and Dr. T S. Ma of the University of Chicago for the micro-analyses.

Summary

1. Using *n*-octenes as the starting material it has been shown that a synthetic cracking catalyst can cause hydrogen transfer in the absence of added cycloparaffins.

2. The hydrogen transfer resulted in the formation of paraffin and aromatic hydrocarbons and a carbonaceous catalyst deposit poor in hydrogen.

3. At least 50% of the hydrogen needed to account for the paraffins found came from the catalyst deposit.

4. Reactions of isomerization, cyclization and polymerization or condensation accompanied the hydrogen transfer reaction.

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[CONTRIBUTION FROM UNIVERSAL OIL PRODUCTS CO.]

Hydrocarbon Reactions in the Presence of Cracking Catalysts. III. Cyclohexene, Decalin and Tetralin

BY HERMAN S. BLOCH AND CHARLES L. THOMAS

Synthetic cracking catalysts were shown to have isomerized olefins and to have severed carbon–carbon bonds of paraffins and olefins.[1,2] It was of interest to examine the reactions of cycloölefins and cycloparaffins in the presence of these synthetic catalysts.

Frost[3] stated that naphthenes cracked in the presence of aluminosilicate catalysts to form olefins, and that the olefins isomerized and decomposed to produce gasolines containing branched chain hydrocarbons. No experimental data were given so that it is not clear whether Frost used pure hydrocarbons or naphthenic petroleum fractions.

The present work describes the reactions at atmospheric pressure of cyclohexene[4] in the presence of a synthetic silica–alumina–thoria catalyst and the reactions of decalin and tetralin in the presence of a synthetic silica–alumina–zirconia catalyst. The conditions of the experiments and a summary of the product distribution are given in Table I. Table II shows the composition of the gaseous products. The liquid products were examined, by methods described in the experimental part, in sufficient detail to permit a semi-quantitative estimation of the principal reaction products or types of product, so that a picture could be drawn of the principal reactions and of the effect on them of the operating variables studied.

Cyclohexene.—The reactions of cyclohexene were studied at constant liquid hourly space velocity (volumes of liquid charge per gross catalyst volume per hour) and approximately constant ratio of hydrocarbon charged to catalyst weight, with temperature as the principal variable. The estimated composition of the liquid products is shown in Table III.

From the data of Table III, it is evident that the principal reactions of cyclohexene, in order of decreasing magnitude, were isomerization, polymerization and hydrogen transfer. These reactions occurred at all three temperatures, and the extent of all of them increased with rise in temperature, within the range studied. In addition, ring scission, which was absent or negligible at 250 and 300°, became more definite at 400°.

The isomerization of cyclohexene yielded methylcyclopentenes. Unidentified methylcyclopentenes were previously reported as cyclohexene isomerization products with titanium oxide or beryllium oxide catalysts at 450°.[5] In our work, two isomers were identified among the reaction products: methylcyclopentene-1 and methylcyclopentene-2. The former was present in much greater quantity than the latter, indicating that isomers having substituents attached to olefinic carbon atoms were formed most readily.[6] Although no evidence of the other two isomers was found, it does not seem unlikely that small quantities of methylcyclopentene-3 were formed.

At 300°, 70% of the cyclohexene that reacted was isomerized. It is clear that the reaction conditions can be controlled to make this reaction predominate. At 400°, more methylcyclopentane was isolated than methylcyclopentenes. The presence of such large amounts of methylcyclopentane in the reaction products and such small amounts of cyclohexane is taken as an indication that isomerization of cycloolefins is a more rapid reaction than hydrogen transfer; however, the situation is not clear-cut, because of the possi-

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(1) G. Egloff, J. C. Morrell, C. L. Thomas and H. S. Bloch, THIS JOURNAL, **61**, 3571 (1939).

(2) C. L. Thomas and H. S. Bloch, U. S. Patents 2,216,284 and 2,216,285 (October 1, 1940); U. S. Patent 2,328,753 (September 7, 1943).

(3) A. V. Frost, *J. Phys. Chem.* (U. S. S. R.), **14**, 1313 (1940).

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(5) Yu. A. Arbusov, and N. D. Zelinsky, *Compt. rend. acad. sci. URSS*, **30**, 717–720 (1941).

(6) That such isomers are the most stable was shown for pentenes by R. H. Ewell and P. E. Hardy, THIS JOURNAL, **63**, 3463 (1941); for hexenes by F. C. Whitmore and P. L. Meunier, *ibid.*, **55**, 3721 (1933) and by P. L. Cramer and A. L. Glasebrook, *ibid.*, **61**, 230 (1939); and for olefins more generally by G. B. Kistiakowsky, *et al.*, *ibid.*, **58**, 137 (1936).

TABLE I

CONVERSION OF CYCLIC HYDROCARBONS WITH CRACKING CATALYSTS AT ATMOSPHERIC PRESSURE

Experiment no.	1	2	3	4	5	6	7	8	9
Hydrocarbon	Cyclohexene			Tetralin			Decalin		
Catalyst	SiO_2–Al_2O_3–ThO_2			SiO_2–Al_2O_3–ZrO_2					
Temperature, °C.	250	300	400	400	450	500	400	500	500
Liquid hourly space velocity	4	4	4	1.33	1.82	3.80	0.95	3.8	4.0
Duration, hours	1	1.27	1	1.58	1	0.5	1	0.5	1[d]
Hydrocarbon charged, g.	320	390	315	204	176	184	290	330	352
Volume, cc.	400	488	395	212	182	190	330	375	400
Catalyst weight, g.	[a]	[b]	47.9	80.0	[e]	80.0	275	157	78.3
Volume, cc.			100[c]	100		100	350	200	100
Products, wt. % of charge									
Gas (b. p. < 10°C.)	0.0	0.02	2.4	0.23	1.9	5.0	9.1	13.8	8.9
Liquid	95.4	99.0	97.1	101.5	99.5	95.3	88.5	86.3	91.5
Catalyst deposit	4.6	1.0	0.5	−1.7	−1.4	−0.3	0.71	0.17	−0.4
Loss							1.7	−0.3	

[a] Regenerated catalyst from Experiment 3 used. [b] Regenerated catalyst from Experiment 1 used. [c] Fresh catalyst. [d] Sixth hour of 6-hour run. [e] Regenerated catalyst from Experiment 7 used.

TABLE II

ANALYSIS OF GASEOUS PRODUCTS

Experiment no.	2	3	4	5	6	7	8	9
Charging stock	Cyclohexene		Tetralin			Decalin		
Gas, wt. % charge	0.02	2.4	0.23	1.9	5.0	9.1	13.8	8.9
Molecular weight	17.7	34.3	...	30.5	36.6	50.9	43.0	41.1
Gas analysis, mole %								
H_2	18	22.4	70	36.2	22.0	5.6	14.2	16.9
CH_4	48	7.3	23.7[a]	3.2	3.4	0.4	2.6	3.0
C_2H_4	26	6.9	6.4[b]	0.9	2.3	1.3	3.9	3.6
C_2H_6	8	6.0		4.0	1.6	1.2	1.8	2.2
C_3H_6		22.5		10.4	21.2	5.5	16.2	20.7
C_3H_8		4.9		19.9	21.4	15.1	10.3	7.0
i-C_4H_8		5.1		0.5	0.7	1.4	2.4	6.1
n-C_4H_8		7.5		3.4	6.3	4.5	6.4	9.5
i-C_4H_{10}		17.4		21.5	21.2	48.3	29.1	21.1
n-C_4H_{10}						16.8	13.0	

[a] Total paraffins: C_nN_{2n+2} where n = 2.83. [b] Total olefins.

TABLE III

PROBABLE COMPOSITION OF LIQUID PRODUCTS OF CYCLOHEXENE CONVERSION

Experiment no.	1	2	3
Temperature, °C.	250	300	400
Products, wt. % of charge			
Aliphatic C_5 and C_6	0	0	3.5
Methylcyclopentane	1.5	2.8	26.3
Methylcyclopentenes	15.6	28.8	23.5
Benzene	Trace	1.5	...
Cyclohexene	68.2	55.0	1.5
Higher-boiling liquids	10.0	11.1	42.2
Dimethylnaphthalenes	..	..	7

bility of isomerization of cyclohexane to methylcyclopentane under the conditions of our work. Although no equilibrium measurements for the cyclohexane–methylcyclopentane isomerization in the region of 400° have been published, "practically complete" conversion of the former to the latter has been reported with a molybdenum–cobalt sulfide catalyst at 500°,[7] and conversions to methylcyclopentane–cyclohexane ratios as high as 12.5 at temperatures in the neighborhood of 400° with molybdenum sulfide catalysts.[8]

The higher-boiling liquid products found in this work were predominantly unsaturated at the 250° reaction temperature but they became increasingly aromatic with rising reaction temperatures. It seems likely that the unsaturated higher-boiling products are polymers of cyclohexene and methylcyclopentenes or simple reaction products of such polymers. From 25% (Expt. 2) to 40% (Expt. 3) of the cyclohexene reacting was converted to these high-boiling liquid products.

In the 400° experiment, because of the increased amount of hydrogen transfer, the high-boiling liquid products consisted principally of

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[7] E. I. Prokopetz, A. N. Filaratov and V. A. Pychko, *J. Appl. Chem.* (U. S. S. R.), **11**, 1631–1635 (1938).

[8] A. V. Frost, *Bull. Acad. Sci. URSS*, cl. Sci. Tech. **1942**, No. 10, 3–10; see also P. V. Puchkov and A. F. Nikolaeva, *J. Gen. Chem.* (U. S. S. R.), **8**, 1153–1158 (1938).

polycyclic aromatic and naphthenic hydrocarbons. Most of the hydrogen made available from the formation of the high-boiling aromatics was used in converting methylcyclopentenes into methylcyclopentane. Little of the hydrogen was set free (see Table II). There was no evidence to indicate that the dehydrogenation of cyclohexene to benzene played any appreciable part in the hydrogen transfer reactions.

The products of Experiment 3 boiling between about 240 and 300° contained high concentrations of dimethylnaphthalenes together with smaller amounts of partially dehydrogenated naphthenes (possibly dimethyltetralins or their isomers). Of the dimethylnaphthalenes, the 2,6 isomer was positively identified as probably the most abundant isomer present, and the 1,6 isomer was tentatively identified as present in much smaller quantity.

Tetralin.—Of the three experiments with tetralin described in Table I, the liquid products of only two (4 and 6) were analyzed in detail. The analyses are shown in Table IV. As in the case of cyclohexene, the reaction temperature was the principal variable; the space velocity and reaction time were also varied, however, so as to maintain a fairly constant and low conversion to gaseous products while approximately the same amount of hydrocarbon per weight of catalyst was charged.

At both 400 and 500°, by far the principal reaction product was naphthalene. Some of the liberated hydrogen was consumed in hydrogen transfer, and the excess was evolved as molecular hydrogen. As a result of hydrogen transfer, cycloparaffins were formed. These appeared to be chiefly bicyclic at both temperatures; in addition, there were smaller quantities of monocyclic paraffins at 400° which were largely absent at 500°.

Scission of the hydrogenated ring should have yielded alkenylbenzene derivatives. Under the conditions here reported these were not found. The hydrogen available from the conversion of tetralin to naphthalene apparently hydrogenated all such olefinic products so that only the corresponding alkylbenzenes were isolated. As a result of these reactions, and dealkylation or cracking of the side-chains, benzene, toluene and *o*-xylene were formed and identified among the products. The presence of ethylbenzene was indicated, but it was not identified with certainty. It is interesting, however, that *m*-xylene or *p*-xylene or both were also formed (to the extent of approximately 30% of the *o*-xylene–ethylbenzene content) in Experiment 6, a clear indication that isomerization of the substituted aromatics occurred either during or after their formation.

In addition to the identified mononuclear aromatics, unidentified higher boiling alkylbenzenes were formed when scission of the hydrogenated ring occurred, as shown in Table IV. The physical constants of the fractions boiling in the $C_{10}H_{14}$ range suggested that methylindanes, formed by isomerization of tetralin, might also have been present.

TABLE IV

COMPOSITION OF LIQUID PRODUCTS OF TETRALIN CONVERSION

Experiment no.	4	6
Temperature, °C.	400	500
Products, weight % of charge		
Olefins	0.0	0.09
Paraffins	0.8	1.0
Cycloparaffins	5.6	7.0
Total aromatic	95	87
Benzene	0.60	6.8
Toluene	0.45	2.4
Ethylbenzene–xylenes	0.32	2.6
Propylbenzene and isomers	0.51	1.2
Butylbenzene and isomers	4.5	6.7
Tetralin[a]	73	32
Naphthalene	14	28
Higher boiling	1.8	7.9

[a] Including possible isomers.

The small amount of paraffinic liquid products probably was formed in secondary reactions by rupture of naphthenic products formed by hydrogen transfer. Thus while the aromatic ring itself appears to be stable to scission under the conditions studied, it may undergo decomposition by such an indirect series of reactions. On the basis of equal conversion, more paraffins and naphthenes were formed at 400° than at 500°; these facts, coupled with the total absence of olefins in the 400° product and their presence in small amounts in the 500° product all indicate that more complete hydrogen transfer was obtained at the lower temperature.

Decalin.—The conditions under which decalin was cracked (as shown in Table I) involved in experiments 7 and 8 variations of both temperature and space velocity designed to counteract each other in order to produce approximately equal conversions. Experiment 9 was conducted at the same conditions as 8 but with a partially spent (carbonized) catalyst. The results of Experiments 8 and 9 may, therefore, be taken as an indication of the manner in which the several reactions are affected by increased on-stream time. The composition of the liquid products is shown in Table V.

The decalin isomers comprised a major reaction product in Experiment 7; under the more severe conditions of Experiment 8, much less remained. It should be emphasized, however, that the estimate of the decalin isomers is based principally on physical constants and that there was no sharp separation between them and the alkylcycloparaffins on the one hand or between them and decalin on the other. The decalin isomers have been taken to be the cycloparaffins of refractive index > 1.46 which boil between about 155 and 185°; the monocycloparaffins boiling in this

TABLE V

COMPOSITION OF LIQUID PRODUCTS OF DECALIN CONVERSION

Experiment no.	7	8	9
Temperature, °C.	400	500	500
State of catalyst	Fresh	Fresh	Used
Products, wt. % of charge			
Olefins	1.6	4.8	7.3
Paraffins	4.0	7.1	6.8[a]
Total cycloparaffins	66.5	52.9	68.4–75.2
Monocyclic[b]	16.8	10.2	...
"Isodecalins"[c]	28	8.7	11.5
Unchanged decalin	21.7	34.0	56.9
Total aromatic	16.5	21.6	9.1
Benzene	0.0	0.08	0.0
Toluene	0.60	1.36	0.54
Xylenes-ethylbenzene	0.57	1.93	0.51
Propylbenzene and isomers	1.03	2.78	0.50
Butylbenzene and isomers	1.57		0.92
Tetralin and isomers	>6.5	10.5	>3.3
Naphthalene and higher-boiling	12.7	5.0	6.6

[a] Including monocyclic naphthenes. [b] Boiling below decalin isomers. [c] Products boiling from 155 to 185° having $n^{20}D$ >1.46.

range have refractive indices of 1.43–1.45. We believe that the decalin isomers formed with the cracking catalyst are probably dimethylbicyclooctanes [0,3,3] or methylhydrindanes. Isomerizations of decalin to dimethylbicyclooctanes have been reported to occur at about 425° in the presence of molybdenum sulfide[9] and at lower temperatures in the presence of aluminum chloride[10] and aluminum bromide.[11]

Ring scission yielded substantial proportions of isobutane and smaller proportions of *n*-butane. The liquid products contained methylcyclopentane and probably cyclohexane. It, therefore, seems likely that decalin undergoes direct scission into C_4 and cyclic C_6 fragments. These fragments may form the corresponding olefins or receive hydrogen from decalin by hydrogen transfer to give saturated products. There are at least three ways in which these could be formed: (1) decalin could give cyclohexane and *n*-butane directly; (2) it could isomerize in one ring and the isomerized product would give (a) cyclohexane plus isobutane, or (b) methylcyclopentane plus *n*-butane; or (3) decalin could isomerize in both rings and the isomerized product would give methylcyclopentane and isobutane.

In each case as conditions become less favorable for hydrogen transfer a larger proportion of the products are olefinic. This is readily apparent in the gases (compare Expt. 7 with Expt. 9, Table II). The liquid products are too complex to permit any certainty that cycloölefins are present.

The substantial proportions of propane and propylene in the gaseous products may have arisen from the cracking of decalin itself, of its isomers, or of the primary products.

The saturated products resulted from both scission and hydrogen transfer. It is worthy of note that at 500° the extent of scission with a fresh catalyst was increased, but the relative amount of hydrogenation by the transfer reaction was decreased from that at 400°, and that the spent catalyst at 500° was less effective for both reactions than the fresh, the decrease in activity being especially noticeable with respect to hydrogen transfer.

The alkylbenzenes formed were similar to those formed by the catalytic cracking of tetralin. It seems likely that some of the decalin was converted by hydrogen transfer to tetralin, and that this (or its isomers) underwent scission in the hydrogenated ring to yield the alkylaromatics found. All of the naphthalene found might have been formed through the tetralin stage rather than directly from decalin.

The formation of alkylaromatics was especially pronounced at 500° with the fresh catalyst. Since these conditions were less favorable for hydrogenation of unsaturates than the lower temperature, the increased yield of aromatics was accompanied by the liberation of increased amounts of molecular hydrogen.

It is evident that the principal reactions found to take place under the influence of cracking catalysts of the type used are common not only to the three types of cyclic hydrocarbons of the present study, but, to a certain extent, to the open-chain compounds previously investigated. Thus both cyclic and aliphatic olefins, as well as cycloparaffin rings, have been shown to isomerize; both cyclic and aliphatic olefins have been shown to polymerize; cycloparaffins as well as open-chain paraffins have been found to undergo scission; and hydrogen transfer has been found to play an important role in determining the nature of the products derived from cyclic as well as from open-chain hydrocarbons.[12]

Experimental

Materials: Cyclohexene.—Redistilled Eastman Kodak Co. cyclohexene having the following properties was employed: b. p. 81.8–82.0° (uncor.), $n^{20}D$ 1.4464, Br no. 195, d^{20}_4 0.80.

Decalin.—Eastman Kodak Co. practical decalin was distilled on a 50-bubble cap column of the Bruun type.[13] The fractions used had the properties

Run no.	B. p., °C. (uncor.)	$n^{20}D$	d^{20}_4	δ
4 and 5	185.0–193.4	1.4768	0.8813	97.5
6	185.0–194.0	1.4768	0.8850	96.9

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(9) E. I. Prokopetz, *J. Appl. Chem.* (USSR) **7**, 159–169 (1934); see also Kadjhinoo, *Ukrain. Chem. J.*, **8**, 333–346 (1933); *C. A.*, **29**, 2161 (1935).

(10) Jones and Linstead, *J. Chem. Soc.*, 616–621 (1936); Zelinsky and Turova-Pollak, *J. Appl. Chem.* (U. S. S. R.), **7**, 753–756 (1934).

(11) Zelinsky and Turova-Pollak, *Ber.*, **58B**, 1292–1298 (1925) obtained unidentified isomers of b. p. 170–175°.

(12) C. L. Thomas, THIS JOURNAL, **66**, 1586 (1944).

(13) Bruun, *Ind. Eng. Chem., Anal. Ed.*, **8**, 224 (1936).

Tetralin.—Eastman Kodak Co. practical tetralin was distilled in vacuum with a 10 in. Vigreux column at the rate of about 1 ml./min. The fraction employed distilled at 77–80° at 10 mm. pressure (199–203°, uncor., at atmospheric pressure) and had the properties d^{20}_4 0.9633, n^{20}_D 1.5432, δ 172.

Catalysts.—The catalyst used for the cyclohexene work had the approximate composition $100SiO_2:5Al_2O_3:0.5ThO_2$; its preparation has been previously described.[4] The catalyst used in the cracking of tetralin and decalin was the same as that of which the composition and preparation are discussed in the preceding paper of this series.[12]

Procedure.—The apparatus and procedure were the same as those previously described.[1]

Analytical Methods.—The collection of the gaseous products, their separation from the liquid products, and their analysis was carried out by the methods reported in our earlier work.[1]

The liquid products were fractionated into a large number of cuts which were characterized by density, refractive index, bromine number, specific dispersion, specific refraction,[14] and the refractivity intercept.[15] The latter two were especially useful in estimating cycloparaffins.

Atmospheric pressure distillations were conducted with a vapor-jacketed column[15a] packed with single-turn glass helices. This column was found to have an efficiency of 17 theoretical plates. In our work, it was operated at very high reflux ratios and slow throughput, in order to obtain the maximum efficiency. In some cases fractions were redistilled.

In Experiments 2 and 3, the high-boiling components were vacuum distilled from a Claisen flask fitted with a 3-in. Vigreux column, and the overhead redistilled at atmospheric pressure with the same equipment. The product of Expt. 4 was vacuum distilled in a similar apparatus with a 10-in. Vigreux column, and the lightest overhead fraction (b. p. 55–75° at 10 mm.) was redistilled on the Fenske-type column.

The refractive indices and specific dispersions were determined with an Abbe refractometer. The determination of the bromine number and the general method by which the composition of fractions was determined followed procedures previously described[16,17]; in the present work, however, the calculations were necessarily modified because of the use of pure hydrocarbons rather than petroleum fractions. Thus in the case of the cyclohexene work the factors used for correcting the specific dispersion of the light fractions for olefins were those of the methylcyclopentenes and cyclohexene (0.129 and 0.109, respectively) rather than the generalized value of 0.16 recommended by Grosse and Wackher.[17]

In the decalin and tetralin work, the refractive index corrections for monocyclic aromatics were weighted in favor of the monoalkyl and *o*-dialkyl isomers. The refractive index corrections for olefins were based on the assumption that they were open-chain unsaturates. This assumption could be considerably in error, however, without greatly affecting the results, since the paraffins and cycloparaffins were separately estimated only for fractions in which the olefin content was low.

In order to determine the composition of the cyclohexene-methylcyclopentene fractions in Experiments 1, 2, and 3, the following values were determined: 1, per cent. olefins, by bromine number; 2, per cent. cyclic compounds, by carbon–hydrogen analysis after hydrogenation; 3, per cent. each of five-membered and six-membered cyclics primarily by refractive index and secondarily by the density of the hydrogenated fractions; 4, per cent. of benzene by the specific dispersion, after correction for the cyclo-olefin content; by the specific dispersion after hydrogenation; and by qualitative nitration tests.

The hydrogenations were carried out in an Ipatieff autoclave with the commercial U. O. P. nickel hydrogenation catalyst[18] at 80°; in all cases the hydrogenated products were saturated to permanganate.

A number of individual compounds present in the reaction products were identified by isolation and the determination of physical constants or by the preparation of solid derivatives. These included the following:

Methylcyclopentene-1 was identified by permanganate oxidation to γ-acetobutyric acid hydrate, m. p. 36–37°, neutralization equivalent 151 (calcd. 148); oxime, m. p. 102–102.5°. Found, N, 9.54; calcd. 9.65. It was present in fractions of Expt. 2 boiling between 71 and 77°.

Methylcyclopentene-2 was identified by permanganate oxidation to α-methylglutaric acid, m. p. 75.5–76.5°, neutralization equivalent, 73.5 (calcd. 73.0); present in fractions of Expt. 2 boiling at 65–71° and a fraction of Expt. 3 boiling at 34–69°.

Benzene was identified by qualitative nitration tests on hydrogenated fractions recovered from Expts. 1 (b. p. 79–82°) and 2 (b. p. 81.8–82.3°). It was identified also in fractions from Expt. 4, b. p. 74–82°, and Expt. 6, b. p. 72–85°, by conversion to dinitro derivative (m. p. 87–88°) which did not markedly depress the melting point of known dinitrobenzene (m. p. 90–91°).

Toluene was identified by conversion to 2,4-dinitrotoluene (m. p. 70.5–71°) which did not depress the melting point of known compound; present in fractions of Expt. 6, b. p. 85–108°.

Ethylbenzene and xylenes by permanganate oxidation of a fraction of b. p. 112–146° from Expt. 6 yielded benzoic acid as the major product (m. p. 121.5–122°, did not depress m. p. of known benzoic acid), which was taken to indicate the presence of ethylbenzene; a trace of phthalic acid, identified by a fluorescein test, which was considered evidence for the presence of *o*-xylene; and 22% of benzene-insoluble acids which sublimed without melting above 284°, were slightly soluble in ethanol, and formed a solid dimethyl ester m. p. 100–120°, with softening from 60°. This material, mixed with dimethyl isophthalate (m. p. 64.5–66°) softened at 58° and melted at 62–63.5°. It was concluded that a mixture of iso- and terephthalic acids was present.

Naphthalene, m. p. 80–81° (no depression when mixed with known naphthalene), was found in large quantities in the higher-boiling fractions from Expts. 4 and 6.

1,6-Dimethylnaphthalene was tentatively identified as a picrate isolated from the fraction of Expt. 3, b. p. 259–267°. The picrate melted at 102–104°, and when mixed with the known picrate (m. p. 110.5–111.5°) depressed the melting point to 106.5–109°.

2,6-Dimethylnaphthalene, m. p. 107–108.5°, picrate m. p. 138.5–141° (neither depressed m. p. of known compounds). Calcd. for $C_{12}H_{12}$: C, 92.31; H, 7.69; mol. wt., 156. Found: C, 92.13; H, 8.00; mol. wt., 157. Present in fractions from Expt. 3, b. p. >237°.

Summary

A study has been made of the reactions, at atmospheric pressure, of cyclohexene in the presence of a synthetic silica–alumina–thoria catalyst at 250–400°; of tetralin with a synthetic silica–alumina–zirconia catalyst at 400–500°; and of decalin with the latter catalyst in both the fresh and partially spent state at 400–500°.

The principal reaction products isolated from cyclohexene were methylcyclopentenes-1 and -2, methylcyclopentane, a mixture of unidentified liquids higher boiling than cyclohexene, and 2,6-

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[14] (a) Vlugter, Waterman and Van Westen, *J. Inst. Petroleum Tech.*, **20**, 255 (1934); (b) Schiessler, Cosby, Clark, Rowland, Sloatman and Herr, *Proc. Am. Petroleum. Inst.*, **23**, [III] 15 (1942).

[15] Ward and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 559 (1938).

[15a] Tongberg, Quiggle and Fenske, *Ind. Eng. Chem.*, **26**, 1212 (1934).

[16] "U. O. P. Laboratory Test Methods for Petroleum and Its Products" Method No. 173-40, pp. H-45 to H-59, Universal Oil Products Company, Chicago, Illinois (1940).

[17] Grosse and Wackher, *Ind. Eng. Chem., Anal. Ed.*, **11**, 614–624 (1939).

[18] Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

dimethylnaphthalene. The principal reactions of cyclohexene under the conditions studied were (1) isomerization, (2) polymerization and (3) hydrogen transfer. The hydrogen transfer was primarily from the polymer resulting in the formation of dimethylnaphthalenes and the hydrogenation of the methylcyclopentenes to methylcyclopentane.

Naphthalene was the product formed most abundantly from tetralin. Scission of the hydroaromatic ring gave benzene, toluene, xylenes, possibly ethylbenzene, and higher boiling alkylated benzenes. No alkenylbenzenes were isolated. They may have been formed and then converted into the corresponding alkyl derivatives by hydrogen made available by the conversion of tetralin to naphthalene. Some of the tetralin was converted to bicycloparaffins, presumably decalin or its isomers. The products can be explained by reactions of (1) scission of the hydroaromatic ring and (2) hydrogen transfer. Apparently, isomerization also occurred, for the xylene fraction contained xylenes other than *o*-xylene.

The chief products formed from decalin were "isodecalins," C_3 and C_4 olefinic and paraffinic gases in which isobutane predominated, methylcyclopentane, and probably cyclohexane and the corresponding olefins. In addition, tetralin or its isomers was found and the aromatic reaction products of tetralin conversion indicated above. The products can be explained by the following reactions of decalin and the intermediate tetralin: (1) isomerization, (2) ring scission and (3) hydrogen transfer.

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Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene and Methyl Methacrylate

BY FRANK R. MAYO AND FREDERICK M. LEWIS

Although considerable progress has been made in interpreting the polymerization of single monomers, a systematic study of copolymerization has been hampered by the absence of a theoretical basis for comparing the behavior of monomers in copolymerization. This paper describes the development of such a basis for addition (vinyl) polymerizations, the application of the general concept to the copolymerization of styrene and methyl methacrylate by a free radical mechanism, and the scope of the present development.

The Problem of Copolymerization.—When two monomers such as styrene (S) and methyl methacrylate (M) copolymerize, there are two kinds of free radicals which form the growing ends of the polymer molecules. These two kinds of radicals will be designated as S· and M·, respectively, depending on whether the active center at the instant chosen ends in a styrene or in a methyl methacrylate unit. The reactions of these radicals are assumed (and will be shown) to be independent of the number and kind of attached units. Each kind of radical may react with either kind of monomer molecule

$$\mathrm{S\cdot + S \xrightarrow{k_1} S\cdot} \qquad (1)$$

$$\mathrm{S\cdot + M \xrightarrow{k_2} M\cdot} \qquad (2)$$

$$\mathrm{M\cdot + M \xrightarrow{k_3} M\cdot} \qquad (3)$$

$$\mathrm{M\cdot + S \xrightarrow{k_4} S\cdot} \qquad (4)$$

The problem is to develop from these equations an expression which will permit correlation of data on products of copolymerizations in the simplest possible terms.

Previous Work.—Norrish and Brookman[1] studied the rates of copolymerization of styrene–methyl methacrylate mixtures. They considered the problem on the basis of the four chain growth steps given above, but they also made an assumption about the concentration of active centers, the validity of which will be discussed later.

Wall[2] has presented a relatively simple basis for studying copolymerizations. In terms of the nomenclature in this paper, he defines the relative reactivity (α) of two monomers in copolymerization as the quotient of the rate constants for the individual polymerizations (k_s and k_m, respectively): *i. e.*,

$$\frac{d[S]}{d[M]} = \frac{k_s[S]}{k_m[M]} = \alpha\frac{[S]}{[M]}$$

where [S] and [M] refer to concentrations of unreacted monomers. Actually, Wall's equation applies only to the limiting case of ideal copolymerizations, where both radical types, S· and M·, have the same relative preferences for reacting with the monomers S and M, *i. e.*, where $k_1/k_2 = k_4/k_3$. If this relation does not hold, then α will vary with the ratio of S·/M·, and since S·/M· will depend on [S]/[M], α will vary with the composition of the monomer mixture. Although Wall's equation seemed at first to be an attractive approach to the problem of copolymerization, our initial experiments with styrene and methyl methacrylate showed that α varied considerably with [S]/[M]. The α-concept also cannot apply to ethylene derivatives which do not polymerize

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[1] Norrish and Brookman, *Proc. Roy. Soc.* (London), **171A**, 147 (1939).

[2] Wall, THIS JOURNAL, **63**, 1862 (1941).