

Reactivities of Some C₆-C₈ Paraffins over Pt-Al₂O₃

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Data are presented showing the effects of molecular size and structure on the rates of dehydrocyclization and hydrocracking of some C₆-C₈ paraffins over a 0.3% platinum on alumina catalyst. Increasing the length of the carbon chain from 6 to 8 carbon atoms increased the rate of dehydrocyclization several fold, but had surprisingly little effect on the rate of hydrocracking. The rates of dehydrocyclization of the normal paraffins were appreciably higher than those of the branched paraffins of the same molecular weight, whereas the reverse was true for hydrocracking. The results appear to be consistent with a carbonium ion mechanism for the reactions.

PLATINUM on alumina catalysts belong to a class of catalysts termed bifunctional, since they possess hydrogenation-dehydrogenation activity and are also active for reactions which are typically promoted by acid catalysts (1). In the presence of hydrogen, important reactions of paraffinic hydrocarbons over such catalysts include isomerization, dehydrocyclization, and hydrocracking. At temperatures below about 400° C., the isomerization reaction is observed almost exclusively, but as temperature is increased further, hydrocracking to lower molecular weight hydrocarbons and dehydrocyclization to aromatics become increasingly important. This article is concerned with the latter two reactions. The results present the effect of molecular size and structure on the rates of dehydrocyclization and hydrocracking of some C₆-C₈ paraffins over a platinum on alumina catalyst.

EXPERIMENTAL

Procedure. The hydrocarbons were contacted with the catalyst in the presence of hydrogen, using a flow reactor technique described previously (6). Catalyst charges ranging from 1.0 to 6.0 grams were used. The reaction products were analyzed chromatographically (7).

Materials. The hydrocarbons used in this work were Phillips pure grade (> 99 mole % purity). The hydrocarbons and hydrogen were dried to less than 5 p.p.m. water using procedures described previously (6). The platinum on alumina catalyst used contained 0.3 wt % platinum. The catalyst was prepared by impregnation of alumina with aqueous chloro-platinic acid, followed by calcination in air for 4 hours at 593° C. The surface area of the alumina was 163 square meters per gram.

RESULTS

When paraffins are passed over platinum on alumina catalyst at the temperatures of the present study, the observed reactions include isomerization, hydrocracking, and dehydrocyclization. Typical product distribution data are shown in Table I. In the case of the normal paraffins, the products of the isomerization reaction are predominantly the singly branched isomers. In the case of 3-methylhexane, the isomerization products are predominantly 2-methylhexane and *n*-heptane. For 2,2,4-trimethylpentane the only observed isomer was 2,2,3-trimethylpentane.

The products of the dehydrocyclization reaction are aromatics and cycloparaffins. In the case of *n*-hexane, the major product of dehydrocyclization is methylcyclopentane, the amount of benzene being much smaller. In the case of the C₇ paraffins and *n*-octane the major products of the dehydrocyclization reaction are aromatics, toluene from the

former and a mixture of ethylbenzene and xylenes from the latter. Very little dehydrocyclization is observed for the 2,2,4-trimethylpentane, and that which is observed is accompanied by cracking, so that the products are aromatics and cycloparaffins of a carbon number lower than eight.

The products of the hydrocracking reaction are hydrocarbons of lower carbon number than the reactant. Of particular interest is the result that cracking of 2,2,4-trimethylpentane strongly favors the formation of isobutane.

Rates of hydrocracking r_c and dehydrocyclization r_d are shown in Table II. The rates were calculated from data taken at moderately low conversions (13 to 20%) using the relation

$$r = \frac{F}{W} \Delta x \quad (1)$$

where F is the feed rate of hydrocarbon reactant in gram moles per hour into the reactor, W is the weight of catalyst in grams, and Δx is the fraction of reactant converted in a particular reaction. The rates were reproducible within about 10%. For hydrocracking Δx represents conversion to hydrocarbons of lower carbon number than the hydrocarbon reactant, while for dehydrocyclization Δx represents conversion to aromatics and cycloparaffins.

The ratio of r_c to r_d varies with the hydrocarbon reactant. Hettlinger and co-workers (4), in a study of the reactivity of *n*-heptane over a platinum on alumina catalyst, found the ratio to vary with reaction conditions. At conditions (24.3 atm., 496° C.) not far removed from the conditions of the present work on *n*-heptane, these authors found a value of about 1.6 for the ratio of initial rates, which is not greatly different from the value of 2.2 obtained in this work.

The data in Table II indicate that the rate of hydrocracking increases only slightly when the length of the carbon chain is increased from 6 to 8 carbon atoms. This is somewhat surprising, since certain of the data of Myers and Munns (5) suggest that the rate of hydrocracking of *n*-heptane over a platinum on alumina catalyst is significantly higher than that of *n*-pentane. Perhaps this reflects a difference in the properties of the specific catalysts used, although it is not clear why this should be the case. However, there is an appreciable difference in the rates of hydrocracking of normal and branched paraffins, particularly in the case of *n*-octane vs. 2,2,4-trimethylpentane, where the latter cracks about six times as fast as the former. The data on the C₇ paraffins indicate that the rate of hydrocracking of 3-methylhexane is about 20 to 30% greater than that of *n*-heptane.

Increasing the size of the normal paraffin molecule from C₆ to C₈ increases the rate of dehydrocyclization appreci-

Table I. Product Distribution Data^a

Reactant	<i>n</i> -Hexane	<i>n</i> -Heptane	3-Methylhexane	<i>n</i> -Octane	2,2,4-Trimethylpentane
Pressure, atm.	11	21	21	11	11
<i>F</i> / <i>W</i> ^b	0.52	0.90	0.89	0.45	0.89
Moles/100 Moles Reactant					
C ₁	1.1	1.2	1.4	1.3	8.6
C ₂	2.8	1.3	1.9	4.1	2.1
C ₃	1.7	2.3	2.8	2.4	3.3
<i>i</i> C ₄	1.2	0.8	1.0	0.4	11.0
<i>n</i> C ₄	1.1	1.1	1.3	1.4	4.9
<i>i</i> C ₅	0.1	0.6	1.6	0.9	0.5
<i>n</i> C ₅	0.1	0.4	0.6	0.5	0.3
Isohexanes	7.2 ^c	0.7	0.5	0.1	0.1
<i>n</i> -Hexane		0.2	0.2	0.5	0.1
Isoheptanes		13.0 ^d	9.0 ^e	0.1	2.3
<i>n</i> -Heptane			3.8	0.6	
Iso-octanes				11.1 ^f	3.3 ^g
Methylcyclopentane	1.3	0.1		0.1	0.5
C ₇ Cycloparaffins		0.2		0.6	
Benzene	0.3				
Toluene		1.6	1.4		0.2
Ethylbenzene				1.6	
Xylenes				2.4	
Mole % Unconverted	87.4	81.0	80.1	79.4	82.6
Mole % Hydrocracked	3.8	4.1	5.7	4.8	13.4

^a 471°C., H₂/hydrocarbon = 5. ^b Gram mole hydrocarbon charged per hour per gram catalyst. ^c 54% 2-methyl and 43% 3-methylpentane, 3% dimethylbutanes. ^d 63% 3-methyl and 33% 2-methyl-

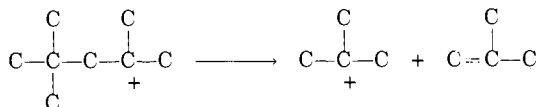
hexane, 4% dimethylpentanes. ^e 90% 2-methyl hexane, 10% dimethylpentanes. ^f Predominantly methylheptanes. ^g 2,2,3-Trimethylpentane.

ably. Thus, the total rate of dehydrocyclization of *n*-octane is about 2.5 times that of *n*-hexane. If we consider only the aromatics formed in the reaction, the rate of dehydrocyclization of *n*-octane to aromatics becomes 12 times as high as that of *n*-hexane. Furthermore, the rate of dehydrocyclization varies appreciably with the structure of the paraffin molecule, the rate being significantly higher for *n*-paraffins than for branched paraffins. For example, the total rate of dehydrocyclization of *n*-octane is about 3.5 times that of 2,2,4-trimethylpentane. On the basis of the aromatics formed in the reaction, however, this difference becomes much larger, since the yield of aromatics from 2,2,4-trimethylpentane is small. In the case of the C₇ paraffins studied, the rate of dehydrocyclization of *n*-heptane is about 40 to 50% greater than that of 3-methylhexane.

From the data on the temperature dependence of the rates of hydrocracking and dehydrocyclization of *n*-heptane and 3-methylhexane, the apparent activation energies for these reactions appear to be of the order of 30 kcal./mole for the catalyst employed in this study.

DISCUSSION

The observed effects of the structure of the paraffin molecule on both the rate and the nature of the products of the cracking reaction are in accord with a carbonium ion mechanism. Applying this to 2,2,4-trimethylpentane, a tertiary ion would readily be formed and then crack as follows:



The cracking of the ion leads to isobutyl structures, which are subsequently converted to isobutane via hydrogenation or hydrogen transfer reactions. This mode of cracking is an

example of the beta scission rule (8), and accounts for the predominance of isobutane in the products from 2,2,4-trimethylpentane.

The observation, that the rate of cracking of 2,2,4-trimethylpentane relative to *n*-octane is high while the rate of cracking of 3-methylhexane relative to *n*-heptane is much smaller, is in line with previously reported results of Ciapetta and Hunter for nickel-silica-alumina catalysts (2, 3). This suggests that the tertiary 2,2,4-trimethylpentyl ion is a particularly reactive configuration for cracking.

The observed data on dehydrocyclization are also in accord with a carbonium ion mechanism, involving an olefinic ion as an intermediate. The formation of olefinic ions presumably involves a dehydrogenation step on platinum sites of the catalyst, followed by interaction of the resulting unsaturates with acidic centers. In the case of normal structures, the olefinic ion could be either a primary or secondary carbonium ion. Since secondary carbonium ions are far more stable than primary ions, they would exist in higher concentration on the surface, and the predominant path in ring closure would involve a secondary carbonium ion intermediate. In the case of *n*-hexane this can lead to formation of a five-membered ring (Figure 1)

Table II. Summary of Rate Data

	Temp., ° C.	Pressure, Atm. ^a	<i>r_c</i> ^b	<i>r_d</i> ^b
<i>n</i> -Hexane	471	11	0.020	0.0084
<i>n</i> -Octane	471	11	0.021	0.021
2,2,4-Trimethylpentane	471	11	0.12	0.006
<i>n</i> -Heptane	471	21	0.037	0.017
	527	21	0.16	0.075
3-Methylhexane	471	21	0.051	0.012
	527	21	0.19	0.048

^a Hydrogen to hydrocarbon ratio = 5.

^b Reaction rate, gram-mole/hour/gram catalyst.

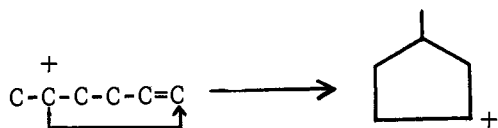


Figure 1. Cyclization of nC_6

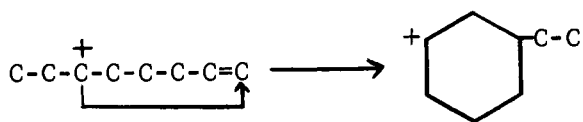


Figure 2. Cyclization of nC_8

but not a six-membered ring; whereas, in the case of n -octane, for example, it can also lead to the formation of a six-membered ring (Figure 2). This accounts for the higher rate of dehydrocyclization of n -octane as compared to n -hexane, and for the fact that the dehydrocyclization reaction results in a much more selective conversion to aromatics in the case of n -octane.

The small extent of dehydrocyclization of 2,2,4-trimethylpentane, particularly to aromatics, is presumably due to the difficulty of rearranging to a structure which can satisfactorily undergo ring closure. The difficulty in rearranging

the structure is also indicated by the observation that essentially no methylheptanes or dimethylhexanes are formed.

The observation that the rate of dehydrocyclization of 3-methylhexane is only moderately lower than that of n -heptane indicates that the former can rearrange to the normal readily. This makes a path available for the direct formation of a six-membered ring via a secondary carbonium ion intermediate.

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Dichromate Catalysis of Deflagrating Ammonium Nitrate

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An experimental technique is described for studying a qualitative catalytic action of heterogeneous solids on the gaseous products from molten, decomposing ammonium nitrate (AN). Freshly prepared chromic oxide ash produced by the thermal decomposition of ammonium dichromate (AD) will (catalytically) decompose a portion of the gaseous products of AN at relatively high temperatures into nitrogen dioxide gas. Further evidence suggests that the NO_2 is produced by the decomposition of nitric acid vapor which is present. The studies show that chromic oxide ash prepared freshly by the thermal decomposition of AD differs in its catalytic behavior from laboratory-grade chromic oxide. This difference in behavior is presumably due to differences in its surface properties (area and/or composition) from those of laboratory-grade chromic oxide, which is usually prepared by a different method.

CHROMATE AND DICHROMATE salts which are soluble in molten ammonium nitrate (AN) are effective catalysts for both the thermal decomposition of molten AN, and the deflagration of solid AN (4, 5). The exact mechanism of the catalytic activity is not known in either case, but it is well established that the catalyzed decomposition of both molten (4, 5) and deflagrating (6) solid AN produces gases containing nitrogen dioxide; whereas, the thermal decomposition of molten pure AN gives nitrous oxide, water vapor, nitric acid, and ammonia. On the basis of the results of the molten catalyzed AN decomposition, it was usually considered that chromates and dichromates influence the deflagration characteristics of solid AN principally through a liquid-phase reaction (5). However, it was subsequently postulated that in the case of ammonium dichromate (AD) it is the chromic oxide produced by thermal decomposition of the AD which is the dominant catalyst, and that it is effective in the gas-phase reactions (1). The possible importance of heterogeneous catalysis of the gas-phase reactions by other catalysts was also

emphasized. This hypothesis was based on the observations that small percentages of AD (and other typical burning catalysts) have no effect on the linear pyrolysis rate of pure solid AN. In addition, for the case of AD, hot freshly-prepared chromic oxide is capable of catalyzing the decomposition or reaction of the gaseous products from vaporizing molten AN, giving NO_2 as one of the products. This latter observation, of which only the final results were briefly reported, has subsequently created some interest. This article describes the experimental technique and results leading to the above conclusion and elaborates on the results.

EXPERIMENTAL TECHNIQUE AND RESULTS

The experiment was designed so that the gaseous products from molten AN would pass through the catalyst. A stainless-steel screen (200 mesh) was placed over a heated platinum crucible about three-fourths full of molten pure AN. Because it was believed that the initial decomposition products of deflagrating AN are predominantly HNO_3 and NH_3 (1), the temperature of the molten AN in the crucible was kept high ($> 240^\circ C.$) to ensure the presence of

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