color was imparted to the solution. The amount of exchange was small following the first three minutes of reaction, but soon increased to a level somewhat above the maximum exhibited in the previously determined exchange curve for β-nitrostyrene (see Table I), and then decreased slowly. The strong adsorption of the nitro compound controls the reaction, reduction taking place first, and then the exchange reaction comes into prominence after the nitro compound has been reduced. The reduction and the exchange are both rapid under these conditions.

The oximes did increase the rate of exchange initially above that shown by acetic acid, but after a given level of exchange was attained the addition of more material failed to increase further the rate of exchange. The final level reached by the oximes in each case was lower than the maximum exhibited by the parent nitro compound. Since in the reduction of nitro compounds, an amine and water are also formed,[2] equimolar solutions of oxime–aniline and oxime–water in acetic acid were studied (see Table II). The oxime–aniline solution exhibited more exchange than did the oxime–water solution, although the exchange in each case was greater than that exhibited by a solution of oxime of the same concentration.

This indicates that in the reduction the α,β-unsaturated nitro compounds probably go through oxime intermediates which then increase the rate of exchange. There was sufficient methyl ethyl ketoxime present to furnish all of the hydrogen found in the gaseous phase, but for phenylacetaldoxime this was not the case so that some of the hydrogen must have come from the acetic acid. There was no color formation during the exchanges involving the oxime–acetic acid systems.

The reaction of a nitro group with hydrogen over a catalyst is greatly affected by the remainder of the molecule. The nitro group in nitromesitylene is attached to an aromatic ring which would indicate that this compound should prevent the exchange as does nitrobenzene. However, the two methyl groups *ortho* to the nitro group reduce the resonance interaction of the nitro group with the benzene ring. Thus the kinetics of the catalytic hydrogenation of nitromesitylene are somewhat different from those for the hydrogenation of nitrobenzene. The lack of interaction of the nitro group with the ring results in a nitro group which in reactivity somewhat resembles one found in an aliphatic compound. Nitromesitylene in solutions of low concentrations decreased the rate of exchange, resembling nitrobenzene, but in solutions of higher concentrations nitromesitylene failed to change further the rate of exchange.

Although the behavior of aniline is similar to that of nitromesitylene different considerations apply. The hydrogenation of aniline over Adams platinum catalyst in acetic acid is zero order with respect to aniline, as is the hydrogenation of nitrobenzene. Aniline, however, is less strongly adsorbed than is nitrobenzene and hence has less effect on the exchange. The fact that nitrobenzene undergoes hydrogenation initially to form aniline which is then desorbed has been shown in previous studies. When all of the nitrobenzene is hydrogenated, the aniline is readsorbed and the benzene ring hydrogenated to give cyclohexylamine.

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KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM THE HOUDRY PROCESS CORPORATION]

Reactions of C_5–C_8 Paraffins with a Silica–Alumina Cracking Catalyst.[1] I. Isomerization

BY S. G. HINDIN, A. G. OBLAD AND G. A. MILLS

RECEIVED JULY 23, 1954

The interaction of C_5–C_8 paraffins with a silica–alumina cracking catalyst at 100–150° was studied by measurement of isomerization and cracking. It was found that two factors are critical if isomerization and cracking are to occur; one, the degree of catalyst hydration, and two, the structure of the hydrocarbon molecule. Small amounts of water added to the highly dehydrated catalyst activate, and larger amounts inactivate the catalyst. Only paraffin molecules possessing a tertiary carbon atom undergo reaction at these conditions; monomethyl and dimethyl paraffins (with methyl groups on separate carbon atoms) show extensive isomerization, whereas normal paraffins and those molecules containing only the quaternary structure show no reaction. With highly branched structures, cracking becomes the predominant reaction, with isobutane the major product.

It has long been observed that cracking catalysts are not isomerization catalysts for paraffins at the usual cracking conditions. For example, Good, Voge and Greensfelder[2] found, from studying the cracking of the isomeric hexanes at 550° and 0.5 LHSV, direct isomerization of hexanes was of small importance, for only in the reaction with 2,3-dimethylbutane was isomerization apparent (approximately 6% of charge). Unpublished data from this Laboratory and data given by Hansford[3] on the reaction of normal butane at cracking conditions similarly disclosed no evidence of isomerization. Pines, in his chapter in "Advances in Catalysis,"[4] stated, "The isomerization in the presence of the oxide catalysts proceeds usually at high temperatures and in the presence of hydrogen.

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[1] Presented before the Petroleum Division, American Chemical Society, March, 1953.

[2] G. M. Good, H. H. Voge and B. S. Greensfelder, *Ind. Eng. Chem.*, **39**, 1032 (1947).

[3] R. C. Hansford, *ibid*., **39**, 849 (1947).

[4] H. Pines, *Advances in Catalysis*, Vol. I (1948).

These catalysts have no significant importance."

The reason why highly active cracking catalysts are not isomerization catalysts has not been clear inasmuch as isomerization, like cracking, is an acid-catalyzed reaction and proceeds through a typical polarized complex or carbonium ion mechanism. Obviously, acidity, though a necessary condition, is not a sufficient condition, as is shown by the fact that sulfuric acid will isomerize only methylparaffins, whereas aluminum halide co-catalyzed with hydrogen halide will isomerize both normal and isoparaffins. In the present work, it has been found that silica–alumina catalyst is indeed capable of isomerizing paraffins to a considerable degree and as will be shown, that the exact condition of hydration of the catalyst is critical to its ability to catalyze the isomerization reaction.

It has been pointed out that studies of hydrocarbon–cracking catalyst interaction at the temperature at which cracking is usually carried out, 425–500°, are made difficult by the complex products which result from the numerous consecutive and competitive reactions. Therefore in the present study, temperatures of 100–150° have been used, where side reactions are very greatly minimized and consequently the major reactions being studied stand out in sharper detail.

Experimental

Reagents. 1.—The following paraffins were used, though not all were studied for both isomerization and exchange.

Normal
n-Hexane
n-Heptane

Dimethyl
2,2-Dimethylbutane
2,3-Dimethylbutane
2,3-Dimethylpentane
2,4-Dimethylpentane
3,3-Dimethylpentane
2,5-Dimethylhexane

Monomethyl
2-Methylbutane
2-Methylpentane
2-Methylhexane
3 Methylhexane
2-Methylheptane

Trimethyl
2,2,3-Trimethylbutane
2,2,4-Trimethylpentane
2,3,3-Trimethylpentane
2,3,4-Trimethylpentane

All were N.B.S. Standard Samples and were used without further treatment except for removal of dissolved gases in one or two samples. This removal was carried out in the usual fashion, by alternate freezing and melting, with pumping on the cooled sample.

2.—The catalyst was prepared by adding known amounts of water to Houdry Type S-45 (a commercial synthetic silica–alumina cracking catalyst) previously evacuated under controlled conditions.[5]

Technique.—All reactions were carried out using high-vacuum technique; fresh samples of hydrocarbon and catalyst were taken for each experiment. The procedure used was as follows: a weighed amount of catalyst was dried (at either 315 or 525°) under constant vacuum ($<10^{-3}$ mm.) for one hour. Under these conditions the catalyst was found earlier[5] to contain 1.1 and 0.7% "structural D_2O," respectively. The catalyst was cooled to liquid nitrogen temperature, predetermined amounts of deuterium oxide and hydrocarbon were distilled onto the cooled catalyst, and the tube containing the reactants sealed off, with evacuation during sealing. The tube was heated to 150° and then held at that temperature for one hour. After reaction, the hydrocarbon was desorbed into a 3 mm. side tube, by cooling the latter in liquid nitrogen. The sample was then analyzed by the mass spectrometer.

Experimental Results

1. Effect of Hydrocarbon Structure.—The variables studied in this work were (1) the effect of hydrocarbon structure on isomerization, (2) catalyst precalcination and rehydration, (3) reaction temperature and (4) effect of change of catalyst–water–hydrocarbon ratio. The experimental results are summarized in Tables I to V.

The data of Table I show that the hydrocarbon structure, at constant catalyst pretreatment, is of great importance in determining both the extent and direction of reaction. A hydrocarbon molecule will not react with the cracking catalyst in one hour at 150° unless it contains at least one tertiary carbon atom. When it does contain a tertiary carbon atom, both the hydrocarbon structure and hydrocarbon molecular weight play parts in determining the course of reaction. Specifically, the following results are found: normal paraffins show no isomerization; monomethylparaffins show extensive isomerization; dimethylparaffins, when the methyl groups are on separate carbon atoms, show extensive isomerization; when the quaternary type structure is present, no isomerization is found; with very highly branched structures, the major reaction is cracking and because of the extensive cracking, interpretation of the isomerization data is ambiguous.

Table I

Relative Amounts of Isomerization and Cracking as a Function of Hydrocarbon Structure

Reactions carried out at 150°

Hydrocarbon	Reaction, % Isomerization	Cracking
2-MeC$_4$	0[a]	3
2-MeC$_5$	11 { 11% 3 MeC$_5$	0
2,2-Me$_2$C$_4$	0	0
2,3-Me$_2$C$_4$	9 { 7% 2MeC$_5$ 2% 3MeC$_5$	5
3,3-Me$_2$C$_5$	0	0
2,3-Me$_2$C$_5$	34 { 28% 2,4Me$_2$C$_5$ 3% 2MeC$_6$ 3% 3MeC$_6$	30
2,4-Me$_2$C$_5$	13 { 13% 2,3Me$_2$C$_5$	36
2,5-Me$_2$C$_6$	6 { 5% 2,4Me$_2$C$_6$ 1% 2,3Me$_2$C$_6$	89
2,3,3-Me$_3$C$_5$	2	97
2,2,4-Me$_3$C$_5$	3	92
2,3,4-Me$_3$C$_5$	2	94
n-C$_6$	0	0
n-C$_7$	0	0

[a] Isomerization to the "3-methyl" position would not be apparent.

Isomerization which does not involve a change in degree of branching occurs to a greater extent than isomerization which does involve such change. However, isomerization with a change in degree of branching does occur as evidenced by the finding that methylhexanes are formed in the isomerization of 2,3-dimethylpentane. (It should be noted that isomerization which involves a change in degree of branching requires in an ionic mechanism the movement of charge along the hydrocarbon

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(5) S. G. Hindin, G. A. Mills and A. G. Oblad, This Journal, **73**, 278 (1951).

chain, since to change the hydrocarbon chain length means that, at some time, the positive charge must have resided on a primary carbon atom.)

The product obtained as a gas after isomerization at these reaction conditions does not contain normal paraffins or paraffins containing a quaternary structure though both structures are thermodynamically stable at the reaction conditions. The fact that they are not found in the gaseous product means that they were never formed in any appreciable amount during reaction since both structures have been found to be relatively stable to cracking or other such reactions.

It is found that the major product of cracking is isobutane and secondarily, isopentane. If the hydrocarbon structure is such that a tertiary butyl fragment and another fragment of three or four carbon atoms can be formed by a single carbon–carbon bond cleavage, cracking becomes the predominant reaction. This product distribution appears even in those cases in which a tertiary-butyl fragment cannot be formed by a single carbon–carbon bond scission as in the case of 2,3-Me_2C_5 or 2,3,4-Me_3C_5. It is believed that in these cases, isomerization, to put a methyl group in the "2-position," first occurs and the isomer thus formed cracks to give the tertiary-butyl fragment. This would mean that the cracking reaction is fast relative to the isomerization reaction.

There is some uncertainty concerning the absolute values of the amounts of cracked and uncracked (isomerized) products. This arises from the fact that higher molecular weight hydrocarbons are sorbed to a greater extent than the lower molecular weight hydrocarbons; orienting experiments have shown that any possible change in distribution so introduced is, however, insufficient to change the general conclusions. In general, for the mono- and dimethyl paraffins, the effect of molecular weight, as seen from the data of Table I, is as follows: the six carbon isoparaffins show more isomerization than cracking; the seven carbon isoparaffins show, roughly, about equal amounts of cracking and isomerization; the eight carbon isoparaffins crack to almost the complete exclusion of isomerization.

2. Effect of Catalyst Precalcination and Rehydration.—Two variables were investigated: (1) the effect of varying the drying temperature of the catalyst, and (2) the effect of rehydration of the dried catalyst to varying water levels. Increase in drying temperature from 315 to 525° has little if any effect on the reaction, whether the reaction is isomerization or cracking. The degree of rehydration of the dried catalyst is, however, most important, as seen in Table II. With 2-methylpentane the freshly dried catalyst shows very little isomerization activity, but does become an active isomerization catalyst when rewetted with small amounts of water. With normal hexane, though the extent of reaction is quite small, the effect of water on the isomerization activity of the catalyst parallels the effect with methylpentane. In both these reactions the maximum reaction rates occur when water is added in amounts approximating 0.05 weight %, whereas, in the hydrogen exchange reaction, the maximum occurred with 0.2 to 0.3 weight % water.[5] Presumably the fact that smaller amounts of water give optimum isomerization activity may be due to the fact that the catalyst sites which are available for reaction with hydrocarbons are energetically heterogeneous and isomerization requires higher energy sites than does hydrogen exchange.

TABLE II

EFFECT OF LEVEL OF REHYDRATION OF THE DRIED CATALYST ON ISOMERIZATION ACTIVITY

Hydrocarbon	Water added to dried catalyst, wt. %	Isomerization, %	Cracking, %
2-MeC_5	0	1	0
reacn.	0.05	21	6
at	.09	15	4
100°	.26	11	0
	.64	4	0
n-C_6	0	2	3
reacn.	.06	5	5
at	.10	4	6
250°	.60	2	3

The effect of water on cracking, shown in the last column of Table II rather closely parallels the effect of water on isomerization. Here the optimum level appears to lie in the neighborhood of 0.05–0.1 weight % water, similarly to the optimum value found for isomerization. Hansford[3] has shown that with butane, at standard cracking conditions, a dried catalyst is less effective than one which has been rewetted to low levels of water content and the present data are in agreement with his results.

This effect of small amounts of water on a freshly dried cracking catalyst is of major interest for, as has been pointed out, silica–alumina catalyst which has been dried at 525° under constant high vacuum still contains about 0.7 weight % water, as water of constitution. Hence, the fact that addition of only 0.05 weight % water gives an active isomerization catalyst and a catalyst which shows increased cracking activity, must mean that the water added back at low temperatures does not become chemically equivalent to water already present as part of the catalyst structure. This conclusion is borne out by the fact that increase in catalyst drying temperature from 315 to 525° has little effect on isomerization despite the decrease in water content.

3. Effect of Variation in Reaction Temperature.—The increase in extent of reaction with increasing temperatures may be seen in Table III; as expected, both isomerization and cracking increase with increasing temperature. In general,

TABLE III

EXTENT OF REACTION AS A FUNCTION OF TEMPERATURE

Conditions: catalyst rehydrated with 0.6 wt. % H_2O.

Hydrocarbon	Reaction T, °C.	Reaction, % Isomerization	Reaction, % Cracking
2-MeC_5	100	4	0
	150	11	0
2,4-Me_2C_5	100	2	0
	150	13	36
n-C_6	150	0	0
	250	2	3

from thermodynamic considerations, cracked products should, of course, predominate in the reaction mixture with increasing temperature of reaction.

4. Effect of Change of Catalyst–Water–Hydrocarbon Ratio.—In Table IV are shown data of two types; first, varying amounts of water were added to varying weights of catalyst to give the same final water concentration, based on catalyst weight, and, secondly, a constant amount of water was added to varying weights of catalyst to give different final levels of water concentration. The amount of hydrocarbon added was constant in all experiments. Increasing the amount of catalyst containing a fixed percentage of water has little effect on the extent of reaction since the original catalyst-hydrocarbon ratio is quite large. However, varying the final water concentration of the catalyst does show a very marked effect on isomerization as has already been indicated by the data of Table II.

TABLE IV

EXTENT OF ISOMERIZATION AS A FUNCTION OF CATALYST–WATER–HYDROCARBON RATIO

Conditions: in all cases, 2.0 (gaseous) cc. of hydrocarbon was used. Reaction was for one hour at 100°.

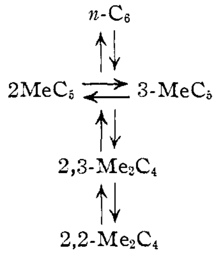
Hydrocarbon	Wt. of catalyst, g.	Wt. of water added, mg.	Isomerization, %
2-MeC_5	2.0	12.0	3
	3.0	18.0	4
	5.0	30.0	4
	1.0	14.0	0
	2 0	14.0	3
	5.0	14.0	12

COMPARISON OF SILICA–ALUMINA WITH ALUMINUM CHLORIDE AS ISOMERIZATION CATALYSTS

Silica–alumina at 150°	Aluminum chloride at 100° [6]
Normal paraffins do not isomerize	Normal paraffins do isomerize
Interconversion of the methylpentanes is rapid	Interconversion of the methylpentanes is rapid
Formation of 2,3-dimethylbutane from methylpentanes is fairly rapid	Formation of 2,3-dimethylbutane from methylpentanes is fairly rapid
Formation of 2,2-dimethylbutane from 2,3-dimethylbutane does not occur	Formation of 2,2-dimethylbutane from 2,3-dimethylbutane does occur

In the paper by Evering and Waugh[6] from which these aluminum chloride data were taken, it was found that the slow step in the over-all isomerization of normal hexane shown below (taken from that paper) is the last step and the next slowest step is the first step. The two intermediate steps, interconversion of the methylpentanes and formation of the 2,3-dimethylbutane, are more rapid than the slower steps by two orders of magnitude. This, therefore, points up the possibility that the reason why the first and last steps are not seen with silica–alumina may relate to the kinetics of the reactions and not to any factor inherent in the catalyst.

STEPS IN ISOMERIZATION OF *n*-HEXANE



Acknowledgment.—The mass spectrometric data and their analyses are due to J. Terrell. Suggestions by other staff members aided in the interpretation of the results. Permission by the Houdry Process Corporation to publish is acknowledged with appreciation.

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[6] B. L. Evering and R. C. Waugh, *Ind. Eng. Chem.*, **43**, 1820 (1951).

MARCUS HOOK, PA.

[CONTRIBUTION FROM THE HOUDRY PROCESS CORPORATION]

Reactions of C_5–C_8 Paraffins with a Silica–Alumina Cracking Catalyst.[1] II. Hydrogen Exchange

BY S. G. HINDIN, G. A. MILLS AND A. G. OBLAD

RECEIVED JULY 23, 1954

Hydrogen exchange between a silica–alumina catalyst and C_5–C_8 paraffins was investigated. The isomerization and cracking reactions which these paraffins undergo have previously been determined (Part I). It was found that, at 150°, only paraffin molecules containing one or more tertiary carbon atoms exchange with catalyst hydrogen; normal paraffins and those containing only the quaternary structure do not exchange. All hydrogens exchange in molecules as 2-methylhexane, regardless of their distance from the tertiary carbon atom. The distribution of poly deuterated species formed parallels the statistical distribution calculated assuming equivalence of hydrogen and deuterium. Therefore, the adsorbed molecule remains on the catalyst surface before desorption for a period of time which is long relative to the time required for exchange. The total number of molecules which exchange is greater than the number which isomerize; and methyl group isomerization is not a required condition for exchange. A mechanism by which exchange occurs is presented. Exchange occurs with hydrogen atoms on the carbon atom alpha to the one bearing the positive charge and proceeds by migration of the positive charge along the hydrocarbon chain through intramolecular hydride ion-positive charge shifts. While formation of a catalyst hydrocarbon complex is the slowest reaction step, the observed products depend on the relative rates of the exchange, isomerization and cracking reactions, which are dependent on the hydrocarbon structure.

Hydrogen exchange reactions between cracking catalyst and hydrocarbons have proven very significant in pointing outt hose factors important in catalyst–hydrocarbon reactivity. Parravano, Hammel and Taylor[2] first reported exchange between methane and deuteromethane in the presence

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[1] Presented before the Petroleum Division, American Chemical Society, March, 1953.

[2] C. Parravano, E. F. Hammel and H. S. Taylor, THIS JOURNAL, **70**, 2269 (1948).