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Alumina: Catalyst and Support.
XVII.* Dehydrocracking of Hydrocarbons over "Nonacidic" Chromia-Alumina Catalyst†

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Dehydrocracking of hydrocarbons over "nonacidic" chromia-alumina catalyst at about 525°C and atmospheric pressure was correlated with the types of carbon–carbon bonds cleaved. In paraffins bond cleavage was preferred between the most substituted carbon atoms. In olefins bond breakage occurred β to the double bond. The cracking pattern over "nonacidic" chromia-alumina catalyst favors a free radical mechanism.

INTRODUCTION

It was shown in previous papers of these series (*1*, *2*) that the aromatization of branched paraffins over chromia-alumina catalyst is accompanied by a cracking reaction. The extent of cracking depends to a great degree upon the structure of the feed paraffins. It was also demonstrated (*1*) that recombination of the products of cracking may produce aromatic hydrocarbons. The importance of this reaction in the case of trimethylpentanes made the investigation of the cracking patterns of hydrocarbons desirable. The primary fragments of cracking accompanying dehydrogenation can be determined on "nonacidic" chromia-alumina, which does not catalyze secondary reactions associated with acid sites (*2*).

DISCUSSION

This study of the cracking characteristic of C_6–C_8 hydrocarbons is based on the detailed analysis of their dehydrogenation products as described in the preceding two papers (*1*, *2*). The experiments were made in a flow type apparatus using chromia-alumina catalyst in which the alumina was made from potassium aluminate; the concentration of chromia was 13.8 wt.%. The reactions were carried out at about 525° and at about 3 seconds contact time. For details of experimental conditions and analytical

TABLE 1
DISTRIBUTION OF REACTIONS IN THE DEHYDROGENATION OF 2,2-DIMETHYLBUTANE OVER Cr_2O_3–Al_2O_3 CATALYST

Cut number	1	2
2,2-Dimethylbutane reacted (Mole %)	13.9	15.2
Type of reaction (Mole % of total conversion)		
Dehydrogenation	33.2	36.5
Dehydroisomerization		
2-Methylpentenes	7.9	8.3
3-Methylpentenes	0.1	0.2
2,3-Dimethylbutenes	0.5	0.7
1,1,2-Trimethylcyclopropane	0.15	0.2
Cracking		
Isobutane and ethylene	42.3	39.4
Isopentenes and methane	14.3	13.2
Neopentane and methane	0.05	0.06
Aromatics	0.3	0.24
Carbonaceous material	1.0	1.0
Other	0.2	0.2

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[*] For paper XVI of these series see H. Pines and S. M. Csicsery, reference (*1*).

[†] Paper IX of the series "Aromatization of Hydrocarbons." For paper VIII see reference (*1*).

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TABLE 2

Distribution of Reactions in the Dehydrogenation of 2,3-Dimethylbutane over Cr_2O_3–Al_2O_3 Catalyst

Cut number	1	2	3
2,3-Dimethylbutane reacted (Mole %)	28.0	31.3	33.0
Type of reaction (Mole % of total conversion)			
Dehydrogenation			
Olefins	51.9	54.4	58.2
Diolefins	10.2	10.2	10.3
Dehydroisomerization			
2-Methylpentenes	3.7	4.5	5.7
3-Methylpentenes	7.0	6.2	4.6
Dehydrocyclization			
Methylcyclopentenes[a]	0.2	0.2	0.1
Cracking			
Methylbutenes and methane	10.0	9.4	8.5
Propane and propylene	14.3	12.3	9.8
Isobutane and $2CH_4$ or C_2H_6[a]	0.5	0.5	0.5
Aromatics			
Benzene	0.2	0.3	0.3
C_7–C_9	0.2	0.2	0.2
Carbonaceous material	1.8	1.8	1.8

[a] Secondary reactions of methylpentenes.

TABLE 3

Distribution of Reactions in the Dehydrogenation of 2,2,4-Trimethylpentane over Cr_2O_3–Al_2O_3 Catalyst

Cut number	1	4
2,2,4-Trimethylpentane reacted (Mole %)	19.4	25.2
Type of reaction (Mole % of total conversion)		
Dehydrogenation	32.0	35.5
Dehydrocyclization		
Naphthenes	1.0	1.0
p-Xylene	10.1	15.5
Toluene	0.9	1.2
Dehydroisomerization		
2,5-Dimethylhexenes	2.6	2.0
Cracking		
Isobutane and isobutylene	39.2	33.0
Neopentane and propylene	2.6	1.8
2,2-Dimethylpentenes and methane	1.6	1.3
2,4-Dimethylpentenes and methane	6.0	5.0
2-Methylpentenes + $2CH_4$[a]	0.5	0.4
Methylbutenes + C_2[b]	1.6	1.5
Carbonaceous material	1.9	1.8

[a] Secondary cracking of dimethylpentenes.

[b] Secondary cracking of 2,5-dimethylhexenes.

procedure see previous papers (*1*, *2*). The distribution of the different reactions occurring on the chromia-alumina catalyst are summarized in Tables 1–8. These data were used in determining the probabilities for bond dissociations between neighboring carbon atoms of different substitution. Statistical weights were applied in the case of two or more identical bonds. The different bond cleavages for each hydrocarbon were expressed as percentages of the feed hydrocarbon passed over the catalyst (Table 9). The values obtained from the different paraffins were similar for each type of bond cleaved (Table 10).

Primary cracking products can react further. *n*-Hexenes were dehydrocyclized to benzene, and part of the dimethylpentanes derived from the trimethylpentanes dissociated to smaller fragments. In the preparation of Tables 1–9 these secondary reactions were also taken into consideration.

The greatest extent of cracking was observed in the dehydrogenation of 2,2,3-trimethylpentane. In this hydrocarbon most of the bond breaking occurred between the quaternary and tertiary carbon atoms. Cracking is limited when normal paraffins are dehydrogenated.

TABLE 4

Distribution of Reactions in the Dehydrogenation of 2,3,4-Trimethylpentane over Cr_2O_3–Al_2O_3 Catalyst

Cut number	1	2	3	4
2,3,4-Trimethylpentane reacted (Mole %)	36.3	34.6	31.3	25.6
Type of reaction (Mole % of total conversion)				
Dehydrogenation				
Monoolefins	35.0	31.2	26.2	21.0
Diolefins	3.2	3.5	3.8	3.4
Dehydrocyclization				
Toluene	1.40	1.46	1.02	0.77
Ethylbenzene	0.14	0.14	0.12	0.03
o-Xylene	4.00	3.80	3.02	2.33
m-Xylene	9.90	5.00	2.00	0.87
p-Xylene	3.76	3.40	1.94	1.10
Cracking				
2,3-Dimethylpentane and methane	4.8	5.6	4.8	5.7
2,4-Dimethylpentane and methane	0.8	0.9	0.8	0.9
Methylpentenes and $2CH_4$	1.1	1.4	1.3	1.4
Methylbutenes and C_3	24.3	31.5	41.0	48.0
Methylbutenes and C_2 + methane	1.6	1.7	2.2	2.4
C_4 and others	2.3	2.4	3.5	3.0
Carbonaceous materials	7.6	7.9	8.2	9.0
Other	0.1	0.1	0.1	0.1

TABLE 5

Distribution of Reactions in the Dehydrogenation of 2,2,3-Trimethylpentane over Cr_2O_3–Al_2O_3 Catalyst

Cut number	1	3
2,2,3-Trimethylpentane reacted (Mole %)	40	37
Type of reaction (Mole % of total conversion)		
Dehydrogenation	6.00	5.25
Dehydrocyclization		
m-Xylene	1.52	2.14
Ethylbenzene, *o*- and *p*-Xylene	0.55	0.50
Toluene and methane	1.86	1.50
1,1,2-Trimethylcyclopropane and C_2	0.02	0.02
Dehydroisomerization		
2,4-Dimethylhexenes	0.34	0.44
2-Methylheptenes	0.17	0.14
Cracking		
2,2-Dimethylbutane and C_2	2.80	3.07
2,3-Dimethylpentane and methane	3.65	3.48
2,2-Dimethylpentane and methane	0.65	0.59
2,2,3-Trimethylbutane and methane	1.50	1.76
i-C_4 and *n*-C_4	63.00	65.30
C_4, C_3, and CH_4 or C_4 and $2C_2$[a]	10.56	8.70
i-C_5, C_2, and CH_4[a]	3.12	2.77
C_6 and $2CH_4$[a]	0.87	0.96
Other	0.83	0.71
Carbonaceous materials	2.56	2.67

[a] Secondary cracking of C_7 or C_6 hydrocarbons.

TABLE 6

DISTRIBUTION OF REACTIONS IN THE DEHYDROGENATION OF 3-ETHYLHEXANE OVER Cr_2O_3–Al_2O_3 CATALYST

Cut number		1	2	3
3-Ethylhexane reacted (Mole %)		29.6	32.4	36.7
Type of reaction (Mole % of total conversion)				
Dehydrogenation				
	Olefins	11.5	11.9	12.0
	Diolefins	2.2	2.3	2.1
Dehydrocyclization				
	Naphthenes	1.2	1.2	1.0
	Ethylbenzene and styrene	24.6	29.5	32.5
	o-Xylene and *m*-xylene	1.1	1.1	1.0
Cracking				
$C_7 + C_1$	3-Ethylpentane and methane	0.8	1.6	1.3
	3-Methylhexane and methane	0.8		
	Toluene and methane	1.6	1.9	2.0
$C_6 + C_2$	*n*-Hexane and C_2	10.0	8.6	7.8
	Benzene and C_2	8.5	9.7	9.4
	3-Methylpentane and C_2	2.9	2.2	2.1
	2-Methylpentane and $2CH_4$[a]	0.3	0.3	0.3
$C_5 + C_3$, etc.	*n*-Pentane and C_3	24.6	20.5	20.0
	Isopentane, C_2 and Methane	0.3	0.2	0.2
C_4 and C_3, C_2, C_1[a]		7.0	6.4	5.7
Carbonaceous materials		2.6	.26	2.6

[a] Secondary cracking.

TABLE 7

DISTRIBUTION OF REACTIONS IN THE DEHYDROGENATION OF 3-ETHYLHEXENES OVER Cr_2O_3–Al_2O_3 CATALYST

Cut number		1	2	3
3-Ethylhexenes reacted (Mole %)		46	35	28.5
Type of reaction (Mole % of total conversion)				
Hydrogenation to paraffin		21.1	24.9	21.4
Dehydrogenation to diolefins		16.7	17.7	20.8
Dehydrocyclization				
	Naphthenes	6.6	6.8	6.9
	Ethylbenzene and styrene	19.3	3.9	3.6
	o-Xylene and *m*-xylene	0.9	0.3	0.2
Cracking				
$C_7 + C_1$	3-Ethylpentane and methane	11.6	5.7	10.2
	3-Methylhexane and methane		8.5	
	Toluene and methane	2.0	1.4	1.1
$C_6 + C_2$	*n*-Hexane and C_2	1.6	1.6	2.3
	Benzene and C_2	0.1	0.1	0.1
	3-Methylpentane and C_2	6.3	10.3	12.0
	2-Methylpentane and $2CH_4$[a]	0.3	0.4	0.4
$C_5 + C_3$ etc.	*n*-Pentane and C_3	2.4	3.9	4.5
	n-Pentane, C_2, and methane[a]	3.1	4.1	4.7
	Isopentane, C_2, and methane	1.3	2.5	2.9
C_4 and C_3, C_2, C_1[a]		3.1	4.3	5.3
Carbonaceous material		3.6	3.6	3.6

[a] Secondary cracking.

TABLE 8
DISTRIBUTION OF REACTIONS IN THE DEHYDROGENATION OF 1-METHYL-2-ETHYLCYCLOPENTANE OVER CR_2O_3–AL_2O_3 CATALYST

Cut number	2
1-Methyl-2-ethylcyclopentane reacted (Mole %)	16.5
Type of reaction (Mole % of total conversion)	
Dehydrogenation	
Monoolefins	24.8
Diolefins	2.8
Dehydroisomerization to Aromatics	
o-Xylene	1.4
m-Xylene	0.6
Ethylbenzene	1.0
Toluene	2.0
Benzene	0.1
Cracking	
Ethylcyclopentane and methane	4.5
Methylcyclopentane and ethylene	8.0
Cyclopentane, ethylene, and methane	1.5
n-Hydrocarbons	4.5
Branched hydrocarbons	0.8
Carbonaceous materials	48.0

CONCLUSIONS

Cracking is independent of the activity and selectivity changes of the catalyst within a dehydrogenation cycle. In open-chain paraffins dissociation of the bond between two carbon atoms increases with the number of their substituents. This effect is the opposite to that observed in the hydrogenolysis over nickel catalyst, where the least substituted bonds break.

Cracking is very much inhibited if neither of the products can be converted to an olefin. An extremely small amount of cracking was observed between the third and fourth carbon atoms of 2,2-dimethylbutane. This reaction should have produced methane and neopentane requiring the consumption of two hydrogen atoms.

Paraffin–monoolefin–diolefin distributions of the products of cracking approach hydrogenation–dehydrogenation equilibria. Cannings *et al.* (*3*) observed very similar radioactivities in isobutane and isobutylene derived from 2,2-dimethyl-4-methyl-C^{14}-pentane. The *n*-butane/*n*-butenes and isobutane/isobutylene ratios were very similar in the dehydrogenation product of 2,2,3-trimethylpentane. Dehydrocracking apparently does not produce an olefin and a paraffin at the moment of bond cleavage but two identical species. This homolytic cleavage indicates a free radical mechanism in the dehydrocracking. The increase in bond breakage with the substitution of the carbon atoms can be explained by the increased stabilities of the free radicals formed since the stability of a free radical increases with substitution. According to Walling (*4*) substitution of a methyl group for a hydrogen on a methyl radical decreases dissociation energy by about 4 kcal/moles.

The cracking pattern of cycloparaffins is different from that of the open-chain paraffins. No ring cleavage of the alkylcyclopentanes occurred during the dehydrogenation reaction. Cracking is limited and it is restricted to the dealkylation of the side chains with the longer side chain dealkylating faster. Twice as much methylcyclopentane than ethylcyclopentane was formed in the dehydrogenation of 1-methyl-2-ethylcyclopentane (Table 8). In the case of methylcyclopentane the only significant cracking reaction is demethanation. Cyclopentane, cyclopentene, and cyclopentadiene were present in the reaction products in substantial quantities (*2*).

Cracking of the 3-ethylhexenes follows a very different pattern than the cracking of 3-ethylhexane (Tables 6 and 7). Probably no cracking of the olefins occurs near the tertiary carbon*. About six times as many bonds are broken between two secondary carbons in the olefin that in the paraffin. It seems that neither the double bond nor any bond adjacent to it can break to form olefins, even if these would be the most preferred bonds in the cracking of the corresponding paraffin. The bond β to the

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* The 3-ethylhexenes undergo much hydrogenation to 3-ethylhexane during the reaction. The limited cracking between the tertiary carbon and any one of the secondary carbons is probably due to the presence of the paraffin.

TABLE 9

CARBON–CARBON BOND BREAKING IN OPEN-CHAIN HYDROCARBONS OVER "NONACIDIC" Cr_2O_3–Al_2O_3 CATALYST AT ABOUT 525°

Type of C—C bond	C—C Bonds broken, Mole % of hydrocarbons passed over the catalyst									
	2,2-Dimethyl butane	2,3-Dimethyl butane	2,2,3-Trimethyl pentane	2,2,4-Trimethyl pentane	2,3,4-Trimethyl pentane	3-Ethyl hexane	*n*-Hexane	*n*-Heptane	*n*-Octane	3-Ethyl hexenes
Secondary–Primary	0.003	—	0.15	—	—	0.34	0.18	0.26	0.21	0.22
Secondary–Secondary	—	—	—	—	—	0.7	0.35	0.52	0.42	4.4
Tertiary–Primary	—	0.69	0.2	0.2	0.68	—	—	—	—	—
Tertiary–Secondary	—	—	1.0	0.52	—	8.8–3.4[a]	—	—	—	0.87
Tertiary–Tertiary	—	3.94	—	—	5.4	—	—	—	—	—
Quaternary–Primary	0.65	—	0.63	0.4	—	—	—	—	—	—
Quaternary–Secondary	5.85	—	—	8	—	—	—	—	—	—
Quaternary–Tertiary	—	—	18.0	—	—	—	—	—	—	—
Total cracking	7.8	6.7	21.2	10.1	14.2	17.3	1.4	2.6	2.5	14.2
Dehydrocyclization to aromatics	0.01	0.06	0.8	2–3.9[b]	6.4–1.1[b]	7.6–12.3[b]	15.5	18	11	4.3–1.1[b]
Dehydrogenation	5	17–22[b]	2.3	6–9[b]	14–6[b]	4.5	9.4	13	11	7

[a] For $C_3 + n\text{-}C_5$ the value is 8.8. For $C_2 + n\text{-}C_6$ or benzene it is 3.4.

[b] Conversions in the first and last cuts of the experiment.

TABLE 10

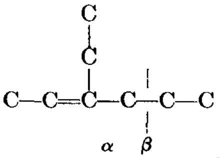
THE RELATIVE CLEAVAGE OF CARBON–CARBON BONDS OF HYDROCARBONS OVER "NONACIDIC" CHROMIA–ALUMINA CATALYST AT 525°

Type of carbon–carbon bonds broken	Carbon–carbon bonds broken (Mole % based on paraffins passed over chromia-alumina)
Secondary–Primary	0.2[a]
Secondary–Secondary	0.4–0.7
Tertiary–Primary	0.2–0.7
Tertiary–Secondary	0.5–8.8[b]
Tertiary–Tertiary	4 –5.4
Quaternary–Primary	0.4–0.6
Quaternary–Secondary	6 –8
Quaternary–Tertiary	18

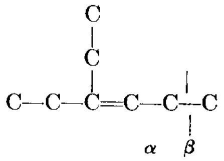
[a] The reaction 2,2-dimethylbutane → neopentane + methane can go only with the consumption of one mole of H_2. Therefore the low value (0.003%) was not included into the average.

[b] The higher value applies to the cracking of 3-ethylhexane producing propylene and *n*-pentane.

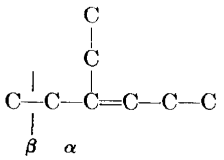
double bond is broken. This preferred bond breakage at the allylic carbon atom may be the consequence of a free radical mechanism.



→ 3-Methylpentenes + Ethylene



→ 3-Ethylpentenes + Methane



→ 3-Methylhexenes + Methane

The differences in the cracking patterns of olefins and paraffins indicate that olefins cannot be intermediates in the cracking reaction of paraffins.

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