# NATURE OF THE ISOSYNTHESIS REACTION

COMPARISON WITH OTHER CATALYTIC PROCEDURES FOR THE HYDROGENATION OF CARBON MONOXIDE

Before the discovery of the isosynthesis, two fundamentally different catalytic procedures were available for the hydrogenation of carbon monoxide. The first made use of metallic catalysts having a high hydrogenation capacity and produced methane and its straight-chain homologues. Chiefly methane, or liquid hydrocarbons, or solid paraffins could be obtained, depending on operating conditions. The second process, carried out in the presence of oxide catalysts, produced methanol, higher alcohols, and other oxygenated compounds. Under different conditions, chiefly methanol, or higher alcohols, or a mixture of alcohols, acids, aldehydes, and ketones (the Synthel synthesis) could be obtained. It was generally assumed in the past that these syntheses followed two completely different courses, despite the possibility that hydrocarbons might be produced by way of intermediary oxygenated compounds. In recent years, however, medium-pressure synthesis with iron catalysts has produced considerable amounts of alcohols instead of the usual hydrocarbons. The isosynthesis over oxide catalysts produced primarily branched-chain aliphatic hydrocarbons; at low temperature and high pressure, oxygenated compounds were obtained. The nature of the reaction for the production of hydrocarbons by the hydrogenation of carbon monoxide is discussed in another report.[37]

As in the synthesis of straight-chain hydrocarbons, the over-all reaction accompanying the synthesis of branched-chain hydrocarbons can be represented by the two equations:

$$nCO + 2nH_2 = (CH_2)n + nH_2O$$

$$2nCO + nH_2 = (CH_2)n + nCO_2.$$
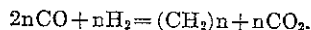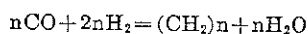
Under the conditions of isosynthesis, the maximum yield of hydrocarbons (208 g./m^3 CO+H$_2$) is obtained when carbon monoxide and hydrogen are present in the ratio in which they are consumed, that is, 1.2:1.

[37] Pichler, H., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen]: Bureau of Mines Special Report, Pittsburgh, Pa., 1947, 159 pp.

ESSENTIAL FEATURES OF THE ISOSYNTHESIS

The essential features of the isosynthesis are the following:

THE CATALYST

The best results are obtained with a thorium oxide catalyst promoted by aluminum oxide and, in certain cases, by traces of alkali. The catalyst must be prepared by a special precipitation process, the details of which have been described earlier in this manuscript. Branched hydrocarbons also were obtained from carbon monoxide and hydrogen in the presence of zirconium oxide, cerium oxide, and zinc oxide-aluminum oxide. The individual components of the last catalyst were not suitable for isosynthesis, however.

In contrast to the straight-chain hydrocarbon synthesis, metals belonging to the iron group produce methane and carbon under the conditions of the isosynthesis. Substances that dilute the active centers, such as kieselguhr, do not improve the activity of the catalyst in the isosynthesis.

SYNTHESIS CONDITIONS

Synthesis pressures range from 100 to 1,000 atmospheres, the best results being obtained at 300 to 600 atmospheres. No perceptible reaction occurs at atmospheric pressure. At pressures above 600 atmospheres, the production of large amounts of dimethylether was difficult to avoid. Reaction temperatures between 400° and 450° C. are optimum. As the temperature decreases, dimethylether production again increases and, in certain cases, alcohols appear. At higher temperatures, methane and the other homologous gaseous hydrocarbons are obtained. Above 500° C., large amounts of carbon are produced.

THE PRODUCTS

The principal synthesis products are saturated, branched-chain, aliphatic hydrocarbons containing four to eight carbon atoms. As the temperature decreases, the amounts of high molecular-weight and unsaturated aliphatic hydrocarbons increase (at 375° C. hydrocarbons in the lubricating oil range are obtained as

secondary products). The formation of oxygenated compounds also increases. At higher temperatures, the degree of saturation of the aliphatic hydrocarbons increases, as well as the naphthene and aromatic hydrocarbon content. Under the best conditions, over 90 percent of saturated aliphatic hydrocarbons are obtained. (As the presence of olefins makes identification of the hydrocarbons by distillation difficult, the product was usually mildly hydrogenated before distilling. The following discussion is concerned primarily with saturated hydrocarbons.)

POSSIBLE MECHANISMS OF THE REACTION

In considering the nature of the reaction, the following questions arise:

1. Can branched hydrocarbons be obtained by isomerization from n-paraffins obtained as primary products?
2. Are alcohols possible primary products of the isosynthesis?
3. Do polymerization, alkylation, and cyclization play a part in the synthesis of the higher hydrocarbons?

ISOMERIZATION OF PRIMARY n-PARAFFINS

The catalyst is an oxide that is not reduced under the conditions of the synthesis. Consequently, the occurrence of carbides and carbonyls as intermediates in the formation of CH_2-chains cannot be postulated. The carbide of thorium (ThC_2) is known; it is not formed at synthesis conditions but at considerably higher temperatures (for example, electric arc).[38]

The equilibrium ratios existing between individual isomers also indicate that the primary production of normal CH_2-chains with subsequent isomerization does not occur under the conditions of the isosynthesis. In recent years, this hypothesis has been examined in detail by a number of workers. True isomeric equilibrium of n-butane with iso-butane was first obtained by Glasebrook and Lovell[39] in the presence of an aluminum bromide catalyst. In the case of higher aliphatic hydrocarbons, the formation of byproducts interfered with true isomeric equilibrium.[40] However, under certain experimental conditions, Koch and Richter[41] obtained a true isomeric equilibrium for the hexanes between 17° and 25° C., which confirmed the calculations of Rossini and his coworkers.[42] Figures 18 and 19 show equilib-

[38] Gmelin-Kraut, [Handbook of Inorganic Chemistry]: Vol. VI, pt. 1, 1928, p. 157.
[39] Glasebrook, A. L., and Lovell, W. G., The Isomerization of Cyclohexane and Methylcyclopentane: Jour. Am. Chem. Soc., vol. 61, 1939, pp. 1717–1720.
[40] Schuit, Hoog, and Verheus, Recueil Trav. chim.: Pays-Bas, vol. 59, 1940, p. 793.
[41] Koch, H., and Richter, H., [Isomerization Equilibrium of Hexane]: Ber. deutsch. chem. Gesell., vol. 77, 1944, pp. 127–132.
[42] Rossini, F. D., and Prosen, E. J. R., Energies of Isomerization of the Five Hexanes: Jour. Am. Chem. Soc., vol. 62, 1940, pp. 2250–2251.
Rossini, F. D., Prosen, E. J. R., and Pitzer, K. S., Free Energies and Equilibria of Isomerization of the Butanes, Pentanes, Hexanes, and Heptanes: Jour. Res., Nat. Bur. Standards, vol. 27, 1941, pp. 529–541.
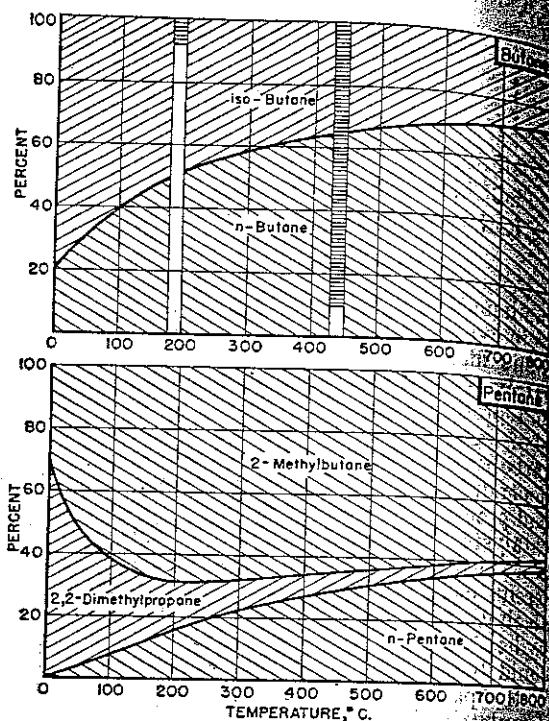

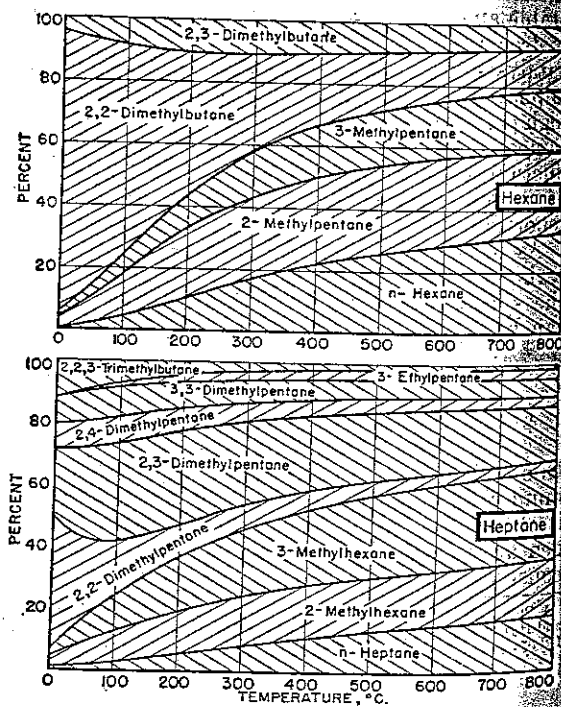FIGURE 18.—ISOMERIZATION EQUILIBRIA OF BUTANE AND PENTANE.

FIGURE 19.—ISOMERIZATION EQUILIBRIA OF HEXANE AND HEPTANE.

rium concentrations at various temperatures for the two butanes, the three pentanes, the five hexanes, and the nine heptanes. They agree with the free energies of isomerization calculated by Rossini, Prosen, and Pitzer.

The curve for butane shows the relative amount of n- and iso-butane present in the C_4 fractions obtained in normal pressure hydrocarbon synthesis at 190° C. and in isosynthesis at 450° C. (cross-hatchings represent iso-butane fraction). Comparison of the values obtained for the two types of synthesis with the equilibrium curve shows that straight (CH_2) chains form as primary products in synthesis at atmospheric pressure (the same is true of medium-pressure synthesis). A state of equilibrium is not attained, and only 7.5 percent of iso-butane and 92.5 percent of n-butane are produced. In the isosynthesis, at equilibrium the relative amounts would be approximately 65 percent of n-butane and 35 percent of iso-butane. The actual composition of the C_4 fraction, however, is 10 percent n-butane and 90 percent iso-butane. As a result, equilibrium is not attained. Consequently, it is believed iso-butane is the primary product in isosynthesis.

Table 27 contains the distribution of the C_4, C_5, and C_6 fractions of isoparaffins and n-paraffins obtained at equilibrium at 425° C., and the actual distribution obtained in isosynthesis at the same temperature. The data show that there is no evidence in support of the hypothesis that branched-chain hydrocarbons are the result of an isomeric rearrangement as primary products.

TABLE 27.—*Distribution at 425° C. of branched hydrocarbons present in the C_4–C_6 paraffin fractions (percent of the individual fractions)*

|	C_4	C_5	C_6
Equilibrium	35	72	77
Isosynthesis	85–90	80–90	92–97

INTERMEDIATE ALCOHOL PRODUCTION

The problem of the formation of alcohols as intermediates is discussed in the light of the following experimental evidence.

OXYGENATED BYPRODUCTS OF THE ISOSYNTHESIS

The byproducts of isosynthesis include dimethylether and methanol. Under certain conditions, there are obtained isobutyl alcohol and small amounts of isopropyl alcohol (in the presence of alkalized catalysts, phenols also were obtained at high temperatures). The production of dimethylether is favored by high pressures and low temperatures.

EFFECT OF THE CATALYST

Oxides, which are known to have a dehydrating action on alcohols, were found to be suitable catalysts for the isosynthesis. Table 28 summarizes a study made by Sabatier and Mailhe[43] on the activity of various oxides as catalysts for the following reaction:

$$C_2H_5OH = C_2H_4 + H_2O.$$
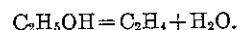
In these experiments, ethyl alcohol vapors were passed over the oxide, and the amounts of gas evolved were determined, together with their ethylene and hydrogen contents. Owing to the fact that the most efficient conditions for preparing oxides were not known at the time, these earlier results have in some instances only a qualitative value. Nevertheless, it is interesting to compare the results in table 28 with table 2.

TABLE 28.—*Decomposition of ethanol vapors in the presence of various catalysts at 340°–350° C.*

Catalyst	Rate, cc./min.	Product, percent	
		C_2H_4	H_2
ThO_2	31	100	Traces
Al_2O_3	21	98.5	1.5
W_2O_5	57	98.5	1.5
Cr_2O_3	4.2	91	9
SiO_2	.9	84	16
TiO_2	7.0	63	37
BeO	1.0	45	55
ZrO_2	1.0	45	55
UO_2	14	24	76
V_2O_3	14	9	91
ZnO	6	5	95
MnO	3.5	0	100
MgO	Traces	0	100
Cu	110	0	100

Thorium, aluminum, and tungsten oxides were most effective in promoting the dehydration of alcohols. These same oxides were most active as catalyst in the isosynthesis, although aluminum and tungsten oxides were undesirable because of their tendency to form carbon and methane. The oxides from chromium to vanadium are not suitable catalysts for dehydration and show little activity under the conditions of the isosynthesis. On the other hand, the dehydrogenating properties increase. The oxide from zinc to copper (the latter prepared at low temperatures) are suitable neither as catalysts for the dehydration of ethanol (table 28) nor as one-component catalysts for isosyn-

43 Sabatier and Mailhe: Ann. Chim. (S), vol. 20, 1910, p. 341.

thesis; they are exclusively dehydrogenation catalysts. In the thorium oxide-20 percent aluminum oxide catalyst, which is the best catalyst for the isosynthesis, the dehydrating action of thorium oxide is promoted by aluminum oxide. Under the conditions of the isosynthesis, the catalytic activity of thorium oxide in both hydrogenating carbon monoxide to alcohol and dehydrating the alcohol far exceeds that of the other oxides.

These observations on the action of thorium oxide in isosynthesis agree to some extent with experiments by Hoover and Rideal [44] on the decomposition of ethyl alcohol in the presence of thorium oxide. Their experiments showed that thorium oxide can act as a catalyst not only for the dyhydration of the alcohol to ethylene and water but also for its dehydrogenation to acetaldehyde and hydrogen. Under certain conditions, the two reactions proceed at approximately the same rate, but their temperature coefficients are different. It was found that the dehydrating action of thorium oxide could be poisoned (with chloroform) without affecting its dehydrogenating property. On the other hand, by changing the method of preparation (decomposition of thorium nitrate on carriers instead of precipitation) thorium oxide could be obtained in such form that it was almost exclusively a dehydrating agent. This indicated that the two reactions occur at different points of the catalyst surface. By blocking certain parts of the surface, selective adsorption [45] is obtained, and primarily catalytic dehydrogenation occurs. On the other hand, inhibiting the development of the dehydrogenating centers causes the catalyst to be solely a dehydrating agent.

Eucken and Wicke [46] have studied the mechanism of the dehydration of alcohols in the presence of oxide catalysts, especially bauxite. Particularly the observation that a certain amount of water retained by the catalyst at excessively high temperatures is necessary for the reaction to take place indicated that surface OH groups are catalytically active centers. The alcohol is adsorbed at the OH group by the formation of OH linkages (weak chemical absorption); simultaneously, a hydrogen atom from an adjacent CH_3-group of the alcohol interacts with an oxygen atom at the catalyst surface. When the olefin and the water are desorbed, a hydrogen atom has shifted from an oxygen atom at the catalyst surface to an adjacent oxygen atom. The twofold activity of thorium oxide in isosynthesis

is emphasized by the fact that it can be replaced to some extent by the two-component catalyst zinc oxide-aluminum oxide, in which one component is a hydrogenating agent and the other is a dehydrating agent.

Earlier reports that thorium oxide is not a suitable dehydrating agent for methanol [47] can probably be attributed to insufficient activity of the adsorption points of the catalyst at which dehydration of the methanol should have taken place.

Dehydration of the higher alcohols has been the subject of numerous studies. For example, the catalytic action of aluminum oxide, thorium oxide, and chromium oxide has been compared. Particularly with thorium oxide, it was found that dehydration of the alcohol to olefin was usually followed by isomerization of the olefin. Comparative isomerization experiments at 400° C. showed that with certain olefins (for example, starting with 2- and 3-methylpentene) a state of equilibrium was reached in the presence of thorium oxide, but not aluminum oxide. Chromium oxide is strongly dehydrogenating and leads to the production of aromatic compounds rather than olefin isomers.[50]

INTERMEDIATE DIMETHYLETHER PRODUCTION

The conversion of mixtures of dimethylether and hydrogen (1:4–1:5) in the presence of thorium oxide under the conditions of the isosynthesis was reported in the experimental part of the present work. The principal products obtained were iso-butane, iso-butene, and liquid hydrocarbons. Carbon monoxide, carbon dioxide, methane, and small amounts of ethylene, ethane, propylene, and propane were produced. In other words, the products were the same as those obtained by isosynthesis from carbon monoxide and hydrogen.

Dimethylether is produced from methanol according to the following equation:

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$
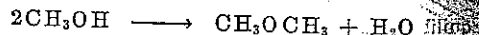
Dimethylether was almost always obtained as byproduct in the isosynthesis, in very small amounts in the presence of highly dehydrating catalysts, and in larger quantities in other cases.

The formation of hydrocarbons from dimethylether can be explained by postulating an initial decomposition process, as follows:

$$CH_3OCH_3 \longrightarrow HCHO \longrightarrow CH_4 + CO + H_2$$
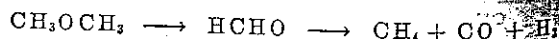
The carbon monoxide reacts with hydrogen

[44] Hoover, G. I., and Rideal, E. K., The Decomposition of Ethyl Alcohol at the Surface of Thoria. II. Adsorption on the Thoria Catalyst: Jour. Am. Chem. Soc., vol. 49, 1927, pp. 116–123.
[45] Springer, Julius: Berlin, 1931, p. 184. Schwab, G., [Catalysis]: Berlin, 1931, p. 184. Taylor: Jour. Phys. Chem., vol. 30, 1926, p. 145.
[46] Eucken, A., and Wicke, E., [The Interpretation of Heterogeneous Dehydrating Catalyses by Exchange of Hydrogen Atoms]: Naturwissen., vol. 32, 1945, pp. 161–162.

[47] Sabatier, P., Work cited in footnote 21, p. 217.
[48] Anissimow: Chem. Zentr., vol. I, 1940, p. 2933.
Goldwasser, S., and Taylor, H. S., Catalytic Dehydration of C₄–C₁ Aliphatic Alcohols: Jour. Am. Chem. Soc., vol. 61, 1939, pp. 1751–1761.
[49] Goldwasser, S., and Taylor, H. S., Isomerization of Alkenes on Alumina and Thoria: Jour. Am. Chem. Soc., vol. 61, 1939, pp. 1762–1765.
[50] Komarewsky, V. I., Reisz, C. H., and Thodos, G., Aromatization of Fatty Alcohols: Jour. Am. Chem. Soc., vol. 61, 1939, pp. 2525–2527.
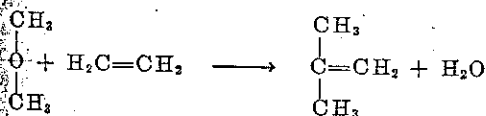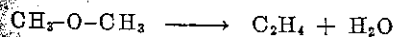
to give branched hydrocarbons by the iso-synthesis process.

Evidence against this hypothesis is based mainly on experiments involving similar reactions between ethylether and hydrogen (1:4). Ethylether reacts largely according to the equation:

$$C_2H_5OC_2H_5 \longrightarrow CO + 2CH_4 + 1/2C_2H_4$$

Carbon monoxide, methane, ethylene, ethane, propylene, and propane were obtained, but neither iso-butane nor iso-butene. If iso-butane was obtained indirectly from carbon monoxide in the dimethylether experiments, it should also be obtained from ethylether. The absence of isohydrocarbon in the latter experiments may be explained by the fact that the partial pressure of carbon monoxide is too low for the isosynthesis to proceed. However, the same effect should also apply in the dimethyl-ether experiments.

The next step in this phase of the work was to outline a reaction for the formation of iso-butane, or iso-butene, from dimethylether, which did not involve the intermediate formation of carbon monoxide and hydrogen. Such a reaction may involve the dehydration of a molecule of dimethylether to produce a molecule of water and a molecule of ethylene; the latter reacts with a second molecule of dimethyl-ether to produce another molecule of water and iso-butene. Thus:

$$CH_3-O-CH_3 \longrightarrow C_2H_4 + H_2O$$

$$\begin{array}{c} CH_2 \\ | \\ O + H_2C=CH_2 \\ | \\ CH_2 \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ C=CH_2 + H_2O \\ | \\ CH_3 \end{array}$$
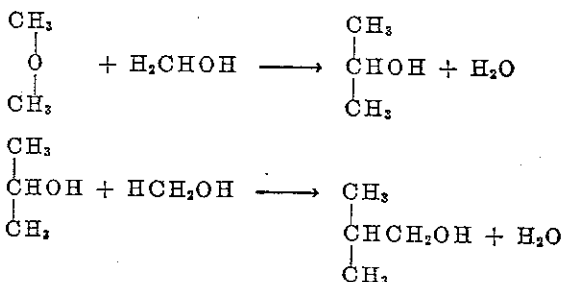
The iso-butene formed in this way either adds hydrogen to give iso-butane or undergoes polymerization and other similar reactions. This hypothesis may be justified on the basis of the relatively high synthesis temperature and the strong dehydrating action of the catalyst.

It subsequently received additional support from studies carried out at the Kaiser Wilhelm Institute to determine the nature of the products obtained from decomposition of methanol over phosphorus pentoxide. In addition to dimethylether, methane, and other gaseous and liquid hydrocarbons, iso-C_4 hydrocarbons were observed.[51] The same reaction carried out with ethyl alcohol gave neither iso-butene nor iso-butane.

In this connection, mention should be made of two earlier studies, now rarely recalled. In

the first, Sernagiotto[52] observed that in the presence of phosphorus pentoxide, methanol suffered a violent reaction with formation of gaseous, liquid, and solid hydrocarbons. In the second, Ostromysslenski and Kielbasinski[53] found butadiene to be one of the reaction products obtained by passing ethylether or mono-chloroethylether over heated aluminum oxide.

In addition to the process involving dimethyl-ether as intermediate product, already discussed, the formation of isobutene from iso-butyl alcohol can be considered, according to the following scheme:

$$\begin{array}{c} CH_3 \\ | \\ O \\ | \\ CH_3 \end{array} + H_2CHOH \longrightarrow \begin{array}{c} CH_3 \\ | \\ CHOH + H_2O \\ | \\ CH_3 \end{array}$$

$$\begin{array}{c} CH_3 \\ | \\ CHOH + HCH_2OH \\ | \\ CH_3 \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ CHCH_2OH + H_2O \\ | \\ CH_3 \end{array}$$

Dehydration reactions are either independent of pressure or should be favored by operation at low pressures. According to Ipatieff,[54] operation at high pressures retards the dehydration of alcohols by raising the temperature at which dehydration begins, increasing the formation of ether and decreasing that of hydrocarbons. The fact that isosynthesis must nonetheless be carried out at higher pressures can probably be attributed to the primary reaction, that is, the formation of alcohols and the stepwise building up of hydrocarbons. However, the fact that, in the experiments using dimethylether in the presence of thorium catalysts, satisfactory results were obtained only at high pressures can probably be explained by absorption phenomena leading to other undesirable reactions that predominate at low pressure.

ISOMERIZATION EQUILIBRIA OF OLEFINS OBTAINED BY DEHYDRATION OF ALCOHOLS

The olefins obtained by dehydration from alcohols (especially C_1–C_4 alcohols) and di-methylether can polymerize to higher olefins. However, higher olefins can also be produced by dehydration of the corresponding alcohols. At the temperatures used in isosynthesis, thorium oxide promotes the isomerization equilibria of olefins[55] but is not a good hydrogenation catalyst. Consequently, it may be assumed that in certain cases isomerization of the olefins

Koch, H., et al, Unpublished work of the Kaiser Wilhelm Institute for Coal Research, Mülheim-Ruhr.

[52] Sernagiotto: Gazz. chim. ital., vol. 44, I, p. 587 (Chem. Zentr., 1914, vol. II, p. 1034).
[53] Ostromysslenski and Kielbasinski: Chem. Zentr., 1914, vol. I, p. 2155.
[54] Ipatieff, V. N., Jour. Soc. Phys. Chim. Russe, vol. 36, 1904, pp. 786, 819; vol. 38, 1906, pp. 63, 92.
Sabatier, P., Work cited in footnote 21, p. 215, reference 711.
[55] Goldwasser, S., et al., Work cited in footnote 49.

proceeds more rapidly than their hydrogenation to paraffins. If, moreover, we assume that the paraffins formed by hydrogenation of the olefins do not isomerize in the presence of thorium oxide, then the composition of the paraffins obtained is determined by the equilibrium composition of the corresponding olefins. In order to evaluate this assumption, a specific example—hexane—was selected, as described below:

1. Values for the composition of the hexanes based on the assumption that the hexane isomers are in equilibrium at 420° C. (values calculated by interpolation of data obtained at 398° C. and 440° C.) and that the olefin isomers are saturated without any subsequent isomerization of the hexanes.

2. Values for the average composition of the hexane fraction obtained by isosynthesis.

3. Values for the isomerization equilibrium of the hexanes corresponding to figure 19.

It will be seen from table 29 that under certain conditions the supposedly primary equilibrium of the olefins could be responsible for the absence of n-hexane. However, the two main components of the hexane fraction obtained by isosynthesis, 2-methylpentane and 2,3-dimethylbutane, cannot be the result of such an isomerization reaction. It is probable that they are produced as primary products.

TABLE 29.—*Mixture of hexane isomers*

(A) At equilibrium of the olefins
(B) From isosynthesis
(C) At equilibrium of the hexanes (420°–450° C.)

Hexane	(A)	(B)[a]	(C)
n-Hexane	0	3–8	23
2-Methylpentane	10–15	28–59	28
3-Methylpentane	80–90	10–20	16
2,2-Dimethylbutane	0–3	1–3	23
2,3-Dimethylbutane	0	12–41	10

[a] The values listed in this column were obtained subsequently by Pichler and Titzenthaler.

The absence of a state of equilibrium between the olefins is particularly evident in the case of 3-methylpentane. The corresponding 3-methyl olefins constitute 80 to 90 percent of the olefins in equilibrium obtained at 420° C. (more than 90 percent at lower temperatures), whereas the isosynthesis products obtained by hydrogenation of the C_6 hydrocarbons contains only 10 to 20 percent of 3-methylpentane.

The same is true of the other hydrocarbon fractions. At 420° C., the n-butene–iso-butene equilibrium contains only 46 percent of iso-butene and 54 percent of n-butene,[56] whereas

[56] Serebrjakowa and Trost: Chem. Jour. Ser. A. J. allg. Chem. (russ. Chimtscheski Shurnal Ssser. A. Shurnal obschtschei Chimii), vol. 7, 1936, p. 122.

approximately 90 percent of the C_4 fraction obtained by isosynthesis is composed of branched compounds (see table 27). Consequently, the establishment of an isomeric equilibrium of the initial olefins appears to have no special significance.

The fact that the composition of the olefins produced by dehydration of higher alcohols in the presence of thoria corresponds to the isomerization equilibrium and that the composition of olefins produced in the isosynthesis does not indicates that the hydrocarbons obtained by isosynthesis are not dehydration products of the corresponding alcohols. Goldwasser and Taylor [57] dehydrated hexanol-1 in the presence of thorium oxide at 398° C. using (a) a throughput of hexanol of 22.5 cubic centimeters per 10 grams of catalyst per hour and (b) a throughput of 3.1 cubic centimeters per 10 grams of catalyst per hour. Table 30 shows the composition of the reaction product obtained in each case.

TABLE 30.—*Dehydration of hexanol in the presence of thoria at 398° C*

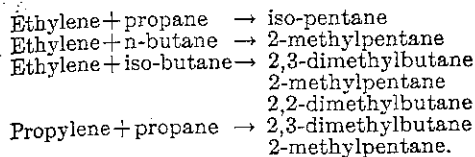| Products, percent	Throughput, cc./10 g. catalyst/hr.	
	(a) 22.5	(b) 3.1
Hexene-1	30	0
2-Methylpentene-2	15	0
3-Methylpentane-2t	35	90
4-Methylpentene-2t	5	0
Polymer	15	10

In the first experiment (a), a short contact time resulted in a mixture of hexenes. Prolonged contact led to isomerization and the almost exclusive formation of 3-methylpentene (10 percent of polymers). The fact that at pressures below 300 atmospheres, alcohols with 5 or more carbons are present only in traces, if at all, also contradicts the theory that higher hydrocarbons are produced by dehydration of the corresponding alcohols in the course of isosynthesis.

POLYMERIZATION, ALKYLATION, AND CYCLIZATION REACTIONS IN THE PRODUCTION OF HIGHER HYDROCARBONS (C_5+)

The C_2-C_4 hydrocarbons, produced as primary products, constitute the essential elements of these reactions. We know that at the temperatures and pressures prevailing in isosynthesis, the unsaturated members of these hydrocarbon series have a marked tendency to polymerize. When a low olefin concentration

[57] Goldwasser, S., and Taylor, H. S., Work cited in footnote 43.

is maintained, as is the case in isosynthesis, polymerization decreases in favor of alkylation.[58] Of the olefins considered, iso-butene is the most reactive towards alkylation in an acid medium and also shows the strongest tendency toward polymerization. In contrast to paraffins, ethylene shows the greatest reactivity under the conditions of thermal alkylation. Under the condition of acid alkylation, a reaction takes place only with a paraffin hydrocarbon containing a tertiary carbon, especially with isobutane; however, even propane and n-butane react under the conditions of thermal alkylation. The following reactions are possible:

Ethylene + propane   →   iso-pentane
Ethylene + n-butane   →   2-methylpentane
Ethylene + iso-butene → 2,3-dimethylbutane
                             2-methylpentane
                             2,2-dimethylbutane
Propylene + propane   → 2,3-dimethylbutane
                             2-methylpentane.

It will be seen from the foregoing discussion that there is little basis for the assumption that the higher hydrocarbons obtained by isosynthesis form by isomerization of primary straight-chain hydrocarbons, or that they are obtained by dehydration of the corresponding alcohol. The direct formation of branched-chain hydrocarbons seems to be most likely. The mechanism of the formation of branched hydrocarbons by alkylation (for example branched hexane, by ethylation of isobutane) has been interpreted in various ways. According to Ipatieff,[59] it is probable that ethylene participates in an addition reaction with the tertiary carbon atom and produces 2,2-dimethylbutane as primary product. On the other hand, Caesar and Francis [60] and Koch [61] believe that 2,3-dimethyl-butane is the first of the butanes with a double methyl group to form. It is probable that this is also the case in isosynthesis, as 2,3-dimethylbutane is far more abundant than the 2,2-dimethyl compound, which, according to equilibrium calculations, should be present in large amounts. One must, therefore, assume that initially the olefin molecule is located between two carbons of the paraffin hydrocarbon. Similarly, in accord with the results obtained in isosynthesis, such compounds as iso-pentane and 2-methylpentane may form as primary products, whereas other hydrocarbons, such as 2,2-dimethylbutane (neo-hexane) and 2,2-di-methylpropane, are produced in small amounts, if at all, as the products of a secondary isomerization.

The aromatics and naphthenes that occur in isosynthesis are obtained by way of primary aliphatic products. In recent years a number of studies have been published on the catalytic cyclization of such compounds in the presence of oxidic catalysts.[62] Best results in aromatizing paraffins are obtained with dehydrogenating catalysts such as chromium oxide. Dehydration catalysts such as aluminum oxide produce poor results. Thorium oxide, which can act both as a dehydrator and as a dehydrogenator, presents an intermediate case.

n-Hexane produces benzene, di-isobutyl produces p-xylene, and di-isoamyl gives m-methyl iso-propylbenzene. As the isosynthesis produces only small amounts of n-hexane, benzene was not present as a rule, but toluene, xylene, hexamethyl benzene, and other cyclic hydrocarbons, particularly the corresponding naphthenes, were obtained. Hydrocarbons belonging to the terpene series are produced by reactions similar to that of di-iso-amyl. As a good many of the hydrocarbons formed in this way can undergo isomerization under the conditions of isosynthesis, the studies made of the equilibrium between n-hexane and 2-methyl-cyclopentane [63, 64, 65] may be mentioned. It will be seen that at the temperature of the isosynthesis, this equilibrium is shifted almost entirely toward 2-methylcyclopentane, which is obtained in relatively large amounts by isosynthesis.

The ratio of naphthenes to aromatics also indicates a state of equilibrium. Under the conditions of the isosynthesis, at 450° C. the equilibrium is shifted towards the naphthenes; at 500° C. it is displaced toward the aromatics. The explanation for the decrease in the ratio of paraffins to olefins at low temperatures (increase in olefins) may be a lower hydrogenating capacity of the thorium catalyst at low temperatures.

Finally, as already noted, at low temperatures (that is, below 400° C.), high-boiling, viscous hydrocarbons form as a result of polymerization reactions favored by low temperatures.

[62] Goldwasser, S., and Taylor, H. S., Aromatization of Heptane, Heptene, and Hexene Isomers on Chromic Oxide: Jour. Am. Chem. Soc., vol. 61, 1939, pp. 1766-1769.
  Karzhev, et al., Chem. Zentr., 1938, vol. II, p. 2055.
  Kasansky and Plate: Ber. deutsch. chem. Gesell., vol. 69, 1936, p. 1862.
  Koch, H., [Catalytic Aromatization of Aliphatic Hydrocarbons]: Brennstoff Chem., vol. 20, 1939, pp. 1-9.
  Komarewsky, V. I., and Riesz, C. H., Aromatization of n-Octane and n-Decane in the Presence of Nickel-Aluminum Catalyst: Jour. Am. Chem. Soc., vol. 61, 1939, pp. 2524-2525.
  Moldawski and Kaumscher: C. F. Acad. Sci., URSS, 1936, vol. I, p. 355, (Chem. Zentr., 1936, vol. II, p. 2339 and 1937, vol. II, p. 1546).
  Moldawski, et al.: Chem. Zentr., 1938, vol. II, p. 1023.
  Universal Oil Products Co., Italian Patent 351,078, 352,747 (1937).
  Zelinsky, Kasansky, Libermann, Lossik, Plate, and Serguienew: Chem. Zentr., 1940, vol. II, p. 3459.
[63] Glasebrook, A. L., and Lovell, W. G., Work cited in footnote 39.
[64] Nenitzescu, C. D., and Cantuniari, I. P., [Aluminum Chloride-catalyzed Reactions. VI. Rearrangement of Cyclohexane to methyl-cyclopentane]: Ber. deutsch. chem. Gesell., vol. 66, 1933, pp. 1097-1100.
  Shingo Ando: Jour. Soc. Chem. Ind., Japan, Suppl. Bind., vol. 42, 1939, 322-324B.
[65] Schuit, et al., Work cited in footnote 40.

[58] Frey, F. E., and Hepp, H. J., Noncatalytic Addition of Ethylene to Paraffin Hydrocarbons: Ind. Eng. Chem., vol. 28, 1936, pp. 1439-1445.
  Oberfell, G. G., and Frey, F. E.: Refiner Natur. Gasoline Manufacturer, vol. 18, 1939, p. 486; Nat. Petrol. News, vol. 31, 1939, p. R502.
[59] Ipatieff, V. N., Chim. et Ind., vol. 42, 1939, p. 215.
  Scheer, W., Feuerungstechn., vol. 29, 1941, p. 273.
[60] Caesar, P. D., and Francis, A. W., Low-temperature Catalytic Alkylation of Isoparaffins: Ind. Eng. Chem., vol. 33, 1941, pp. 1426-1428.
[61] Koch, H., et al., Work cited in footnote 51.