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A Mechanism for the Isomerization of the Hexanes Using Zeolite Catalysts

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The isomerization of the hexane isomers was studied at low conversion levels using a palladium-loaded zeolite catalyst. The primary products derived from the individual hexane isomers cannot be explained in terms of an intramolecular rearrangement of a carbonium ion intermediate.

It was observed that isomerization is invariably accompanied by hydrocracking, but the hydrocracked products are not consistent with a simple cleavage of the hexane molecules. A bimolecular mechanism is proposed which satisfactorily explains both the observed products from the isomerization and hydrocracking reactions as well as the presence of heptanes in the product.

INTRODUCTION

The skeletal isomerization of the alkanes using acid catalysts has been extensively studied (*1*, *2*) and the reaction is generally considered to proceed via a carbonium ion mechanism. The isomerization activity of dual function catalysts of the platinum on alumina type has also been studied. A correlation between the dehydrogenation activity and the isomerization activity was established (*3*, *4*) and it has been proposed that the role of the metal is to dehydrogenate the alkane to an olefin which is subsequently isomerized via a carbonium ion on the acidic sites. However, the close similarity between the initial product distribution from the isomerization of the hexanes and the hydrogenolysis of methylcyclopentane led to the proposal (*5*) of an alternative mechanism involving a cyclic transition state. Recent work (*6*) using platinum and palladium films has introduced the possibility that the primary isomerization reaction on the dual function catalyst is augmented by another mechanism occurring on the metal surface alone. The isomerization activities of noble metal-loaded zeolite catalysts (have) previously been investigated (*7*). It was shown that activity increases linearly with metal concentration up to particular loadings which depend on the metal being used. The objective of this study was to carefully follow the isomerization of the individual hexane isomers at low conversions and determine the initial reaction products. From these data, it was hoped that the path of hexane isomerization could be deduced and insight could be obtained into the reaction mechanism.

EXPERIMENTAL METHODS

Phillips research grade hydrocarbons, greater than 99.8-mole % purity, were used in these experiments. The crystalline catalyst was synthesized from Type Y zeolite with a SiO_2/Al_2O_3 molar ratio of 5.0 by partial rare-earth cation exchange (45% rare earth) and partial ammonium exchange (50%). The balance of the cations was sodium. Palladium (0.5 wt %) was introduced onto the zeolite by an ion-exchange technique (*7*). The catalyst was used in the form of ⅛-in. long by ⅛-in. diameter tablets. Prior to use, the tablets were calcined in air at 550°C in an oven; they were then reduced in hydrogen at 510°C in the test reactor. The isomerization reactions were carried out using between 5–20 mls of catalyst in a continuous flow unit of conventional design. The stainless steel reactor was surrounded by aluminum blocks heated by a Glas Col heating mantle enabling isothermal operation. Reaction temperature and pressure were maintained at 285°C and 500 psig, respectively, in all experiments. The space velocity was varied from 2 to 90 g of hydrocarbon/g of catalyst/hr and the hydrogen to hydrocarbon ratio from 5:1 to 20:1. To ascertain that channeling of the feed was not taking place in the catalyst bed at the higher space velocities required to obtain the lower conversion levels, the exect of different flow rates was evaluated using the same weight of catalyst to flow rate ratio. Identical conversions and product selectivities were obtained using different flow rates which demonstrated that channeling did not occur and also that external diffusion on the catalyst surface was insignificant (*8*). Sufficient evidence exists in the current litterature showing internal diffusion in zeolite catalysts to be negligible (*9*, *10*). Reaction periods of 2 hr were allowed for attainment of steady state before sampling and material balances were taken over 1-hr time intervals. The reaction products were collected at Dry Ice temperature. Gas analyses were determined on a Perkin-Elmer 154D fractometer equipped with a 20-ft alumina column and thermal conductivity detector. The analyses of the liquid products were made using a Perkin-Elmer 880 chromatograph equipped with a 150-ft squalene column and a flame ionization detector.

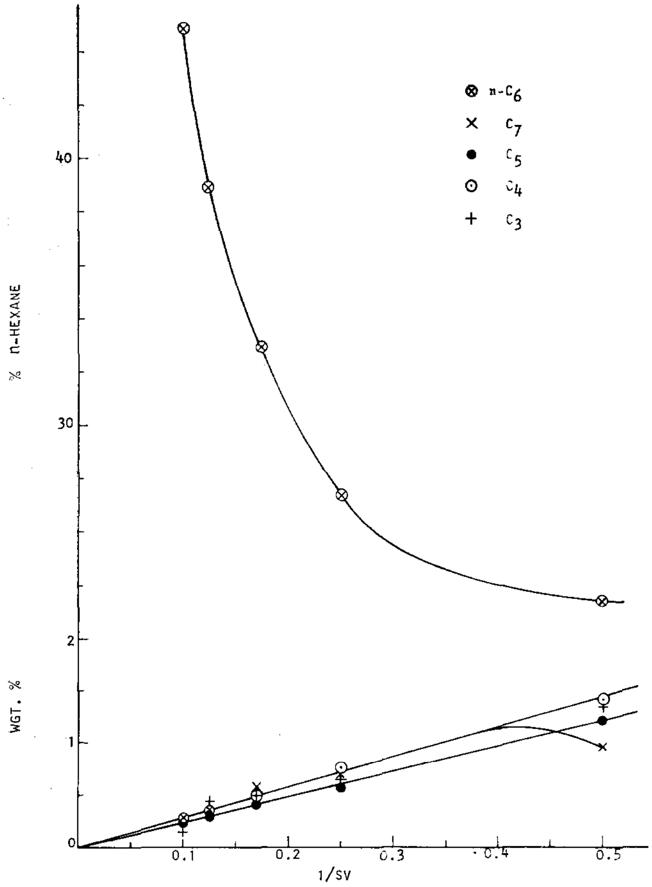


FIG. 1. Product distribution from *n*-hexane isomerization.

RESULTS

The isomerization of *n*-hexane was studied over a range of conversion levels, the extent of conversion being controlled by the space velocity. The results, presented in Fig. 1, show the isomerization reaction to be accompanied by a cracking reaction and also that heptanes are present in the product.

The isomerization of the five individual hexane isomers was then studied under carefully controlled conditions at different conversion levels. The experimental data from these studies are shown in Tables 1 to 5. The variation in conversion level was controlled by the space velocity of the feed in the studies with *n*-hexane, 2,2-dimethylbutane and 2,3-dimethylbutane. However, in the case of the 2- and 3-methylpentanes, the low conversion levels could be achieved only with increased hydrogen flow rates. From the contact times and the product

TABLE 1

THE ISOMERIZATION OF *n*-HEXANE AT 285°C

	Product composition (mole %)					Normalized			
Conversion (%)	2,2-DMB	2,3-DMB	2-MP	3-MP	*n*-hexane	2,2-DMB	2,3-DMB	2-MP	3-MP
4.1	0	0.41	2.19	1.51	95.90	0	10.0	53.4	36.8
4.85	0	0.48	2.60	1.77	95.85	0	9.9	53.6	36.5
4.81	0	0.43	2.63	1.75	95.18	0	8.9	54.7	36.4
6.5	0	0.57	3.45	2.51	93.50	0	8.8	53.1	38.6
8.9	0	0.87	4.68	3.35	91.10	0	9.8	52.1	38.1
12.0	0.11	1.17	6.23	4.56	88.0	0.9	9.8	51.9	38.0
15.0	0.17	1.39	7.63	5.80	85.0	1.1	9.3	50.9	38.7

TABLE 2

THE ISOMERIZATION OF 2-METHYLPENTANE AT 285°C

	Product composition (mole %)					Normalized			
Conversion (%)	2,2-DMB	2,3-DMB	2-MP	3-MP	*n*-hexane	2,2-DMB	2,3-DMB	3-MP	*n*-hexane
11.18	0.44	9.60	88.83	0.89	0.24	2.1	8.0	85.9	3.9
6.80	0.31	5.35	93.23	0.94	0.17	2.5	13.9	79.0	4.6
5.46	0.12	4.51	94.56	0.66	0.15	2.2	12.1	82.9	2.8
4.52	0.09	3.46	95.50	0.83	0.12	2.0	18.4	76.9	2.7
2.47	0.04	1.71	97.56	0.67	0.02	0.8	27.5	70.1	1.6

TABLE 3

THE ISOMERIZATION OF 3-METHYLPENTANE AT 285°C

	Product composition (mole %)					Normalized			
Conversion (%)	2,2-DMB	2,3-DMB	2-MP	3-MP	*n*-hexane	2,2-DMB	2,3-DMB	2-MP	*n*-hexane
9.7	0.10	0.45	8.26	90.29	0.89	0.9	4.6	85.2	9.2
8.3	0.10	0.36	7.05	91.67	0.85	0.8	4.3	84.6	10.0
6.9	0.06	0.29	5.87	93.04	0.72	0.9	4.2	84.6	10.4
6.2	0.05	0.20	5.28	93.75	0.70	0.8	3.2	84.8	11.2
4.7	0.0	0.0	4.02	95.30	0.64	0.0	0.0	86.5	13.5
3.0	0.0	0.0	2.60	97.0	0.40	0.0	0.0	85.0	15.0

TABLE 4

THE ISOMERIZATION OF 2,3-DIMETHYLBUTANE AT 285°C

	Product composition (mole %)					Normalized			
Conversion (%)	2,2-DMB	2,3-DMB	2-MP	3-MP	*n*-hexane	2,2-DMB	2-MP	3-MP	(*n*-hexane)
10.8	3.33	89.25	5.17	2.23	0	31.0	48.2	20.8	0
9.3	2.59	90.72	4.80	1.87	0	28.0	51.8	20.2	0
8.7	2.62	91.34	4.45	1.58	0	30.3	51.4	18.3	0
7.2	2.16	92.83	3.54	1.45	0	30.2	49.5	20.3	0
6.6	2.02	93.41	3.30	1.25	0	30.7	50.2	19.1	0
4.1	1.22	95.90	2.26	0.62	0	29.5	55.3	15.1	0
2.3	0.71	97.70	1.26	0.23	0	30.9	59.2	9.9	0

TABLE 5

THE ISOMERIZATION OF 2,2-DIMETHYLBUTANE AT 285°C

	Product composition (mole %)					Normalized			
Conversion (%)	2,2-DMB	2,3-DMB	2-MP	3-MP	*n*-hexane	2,3-DMB	2-MP	3-MP	*n*-hexane
13.8	86.21	5.16	4.51	2.78	1.31	37.5	32.8	20.2	9.5
6.6	93.45	3.64	1.62	0.91	0.36	55.7	24.8	13.9	5.5
4.4	95.60	2.71	1.0	0.44	0.21	62.2	22.9	10.1	4.8
2.8	97.18	1.86	0.73	0.21	0.0	67.0	25.9	7.5	0.0
1.0	98.98	0.71	0.24	0.06	0.0	71.0	24.0	6.0	0.0

distributions, rates of reaction were calculated as shown in Table 6. According to the method of Schneider and Frolich (*11*), insight may be gained into the path of the reaction by plotting conversion against the hexane product distribution and extrapolating to zero conversion. A primary reaction product is indicated when the ordinate is intersected at a positive value and a secondary product is indicated when the ordinate is intersected at a negative value. It was necessary in these studies to obtain data at conversions lower than 10% to minimize errors in extrapolation and thus avoid erroneous conclusions resulting from rates of secondary reactions being large compared to the rates of formation of the primary products.

TABLE 6

RATES OF ISOMER INTERCONVERSION AT 285°C

Reaction	Reaction rate (G moles/g of catalyst/hr × 10)
$n\mathrm{C}_6 \rightarrow 2\text{-}\mathrm{MeC}_5$	14.0
$n\mathrm{C}_6 \rightarrow 3\text{-}\mathrm{MeC}_5$	10.0
$n\mathrm{C}_6 \rightarrow 2,3\text{-}\mathrm{Me}_2\mathrm{C}_4$	2.4
$2\text{-}\mathrm{MeC}_5 \rightarrow 3\text{-}\mathrm{MeC}_5$	9.0
$2\text{-}\mathrm{MeC}_5 \rightarrow 2,3\text{-}\mathrm{Me}_2\mathrm{C}_4$	13.0
$3\text{-}\mathrm{MeC}_5 \rightarrow 2\text{-}\mathrm{MeC}_5$	37.0
$3\text{-}\mathrm{MeC}_5 \rightarrow n\mathrm{C}_6$	5.0
$2,3\text{-}\mathrm{Me}_2\mathrm{C}_4 \rightarrow 2\text{-}\mathrm{MeC}_5$	54.0
$2,3\text{-}\mathrm{Me}_2\mathrm{C}_4 \rightarrow 2,2\text{-}\mathrm{Me}_2\mathrm{C}_4$	23.0
$2,2\text{-}\mathrm{Me}_2\mathrm{C}_4 \rightarrow 2\text{-}\mathrm{MeC}_5$	2.8
$2,2\text{-}\mathrm{Me}_2\mathrm{C}_4 \rightarrow 2,3\text{-}\mathrm{Me}_2\mathrm{C}_4$	4.9

The primary products from the isomerization of *n*-hexane, Fig. 2, are shown to be 2- and 3-methylpentanes and 2,3-dimethylbutane in agreement with the work of Evering and Waugh (*12*). Figures 3 and 4 show that there are only two primary products from the methylpentanes. 2-Methylpentane yields the other methylpentane and 2,3-dimethylbutane at low conversions while 3-methylpentane yields 2-methylpentane and *n*-hexane. The 3-methylpentane is the only isomer that yields *n*-hexane as a primary product. The products from 2,3-dimethylbutane, Fig. 5, show that 2-methylpentane and 2,2-dimethylbutane are primary products. 3-Methylpentane is considered as a secondary

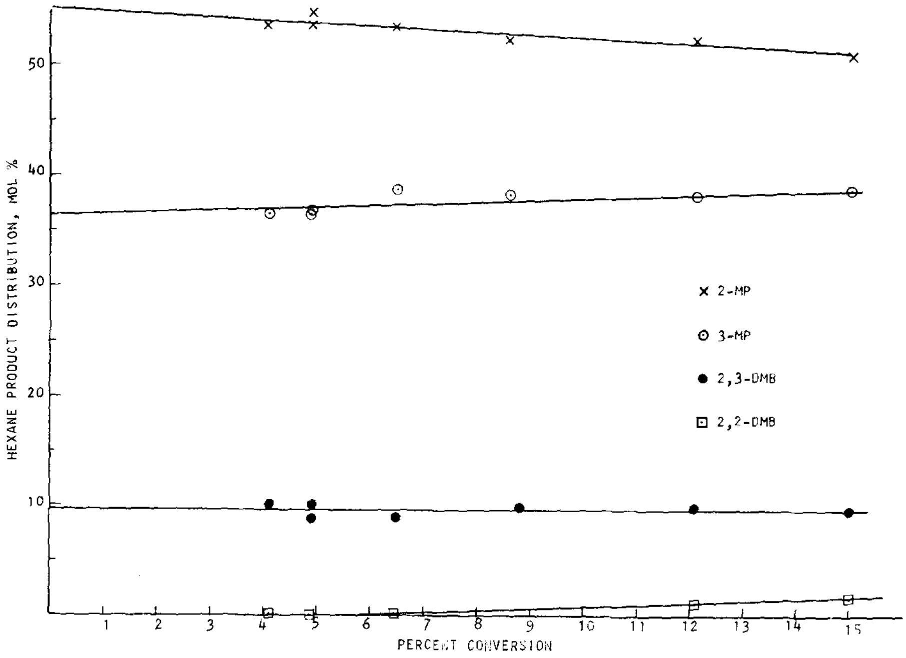


FIG. 2. The isomerization of *n*-hexane.

product since the relative concentration of this isomer at higher conversions is adequately explained by the rate of interconversion between the methylpentanes as shown in Table 6. The initial products from 2,2-dimethylbutane, Fig. 6, are 2-methylpentane and 2,3-dimethylbutane. The presence of some 3-methylpentane is again attributed to its relatively rapid formation from the 2-methylpentane.

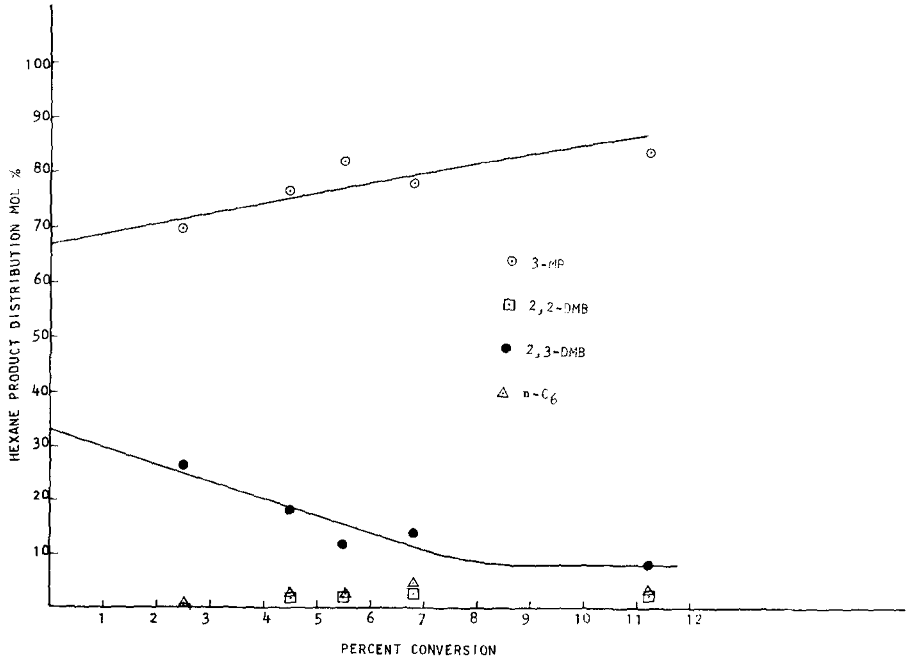


FIG. 3. The isomerization of 2-methylpentane.

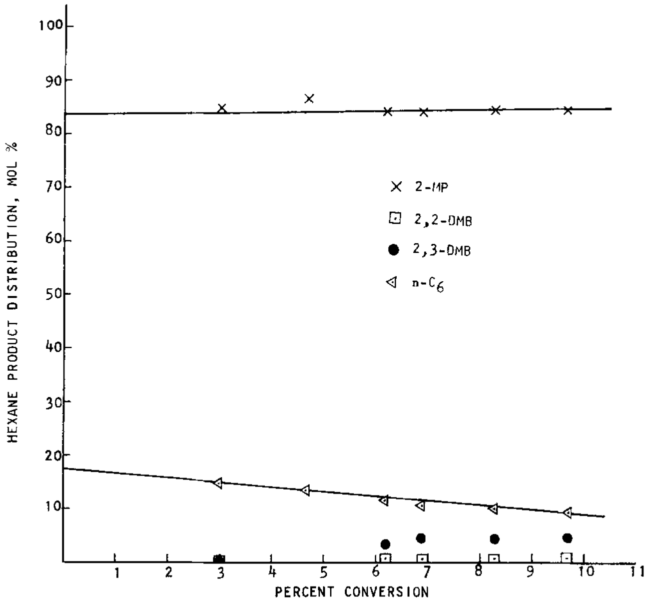


Fig. 4. The isomerization of 3-methylpentane.

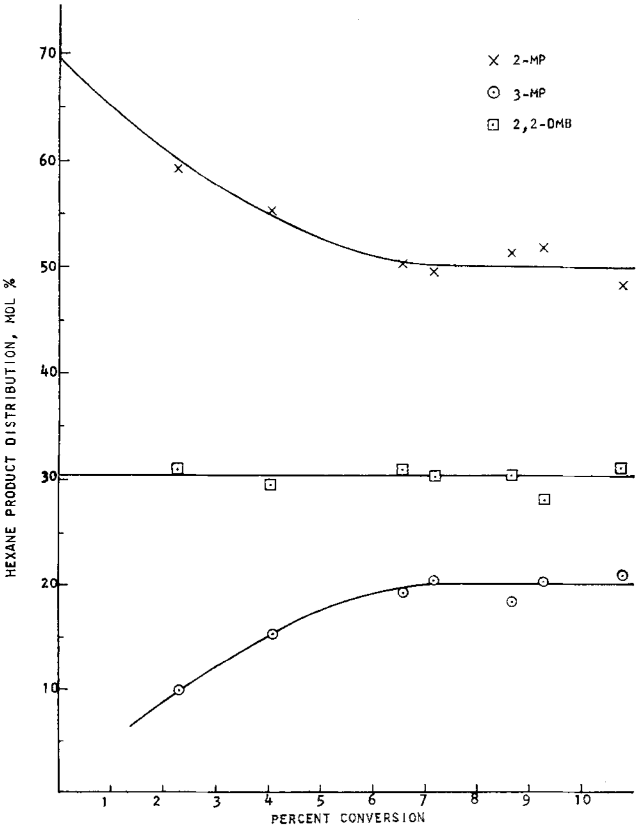


Fig. 5. The isomerization of 2,3-dimethylbutane.

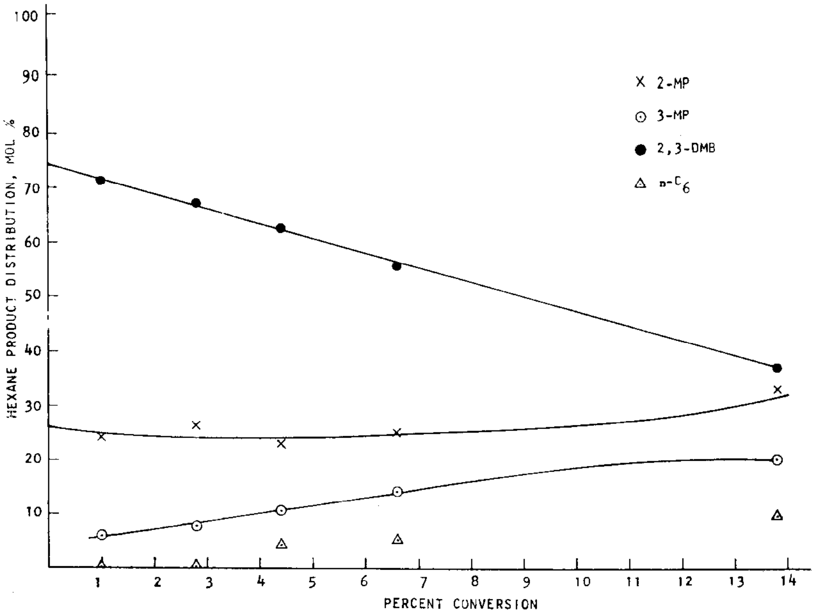
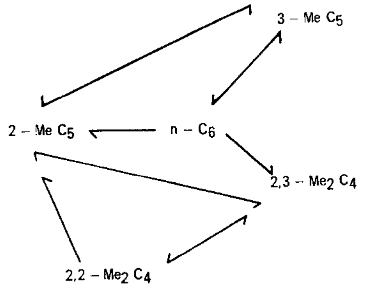


FIG. 6. The isomerization of 2,2-dimethylbutane.

DISCUSSION

The experimental results in Tables 1 to 5 show that the isomerization of the hexane isomers proceeds toward equilibrium distribution via the following reaction scheme:

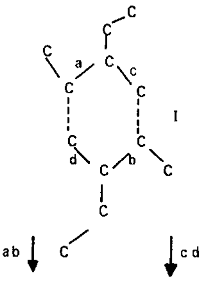


The experimental results do not imply that the isomers convert only in the directions represented by the arrows but that the isomerization reactions not indicated have slow reaction rates and do not contribute significantly to the attainment of equilibrium distribution.

This reaction scheme is not consistent with the presently accepted mechanism derived from an acid-catalyzed system because of the following discrepancies (*13*): the formation of 2,3-dimethylbutane from *n*-hexane, the formation 2-methylpentane from 2,2-dimethylbutane and the absence of *n*-hexane from the primary products of 2-methylpentane. Thus, a simple molecular rearrangement of a carbonium ion intermediate does not adequately explain these observed results. A cyclic reaction mechanism (*5*), involving a methylcyclopentane intermediate, is also unsatisfactory since, like the carbonium ion theory, it does not allow for the direct formation of 2,3-dimethylbutane from *n*-hexane. The results in Fig. 1 show that hexane isomerization over zeolite catalysts does not occur in the absence of cracking. This would suggest that cracking is an integral part of the isomerization reaction. Anderson and Avery (*6*, *14*) concluded from studies on metal films that the isomerization and cracking of butane proceed through a common surface intermediate. This intermediate, a 1–3 diadsorbed species, adequately accounts for the isomerization and cracking of butane and pentane but fails to allow for some of the hexane isomer interconversions shown to occur experimentally. Any proposed mechanism for hexane isomerization, as well as accounting for the accompanying cracking reaction, should also provide an explanation for the presence of heptane isomers in the product.

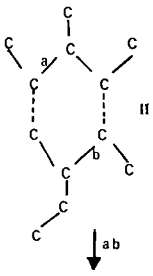
A reaction mechanism is proposed which envisages the isomerization, cracking, and disproportionation reactions to proceed through a common transition state. Two hexane molecules, diadsorbed adjacently on the catalyst surface provide a bimolecular transistion state from which the observed products from the three reactions may be obtained. A suitable configuration for a bimolecular transition state, comprising two hexane molecules, is that in which the thermodynamically favored six-membered ring is formed. Such a species may occur if the alkane molecules are 1,3 diadsorbed onto a pair of active sites or, alternately, are diadsorbed onto sites in close proximity to each other. In accordance with the theory of dual functional nature, the initial step after adsorption may well be the dehydrogenation of the alkanes to olefins followed by the formation of a cyclohexane-type intermediate (*4*). This intermediate could then be catalytically cracked into the various hexenes which would subsequently be hydrogenated to the hexane isomers. The possible configurations of the six-membered ring intermediates are thought to be limited by bond formation between the carbon atoms of the two alkene molecules. Bond formation between two secondary carbon atoms and between a secondary carbon atom and a primary carbon atom is considered possible but between two primary carbon atoms, unlikely. Another limitation to the formation of a bimolecular transition state could be the avoidance of tertiary carbon atom adsorption at an active site. This would give rise to a highly strained species.

There are two cyclohexane-type transition states that may be derived from 3-methylpentane using the previously defined limitations and these are represented by the following carbon skeletons:



I

n – hexane 2 – methylpentane

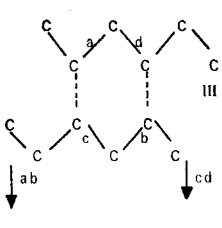


II

n – hexane + 3 – methylpentane

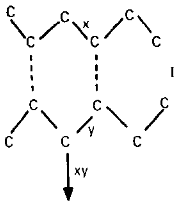
The rupture of carbon–carbon bonds in Transition State I at a and b yields two molecules of *n*-hexane while rupture at c and d yields two molecules of 2-methylpentane. Transition State II will yield a molecule of *n*-hexane together with a molecule of 3-methylpentane. In agreement with the experimental data, the formation of the dimethylbutanes is not possible via a cyclohexane-type transition state derived from two molecules of 3-methylpentane.

Four different transition states may be formed from two *n*-hexane molecules,



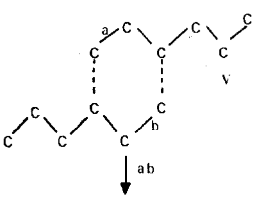
III

3 – Methylpentane 2 – Methylpentane



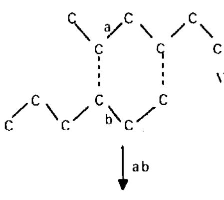
IV

2,3 – Dimethylbutane + n – Hexane



V

2 – Methylpentane

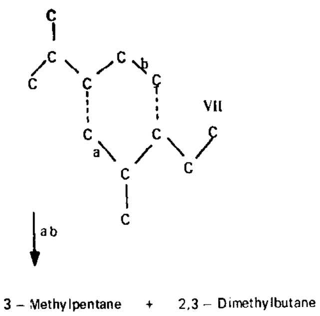


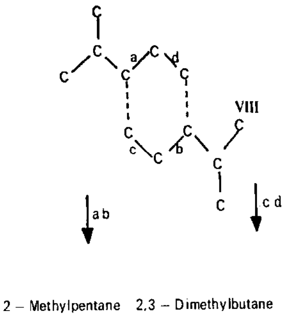
VI

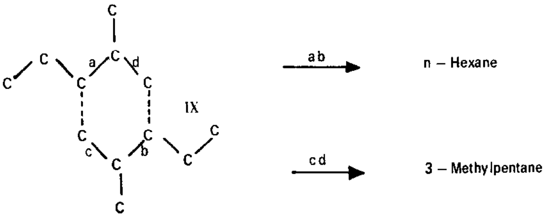
3 – Methylpentane + n – Hexane

from which only three hexane isomers may be derived as required by the exeprimental results. It is not possible to form a cyclohexane-type intermediate from two *n*-hexane molecules that can yield 2,2-dimethylbutane.

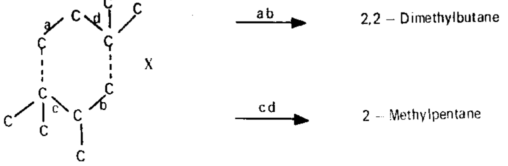
Three intermediates may be derived from 2-methylpentane,





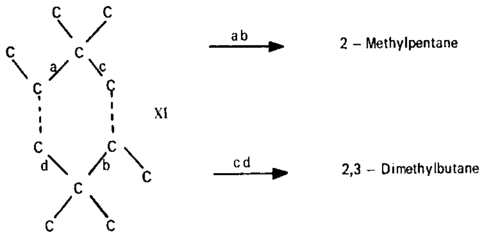


and these account for those isomers found experimentally. However, *n*-hexane is also predicted to be a primary product by intermediate IX which is contrary to the observed results. It is assumed that the formation of *n*-hexane from Transition State IX is slow compared to the formation of 3-methylpentane.

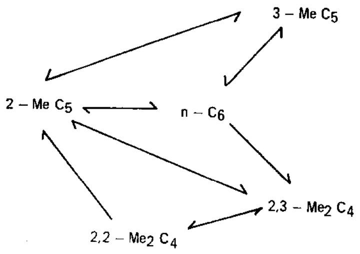


The two primary isomers that are observed from the isomerization of 2,3-dimethylbutane may be derived from intermediate X which is the only intermediate that may be formed from this isomer.

It is necessary, in this instance, to allow for the adsorption of a tertiary carbon atom at an active site since no alternative configuration is possible without resorting to primary–primary carbon atom bond formation. The formation of 2-methylpentane and 2,3-dimethylbutane, the principal products from the isomerization of 2,2-dimethylbutane may be accounted for by Transition State XI which again is the only intermediate that may be derived from this isomer.



The following reaction scheme may be derived assuming a cyclohexane-type intermediate:



Comparison with the experimentally derived reaction scheme shows that the two schemes are very similar. The only difference being that the conversion, 2-methylpentane to *n*-hexane is not observed experimentally. However, the absence of this conversion may well be due to a relatively slow reaction rate.

The isomerization of hexane is invariably accompanied by hydrocracking and this is shown in Fig. 1. Anderson and Avery proposed (*14*) that, since hydrocracking and isomerization on platinum and palladium films have the same activation energies, these reactions proceed from a common surface intermediate. Bond rupture prior to complete bond formation during the formation of the cyclohexane-type intermediate would result in the formation of low molecular weight hydrocarbons. Such a mechanism would partially explain the disparity in the concentrations of methane and the pentanes in the products at these low conversions. The cracking of an hexane molecule by a monomolecular mechanism would be expected to give rise to the following pairs per mole of hexane: C_3 plus C_3, C_4 plus C_2, and C_1 plus C_5. The amount of methane formed at these low concentrations was found to be negligible, a characteristic of zeolite catalysts. Other similar discrepancies have previously been observed (*15*).

The formation of a product with a carbon number in excess of the parent hydrocarbon molecule has been attributed to either recombination processes among surface residues (*14*) or to a disproportionation reaction (*16*). Disproportionation products from hexane may be adequately described in terms of a cyclohexane-type transition state. Intermediate II may yield two C_6 molecules, an isomerization reaction, or one C_7 molecule plus one C_5 molecule, a disproportionation reaction. It was observed, however, that although the isomerization of every hexane isomer was accompanied by cracking, only three isomers, *n*-hexane, 2-methylpentane, and 3-methylpentane yielded heptanes at low conversions. The proposed transition states from the various hexane isomers show that in accordance with the experimental results only those derived from *n*-hexane and the methylpentanes have the required geometry to yield a C_7 plus a C_5 molecule.

The bimolecular mechanism correlates satisfactorily with the observed results from the isomerization of hexanes and provides an explanation of the accompanying cracking and disproportionation reactions. Perhaps of more significance is that insight may be provided into the high reaction rates exhibited by zeolite catalysts. Weisz and Miale (*17*) have estimated that zeolite cracking catalysts have activities several orders of magnitude higher than conventional heterogeneous catalysts. This, together with the observation that nonmetal-loaded zeolites isomerize hexane while silica–alumina does not, might well be explaned in terms of the unique adsorptive characteristics of the zeolites (*18*). While a monomolecular reaction occurring on a heterogeneous catalyst needs but a catalytically active site, a bimolecular reaction requires the simultaneous presence of two reactant molecules at a suitable surface. Thus the latter reaction is statistically less favorable than the former. The zeolite with its high hydrocarbon adsorption characteristics will greatly facilitate the bringing together of the reactant molecules at the catalyst surface necessary for a bimolecular reaction. Further proof as to the validity of this mechanism for hexane isomerization is required and may possibly be provided by a detailed analysis of both the hydrocracked and disproportionated products. These products, like those derived from the isomerization reactions, should also be a reflection of the geometry of the transition intermediates from which they are derived. Such a study is presently being undertaken in this laboratory.

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