

ISOMERIZATION OF THE METHYLNONANES AND 2-METHYLOCTANE ON A BIFUNCTIONAL ZEOLITE CATALYST

By

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(Received 1st February, 1978)

2-Methyl-, 3-methyl-, 4-methyl-, 5-methylnonane, and 2-methyloctane were hydroisomerized on a Pt/Ca-Y-zeolite catalyst at a total pressure of 4.1 MPa and temperatures ranging from 210 to 230 °C. No hydrocracking occurred under these conditions. The product distributions were determined by temperature programmed capillary GLC using different stationary phases. The mechanism is discussed in terms of nonbranching (type *A*) and branching (type *B*) carbenium ion rearrangements. Unknown selectivities in the rearrangement behaviour of long chain alkyl carbenium ions are revealed.

Introduction

Catalytic isomerization of alkanes is of considerable importance in petroleum refining. Commercial objectives are improvement of octane rating of light gasoline components or the production of *isobutane*. Another potential application is pour point lowering of heavier petroleum fractions, *e.g.*, of jet fuel or diesel fuel [1, 2].

Whereas there is a vast number of publications dealing with product distributions, kinetics and possible mechanisms of isomerization of *light* hydrocarbons containing up to six or seven carbon atoms, hardly any information is available concerning the isomerization of *long chain* alkanes. Such informations are desirable both for a better understanding of potential processes for pour point lowering and for a more detailed insight into the mechanisms of hydrocracking and catalytic cracking where cleavage is preceded by skeletal rearrangement. The existing gap in our knowledge on isomerization of long chain alkanes is due to both the difficulties encountered in product analysis and the fact that cracking reactions often interfere if the feed hydrocarbon contains more than six carbon atoms.

Recently it has been shown [3] that long chain alkanes may be hydroisomerized in high yields if special bifunctional catalysts, *e.g.*, of the noble metal/zeolite type are used. With the *n*-alkanes of 13 to 16 carbon atoms remarkable selectivities were encountered which are not observable with light *n*-alkanes [4]. The present paper reports on the hydroisomerization of long chain alkanes containing one methyl branching.

Experimental

Principally, the apparatus consisted of a high pressure saturator for loading the hydrogen with hydrocarbon vapor, and a downflow fixed bed reactor. Details are given elsewhere [5]. 0.45 g of the Union Carbide SK 200 catalyst, *i.e.*, 0.5% Pt/Ca-Y-zeolite were used. Drying and activation of the catalyst were carried out *in situ* by purging with nitrogen and hydrogen, respectively, at 0.1 MPa and a maximum temperature of 400 °C.

Purities of the feed hydrocarbons as determined by capillary GLC were as follows: 2-methylnonane 99.7%, 3-methylnonane 99.95%, 4-methylnonane 97.4%, 5-methylnonane 99.95%, and 2-methyloctane 98.2%. Product distributions were corrected under the assumption that the feed impurities underwent no reaction. All experiments were conducted at a hydrogen partial pressure of 4.0 MPa and a hydrocarbon partial pressure of 0.1 MPa.

The required high resolution analyses of the products could be achieved by capillary GLC with squalane and polypropylene glycol as stationary phases. Length and internal diameter of the capillaries were 100 m and 0.25 mm, respectively. Starting at ambient temperature the column oven was heated with 1 °C/min. A flame ionization detector and an electronic integrator were used.

As a whole the resolution of the peaks either on squalane or polypropylene glycol was good. The only major analytical problem was the separation of 3-ethyloctane from 2-methylnonane when the latter was the feed. For assignment of the peaks the experience from earlier work on hydrocracking [3, 6] was available. In addition to this, use was made of retention index values reported in the literature [7, 8]. 4-Propylheptane was purchased as a reference substance from Roth, Karlsruhe and its structure ascertained by mass spectrometry. Its retention index reported in [8] for Apiezon L was found to be approximately valid for polypropylene glycol while that given in [7] did not agree with the experimental value.

Results

Hydrocarbons with a carbon number exceeding that of the feed were never observed. Undesired hydrocracking reactions were absent or negligible under the conditions applied. The highest degree of cracking conversion was 0.3%. In this case the distribution of the cracked products showed all features of an ionic hydrocracking rather than those of hydrogenolysis over platinum [3].

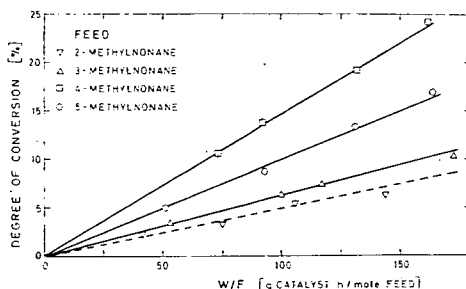


Fig. 1. Hydroisomerization of the methylnonanes on Pt/Ca-Y-zeolite ($T = 210\text{ }^{\circ}\text{C}$)

Table I

Distributions of the Products (mole-%) Formed from the Methylnonanes at Low Degrees of Conversion X ($T=210^\circ\text{C}$)

Feed $W/F \left[\frac{\text{g catalyst} \cdot \text{h}}{\text{mol feed}} \right]$ X [%]	2-ME-Nonane	3-ME-Nonane	4-ME-Nonane	5-ME-Nonane
	41	53	74	51
	2.4	3.4	10.7	4.9
2-ME-Nonane	—	27.3	0.8	0.4
3-ME-Nonane	77.5	—	27.4	9.3
4-ME-Nonane	6.9	36.6	—	52.7
5-ME-Nonane	0.9	5.1	31.8	—
3-ET-Octane	(1)	13.7	14.5	6.2
4-ET-Octane	0.5	8.4	20.5	28.0
4-PR-Heptane	0	0.1	1.6	2.4
<i>n</i> -Decane + DM-Octanes	14.2	8.8	3.4	1.0
	100.0	100.0	100.0	100.0

(1) Not determined

Table II

Distributions of the Products (mole-%) Formed from the Methylnonanes at Medium Degrees of Conversion X ($T=230^\circ\text{C}$)

Feed $W/F \left[\frac{\text{g catalyst} \cdot \text{h}}{\text{mol feed}} \right]$ X [%]	2-ME-Nonane	3-ME-Nonane	4-Me-Nonane	5-ME-Nonane
	127	168	95	91
	31	39	38	37
2-ME-Nonane	—	26.2	2.9	1.6
3-ME-Nonane	55.0	—	30.9	13.1
4-ME-Nonane	14.0	34.6	—	46.7
5-ME-Nonane	4.5	9.1	26.8	—
3-ET-Octane	(1)	10.0	12.8	7.3
4-ET-Octane	4.1	9.2	17.8	23.0
4-PR-Heptane	0.1	0.6	1.8	2.1
<i>n</i> -Decane + DM-Octanes	22.3	10.3	7.0	6.2
	100.0	100.0	100.0	100.0
<i>n</i> -Decane	9	13	15	18
2,3-DM-Octane	13	6	15	13
2,4-DM-Octane	17	10	12	15
2,5-DM-Octane + 3,5-DM-Octane	24	26	28	24
2,6-DM-Octane	14	8	3	3
2,7-DM-Octane	9	6	4	3
3,4-DM-Octanes ⁽²⁾	3	7	5	7
3,6-DM-Octanes ⁽²⁾	4	13	5	5
4,5-DM-Octanes ⁽²⁾	1	2	5	3
Others ⁽³⁾	6	9	8	9
	100	100	100	100

(1) Not determined.

(2) Both diastereomers.

(3) Essentially 4 unidentified peaks; possibly including 2,2-DM- and 3,3-DM-octane.

branching in the carbon skeleton is not changed whereas in type *B* rearrangements a ramification is created or vanished. Type *A* rearrangements are considered to proceed *via* a classical sequence of hydride and alkyl shifts. Type *B* rearrangements of light alkanes were shown to be best interpreted in terms of protonated cyclopropane intermediates [10, 11].

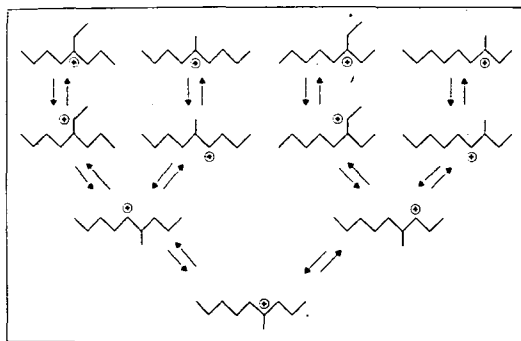
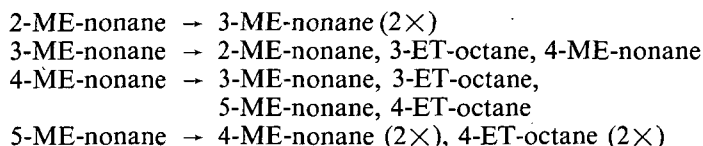


Fig. 2. Reaction sequences in type *A* rearrangements of the tertiary carbenium ion derived from 4-methylnonane.

In Fig. 2 the type *A* mechanism is applied, as an example, to the tertiary carbenium ion derived from 4-methylnonane. Applying the same procedure to all positional isomers results in the following prediction of primary products (relative statistical probabilities other than unity are given in brackets):



The actual product distributions at low degrees of conversion (Table I) essentially confirm the assumed mechanism. In particular, the methyl shift along the main chain is clearly found to be a stepwise reaction and the ethyloctanes are formed as predicted. As expected 4-propylheptane occurs as a secondary product of 4-ethyloctane. A more subtle consideration, however, reveals two systematic deviations from the simple statistic prediction of primary products: A methyl shift is always faster than a competing shift of a bulkier alkyl group. As a consequence, *e.g.*, the rate of formation of 4-methylnonane from 5-methylnonane is *ca.* twice that of 4-ethyloctane. Furthermore, competing methyl shifts do not proceed at equal rates. The preferred methyl shift is the one towards the center of the main chain. *E.g.*, 3-methylnonane yields 4-methylnonane with a higher rate than 2-methylnonane.

At higher degrees of conversion the selectivities are still visible though less pronounced due to secondary reactions, *cf.* Table II. At $X=38\%$ 4-methylnonane yields somewhat more 3-methylnonane than 5-methylnonane. This is due to the higher thermodynamic equilibrium concentration of 3-methylnonane. The behaviour of

2-methyloctane (Table III) in type *A* rearrangement is quite analogous to 2-methylnonane.

Possible type *B* rearrangements of carbenium ions derived from 2-methyloctane represented in Fig. 3. For the sake of brevity the protonated cyclopropane intermediates are written in a face-protonated form although corner- or edge-protonated entities appear to be more likely [10, 12]. If the branching is assumed to start from the most stable ion, *i.e.*, the tertiary 2-methyl-(2)octyl-cation then 2,2-DM- and 2,3-DM-heptane are expected as the only primary products.

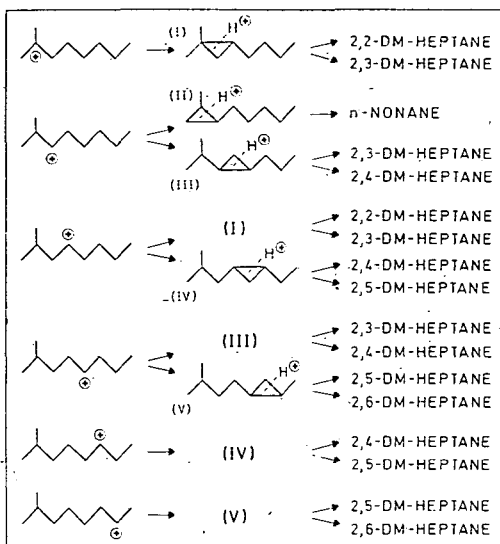


Fig. 3. Possible pathways for type *B* rearrangement of carbenium ions derived from 2-methyloctane

Table III unambiguously shows that such a mechanism is not consistent with the experimental result. If, on the other hand, branching is assumed to start from the mixture of secondary carbenium ions and to be governed by mere statistics, then the expected distribution is:

n-nonane:	$100/15 \approx 6.5\%$
2,2-DM-heptane:	$100/15 \approx 6.5\%$
2,3-DM-heptane:	$300/15 = 20\%$
2,4-DM-heptane:	$400/15 \approx 26.5\%$
2,5-DM-heptane:	$400/15 \approx 26.5\%$
2,6-DM-heptane:	$200/15 \approx 13\%$

which is in rather good agreement with the actual distribution shown in Table III. In particular, the relatively low rates of formation of *n*-nonane, 2,2-DM-heptane, and 2,6-DM-heptane are correctly predicted.

Application of the same formalism to the methylnonanes is less straightforward. One reason for this is the incomplete analysis of individual dimethyloctanes. It is

interesting to note, however, that 2-methylnonane is the most reactive isomer for type *B* rearrangement while it is the least reactive for type *A* rearrangement, cf. Tables I and II. Additional systematic investigations are required to arrive at a full understanding of the selectivities encountered in ionic rearrangement of long chain alkanes containing one methyl branching.

Conclusions

Hydroisomerization of higher alkanes on properly balanced bifunctional catalysts is a powerful tool for studying the details of rearrangement of long chain alkyl carbenium ions. Both the non-branching and the branching rearrangements exhibit distinct features which are not observable with C₆ or lower molecules. In a sense the latter are special cases which do not contain enough carbon atoms to reveal the detailed information on the most favorable rearrangement routes.

Acknowledgement

The authors thank PROF. DR. K. HEDDEN, Head of the Division of Gas, Oil, and Coal of the Engler-Bunte-Institute, who generously supported this work. H. FARAG acknowledges a post-doctoral scholarship granted by International Seminar for Research and Education in Chemical Engineering and Physical Chemistry at the University of Karlsruhe.

Abbreviations

DM = dimethyl-, ET = ethyl-, ME = methyl-, PR = propyl-.

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