...
Methyl isobutyl ketone	....	....	0.9	0.7	...	...	...
Methylpentenes and methylpentadienes	14.8[d]	17.2[e]	17.8[e]	6.04	...	...	...

[a] Duration of experiments was six hours, temperature 490°, liquid hourly space velocity, 0.9. [b] Based on isopropyl alcohol reacted. [c] Alcohol decomposition was complete with all the molybdena catalysts. [d] Cyclic hydrocarbons are present. [e] Contains 2-methylpentane.

which contained 20% of molybdena increased the dehydrogenation properties of the catalyst. Similar results were obtained when pure molybdena was used as a catalyst.

Experimental

I. MATERIALS

Purification of Alcohols and Ketones.—Isopropyl alcohol was purified by being dried with anhydrous potassium carbonate followed by distillation. Acetone, isophorone, mesityl oxide, methyl isobutyl ketone, and diisobutyl ketone of C. P. grade were also purified in the analogous manner.

Preparation of Catalysts. (A) Stock Magnesia.—The stock magnesia was prepared by precipitation of the hydroxide from J. T. Baker C. P. magnesium nitrate hexahydrate in 1.5 molar solution with ammonium hydroxide at 85–95°. The filter cake, after being washed with copious amounts of water until no test for nitrate ion was observed, was dried in an oven at 245° for sixteen hours, sieved and granules of 10–20 mesh were introduced into the reaction and further dried *in situ*. Magnesium oxide was also prepared by precipitation with sodium and ammonium hydroxide at 25°.

(B) **Preparation of Mixed Oxides.**—1. **By Impregnation.**—The preparation of impregnated metallic oxide catalysts consisted of treating powdered stock magnesia, previously heated to about 400° for one hour with the desired C. P. metal nitrate solution, except in the case of molybdena-promoted catalysts where ammonium molybdate was employed. The stirred slurry was evaporated on a steam-bath, and heated for sixteen hours at 245° followed by one hour at 400–500° to ensure complete nitrate decomposition. The resulting solid was then passed through a 10–20 mesh sieve and reserved for the experiments.

2. **By Coprecipitation.**—Magnesia which contained 10 and 20% alumina as well as 10% zinc oxide was prepared by coprecipitation of the hydroxides employing the respective nitrate solutions and ammonium hydroxide at 90°. The procedure as outlined in (A) was then followed.

(C) **Preparation of Magnesia-Containing Metallic Aluminum Promoter.**—The catalyst which comprised magnesia with 2% metallic aluminum was prepared by stirring the moistened stock magnesia with the required amount of powdered aluminum obtained from the Metals Disintegrating Company. It was gently heated on a steam-bath, briqueted and further dried after introduction into the reaction tube.

(D) **Preparation of Molybdena.**—The catalyst consisting of molybdena alone was obtained by decomposition of the ammonium molybdate hydrate at 400–500° for a period of four hours.

II. APPARATUS AND PROCEDURE

The apparatus consisted of a Pyrex reaction tube of 21 mm. outside diameter heated by a thermostatically controlled vertical furnace. The alcohol or alcohol mixture was fed into the reaction tube containing about 80 cc. of the appropriate catalyst by means of a liquid feed pump[7] and was preheated before reaching the catalyst bed. The lower end of the tube was connected to a liquid receiver, which in turn was attached through an ice and Dry Ice-acetone cooled trap to a gas sampling bottle and to a wet-test meter. The reaction tube also contained an inlet tube through which nitrogen or hydrogen could be introduced into the reaction zone.

The procedure was as follows: The catalyst was heated in a stream of nitrogen to 490° and kept at this temperature for a period of thirty to forty-five minutes, after which time hydrogen was introduced into the system

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(7) H. Tropsch and W. J. Mattox, *Ind. Eng. Chem.*, **26**, 1338 (1934).

for about the same period of time. The gas stream was then discontinued and the liquid reactant was pumped in at an hourly liquid space velocity of about 0.90. When constant conditions had been established, usually about twenty minutes after the start of the liquid passage, the condensing train was connected to the reaction tube, and the actual experiment was begun. Liquid product accumulated in the receivers, whereas condensable gases collected in the tubes chilled to −78°. Non-condensable gases which passed into the wet-test meter were sampled from time to time and analyzed. The duration of each experiment was six hours, at the conclusion of which the liquid product was removed and the reaction tube flushed with nitrogen. The condensable gases were vaporized into a gas-collecting bottle and analyzed.

III. ANALYTICAL PROCEDURE

A. **Gas Analysis.**—The analysis of the gaseous mixtures was carried out by absorption.[8]

B. **Liquid Product.**—The total liquid product obtained from the respective experiments was dried with anhydrous potassium carbonate; when large amounts of water were produced, the organic material was salted out with potassium carbonate and then dried over this reagent. The difference in weight was assumed to correspond to the amount of water formed. The dried contents were distilled in a column of ten plate efficiency and the fraction which boiled to 85° collected. The chilled distillate was then treated with ice water in a glass-stoppered graduated cylinder whereby separation into layers resulted. When no further change in volume occurred, the upper hydrocarbon layer was separated and washed with further amounts of water, the initial washings being incorporated in the aqueous solution. The latter, on salting out with potassium carbonate, followed by drying, yielded on distillation in a 30-plate column, acetone and isopropyl alcohol. The water insoluble layer, after being dried over calcium chloride, was redistilled over sodium.

The original liquid product boiling above 85° was dried, distilled and the various fractions were identified by means of conversion into suitable derivatives.[9]

IV. IDENTIFICATION OF THE LIQUID PRODUCTS

A. **Acetone.**—Acetone was identified on the basis of physical constants and solid derivatives such as 2,4-dinitrophenylhydrazone and semicarbazone which melted, respectively, at 128 and 190°. They did not show depression in melting point when mixed with the corresponding derivatives of a known sample of acetone.

B. **Liquid Hydrocarbons Obtained in the Fraction Boiling, 55–85°.**—The liquid hydrocarbons separated from the acetone-alcohol distillate boiled in the range 54–134°. These hydrocarbons were redistilled and the various fractions were analyzed as follows:

1. **2-Methylpentenes.**—These hydrocarbons which were taken over in a range of 55–70° were usually redistilled after treatment with small amounts of maleic anhydride to remove any conjugated dienes present. The diolefin-free product distilled at 62–67°, $n^{20}D$ 1.397–1.399, d^{23}_4 0.690. Except in the molybdena-promoted runs, 2-methylpentane was absent.

Hydrogenation.—The 2-methylpentene fraction yielded on hydrogenation 2-methylpentane which boiled at 59.5–61.5°, $n^{20}D$ 1.3709. The hydrogenation was carried out in a 125-cc. rotating autoclave which was charged with 6 g. of product, 15 ml. of isopentane, 0.7 g. of a nickel-kieselguhr catalyst[10] and hydrogen at 100 atmospheres of pressure. The hydrogenation was made at 35°. It was found that in all the experiments with exception of those when molybdena was used as a catalyst, one mole of hydrogen was absorbed per one mole of hydrocarbon charged. In the molybdena experiments the absorption of hydrogen was smaller because of the presence of 2-methylpentane.

2. **2-Methylpentane.**—The presence of 2-methylpentane in admixture with 2-methylpentenes was determined by means of alkylation which is based on the observation[11] that under the experimental conditions used, alkylation of aromatic hydrocarbons proceeds faster than polymerization. The product obtained from such a treatment was stirred with 15% fuming sulfuric acid which removed only the aromatic hydrocarbons. The hydrocarbon layer which remained after such treatment consisted only of paraffinic hydrocarbons.

The procedure used was as follows: To a chilled mixture consisting of 12 ml. of benzene and 11 ml. of 96% sulfuric acid placed in a glass-stoppered graduate was added 5 ml. of the methylpentene boiling fraction (b. p., 59–69°); the contents were shaken. The hydrocarbon layer was separated and heated twice with an equal volume of sulfuric acid containing 15% of sulfur trioxide. The hydrocarbon layer which remained after such a treatment was washed, dried, and distilled in a microcolumn. The hydrocarbon layer which was stable to a nitrating mixture (two volumes of 96% sulfuric acid and one volume of 70% nitric acid) corresponded according to physical constants to 2-methylpentane.

3. **2-Methylpentadienes.**—2-Methylpentadienes were present in the fraction that boiled at 75–77°, $n^{20}D$ 1.4465, d^{20}_4 0.716. It was found that on catalytic hydrogenation, made under conditions previously described above, two moles of hydrogen were absorbed per one mole of hydrocarbons charged.

Adduct with Maleic Anhydride.—Treatment of these diolefins with maleic anhydride formed an adduct of melting point of 55° in almost quantitative yield, the corresponding acid melting at 154° resulted on hydrolysis of the adduct. Both the acid and anhydride gave no depression in melting point when these were mixed with the respective authentic samples obtained from 2-methyl-1,3-pentadiene.[11a]

4. **Cyclic Diolefins.**—1,5,5-Trimethyl-1,3-cyclohexadiene was present in the fraction that boiled at 131–134°.

Anal. Found: C, 88.38; H, 11.29; $n^{20}D$ 1.4674. Calcd. for C_9H_{14}: C, 88.52; H, 11.47.

Maleic Anhydride Adduct.—One and a half grams of maleic anhydride in 12 ml. of benzene was treated with 2.0 g. of the hydrocarbon dissolved in 8 ml. of benzene; a yellow colored solution resulted which after prolonged heating on a steam-bath yielded a resinous product. All of the maleic anhydride reacted. Similar results were obtained when the reaction was carried out at room temperature for four days.

Catalytic Hydrogenation.—The cyclic diolefinic hydrocarbon C_9H_{14} absorbed on hydrogenation two moles of hydrogen per mole of hydrocarbons used. The resulting product boiled at 128–135°, $n^{20}D$ 1.4254, and was stable to nitrating mixture.

Anal. Found: C, 86.29; H, 13.98. Calcd. for C_9H_{18}: C, 85.63; H, 14.37.

Dehydrogenation.—Two and a half grams of the hydrogenated product was passed thrice over platinized alumina catalyst at 266–275°; 825 cc. of gas was liberated. The liquid material from the dehydrogenation distilled at 134–140°. On nitration with a solution composed of two volumes of 96% sulfuric acid and one volume concentrated nitric acid at 70–80° a solid was obtained which, after crystallization from ethanol, melted at 174°; it corresponded to 2,4,6-trinitro-*m*-xylene. A mixed melting point with a known sample of trinitro-*m*-xylene showed no depression.

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[8] "U. O. P. Laboratory Test Methods for Petroleum and its Products," Universal Oil Products Company, Chicago, Illinois, 1940.

[9] The preparation of derivatives, unless otherwise stated, was effected by the methods given in the book by Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1940.

[10] V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

[11] V. N. Ipatieff, B. B. Corson and H. Pines, THIS JOURNAL, **58**, 919 (1936).

[11a] The authors are indebted to Professor G. B. Bachman of Purdue University for determining the mixed melting points.

Anal. Found: N, 17.08. Calcd. for $C_8H_7N_3O_6$: N, 16.42.

C. Liquid Components Found in the Fraction Boiling Above 85°. 1. Mesityl Oxide.—This ketone was found mainly in the fraction that boiled at 125–135°. On redistillation a product was separated in a relatively pure form in the fraction that boiled at 128.5–130.5°, $n^{20}D$ 1.441–1.443. It formed a semicarbazone that melted at 164° and a 2,4-dinitrophenylhydrazone that melted at 201°. No depression in melting point was noticed with the respective derivatives of a known sample of mesityl oxide.

2. Methyl Isobutyl Ketone.—This ketone was present in a fraction that boiled at 110–122°. On redistillation a product was obtained that boiled at 115–119°, $n^{20}D$ 1.394–1.413, $d^{20}{}_4$ 0.801, and corresponding to relatively pure methyl isobutyl ketone. It formed a semicarbazone which melted at 132° and which did not cause a depression in melting point when mixed with the corresponding derivative of a known sample of methyl isobutyl ketone.

3. 2,6-Dimethylheptenes.—This hydrocarbon was separated from the fractions which boiled at 129–140°. After the removal of ketones and redistillation, a hydrocarbon was obtained which boiled at 132–135°, $n^{23}D$ 1.4369, $d^{23}{}_4$ 0.761, $M^{23}D$ 43.39 (calcd. for C_9H_{11}, MD 43.37). On catalytic hydrogenation a compound was obtained which distilled at 133–136°, $n^{20}D$ 1.4017; it corresponded to 2,6-dimethylheptane.

4. Diisobutyl Ketone.—Diisobutyl ketone was present in the fraction that boiled at 159–173°. On redistillation, a product was separated which boiled at 163–167°, $n^{20}D$ 1.412–1.414; it corresponded to diisobutyl ketone. The melting points of the semicarbazone and 2,4-dinitrophenylhydrazone as well as the latter mixed with the authentic samples were 121–122° and 93–94°, respectively.

5. Isophorone.—Isophorone was separated on redistillation from the fractions which boiled at 170–190°. It distilled at 88° at 7 mm. It formed a semicarbazone which melted at 190–191° and decomposed at 193–195°.

Decomposition of Isopropyl Alcohol Containing Isophorone over Magnesia

A solution consisting of 80 mole per cent. of isopropyl alcohol (117 g., 1.96 moles) and 20 mole per cent. of isophorone (69 g., 0.50 mole) was passed over 80 g. of magnesia at an hourly liquid space velocity of 0.9. The duration of the experiment was three hours and the temperature 493°.

The product of the reaction was analyzed by the usual method. Sixty-two per cent. of the isopropyl alcohol and 27% of the isophorone were recovered unchanged. On the basis of the reacted isopropyl alcohol the reaction product consisted of 75.5% of acetone. Fourteen and one-half grams (0.12 M) of liquid hydrocarbon was separated boiling at 130–132°, $n^{20}D$ 1.4672, and identified as 1,5,5-trimethyl-1,3-cyclohexadiene.

Summary

The decomposition of isopropyl alcohol over magnesia and magnesia which contained dehydrogenation and dehydration promoters at 490° has been studied.

Magnesia alone or in the presence of dehydrogenation promoters decomposes isopropyl alcohol to form propene, acetone, mesityl oxide, isophorone and liquid hydrocarbons. The latter consisted of 2-methylpentenes, 2-methylpentadienes and 1,5,5-trimethyl-1,3-cyclohexadiene.

The incorporation of molybdena in magnesia results in increased dehydration property of the catalyst as the content of the promoter is increased.

The introduction of alumina to magnesia results in the increase of propene formation. The liquid product consists of acetone, methyl isobutyl ketone, diisobutyl ketone, 2-methylpentene, 2-methylpentadienes and 2,6-dimethylheptenes.

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Effects of Cross-Linking and Branching on the Molecular Constitution of Diene Polymers[1]

BY PAUL J. FLORY

The polymerization of dienes usually is accompanied by cross-linking reactions. While the percentage of the structural units which are cross-linked almost always is too small to be determined by chemical methods, frequently they are sufficient in number to seriously alter some of the physical properties of the polymerization products and to complicate their structural interpretation. Only a very small degree of cross-linking is sufficient to cause formation of a gel fraction which is insoluble in the usual solvents for the particular type of polymer and, hence, is not amenable to ordinary physico-chemical methods of characterization. Even if the number of cross linkages is insufficient to cause gelation, the molecular weight distribution may be severely distorted by them. The molecular weight distribution under these circumstances does not occupy its usual significance, either in reference to the physical characteristics of the product, or to the kinetic mechanism of the primary polymerization reaction.

In the present paper the probable origin of the cross linkages formed during the polymerization of dienes will be considered, and their effects on the polymer constitution and properties will be analyzed in the light of the statistical theory of three dimensional polymerizations.

I. Reaction Mechanisms

Cross-Linking.—The most likely mechanism for the formation of cross-linkages during polymerization (or copolymerization) of a 1,4-diene consists in the occasional addition of a growing free radical chain to an unsaturated carbon of a previously polymerized diene unit. The process, in the case of butadiene polymerizations, can be represented as follows

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