

# ISOMERIZATION AND CRACKING OF SATURATED HYDROCARBONS ON HYDROGEN-MORDENITE AND PLATINUM-HYDROGEN-MORDENITE CATALYSTS

By

G. LOPEZ, G. PEROT, C. GUEGUEN and M. GUISET

Groupe de Recherches sur la Catalyse en Chimie Organique, Université de Poitiers  
(E. R. A. C. N. R. S.) 86022 POITIERS France

(Received 9<sup>th</sup> February, 1978)

Cracking and isomerization of *n*-hexane, 2-methylpentane, 2,4-dimethylpentane and *isooctane* have been studied at 250 °C and 400 °C on hydrogen-mordenite and 0.6% platinum-hydrogen-mordenite.

On hydrogen-mordenite, at 400 °C, no isomerization is observed and the selectivities are roughly those expected from a classical carbonium ion mechanism in which the adsorption-desorption of the alkanes constitutes the rate-determining step. At 250 °C, products from cracking are mainly saturated hydrocarbons with very small quantities of C<sub>1</sub>, C<sub>2</sub> but comparatively large amounts of C<sub>4</sub>, C<sub>5</sub> resulting from bimolecular reactions among the products.

Isomerization occurs on platinum-hydrogen-mordenite at both temperatures, but only at 250 °C on hydrogen-mordenite. Hence it is suggested that the rate-limiting step is no longer the formation and desorption of carbonium ions but rather their isomerization and  $\beta$ -scission.

## Introduction

Cracking and isomerization of hydrocarbons constitute the major industrial application of zeolite catalysis in petroleum chemistry [1]. Synthetic mordenites in particular are known to be very active in this field [2-4] and their use will probably become more and more widespread in the near future.

Carbonium ions are the most commonly proposed intermediates for the acid catalyzed isomerization and cracking of alkanes [4, 5] according to the mechanism presented in Fig. 1. The most frequent ways of forming carbonium ions from alkanes, (reactions (1) and (4)), are: direct cracking of alkanes by protons, hydride abstraction by Lewis acid sites or protons of Brønsted acid sites, or intermolecular hydride transfer from the alkane to a preadsorbed carbonium ion. These carbonium ions can then undergo what POUTSMA calls "three basic reactions" [4]: intermolecular rearrangements (2),  $\beta$ -scission (3,3') and hydride transfer.

Our objective was to study the main factors that can affect the formation and transformation of carbonium ions and, therefore, change the selectivities of the reaction. The effect of the structure of the reactant itself was studied by using 4 alkanes: *n*-hexane, 2-methylpentane, 2,4-dimethylpentane and *isooctane*. The influence of the reaction temperature was investigated by comparing the results obtained at

400 °C and 250 °C. Finally, the effect of the addition to the mordenite, of a metal component which can dehydrogenate the alkane into alkenes (reactions (1') and (4')), and hence facilitate the formation of carbonium ions, was studied by using a platinum-hydrogen-mordenite catalyst.

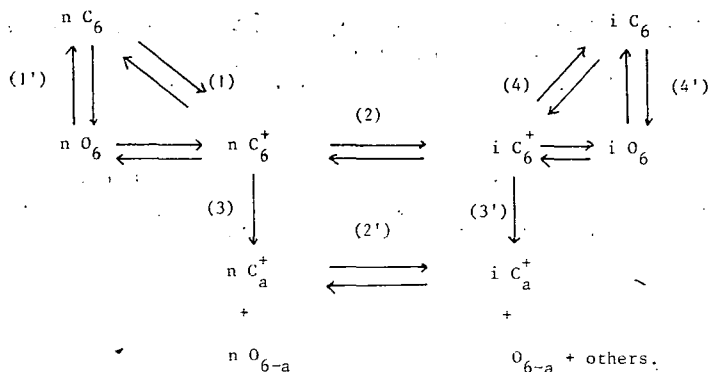


Fig. 1. Carbonium ion mechanism for *n*-hexane cracking and isomerization: *n* normal; *i* isomeric;  $C_6$  hexane;  $O_6$  hexene;  $C^+$  carbonium ion  $1 \leq a \leq 4$

### Experimental part

All the reactants were Fluka pure grade reagents percolated through alumina before use.

The 900-H zeolon hydrogen-mordenite (H-M) was purchased from Norton. Each sample was preheated overnight at 500 °C under hydrogen. The platinum-hydrogen-mordenite (Pt-H-M) was obtained by impregnation of the hydrogen-mordenite with an aqueous solution of  $H_2PtCl_6$  and reduced overnight in hydrogen at 500 °C. The  $H_2$ - $O_2$  gravimetric titration of the 0.2, 0.6 and 1 w% Pt-H-M gives respectively a metal surface area of 0.37, 0.6 and 1.0 m<sup>2</sup> per gram of catalyst (Pt dispersion 80%, 42% and 36% respectively).

All the results were established in a dynamic flow reactor with 0.1 atmosphere hydrocarbon pressure and 0.9 atmosphere hydrogen pressure.

Table I

Activities (Mole hr<sup>-1</sup>g<sup>-1</sup>) of Hydrogen-Mordenite (H-M) and 0.6% Platinum-Hydrogen-Mordenite (0.6% Pt-H-M) after 20 min reaction time ( $a_{20}$ ) and after deactivation extrapolated at zero conversion ( $a_0$ )

Catalysts		Isooctane		n-Hexane		
		$10^4 a_{20}$	$10^4 a_0$	$10^4 (a_1)_0$	$10^4 (a_c)_0$	$(a_1)_0 / (a_c)_0$
		(cracking)		(Isomerization)	(cracking)	
H-M	400 °C	45	5.5	0.05	2.2	0.02
	250 °C	10-15	1.5	0.6	0.75	0.8
0.6% Pt-H-M	400 °C	1200	400	160	200	0.8
	250 °C	55	15	10	1.5	6.6

The analysis of the reaction mixture was performed on a Perkin-Elmer F—20 gas-chromatograph equipped with a S. C. O. T. capillary column of squalane.

The activity of all the catalysts decreased very rapidly during the first 2 hours of use, then became stable. For *isooctane* cracking, the activity after 20 minutes reaction time ( $a_{20}$ ) of the hydrogen-mordenite is approximately 10 times the extrapolated activity after deactivation ( $a_0$ ), while on platinum-hydrogen-mordenite  $a_{20} \approx 3a_0$  (Table I). The product distribution was determined after deactivation of the catalyst and at a very low conversion (less than 5%).

### Results and discussion

#### Hydrogen-mordenite

At 400 °C, the main products are those expected from carbonium ion  $\beta$ -scission (Tables II and III). The distribution is almost the same as on silica-alumina [6]: *n*-hexane and 2-methylpentane give mainly  $C_3$  products, 2,4-dimethylpentane mainly  $C_3$  and  $C_4$  products and *isooctane*  $C_4$  products. However, if one looks at the product distribution in detail, it appears not to correspond exactly to a primary cracking of carbonium ions resulting from the reactant.

The amounts of  $C_1$  and  $C_2$  are always larger than the amounts of the complementary heavy products: one finds 4.4%  $C_1$  and 16.6%  $C_2$  from *n*-hexane while the corresponding amounts of  $C_5$  and  $C_4$  are only 0.5% and 10.5% respectively (Table II).

Table II

Cracking of *n*-hexane and 2-methylpentane. Product composition (mole %)

Starting material	Catalysts Products	H—M		0.6% Pt—H—M	
		400 °C	250 °C	400 °C	250 °C
<i>n</i> -Hexane	Methane	4.4	0	0.2	0
	Ethylene	12	0	0	0
	Ethane	4.6	0.5	4.7	1.3
	Propene	28.5	0.2	6.3	0
	Propane	39.5	43.9	72.2	31.2
	Isobutene	1.7	0	0.9	0
	Isobutane	3.6	22.1	4.7	39.2
	<i>n</i> -butane	4.2	17.1	6.3	8.3
	2-butene	1	0	0.5	0
	Isopentane	0.5	7	1.8	15.7
	<i>n</i> -pentane	0	9.2	2.4	4.3
2-methyl-pentane	Methane	6.3	0	0.75	0
	Ethylene	12.5	0	0	0
	Ethane	4.6	1.2	4.9	4.6
	Propene	33.2	0.85	1.3	0
	Propane	30.7	33.9	81.5	21.4
	Isobutene	0.4	0	0.05	0
	Isobutane	6.7	34.15	4.1	42.5
	<i>n</i> -butane	1	14.45	4.3	7.7
	2-butene	0.8	0.2	0.1	0
	Isopentane	3.8	12.8	2.25	21.6
	<i>n</i> -pentane	0	2.45	0.75	2.2

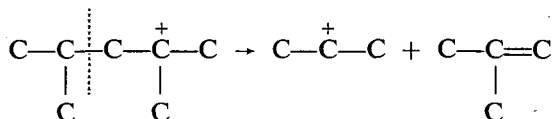
Table III  
Cracking of 2,4-dimethylpentane and isooctane. Product composition (mole %)

Starting material	Catalysts Products	H—M		0.6% Pt—H—M	
		400 °C	250 °C	400 °C	250 °C
2,4-dimethyl-pentane	Methane	0.4	0.05	0.4	0
	Ethylene	2.1	0	0	0
	Ethane	0.2	0.15	2.2	0
	Propene	38.6	2.45	1.1	0
	Propane	7.0	27.4	47.0	42.0
	Isobutene	4.2	0.6	4.6	0
	Isobutane	45.0	47.6	34.7	46.5
	n-butane	0.2	9.5	7.3	3.0
	2-butene	2.1	0.15	0.4	0
	Isopentane	0.2	6.7	0.2	4.8
	n-pentane	0	1.2	0.1	0.5
Hexanes	0	4.2	2.0	3.2	
Isooctane	Methane	11.4	0	2.5	0
	Ethylene	3.7	0	0	0
	Ethane	2.8	0	2.2	0
	Propene	14.6	0.8	0	0
	Propane	9.7	13.7	7.2	7.8
	Isobutene	15.8	7.6	16.0	0
	Isobutane	28.35	54.8	54.5	74.0
	n-butane	1.8	11.6	15.0	11.5
	2-butene	7.1	0.4	0	0
	Isopentane	2.6	7.9	1.4	5.1
	n-pentane	0.8	1.9	1.2	1.1
Pentenes	1.3	0.7	0	0	
Hexanes	0.05	0.6	0	0.5	

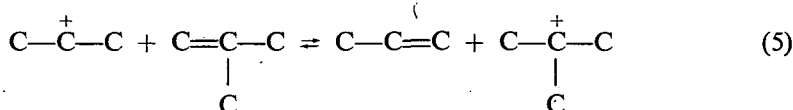
This implies that the alkenes or carbonium ions formed in reactions (3) and (3') undergo a secondary cracking before desorption.

The quantity of alkenes is in every case smaller than the amount of alkanes. This result is generally supposed to be due to hydrogen transfer with formation of aromatics or coke [7]. No aromatics are detected here, but the catalyst is deactivated by coke formation (Table I).

Another observation is that 2,4-dimethylpentane yields *isobutane* and propane (Table III) instead of propane and *isobutene* according to:



This indicates that a reaction of proton transfer (reaction (5)) takes place very readily on the surface:



No isomers of the starting material are detected but one observes an unexpected formation of *i*-C<sub>4</sub> from *n*-hexane (Table II) and *n*-C<sub>4</sub> from *isooctane* and 2,4-dimethylpentane (Table III). The fact that no isomers of the starting material are observed means that (1) and (4) or (2) are slow compared to (3) and (3'). Since isomeric fragments are found among the products, reactions (2) and (2') must take place at an appreciable rate. Moreover it is known that butanes are much more difficult to isomerize than larger alkanes [8—9]. Thus, the principal way in which the isomeric fragments are formed is probably (2) followed by (3'). One must then conclude that the carbonium ion formation and desorption are rate-determining.

At 250 °C, the selectivities differ markedly from what is observed at 400 °C and one notices especially that isomerization now accompanies cracking except for *isooctane*.

The light products are formed in very small quantities but the C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub> products are found in rather large amounts (Tables II and III). For example, no C<sub>1</sub> and C<sub>2</sub> are formed from *n*-hexane whereas one finds respectively 16% and 39% of C<sub>5</sub> and C<sub>4</sub>. However, no products heavier than the reactant are found. All the products are mainly saturated and very few alkenes are found. The large amount of heavy products (C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub>) can only be accounted for by supposing that a bimolecular intermediate is formed, either between two molecules of reactant, or one molecule of reactant and one molecule of product, or between two molecules resulting from a primary cracking of the reactant. The primary products of cracking (alkenes and carbonium ions) are highly reactive and may interact together very readily through alkylation which is the reverse reaction of  $\beta$ -cracking of carbonium ions. This reaction will occur very rapidly especially if small, unstable, primary carbonium ions are involved [10], with a consequent decrease in the amount of light hydrocarbons and alkenes and an increase in the amount of heavier products. The formation of a dimer of the rather unreactive starting alkane [11] is unlikely without its previous transformation into alkenes. Moreover this should lead to products heavier than the reactant, but this is not observed.

At this temperature, cracking is only 3 to 4 times slower than at 400 °C (apparent activation energy: 5 kcal mole<sup>-1</sup>) whereas isomerization is up to 10 times faster at 250 °C than at 400 °C (Table I). The existence of isomerization shows that at 250 °C the cracking of carbonium ions (3 and 3') is no longer infinitely faster than their desorption (4) as it is the case at 400 °C. Adsorption-desorption of alkanes is no longer rate-limiting. Moreover, the peculiar enhancement of the overall isomerization rate (Table I) leads one to suppose that the formation and desorption of the carbonium ions (1 and 4) themselves occur at a higher rate than at 400 °C. This phenomenon can easily be accounted for by assuming that these reactions involve intermolecular hydride transfer between alkanes and carbonium ions at the surface. This exchange would be more important at a lower temperature because of a larger concentration of adsorbed species on the catalyst.

#### *Platinum-hydrogen-mordenite*

At 400 °C the fact that platinum has been deposited on the mordenite has an effect similar to a lowering of the reaction temperature: disappearance of alkenes among the products and also a decrease in the amount of C<sub>1</sub>, C<sub>2</sub> products and an increase in that of C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub> (Tables II and III). But the main point is that the cracking

activity is considerably increased and that an important isomerization activity appears (Table I). The isomerization to cracking ratio in the case of *n*-hexane increases in the same way as when the reaction temperature is lowered on hydrogen-mordenite.

The effect of platinum content (Figure 2) or metal area on the activity is typical

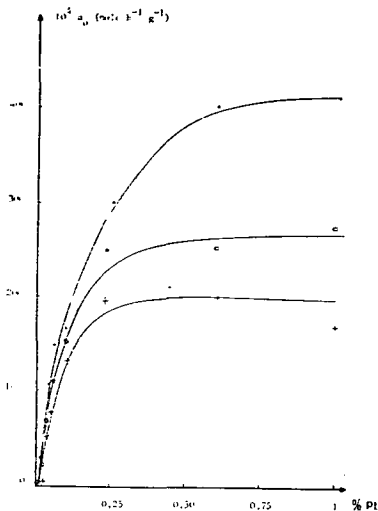


Fig. 2. Influence of platinum content on the activity of platinum-hydrogen-mordenite at 400 °C: • cracking of *isooctane*; ○ cracking of *n*-hexane; + isomerization of *n*-hexane.

plied by 15 (Table I). Thus, the ratio of isomerization to cracking is highly increased. One can again assume that the rate of adsorption-desorption of the alkane is increased by adding (1') and (4') to (1) and (4). The weakness of the effect of platinum deposit is probably due to the fact that at this temperature the metal area is not sufficient to attain the equilibrium between the alkanes and corresponding alkenes.

### Conclusion

The classical mechanism involving carbonium ions as intermediates can explain the results of cracking and isomerization of alkanes on hydrogen-mordenite and platinum-hydrogen-mordenite. At 400 °C, the formation and desorption of carbonium ions is rate-determining for cracking. Isomerization does not take place because the desorption of isomeric carbonium ions is slow compared to their  $\beta$ -scission. A decrease in reaction temperature or an addition of platinum to the hydrogen-mordenite improves the rate of adsorption and desorption of carbonium ions and consequently favors isomerization compared to cracking. The alkenes and carbonium ions resulting from cracking react together. This reaction is faster at 250 °C because of the larger concentration of adsorbed species.

of a bifunctional behaviour: the activity first increases proportionally to platinum content, then remains constant. For *n*-hexane a metal area of approximately 0.4 m<sup>2</sup>g<sup>-1</sup> (0.2 w% Pt) is sufficient to obtain the maximum level of activity. On the catalysts with high platinum content (metal area >0.4 m<sup>2</sup>g<sup>-1</sup>) the carbonium ion formation occurs readily through dehydrogenation of the reactant into alkenes (1'). The limiting step for the cracking reaction becomes the  $\beta$ -cracking of the carbonium ions (3 and 3') while (2) is the limiting step for isomerization. This effect of platinum demonstrates that an increase in the rate of carbonium ion formation improves the selectivity in isomerization as opposed to cracking, and this provides good evidence for our interpretation of the effect of lowering the reaction temperature.

At 250 °C the effect of platinum is much less pronounced than at 400 °C. The activity for *n*-hexane cracking only doubles while the isomerization activity is multi-

### Acknowledgments

One of the authors (C. GUEGUEN) gratefully acknowledges the "Société Nationale Elf-Aquitaine" for supporting his research. Thanks also go to J. BOUSQUET from this company for carrying out measurements of platinum content in the catalysts.

### References

- [1] *Marcilly, Ch.*: Revue de l'Institut Francais du Pétrole **30**, 969 (1975); *Magee, J. S.*: Molecular Sieves II, *J. R. Katzer*: A. C. S. Symposium Series 40, Washington, 650 (1977); *Bolton, A. P.*: Zeolite Chemistry and Catalysis, *Rabo J. A.*, A. C. S. Monograph 171, Washington, 714 (1976).
- [2] *Weisz, P. B., J. N. Miale*: J. Catal. **4**, 527 (1965).
- [3] *Benesi, H. A.*: J. Catal. **8**, 368 (1967).
- [4] *Poutsma, M. L.*: Zeolite Chemistry and Catalysis, *J. A. Rabo*, A. C. S. Monograph 171, Washington, 437 (1976).
- [5] *Ricard, J. M., L. Maury*: Le pétrole Raffinage et Génie Chimique, *P. Wuithier*: Technip, Paris, **1**, 715 (1972).
- [6] *Lopez, G., G. Perot, M. Guisnet*: to be published.
- [7] *Thomas, C. L., D. S. Barmby*: J. Catal. **12**, 341 (1968). *Walsh, D. E., L. D. Rollmann*: J. Catal. **49**, 369 (1977).
- [8] *Brouwer, D. M., J. M. Oelderick*: Rec. Trav. Chim. **87**, 721 (1968).
- [9] *Chevalier, F., M. Guisnet, R. Maurel*: Proc. Inter. Congr. Catal. 6th London, 1976, **1**, 478 (1977).
- [10] *Fejes, P., P. H. Emmett*: J. Catal. **5**, 193 (1966).
- [11] *Bolton, A. P., M. A. Larewala*: J. Catal. **18**, 1 (1970).