[CONTRIBUTION FROM THE PHILLIPS PETROLEUM COMPANY, RESEARCH DIVISION]

Aluminum Bromide Isomerization of 2,2,4-Trimethylpentane Alone and in the Presence of Naphthenes. Mechanism of the Inhibition by Naphthenes of Side Reactions during Paraffin Isomerization

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Aluminum bromide isomerization of 2,2,4-trimethylpentane at 26° gave 18% isobutane, 6% isopentane, 12% hexanes and heptanes, 26% isomeric octanes and 38% heavier products, including catalyst sludge oil. In the presence of *trans*-decalin or cyclohexane, these yields were practically unchanged. In the presence of *cis*-decalin or methylcyclopentane, the yield of isomers increased regularly with the initial amount of added naphthene and the yields of other products, except isobutane, were correspondingly reduced. *cis*-Decalin was simultaneously isomerized to *trans*-decalin with a specific rate 7.6 times the rate of conversion of 2,2,4-trimethylpentane to all products; and methylcyclopentane was simultaneously isomerized to cyclohexane with a specific rate 0.13–0.16 times the rate of conversion of 2,2,4-trimethylpentane. In concordance with these relative rates, *cis*-decalin was isomerized about 46–49 times faster than methylcyclopentane in experiments in which these two naphthenes were isomerized in admixture. In addition to being less effective as an inhibitor of side reactions, *trans*-decalin was much less reactive than *cis*-decalin in aluminum chloride-catalyzed halogen–hydrogen exchange with *t*-butyl chloride at 1°. A mechanism of the inhibition by naphthenes of side reactions during paraffin isomerization is presented.

Much work by others has shown that the aluminum halide-catalyzed isomerization of a paraffin is accompanied by side reactions that convert a part of the paraffin to other paraffins of both higher and lower molecular weight, and a part to substances that complex with the aluminum halide to form a sludge.[1] Other work has shown that, if the isomerization is conducted in the presence of a naphthene,[2a,c] an aromatic hydrocarbon,[2c,d] or hydrogen,[2] the side reactions are inhibited and the ultimate yield of isomers is correspondingly increased.

In the work reported here, part of an investigation of the mechanism of the inhibition of side reactions during paraffin isomerization, 2,2,4-trimethylpentane was isomerized with aluminum bromide alone and in the presence of *cis*-decahydronaphthalene, *trans*-decahydronaphthalene, methylcyclopentane, or cyclohexane as an inhibitor of side reactions. (Hereinafter, "decalin" is used for "decahydronaphthalene.")

Experimental Part

Materials.—Phillips Petroleum Company Pure Grade 2,2,4-trimethylpentane was used.

Eastman Kodak Company Practical Grade decalin was fractionated in a Podbielniak Hypercal column with Heligrid packing,[3] 1 m. × 13 mm. The concentrates of *cis*-decalin and *trans*-decalin so obtained were separately refractionated for further purification. The infrared spectra of the purified compounds indicated that the *trans*-decalin (lower-boiling isomer) was free of *cis*-decalin, that the *cis*-decalin contained about 1% of *trans*-decalin, and that both compounds were free of tetralin and naphthalene.

Phillips Petroleum Company Technical Grade methylcyclopentane and Pure Grade cyclohexane were passed separately through columns of silica gel. Fractions from this treatment which contained less than 0.01% benzene, according to ultraviolet spectrophotometry, were combined and were distilled through the Hypercal column with rejection of approximately the first and last 10% fractions.

C.P. anhydrous aluminum bromide from the Eimer and Amend division of Fisher Scientific Company was used.

Procedure.—The hydrocarbons were weighed into a tared 500-ml. three-necked flask, and the flask was fitted with a mercury-sealed Hershberg stirrer,[4] a thermometer and a reflux condenser, the top of which communicated through a sodium hydroxide-filled drying tube with a Dry Ice-cooled trap. The stirrer was started and the temperature was adjusted to 26° by means of a water-bath. The stirrer was stopped, the thermometer was removed and aluminum bromide was quickly added from a weighed container. The thermometer was replaced, the stirrer was restarted and the weight of aluminum bromide added was obtained from the loss in weight of its container.

In two experiments, anhydrous hydrogen bromide (generated from bromine and tetralin, caught in a Dry Ice-cooled trap and distilled to a second trap before use) was introduced during the stirring period.

After a timed stirring period, an upper hydrocarbon layer in the flask was decanted from a lower sludge layer into a separatory funnel. The sludge was weighed and was decomposed with ice; the hydrocarbon layer was washed with three small portions of ice and water. An aliquot portion of each resulting aqueous solution was analyzed for aluminum bromide by titration with 1 *N* sodium hydroxide with phenolphthalein. The hydrocarbon content of the sludge was calculated by difference. A small amount of sludge remaining on the stirrer, thermometer and tip of the reflux condenser was similarly analyzed for aluminum bromide and was assumed to have the same hydrocarbon content as the bulk.

In several of the experiments with methylcyclopentane, a modification of this procedure was adopted in an attempt to improve the reproducibility of the results, but without marked success. In this modification, the reaction was "shortstopped," after the timed stirring period, by rapid addition of about 10 ml. of purified 1,4-dioxane, followed by water, while the temperature was held as near as possible to 26° by simultaneous cooling of the flask with ice. This method of operation made impossible a determination of the amount of sludge; but in the experiments with methylcyclopentane, where it was used, sludge formation was comparatively slight.

Hydrocarbon Analysis.—The hydrocarbon product, dried overnight with a small amount of anhydrous potassium carbonate, was fractionated in the above-mentioned Podbielniak Hypercal column. The first few ml. of liquid distillate was added to the light ends caught in a Dry Ice-cooled trap, and the whole was analyzed by fractional distillation in a Podbielniak Heligrid low-temperature column. For each product, the contents of isobutane, isopentane, hexanes-plus-heptanes (boiling to 95°), 2,2,4-trimethylpentane (boiling 95–105°), other octanes (boiling 105–122°), heavier (boiling above 122°), and sludge oil (where possible) were calculated as weight per cent. of the material recovered after fractional distillation, which generally exceeded 96% of the hydrocarbons charged.

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[1] (a) Calingaert and Beatty, THIS JOURNAL, **58**, 51 (1936); (b) Ipatieff and Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936); (c) Glasebrook, Phillips and Lovell, THIS JOURNAL, **58**, 1944 (1936); (d) Grummitt, Sensel, Smith, Burk and Lankelma, *ibid.*, **67**, 910 (1945); (e) Bishop, Burk and Lankelma, *ibid.*, **67**, 914 (1945); (f) Grummitt, Case and Mitchell, *Ind. Eng. Chem.*, **38**, 141 (1946); (g) Pines and Wackher, THIS JOURNAL, **68**, 595, 599 (1946).

[2] (a) Evering and d'Ouville, *ibid.*, **71**, 440 (1949); (b) Ipatieff and Schmerling, *Ind. Eng. Chem.*, **40**, 2354 (1948); (c) Evering, d'Ouville, Lien and Waugh, Paper presented before the Petroleum Division, ACS Meeting, Atlantic City, N. J., April, 1947; (d) Mavity, Pines, Wackher and Brooks, *Ind. Eng. Chem.*, **40**, 2374 (1948); (e) Evering and Waugh, Paper presented before the Petroleum Division, ACS Meeting, Chicago, Ill., April, 1948. Other references are cited by some of these authors.

[3] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **13**, 639 (1941).

[4] Hershberg, *ibid.*, **8**, 313 (1936).

TABLE I

ALUMINUM BROMIDE ISOMERIZATION OF 2,2,4-TRIMETHYLPENTANE ALONE AND IN THE PRESENCE OF NAPHTHENES[a]

Expt.[b]	1	2	3	4	5	6[c]	7	8	9[d]	10	T11	T12	T13	C14	C15	C16	C17	C18	C19	C20
$AlBr_3$, wt. % of octane	9.6	9.6	9.3	5.9	9.5	9.5	9.3	9.0	9.4	13.3	9.8	9.5	9.2	9.3	9.6	9.5	9.5	9.4	11.2	12.1
Contact time, min.	60	40	90	220	240	180	150	120	120	135	120	155	200	120	120	120	120	120	260	300
Charge composition, wt. %																				
2,2,4-trimethylpentane	100										94.5	89.7	80.2	99.22	97.47	95.9	93.25	87.1	76.0	66.7
naphthene	0										5.5	10.3	19.8	0.78	2.53	4.1	6.75	12.9	24.0	33.3
Product composition, wt. %																				
isobutane	2.25	2.52	2.81	3.17	3.77	3.95	4.74	5.78	6.02	6.41	3.49	2.69	2.26	3.05	2.05	2.01	1.84	1.74	1.20	1.73
isopentane	0.76	0.83	1.04	1.13	1.14	1.2	1.42	1.82	1.67	1.82	1.04	0.68	0.49	0.77	0.31	0.17	0.20	0.29	0.067	0.028
hexanes and heptanes	1.2	1.7	1.65	2.22	2.53	2.5	3.7	3.6	3.7	4.06	2.5	2.3	2.3	2.3[e]	1.15[e]	1.2[e]	1.16[e]	0.79[e]	0.16	...
2,2,4-trimethylpentane	88.2	87.0	84.5	82.1	79.65	78.05	71.3	69.4	66.8	64.9	74.87	72.3	66.75	82.88	88.2	86.41	83.34	76.28	69.5	58.8
other octanes	3.0	3.5	4.0	4.65	5.35	4.9	7.5	7.4	8.3	10.4	5.3	4.7	4.0	5.3	3.8	4.2	4.8	5.8	4.3	5.14
trans-decalin	...	...	...	...	...	...	...	...	...	...	12.0	15.13	22.3	3.7	3.4	4.66	7.16	13.4	10.1[f]	20.0[f]
cis-decalin	...	...	...	...	...	...	...	...	...	...									12.7[f]	11.8[f]
other hydrocarbons	4.0	3.9	5.0	6.7	6.25	7.4	8.6	12.0	10.4	12.4									1.1	1.2
sludge oil	0.55	0.55	1.0		1.3	2.0	2.7		3.1		0.8	2.2	1.9	2.0	1.1	1.35	1.5	1.7	0.9	1.3
Conversion, wt. %																				
2,2,4-trimethylpentane	11.8	13.0	15.5	17.9	20.35	21.95	28.7	30.6	33.2	35.1	20.8	19.4	16.8	16.5	9.5	9.9	10.6	12.4	8.5	11.8
$AlBr_3$ to sludge	20	24	33	...	53	56	78	...	77	...	58	59	64	60	40	39	48	55	33	45
Ult. yield, wt. % octane																				
isobutane	19.1	19.4	18.1	17.7	18.5	18.0	16.5	18.9	18.1	18.3	17.8	15.7	16.8	18.6	22.0	21.2	18.6	16.1	18.5	22
isopentane	6.4	6.4	6.7	6.3	5.6	5.5	5.0	5.9	5.0	5.2	5.3	3.9	3.7	4.7	3.3	1.8	2.1	2.7	1.0	0.35
hexanes and heptanes	10.2	13.2	10.6	12.4	12.5	11.4	12.9	11.7	11.1	11.6	12.8	13.2	17.1	14.1[e]	12.4[e]	13[e]	11.7[e]	7.3[e]	2.5	...
other octanes	25.6	26.9	26.0	26.0	26.0	22.3	26.1	24.2	25.0	29.6	27.0	27.0	29.7	32.5	40.8	44	48.5	53.6	65.7	65
other hydrocarbons	34.1	29.9	32.1	37.6	31.0	33.7	30.1	39.3	31.3	35.4	37.0	40.2	32.7	30.1	21.4	20	19.1	20.3	12.3	12.7
sludge oil	4.6	4.2	6.5		6.4	9.1	9.4		9.3											
Expt.[b]	H21	H22	M23	M24	M25	M26	M27	M28	M29	M30	M31	M32	M33	M34	M35	M36	M37	M38	M39	M40
$AlBr_3$, wt. % of octane	9.8	9.3	9.4	9.2	9.9	9.1	9.8	10.5	10.2	9.2	9.4	10.9	10.0	9.7	9.5	11.2	5.1	10.5	12.5	9.4
Contact time, min.	130	180	120	120	390	110	120	300	230	110	60	5	35	15	3	5	5	60	165	10
Charge composition, wt. %																				
2,2,4-trimethylpentane	88.8	76.7	98.8	97.8	96.2	95.1	94.5	94.5	93.6	92.5	92.4	89.7	89.7	87.7	83.8	83.8	83.6	83.8	82.0	74.8
naphthene	11.2	23.3	1.2	2.2	3.8	4.9	5.5	5.5	6.4	7.5	7.6	10.3	10.3	12.3	16.2	16.2	16.4	16.2	18.0	25.2
Product composition, wt. %																				
isobutane	1.93	1.57	2.36	3.02	4.78	3.72	3.06	4.00	5.07	4.61	4.57	2.33	2.88	3.29	2.97	4.23	4.04	6.47	8.56	2.06
isopentane	0.55	0.48	0.46	0.45	0.54	0.23	0.14	0.25	0.32	0.17	0.16	0.027	0.09	0.034	0.030	0.044	0.03	0.06	0.19	0.013
hexanes and heptanes	13.2	24.7	1.1	1.5	2.05	1.45	3.3	2.6	2.2	2.7	2.75	7.7	7.3	...	12.6	10.7	10.75	8.6	7.0	0.013[g]
methylcyclopentane														7.28[g]						21.2[g]
cyclohexane														0.33[g]						0.54[g]
2,2,4-trimethylpentane	77.2	67.3	88.24	85.0	74.4	81.1	80.9	76.5	72.0	73.1	72.6	77.1	75.5	71.0	67.1	63.7	63.5	54.4	48.1	62.3
other octanes	3.0	2.4	3.8	5.1	8.9	6.3	6.7	8.3	10.4	9.7	10.6	7.0	8.2	10.5	10.0	11.0	11.25	15.2	16.5	8.0
other hydrocarbons	3.4	2.9	3.4	4.3	7.0	6.7	5.9	6.9	9.4	9.2	9.0	5.5	6.0	7.4	7.3	10.3	10.4	15.3	19.1	5.7
sludge oil	0.67	0.65	0.6	0.6	2.3	0.5		1.4	0.6	0.5	0.3	0.3		0.2					0.6	0.15
Conversion, wt. %																				
2,2,4-trimethylpentane	13.1	12.2	10.7	13.1	22.8	14.7	14.4	19.1	23.2	21.0	21.4	14.0	15.8	19.0	19.9	24.0	24.0	35.1	41.4	16.7
$AlBr_3$ to sludge	33	28	20	31	61	18	...	...	29	17	12	9	...	9	...	...	...	...	22	5
Ult. yield, wt. % octane																				
isobutane	16.6	16.7	22.3	23.6	21.9	26.6	22.5	22.1	23.4	23.8	23.1	18.5	20.3	19.7	17.8	21.0	20.1	22.0	25.2	16.5
isopentane	4.8	5.1	4.3	3.5	2.5	1.6	1.0	1.4	1.45	0.88	0.79	0.20	0.60	0.20	0.18	0.20	0.15	0.20	0.57	0.10
other octanes	25.9	25.4	36.0	49.8	40.9	45.0	49.3	46.1	48.0	50.0	53.5	55.5	57.8	62.8	60.0	54.7	56.0	51.8	48.7	64.0
other hydrocarbons	52.7	52.8	37.4	33.1	34.7	26.8	27.2	30.3	27.2	25.3	22.6	25.8	21.3	17.3	22.0	24.1	23.7	26.0	25.5	19.4
sludge oil																				

[a] The temperature was 26° in all the experiments. [b] T = *trans*-decalin, C = *cis*-decalin, H = cyclohexane, M = methylcyclopentane. [c] About 1% of HBr was added. [d] About 2% of HBr was added. [e] A not very accurate maximum; see text. [f] From refractive index measurements. [g] From infrared analyses of C6-C7 fractions.

In addition, the hexanes-plus-heptanes and the 105–122° octane fractions from several experiments conducted in the absence of a naphthene were combined and refractionated and the fractions were analyzed by infrared spectrophotometry. The same fractions from several experiments with *cis*-decalin, and the 105–122° octane fractions from several experiments with methylcyclopentane, were treated in the same way.

Results

In Table I, Expts. 1–10, in order of increasing conversion of the 2,2,4-trimethylpentane, show that, except for some irregular variation, the ultimate yields of the several products (or groups of products) are substantially independent of the conversion—all these products are "primary" products.[5] The ultimate yields were practically unchanged when hydrogen bromide was added (Expts. 6 and 9), indicating that an accidental variation in the amount of hydrogen bromide (possibly formed by hydrolysis of a part of the aluminum bromide) was not the cause of the irregular variation in ultimate yields. This variation is largely attributable to limitations of the analytical method (fractional distillation).

Experiments C14–C20, in order of increasing weight per cent. of *cis*-decalin in the charge, show that *cis*-decalin is an effective inhibitor of most of the side reactions of 2,2,4-trimethylpentane, so that the ultimate yield of isomers increases regularly with the weight per cent. of *cis*-decalin in the charge; but *cis*-decalin does not decrease the ultimate yield of isobutane. (The values for hexanes and heptanes in Expts. C14–C18 are regarded as not very accurate maxima, for on refractionation of the accumulated fractions, less hexanes and heptanes were found than were expected from the results of the original fractionations; the balance was 2,2,4-trimethylpentane. In Expt. C19, following realization of the difficulty of accurately determining by fractional distillation the small amount of hexanes and heptanes produced, this fraction was redistilled in a very small column, and a more nearly accurate determination was made. In Expt. C20, the amount of hexanes and heptanes appeared very small (the initial boiling point of the liquid product was 94.5°) and was simply neglected, although the ultimate yield of hexanes and heptanes in this experiment may have been about 1%.)

The data of Expts. C19 and C20 show that a large part of the *cis*-decalin was simultaneously isomerized to *trans*-decalin. *trans*-Decalin had comparatively little effect on the ultimate yields of the several products from 2,2,4-trimethylpentane (Expts. T11–T13).

Methylcyclopentane was an effective inhibitor of most of the side reactions accompanying the isomerization of 2,2,4-trimethylpentane and served to increase the ultimate yield of isomers; but it did not serve to decrease the ultimate yield of isobutane; in fact, in most of the experiments with methylcyclopentane, the ultimate yield of isobutane was greater than was generally found in the absence of a naphthene (Expts. M23–M40). A small amount of isomerization of methylcyclopentane to cyclohexane accompanied its conversion to other products in the presence of isomerizing 2,2,4-trimethylpentane (Expts. M34 and M40). Cyclohexane had comparatively little effect on the ultimate yields of products from 2,2,4-trimethylpentane (Expts. H21 and H22).

The data of Table II indicate that naphthenes have some effect on the proportions of isomeric hydrocarbons produced from 2,2,4-trimethylpentane, principally increasing the proportion of methylpentanes to 2,3-dimethylbutane, and the proportion of 2,3,4-trimethylpentane to 2,3,3-trimethylpentane. However, many of the data in Table II are regarded as only semi-quantitative, in view of the varied sources of the fractions combined and analyzed, the rather lengthy procedure used for obtaining the data, and inherent uncertainties of the infrared spectrophotometric determination of those compounds present in small amounts.

TABLE II

HEXANES, HEPTANES AND OCTANES FROM ALUMINUM BROMIDE ISOMERIZATION OF 2,2,4-TRIMETHYLPENTANE[a]

Expts.	1–10[b]	C14–C18[c]	M33[d]
Hexanes, wt. %			
2,2-dimethylbutane	1.2	3	..
2,3-dimethylbutane	72.8	53	..
2-methylpentane	18.0	26	..
3-methylpentane	8.0	18	..
Heptanes, wt. %			
2,2,3-trimethylbutane	6.0	..	..
2,2-dimethylpentane	0.2	..	..
2,3-dimethylpentane	17.0	20	..
2,4-dimethylpentane	71.0	70	..
2-methylhexane	3.0	4.5	..
3-methylhexane	2.8	5.5	..
Octanes, wt. %			
2,2,3-trimethylpentane	5.8	5.5	5.7
2,3,3-trimethylpentane	34.6	24.6	32.0
2,3,4-trimethylpentane	45.0	61.2	54.6
2,2-dimethylhexane	0.2	..	0.2
2,3-dimethylhexane	3.8	0.65	2.2
2,4-dimethylhexane	4.7	4.0	3.5
2,5-dimethylhexane	5.9	4.0	1.0
3,4-dimethylhexane	..	..	0.8

[a] Infrared analyses. [b] Plus three similar expts. not reported; and except Expts. 4, 6, 8 and 9. Hexane to heptane weight ratio = 1.2. [c] Plus four similar expts. not reported. Hexane to heptane weight ratio = 0.9. [d] Plus three similar expts. not reported.

The difference in effectiveness of *cis*-decalin and *trans*-decalin as inhibitors of side reactions during isomerization of 2,2,4-trimethylpentane indicated an unexpected difference in chemical reactivity. This difference was exhibited also in halogen–hydrogen exchanges[6] with *t*-butyl chloride carried out with two samples of decalin, one a sample of pure *trans*-decalin, the other containing some *cis*-decalin (Table III).

Very little reaction of the *t*-butyl chloride and very little production of isobutane occurred in the experiment with pure *trans*-decalin compared with that in the experiment with *cis*-decalin.[7] This

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(5) *Cf.* Schneider and Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931).

(6) Bartlett, Condon and Schneider, THIS JOURNAL, **66**, 1531 (1944).

(7) R. W. Blue and C. J. Engle of this Laboratory have found that *cis*-decalin is several times more reactive than *trans*-decalin in hydrogen transfer with isobutylene over silica–alumina cracking catalysts at 350°, *Ind. Eng. Chem.*, **43**, 494 (1951).

TABLE III

HALOGEN–HYDROGEN EXCHANGE BETWEEN *t*-BUTYL CHLORIDE AND DECALINS

Temperature, °C.	1	1
Contact time, min.	1.5	1.5
Charge composition, mole %		
t-butyl chloride	52.5	53.4
trans-decalin	27.8	46.6
cis-decalin	19.7	..
$AlCl_3$, wt. % of charge	2.2	2.7
Product composition, mole %		
isobutane	14.5	0.61
isopentane	0.2	0.02
t-butyl chloride	35.2	52.2
decalins	32.5	..
residue	17.6[a]	47.2[b]

[a] Calculated as chlorodecalin. [b] Calculated as decalin.

finding is in agreement with the views that both paraffin or naphthene isomerization[1g] and halogen–hydrogen exchange[6] have carbonium ion mechanisms. Both decalins yield the same tertiary carbonium ion; and provided that there are no higher energy states between the molecular ground states and the carbonium ion state, and since *trans*-decalin is 2390 calories more stable than *cis*-decalin,[8] formation of the carbonium ion is easier from *cis*-decalin than from *trans*-decalin by the factor, $e^{2390/RT}$ (= 80 at 1°, 56 at 26°). The ineffectiveness of cyclohexane is attributable to its lack of a tertiary carbon.

The difference at 2390 calories corresponds to less than 2% of *cis*-decalin at equilibrium at 26°. Thus the isomerization of *cis*-decalin to *trans*-decalin is practically irreversible at this temperature. The isomerization of *trans*-decalin gives *trans*-2,6-dimethylbicyclo[3,3,0]octane and other low-boiling naphthenes,[9] which might be expected to inhibit side reactions during isomerization of 2,2,4-trimethylpentane. However, no *trans*-2,6-dimethylbicyclo[3,3,0]octane or other low-boiling naphthenes were found in this work, which indicates that the conversion of *trans*-decalin is very much slower than the isomerization of *cis*-decalin to *trans*-decalin.

Discussion

General Mechanism.—The fact that propane was not produced during the isomerization of 2,2,4-trimethylpentane under the conditions used here indicates that the isopentane, which was always produced, was not formed as a result of a breakdown of an eight-carbon fragment

$$C_8 \longrightarrow C_5 + C_3 \qquad (1)$$

Such a breakdown must be expected to yield some propane, inasmuch as propyl chlorides yield propane in the presence of paraffins and aluminum halides,[10] and propylene yields propane during $AlCl_3{\cdot}CH_3OH$-catalyzed alkylation of isobutane.[11] The isopentane must have been formed from at least a nine-carbon intermediate. Similarly, because neither ethane nor methane was produced, the hexanes and heptanes must have been formed from intermediates having at least ten and eleven carbons, respectively. *It appears that, under mild conditions, breakdown of paraffinic reaction intermediates is limited to production of fragments with at least four carbons.*

The isobutane may result, at least in part, from a breakdown of the 2,2,4-trimethylpentane, or C_8 intermediates derived therefrom, which would also give isobutylene

$$C_8H_{18} \longrightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_8 \qquad (2)$$

In the presence of benzene, apparently the isobutylene alkylates the benzene, for *t*-butylbenzene is produced.[12] In the absence of benzene or other alkylatable hydrocarbon, the isobutylene presumably alkylates 2,2,4-trimethylpentane and other octanes derived from it by isomerization (*cf.* reference 1b)

$$i\text{-}C_4H_8 + C_8H_{18} \longrightarrow C_{12}H_{26} \qquad (3)$$

Such a paraffin alkylation reaction, as is well understood, would not give solely a dodecane, for the dodecane (or twelve-carbon intermediate) is subject to secondary reactions of alkylation, rearrangement and dealkylation. In particular, a part of the twelve-carbon intermediate, most likely after intramolecular rearrangements, may break-down to two six-carbon fragments, or to one five- and one seven-carbon fragment, and these account for at least a part of the isopentane, hexanes and heptanes found in the reaction product. In addition, a part of the twelve-carbon intermediate may be further alkylated to a sixteen-carbon intermediate, and a part of this, most likely after intramolecular rearrangements, may break down to a variety of fragments with from five to eleven carbons.

Although these additional reactions must be admitted, it is noteworthy that reactions 2 and 3 alone plus the isomerization reaction

$$C_8H_{18} \longrightarrow C_8H_{18}' \qquad (4)$$

can be made to account for 97% of the 2,2,4-trimethylpentane converted, simply by the use of stoichiometry and the observed average values, 18% isobutane and 26% isomeric octanes.

In the presence of a naphthene, a part of the isobutylene formed in reaction 2 may react with the naphthene; tentatively

$$i\text{-}C_4H_8 + C_nH_{2n} \longrightarrow C_{n+4}H_{2n+8} \qquad (5)$$

Consequently, the amount of 2,2,4-trimethylpentane and other octanes consumed by reaction 3 is correspondingly reduced, and with them is reduced the amount of by-products formed as a result of reaction 3 *et seq.* Apparently a naphthene does not inhibit reaction 2 (neither *cis*-decalin nor methylcyclopentane reduced the ultimate yield of isobutane); and consequently, it would not be expected to inhibit reaction 1, which is analogous to reaction 2, if it occurred. Furthermore, inasmuch as about 35% of 2,2,4-trimethylpentane is consumed in producing the observed average 18% of isobutane by the uninhibited reaction 2, it follows that the ultimate yield of isomeric octanes may not

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[8] Parks and Hatton, THIS JOURNAL, **71**, 2773 (1949).

[9] Egloff, Hulla and Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1942, pp. 113–114.

[10] Nenitzescu and Dragan, *Ber.*, **66**, 1892 (1933).

[11] Schmerling, THIS JOURNAL, **68**, 275 (1946).

[12] Grosse and Ipatieff, *ibid.*, **57**, 2415 (1935).

exceed 65% (at the one temperature employed in all the experiments). As a matter of fact, in none of the experiments with an inhibitor did the ultimate yield of isomeric octanes exceed about 65%.

Reaction 5 is certainly an oversimplification of the reaction between isobutylene and a naphthene. Indeed, the reaction between isobutylene and methylcyclopentane in the presence of 100% sulfuric acid has been studied in some detail.[13] A considerable part of the reaction comprises hydrogen transfer from methylcyclopentane to isobutylene, forming dicyclic saturated hydrocarbons and isobutane

$$i\text{-}C_4H_8 + C_6H_{12} \longrightarrow i\text{-}C_4H_{10} + C_6H_{10} \quad (6)$$

$$C_6H_{10} + C_6H_{12} \longrightarrow C_{12}H_{22} \quad (7)$$

Such hydrogen transfer may account for at least a part of the increase in ultimate yield of isobutane in the presence of methylcyclopentane (Table I). A minor part of the reaction between methylcyclopentane and isobutylene, and a major part of the reaction between methylcyclopentane and *n*-butenes, in the presence of 100% sulfuric acid, was the formation of ten-carbon polyalkylcyclopentanes and polyalkylcyclohexanes.[13]

As part of the present investigation, in order to learn of the fate of the methylcyclopentane, the C_9^+ materials from several 2,2,4-trimethylpentane–methylcyclopentane experiments were combined and fractionated. About 75% distilled at 161–171° and about 15% distilled at about 220–240°, giving a distillation curve very similar to that of the product from methylcyclopentane and *n*-butenes in the presence of 100% sulfuric acid (Fig. 1, reference 13), and indicating the presence of ten-carbon monocyclic and twelve-carbon dicyclic naphthenes. The several fractions distilling at 161–171° were separately dehydrogenated by passage over a 7% platinum-on-alumina catalyst at about 250°[13] and gave hydrogen corresponding to contents of 25–53% (44% in all) of polyalkylcyclohexanes. Infrared and ultraviolet spectrophotometric examination of the dehydrogenated fractions indicated many different polyalkylbenzenes, including *o*-cymene and *m*-cymene (but not *p*-cymene) and 1-ethyl-3,5-dimethylbenzene.

In extending the mechanism outlined above to paraffins with less than eight carbons, it is noteworthy that by-products with less than four carbons are usually absent.[1] In this circumstance, all by-products must result from intermediates with at least eight carbons, which can only be formed by alkylation of the paraffin with olefin introduced into the reaction mixture or formed from the paraffin by hydrogen transfer to olefin introduced into the reaction mixture. (It has been found that traces of olefin or olefin-generating substances are essential to low-temperature paraffin isomerization by aluminum halides.[1g]) Provided the alkylation is much faster than the isomerization, only a small amount of olefin may result in conversion of a large amount of paraffin to by-products, for the first-formed alkylation product, on undergoing dealkylation, regenerates olefin. A naphthene may inhibit the formation of by-products, then, by preferentially reacting with olefins; and since only a small amount of olefin may be parent to a large amount of by-products, only a small amount of naphthene need be consumed in inhibiting the formation of these by-products.

With paraffins with more than eight carbons, there become an increasing number of possible dealkylation reactions like 2 above, which are not inhibited by naphthenes. Consequently, naphthenes are increasingly less effective in inhibiting side reactions during paraffin isomerization as the number of carbon atoms in the paraffin increases.[2c]

Butane isomerization presents a special case. Alkylation of butane with butylene (present as impurity or formed by hydrogen transfer from the butane) gives first an eight-carbon product which, in principle, can only dealkylate so as to regenerate four-carbon fragments. Only by further alkylation of the eight-carbon first-formed alkylation product, can there be produced intermediates capable of breaking down to other than four-carbon fragments. Inasmuch as the further alkylation is unlikely in the presence of a vast excess of butane, butane isomerization is practically free of side reactions.[1g]

Details of Mechanism and Kinetics.—According to the mechanism outlined above, an amount of naphthene is consumed, by reactions such as 5, 6 and 7, in inhibiting side reactions during isomerization of 2,2,4-trimethylpentane. Let this amount of naphthene be given by $(N_0 - N' - N)$ where N_0 is the initial mole fraction of naphthene, N' is the final mole fraction of isomeric naphthene, and N is the final mole fraction of naphthene. Then the amount of isobutylene consumed by the naphthene in reactions such as 5, 6, and 7 may be $n(N_0 - N' - N)$, where n is a constant. (If the reaction between isobutylene and the naphthene were described solely by reaction 5, n would be unity; but, in general, n may be different from unity.) The amount of 2,2,4-trimethylpentane *not* consumed by isobutylene in reaction 3 may then be $mn(N_0 - N' - N)$, where m is a constant. (Again, if reaction 3 were the sole source of by-products, m would be unity; but, in general, m also may be different from unity.) The use of constants, m and n, supposes a simple stoichiometry governing reactions such as 5–7 and reaction 3. Indirect evidence for such a simple stoichiometry lies in the data of Expts. 1–10, Table I, wherein the distribution of products from 2,2,4-trimethylpentane is substantially independent of conversion.

Now either (I) an amount of 2,2,4-trimethylpentane, $mn(N_0 - N' - N)$, is not converted at all in the presence of the naphthene, in which case the percentage ultimate yield of isomeric octanes, z, will be given by

$$\begin{aligned} z &= z_0((c_0 - c + mn(N_0 - N' - N))/(c_0 - c)) \\ &= z_0 + z_0mn(N_0 - N' - N)/(c_0 - c) \quad \text{(I)} \end{aligned}$$

where z_0 is the percentage ultimate yield of isomeric octanes in the absence of a naphthene, and c_0 and c are the initial and final mole fractions of 2,2,4-trimethylpentane, respectively; or (II) an amount of 2,2,4-trimethylpentane, $mn(N_0 - N' - N)$, is isomerized in the presence of a naphthene, *instead of* being converted to by-products by reaction 3, in which case the total conversion of 2,2,4-tri-

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[13] Pines and Ipatieff, THIS JOURNAL, **67**, 1631 (1945).

methylpentane is unchanged by the presence of a naphthene, and the percentage ultimate yield of isomeric octanes will be given by

$$z = z_0 + 100mn(N_0 - N' - N)/(c_0 - c) \qquad \text{(II)}$$

In any case, it is apparent that a knowledge of the kinetics of the reacting system (N, N' and c as a function of time) may permit calculation of z as a function of the initial composition (given by N_0 and c_0) and of the conversion (measured by $c_0 - c$ or $N_0 - N' - N$). With this end in view, kinetic analyses of the reacting systems, 2,2,4-trimethylpentane–*cis*-decalin and 2,2,4–trimethylpentane–methylcyclopentane, were made, as follows.

First of all, the fact that the ultimate yield of isobutane from 2,2,4-trimethylpentane in the presence of a naphthene was the same (within a factor about 1.2) as that in the absence of a naphthene, while the ultimate yield of isomeric octanes increased by a maximum factor about 2.5, is evidence in favor of alternative (II) above, rather than (I). In view of the general mechanism outlined above, if (I) were correct, the ratio of isobutane to isomeric octanes would be constant. The relatively slight increase in ultimate yield of isobutane in the presence of a naphthene, especially methylcyclopentane, is attributable, at least in part, to the hydrogen transfer reaction 6.

Thus the total conversion, or the rate of conversion, of 2,2,4-trimethylpentane is independent of the inhibition of side reactions by a naphthene—the side reactions are replaced by isomerization. A mechanism in accord with this conclusion is (*cf.* general mechanism above, and reference 1g)

$$R^+ + C_8H_{18} \xrightarrow[k]{\text{slow}} RH + C_8H_{17}^+ \qquad (8)$$

$$C_8H_{17}^+ \xrightarrow{\text{fast}} C_8H_{17}^{+\prime}\ (R^+)(\text{isomerization}) \qquad (9)$$

$$C_8H_{17}^+ \xrightarrow{\text{fast}} t\text{-}C_4H_9^+\ (R^+) + \text{i-}C_4H_8 \qquad (10)$$

$$C_8H_{17}^+ + i\text{-}C_4H_8 \xrightarrow{\text{fast}} C_{12}H_{25}^+\ (R^+) \qquad (11)$$

$$C_8H_{17}^{+\prime} + i\text{-}C_4H_8 \xrightarrow{\text{fast}} C_{12}H_{25}^{+\prime}(R^+) \qquad (12)$$

where C_8H_{18} is $(CH_3)_3CCH_2CH(CH_3)_2$, $C_8H_{17}^+$ is $(CH_3)_3CCH_2C^+(CH_3)_2$, $C_8H_{17}^{+\prime}$ represents isomeric octyl carbonium ions derived from $C_8H_{17}^+$ by H: and CH_3: shifts, $C_{12}H_{25}^+$ is $(CH_3)_3CCH_2C(CH_3)_2CH_2C^+(CH_3)_2$, and $C_{12}H_{25}^{+\prime}$ represents isomeric dodecyl carbonium ions. Additional reactions, such as are mentioned in the general mechanism, are needed to produce the isopentane, hexanes, heptanes and other paraffins formed in the absence of a naphthene.

In the presence of a naphthene, for example, methylcyclopentane

$$R^+ + C_6H_{12} \xrightarrow{\text{slow}} RH + C_6H_{11}^+ \qquad (13)$$

$$C_6H_{11}^+ \xrightarrow{\text{fast}} C_6H_{11}^{+\prime}\ (R^+)\ (\text{isomerization}) \qquad (14)$$

$$C_6H_{11}^+ + i\text{-}C_4H_8 \xrightarrow{\text{fast}} C_{10}H_{19}^+\ (R^+) \qquad (15)$$

where $C_6H_{11}^+$ is the tertiary carbonium ion corresponding to methylcyclopentane. Undoubtedly, also (*cf.* reference 13)

$$C_{10}H_{19}^+ \xrightarrow{\text{fast}} C_{10}H_{19}^{+\prime}\ (R^+)(\text{isomerization}) \qquad (16)$$

but this is not pertinent.

Summarizing, reaction 8 is slow and rate-controlling, its rate independent of the presence of a naphthene, other things being equal (but see below); reaction 11 robs from reactions 9 and 10; reaction 12, in particular, destroys intermediates which would otherwise give isomeric octanes; in the presence of a naphthene, reaction 15 replaces, in part, reactions 11 and 12. Replacement of reaction 11 by 15 would be expected to increase the extents of both reactions 9 and 10, and may account for some of the increase in the ultimate yields of both isobutane and isomeric octanes in the presence of a naphthene; replacement of reaction 12 by 15 would be expected to increase only the yield of isomeric octanes. Inasmuch as the yield of isomeric octanes is increased more than that of isobutane, it appears that reaction 12 occurs to a greater extent than reaction 11. This conclusion is in agreement with the view that the "abnormal" products of alkylation of isobutane with butenes result from further reaction of *dimethylhexanes*.[14]

From rate-controlling reaction 8, and, for simplicity, neglecting the reverse reaction

$$dc/dt = -k(R^+)c$$

Under steady state conditions

$$d(R^+)/dt = 0 \text{ and } (R^+) = \text{a constant}$$

Therefore

$$dc/dt = -k'c$$

More generally, however

$$dc/dt = -kf_1(\text{catalyst})c \qquad \text{(III)}$$

That is, the rate is also a function of catalyst concentration (or "activity").

Ex post facto evidence presented below indicates that the conversion of a naphthene in inhibiting side reactions during 2,2,4-trimethylpentane isomerization takes place *in addition to* its isomerization. That is, supposing the isomerization of the naphthene is first order in naphthene,[15] and, in addition, a part of the naphthene reacts with products from the 2,2,4-trimethylpentane, then, in the case of *cis*-decalin, neglecting, for simplicity, *cis*-decalin-forming reactions

$$dC/dt = -k'f_2(\text{catalyst})C + bf_3(\text{catalyst})f(C)dc/dt \qquad \text{(IV)}$$

and

$$dT/dt = k'f_2(\text{catalyst})C \qquad \text{(V)}$$

where C and T are the mole fractions of *cis*-decalin and *trans*-decalin, respectively, k' is a first order rate constant, and b is a constant. In the case of methylcyclopentane, its isomerization to cyclohexane appears slow compared with its conversion to other products in the presence of 2,2,4-trimethylpentane; therefore, approximately

$$dM/dt = b'f_4(\text{catalyst})f(M)dc/dt \qquad \text{(VI)}$$

where M is the mole fraction of methylcyclopentane and b' is a constant. The use of mole fractions presumes that the total number of moles remains constant during the reaction. This is true for

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[14] Schneider and Kennedy, paper presented before the Petroleum Division, ACS Meeting, Chicago, Ill., September, 1950.

[15] *Cf.* Seyer and Yip, *Ind. Eng. Chem.*, **41**, 378 (1949).

isomerization. It is also true for reactions 2 and 5 in combination. Experimentally, it was true within the accuracy of the analyses.

It is stated above that, in principle, the rate of conversion of 2,2,4-trimethylpentane is independent of the presence of a naphthene, *other things being equal*. Actually, as inspection of the data of Table I will show, the apparent rate of conversion depended upon the presence of a naphthene, being usually less in the presence of much *cis*-decalin and greater in the presence of much methylcyclopentane. These differences may be largely owing to the fact that formation of sludge (catalyst fouling) was generally greater in the presence of *cis*-decalin and less in the presence of methylcyclopentane than in the absence of a naphthene. Furthermore, inadequate control of some variables, such as the access of oxygen, which has been shown to be a promoter of aluminum bromide-catalyzed paraffin isomerization,[10] may have been partly responsible for the general lack of regular dependence of conversion on contact time. Therefore, the experimental data are of little value for computing absolute values of rate constants, such as k and k'. However, supposing that the factors affecting conversion are all contained in the f_n (catalyst) terms in equations (III–VI) and that these several terms are actually identical, these factors and the time factor, dt, cancel out when (IV), (V), and (VI) are divided by (III), and there are obtained

$$\text{(IV)/(III)} \quad \mathrm{d}C/\mathrm{d}c = aC/c + bf(\mathrm{C}) \qquad \text{(VII)}$$

$$\text{(V)(III)} \quad \mathrm{d}T/\mathrm{d}c = aC/c \qquad \text{(VIII)}$$

$$\text{(VI)(III)} \quad \mathrm{d}M/\mathrm{d}c = b'f(\mathrm{M}) \qquad \text{(IX)}$$

where $a = k'/k$, the ratio of the specific rate of isomerization of *cis*-decalin to the specific rate of conversion of 2,2,4-trimethylpentane.

Equations (VII) and (IX) were integrated for three cases, $f(\mathrm{C}) = C^0 = 1$ or $f(\mathrm{M}) = M^0 = 1$, $f(\mathrm{C}) = C^{1/2}$ or $f(\mathrm{M}) = M^{1/2}$ and $f(\mathrm{C}) = C$ or $f(\mathrm{M}) = M$. For Case I, $f(\mathrm{C}) = C^0 = 1$ or $f(\mathrm{M}) = M^0 = 1$, integration of equation (VII) gives

$$C = \left(C_0 + \frac{bc_0}{(a-1)}\right)\left(\frac{c}{c_0}\right)^a - \frac{bc}{(a-1)} \qquad \text{(X)}$$

where c_0 and C_0 are the initial mole fractions of 2,2,4-trimethylpentane and *cis*-decalin, respectively; and integration of equation (IX) gives

$$M = M_0 + b'(c - c_0) \qquad \text{(XI)}$$

where M_0 is the initial mole fraction of methylcyclopentane.

For Case II, $f(\mathrm{C}) = C^{1/2}$ or $f(\mathrm{M}) = M^{1/2}$, integration of equation (VII) gives

$$C = \left[\left(C_0^{1/2} + \frac{bc_0}{(a-2)}\right)\left(\frac{c}{c_0}\right)^{a/2} - \frac{bc}{(a-2)}\right]^2 \qquad \text{(XII)}$$

and integration of equation (IX) gives

$$M = [M_0^{1/2} + b'(c - c_0)/2]^2 \qquad \text{(XIII)}$$

For Case III, $f(\mathrm{C}) = C$ or $f(\mathrm{M}) = M$, integration of equation (VII) gives

$$C = C_0(c/c_0)^a e^{b(c-c_0)} \qquad \text{(XIV)}$$

and integration of equation (9) gives

$$M = M_0 e^{b'(c-c_0)} \qquad \text{(XV)}$$

Substituting for C in equation (VIII) its equivalent from equation (X), (XII) or (XIV), and integrating gives (for a reaction mixture initially containing no *trans*-decalin) for Case I

$$T = \frac{ab(c - c_0)}{(a-1)} - \left(C_0 + \frac{bc_0}{(a-1)}\right)\left(\frac{(c^a - c_0^a)}{c_0^a}\right) \qquad \text{(XVI)}$$

for Case II

$$T = -\left(C_0^{1/2} + \frac{bc_0}{(a-2)}\right)^2\left(\frac{c^a - c_0^a}{c_0^a}\right) + \left(\frac{4ab}{(a^2-4)c_0^{a/2}}\right)\left(C_0^{1/2} + \frac{bc_0}{(a-2)}\right)(cc^{a/2} - c_0c_0^{a/2}) - \frac{ab^2(c^2 - c_0^2)}{2(a-2)^2} \qquad \text{(XVII)}$$

and for Case III (and only for integral values of a)

$$T = -\frac{aC_0}{b^a c_0^a e^{bc_0}}\left[e^{bc}\sum_{n=0}^{a-1}(-1)^n\frac{(a-1)!}{(a-1-n)!}(bc)^{(a-1-n)}\right]_{c_0}^{c} \qquad \text{(XVIII)}$$

Equations (II) and (X) through (XVII) and the data of Expts. C20 and M34 were used to calculate theoretical curves relating z, the percentage ultimate yield of isomeric octanes from 2,2,4-trimethylpentane, and C_0 or M_0, the initial mole fraction of *cis*-decalin or methylcyclopentane, respectively. Use of equation (XVIII) was too laborious and was replaced by an approximate method described below. The Expts. C20 and M34 product compositions were converted to mole fractions on the approximation that each product contained the same number of moles as the charge. The small amount of cyclohexane in the product of Expt. M34 was treated as methylcyclopentane. The steps in calculation of the theoretical curves were as follows:

1. Evaluation of the constants, a, b, b' and mn (equation (II)): In Case I, $b = (C_0 - C - T)/(c_0 - c)$ and $b' = (M_0 - M)/(c_0 - c)$. Evaluation of b in this way from the data of Expt. C20 gave $b = 0.156$; evaluation of b' from the data of Expt. M34 gave $b' = 0.39$. The above value of b and the data of Expt. C20 were then substituted into equation (X) for the evaluation of a and gave $a = 7.6$. In Cases II and III, a was approximated by means of the well-known relationship

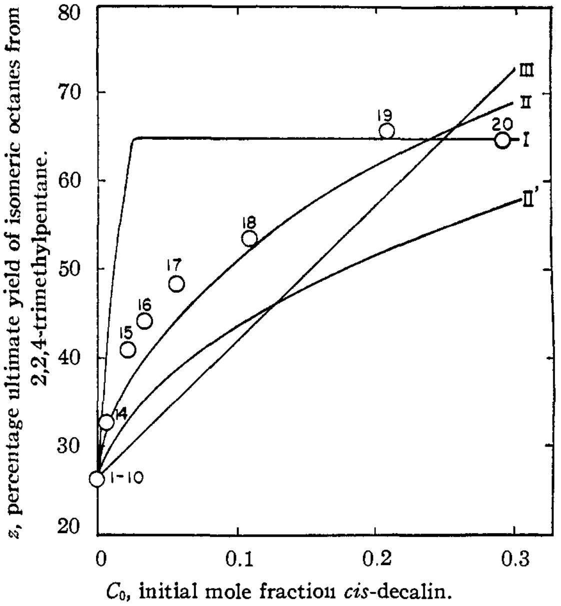
$$K/k = (\log C/C_0)/(\log c/c_0) \qquad \text{(XIX)}$$

derivable from the rate equations (III) and (XX), below

$$\mathrm{d}C/\mathrm{d}t = -Kf_1(\text{catalyst})C \qquad \text{(XX)}$$

which is based upon the approximation that *cis*-decalin is wholly converted in first order reactions with a total rate constant, K. Than $a = ZK/k$, where Z is that fraction of the converted *cis*-decalin that was isomerized to *trans*-decalin. Evaluation of a in this way from the data of Expt. C20 (where $Z = 0.93$) gave $a = 7.6$. This value of a and the data of Expt. C20 were then substituted into equations (XII) and (XIV) for evaluation of b, and gave, in Case II (from equation (XII)), $b = 0.39$, and in Case III (from equation (XIV)), $b = 0.89$. In Case II, $b' = 1.06$ (evaluated from equation (XIII) and the data of Expt. M34). In Case III, $b' = 1.29$ (evaluated from equation (XV) and the data of Expt. M34). In all cases,

mn = 2.5 when *cis*-decalin was the inhibitor (evaluated from equation (II) and the data of Expt. C20), and mn = 0.95 when methylcyclopentane was the inhibitor (evaluated from equation (II) and the data of Expt. M34).



Fig, 1.—Aluminum bromide isomerization of 2,2,4-trimethylpentane in the presence of *cis*-decalin: Curves I, II and III: calculated for 10% conversion of 2,2,4-trimethylpentane; Curve II': calculated for 20% conversion of 2,2,4-trimethylpentane. Experimental points: 8.5–16.5% (average 11.3%) conversion of 2,2,4-trimethylpentane. Numbers designate Expts. (Table I).

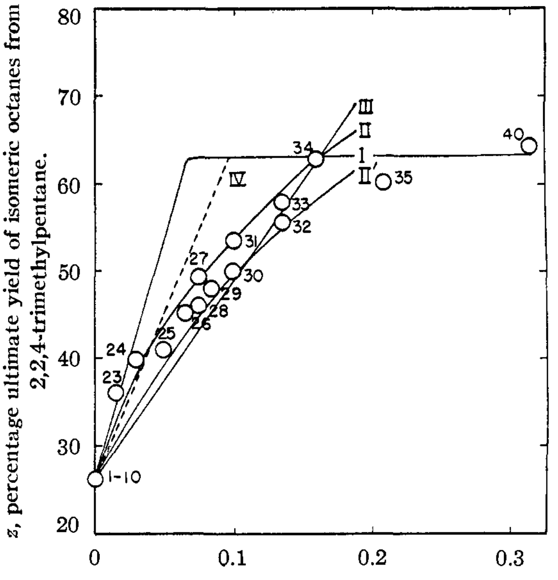


Fig. 2.—Aluminum bromide isomerization of 2,2,4-trimethylpentane in the presence of methylcyclopentane: Curves I, II and III: calculated for 18% conversion of 2,2,4-trimethylpentane; Curve II': calculated for 35% conversion of 2,2,4-trimethylpentane; Curve IV: hypothetical for irreversible isomerization of 2,2,4-trimethylpentane. Experimental points: 10.7–23.2% (average 17.6%) conversion of 2,2,4-trimethylpentane. Numbers designate Expts. (Table I).

2. Calculation of C and T (or M) for a number of values of C_0 (or M_0) and c_0 (equals $1 - C_0$ or $1 - M_0$) and for assigned conversions of the 2,2,4-trimethylpentane (10% and 20% in the case of *cis*-decalin inhibition; 18% and 35% in the case of methylcyclopentane inhibition): Then the amount of *cis*-decalin or methylcyclopentane consumed in inhibiting side reactions of the 2,2,4-trimethylpentane was $(C_0 - C - T)$ or $(M_0 - M)$, respectively.

3. Calculation of z, the percentage ultimate yield of isomers from 2,2,4-trimethylpentane by means of equation (II).

In Case III, where the use of equation (XVIII) was impracticable, the amount of *cis*-decalin consumed in inhibiting side reactions of the 2,2,4-trimethylpentane was approximated as $(C_0 - C - T) = b(c_0 - c)(C_0 + C)/2$, which is an approximate solution of the differential equation

$$\mathrm{d}C/\mathrm{d}c = bC$$

which is that part of equation (VII) dealing with inhibition.

Calculated curves relating z and C_0, and z and M_0, are compared with experimental data in Figs. 1 and 2. Calculated curves relating M and M_0 are compared with experimental data in Fig. 3. Experimental points for Fig. 3 were obtained from the data of Expts. 23–40 (Table I) on the approximation that each product contained twice as much hexanes and heptanes as isopentane (*cf.* Expts. 1–10); the methylcyclopentane–cyclohexane content was then obtained by difference, and cyclohexane was considered as methylcyclopentane.

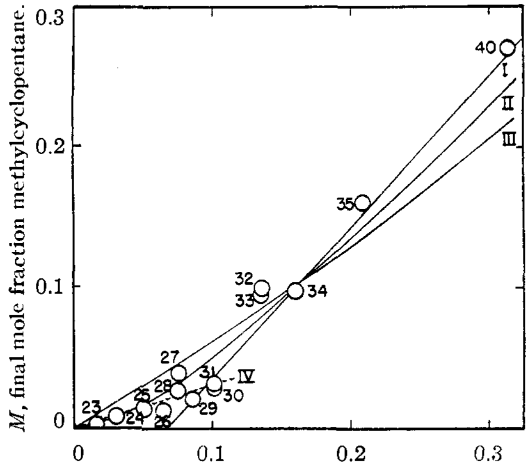


Fig. 3.—Conversion of added methylcyclopentane during aluminum bromide isomerization of 2,2,4-trimethylpentane. Curves I, II and III: calculated for 18% conversion of 2,2,4-trimethylpentane; Curve IV: hypothetical for irreversible isomerization of 2,2,4-trimethylpentane. Experimental points: 10.7–23.2% (average 17.6%) conversion of 2,2,4-trimethylpentane. Numbers designate Expts. (Table I).

The figures show that, when the initial mole fraction of naphthene was high enough to effect maximum inhibition, the naphthene was consumed by a reaction that was zero order in naphthene.

This is understandable in terms of the mechanism outlined above, for the rate-controlling step for interaction of paraffin and naphthene is a decomposition of the paraffin producing olefin. However, when the initial mole fraction of naphthene is below that required to effect maximum inhibition, the naphthene-consuming reaction appears to be half-order in naphthene. (In Fig. 2, the points of Expts. 23–33 fit Curve II with an average deviation of 2.1 percentage units, while they fit Curve III with an average deviation of 3.9 percentage units.) One possible explanation of this is that, under these conditions, there is a competition for olefin between paraffin and naphthene, each competing reaction being first-order with respect to the saturated hydrocarbon; then the observed nonlinear relationship between z and C_0 (or M_0) may be a result of an approach to an equilibrium among octanes augmenting 2,2,4-trimethylpentane-forming reactions which were neglected, for the sake of simplicity, in the mathematic analysis, accompanied by an irreversible sequence of reactions 2 and 5. On this point of view, the broken lines in Figs. 2 and 3 (Curve IV) illustrate relationships hypothesized for a first order reaction of methylcyclopentane and irreversible isomerization of 2,2,4-trimethylpentane.

In the figures, deviations of experimental points from calculated curves are partly attributable to differences between experimentally obtained conversions and the 2,2,4-trimethylpentane conversion selected in calculating each curve. Since naphthene is consumed in inhibiting side reactions as the isomerization progresses, its concentration, and hence its effectiveness as an inhibitor, decreases as the conversion increases. If, in addition, the naphthene simultaneously isomerizes or is otherwise converted rapidly to a substance ineffective as an inhibitor, as is especially so with *cis*-decalin, the decrease in ultimate yield of isomeric octanes with conversion will be more marked. Thus, in Fig. 1, pertaining to *cis*-decalin, there is a greater difference between the curves calculated for 10 and 20% conversion than there is between the curves calculated for 18 and 35% conversion in Fig. 2, pertaining to methylcyclopentane. However, the actually observed decrease in ultimate yield of isomeric octanes with conversion, in Expts. 35–39, for example, is much greater than can be accounted for simply by a spending of the naphthene. This, too, appears to be a result of an approach to an equilibrium among octanes, accompanied by an irreversible sequence of reactions, 2 and 5; for most of the 2,2,4-trimethylpentane converted in the presence of much naphthene can be accounted for as products of isomerization and of reactions 2 and 5.

Ex post facto evidence for the correctness of the form of equation (IV), that is, that a naphthene is consumed in inhibiting side reactions during 2,2,4-trimethylpentane isomerization *in addition to*, rather than *instead of*, its isomerization, comes from direct experimental comparison of the rates of isomerization of *cis*-decalin and methylcyclopentane. The constant, a, is identical with k'/k, the ratio of the specific rates of isomerization of *cis*-decalin and of total conversion of 2,2,4-trimethylpentane. Another constant, a', may now be defined as k''/k, the ratio of the specific rates of isomerization of methylcyclopentane and of total conversion of 2,2,4-trimethylpentane. While the amount of isomerization of methylcyclopentane was small and was neglected in making the above correlations, a' may be approximated in a manner analogous to that used for approximating a for Cases II and III; that is, equation (XXI)

$$K'/k = (\log M/M_0)/(\log c/c_0) \qquad \text{(XXI)}$$

analogous to equation (XIX), is derivable from the rate equations (III) and (XXII), below

$$\mathrm{d}M/\mathrm{d}t = K'f_1(\text{catalyst})M \qquad \text{(XXII)}$$

which is analogous to equation (XX) and is based on the approximation that methylcyclopentane is wholly converted in first order reactions with a total rate constant, K'. Then $a' = Z'K'/k$, where Z' is that fraction of the converted methylcyclopentane that is isomerized to cyclohexane. Evaluation of a' in this way from the data of Expt. M34 (where $Z' = 0.066$) gave $a' = 0.16$; evaluation of a' from the data of Expt. M40 (where $Z' = 0.13$) gave $a' = 0.13$. Since $a = 7.6$, $a/a' = k'/k'' = 48$ or 58; that is, the specific rate of isomerization of *cis*-decalin is predicted to be 48–58 times the specific rate of isomerization of methylcyclopentane. If, however, the conversion of a naphthene in inhibiting side reactions subtracts from its isomerization, then the ratio of the specific rates of isomerization of *cis*-decalin and methylcyclopentane would be given by K/K' and would be predicted to have the value 3.4–8.2.

For the direct experimental determination of the ratio of the specific rates of isomerization, of *cis*-decalin and methylcyclopentane, these hydrocarbons, in admixture, were isomerized with aluminum bromide by a procedure identical to that used in the 2,2,4-trimethylpentane experiments. In such a reaction mixture

$$\mathrm{d}C/\mathrm{d}t = -k_Cf_5(\text{catalyst})C + k_Tf_6(\text{catalyst})T \qquad \text{(XXIII)}$$

and

$$\mathrm{d}M/\mathrm{d}t = -k_Mf_7(\text{catalyst})M + k_Hf_8(\text{catalyst})H \qquad \text{(XXIV)}$$

where k_C and k_M are the first order rate constants (specific rates) of isomerization of *cis*-decalin to *trans*-decalin and of methylcyclopentane to cyclohexane, respectively; k_T and k_H are the rate constants of the corresponding reverse reactions; C, T and M have the same meaning as before; and H is the mole fraction of cyclohexane.

Starting with a mixture containing only *cis*-decalin and methylcyclopentane, if the conversion of each compound to its isomer be low, that is, if the system is far from equilibrium, the second term on the right-hand side of equations (XXIII) and (XXIV) may be neglected in comparison with the first terms, and

$$\mathrm{d}C/\mathrm{d}t = -k_Cf_5(\text{catalyst})C \qquad \text{(XXV)}$$

and

$$\mathrm{d}M/\mathrm{d}t = -k_Mf_7(\text{catalyst})M \qquad \text{(XXVI)}$$

Dividing (XXV) by (XXVI), and assuming $f_5(\text{catalyst}) = f_7(\text{catalyst})$,

$$\text{(XXV)(XXVI)} \quad \mathrm{d}C/\mathrm{d}M = k_CC/k_MM \qquad \text{(XXVII)}$$

Integrating (XXVII) gives

$$k_C/k_M = (\log C/C_0)/(\log M/M_0) \quad \text{(XXVIII)}$$

Equation (XXVIII) and the data presented in Table IV were used to calculate k_C/k_M. The result, 46–49 (after correction by the factor, Z/Z'), is in good agreement with the 48–58 predicted from the comparison of the individual isomerization rates with the total rate of conversion of 2,2,4-trimethylpentane. That is, k_C/k_M is more nearly equal to k'/k'' than to K/K', which means that the conversion of a naphthene in inhibiting side reactions is added to, rather than subtracts from, its isomerization. Apparently reaction (13), presumably rate-controlling as far as conversion of naphthene is concerned, is more extensive in the presence of reacting 2,2,4-trimethylpentane than in its absence. This conclusion is analogous to the fact that isoparaffin alkylation is absolutely and relatively faster than isoparaffin isomerization, although for both reactions, formation of a carbonium ion from the isoparaffin is probably rate-controlling as far as reaction of the isoparaffin is concerned.

TABLE IV

RELATIVE RATES OF ISOMERIZATION OF *cis*-DECALIN AND METHYLCYCLOPENTANE AT 26°

Expt.	41	42
$AlBr_3$, wt. % of naphthenes	10.7	10.2
Contact time, min.	435	350
Charge compn., mole fract.		
methylcyclopentane	0.914	0.919
cis-decalin	.079	.081
benzene	.007[a]	...
Product compn., mole fract.[b]		
benzene	.004	...
methylcyclopentane	.853	.825
cyclohexane	.056	.089
trans-decalin	.076	.078
cis-decalin	.0038	> .00064[c]
residue	.003	< .004[c]
sludge oil	.004	.003
k_C/k_M	49	46[d](32)[e]

[a] Impurity in the methylcyclopentane. [b] Analyses by fractional distillation, supplemented by infrared analysis in Expt. 41, by refractive index determinations in Expt. 42. [c] Not all the *cis*-decalin was distilled. [d] Assuming no *cis*-decalin in the residue. [e] Assuming balance of *cis*-decalin in the residue.

The conversion of *cis*-decalin was so great in each of the experiments in Table IV as to cast doubt on the validity of the approximation made in transforming equations (XXIII) and (XXIV) into equations (XXV) and (XXVI). Actually, the neglected term on the right-hand side of equation (XXIII) was 0.36 the term retained, at the end of Expt. 41 (and, of course, many times less during most of the Expt.), while the neglected term on the right-hand side of equation (24) was 0.008 the term retained, at the end of Expt. 41. This follows from the facts that at equilibrium at 26°, $T/C = 56$,[8] and $H/C = 7.9$.[16] That is, since at equilibrium, $k_C f_5(\text{catalyst})C = k_T f_6(\text{catalyst})T$ and $k_M f_7(\text{catalyst})M = k_H f_8(\text{catalyst})H$, $k_T f_6(\text{catalyst})/k_C f_5(\text{catalyst}) = 1/56$ and $k_H f_7(\text{catalyst}) = 1/7.9$. Therefore, at the end of Expt. 41, $k_T f_6(\text{catalyst})T/k_C f_5(\text{catalyst})C = (0.076)/(0.0038)(56) = 0.36$, and $k_H f_8(\text{catalyst})H/k_M f_7(\text{catalyst})M = (0.056)/(0.853)(7.9) = 0.008$. The proximity to the *cis*-decalin–*trans*-decalin equilibrium in the experiments of Table IV has the effect of making the observed k_C/k_M value lower than reality.

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[16] Stevenson and Morgan, THIS JOURNAL, **70**, 2773 (1948).