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NOTE

Olefinic Intermediates in Catalytic Hydrocracking of Paraffins

Olefins have been visualized to be true intermediates during the conversion of saturated hydrocarbons over bifunctional catalysts in the presence of hydrogen as in catalytic reforming, hydrocracking or hydroisomerization processes (*1, 2*). The independent action of acidic sites for rearrangement reactions and of metallic sites for hydrogenation/dehydrogenation reactions was shown by Weisz and Swegler (*2*) and Weisz (*3*) with bifunctional catalysts consisting of mechanically mixed particles of the two catalyst components. Low thermodynamically controlled concentrations of hexenes in the reaction product of *n*-hexane hydroisomerization have been detected by means of mass spectrometry (*2*). However, no results concerning the occurrence or quantitative determination of olefins in low temperature "ideal" bifunctional hydrocracking have been reported up to now.

Important influences of the catalyst hydrogenation activity upon *n*-hexadecane hydrocracking reactions were shown by Coonradt and Garwood (*4*). Recently, the application of high resolution capillary gas chromatography for the analysis of products from *n*-dodecane hydrocracking over various noble metals on zeolites by Schulz and Weitkamp (*5, 6*) and Pichler *et al.* (*7*) led to a detailed picture of primary and secondary cracking and isomerization reactions. It follows from this that the degree of reversibility of hydrogenation/dehydrogenation reactions is a very important factor for the course of reactions and the products obtained. It was further established that competitive chemisorption of olefins of different size at the acidic centers plays an important role in catalytic hydrocracking.

EXPERIMENTAL METHODS

The feed hydrocarbon (*n*-dodecane, Fluka purum) was hydrocracked in a small tube reactor filled with the catalyst in the zone of constant temperature. The products were recovered by condensation and adsorption and separated into gaseous and liquid fractions which were analyzed by gas chromatography. The experimental and analytical procedures have been described in recent publications (*5, 8, 9*).

The experiments were carried out with a 0.5% Pd/Ca-Y-zeolite catalyst (SK 310, Union Carbide) at a molar ratio H_2/*n*-dodecane of 20, a pressure of 40 kP/cm^2, a space velocity of LHSV = 1.2 hr^{-1} (except one run with LHSV = 4.0 hr^{-1}) and various temperatures in the range of 250 to 500°C.

RESULTS AND DISCUSSION

In Table 1 the composition of the crackproducts from *n*-dodecane is given in dependence of reaction conditions. With the Pd/Ca-Y-zeolite catalyst, hydrocracking starts below 250°C and a 100% cracking conversion is attained at 300°C. The distribution of the crackproducts with almost no C_1 and C_2 fragments indicates a pure cationic cracking mechanism in the low temperature range up to 100% cracking conversion. The total number of moles of crackproducts per 100 moles of dodecane hydrocracked is comparatively low, as corresponding to only minor secondary cracking and a relatively high hydrogenation

TABLE 1

COMPOSITION OF THE CRACKPRODUCTS[a]

Temp (°C):	250	250	265	275	285	300	310	325	350	400	450	500
LHSV (hr^{-1}):	4.01	1.13	1.15	1.40	1.11	1.27	1.18	1.28	1.14	1.14	1.25	1.15
C_{12}-Cracking conversion (%):	3.6	14.8	40.3	57.9	77.7	99.9	100	100	100	100	100	100
C_1	—	—	—	—	—	—	0.1	0.1	0.2	0.5	1.7	10.2
C_2	0.1	—	—	—	0.1	0.1	0.1	0.2	0.5	1.3	2.7	14.0
C_3	9.7	8.6	11.2	12.4	15.3	20.0	26.5	31.2	44.6	60.7	64.2	81.0
C_4	44.7	40.8	44.5	46.1	53.0	59.4	69.9	75.9	94.1	107.1	104.1	101.4
C_5	46.5	45.1	46.6	47.1	49.9	51.8	57.0	57.4	62.3	62.4	62.8	57.7
C_6	40.2	40.1	40.7	40.4	40.5	41.1	42.7	42.6	44.4	42.3	39.0	27.4
C_7	38.6	39.7	38.8	38.3	36.3	34.7	31.1	29.2	15.1	2.9	4.5	4.2
C_8	27.0	28.5	25.7	24.9	21.3	17.3	9.7	6.8	0.5	—	0.5	3.0
C_9	3.5	4.1	3.6	3.6	2.7	1.7	0.4	0.2	—	—	—	0.7
C_{10}	—	0.2	0.2	0.1	0.1	—	—	—	—	—	—	0.1
C_{11}	—	—	—	—	—	—	—	—	—	—	—	—
Total moles	210.3	207.1	211.3	212.9	219.2	226.1	237.5	243.6	261.7	277.2	279.5	299.7
Aromatics (wt %)	—	—	—	—	—	—	—	—	—	0.022	0.58	3.72
Naphthenes (wt %)	0.03	0.18	0.37	0.66	0.75	0.72	0.62	0.50	0.44	0.42	0.40	0.35
Olefins[b] (wt %)	0.015	0.017	0.010	0.009	0.011	—	—	—	—	0.003	0.020	0.160

[a] Molar Distribution (moles/100 moles of C_{12} cracked) and Content of Nonparaffinic Hydrocarbons (wt %).

[b] From C_6 onwards olefin analysis was not complete.

activity of the bifunctional catalyst (*4*, *5*, *7*).

The content of nonparaffinic hydrocarbons in the reaction products is low throughout the whole range of reaction conditions (Table 1, bottom lines). Above 400°C increasing amounts of aromatics are formed whereas the concentration of naphthenes goes through a maximum because at higher temperatures (>300°C) they are

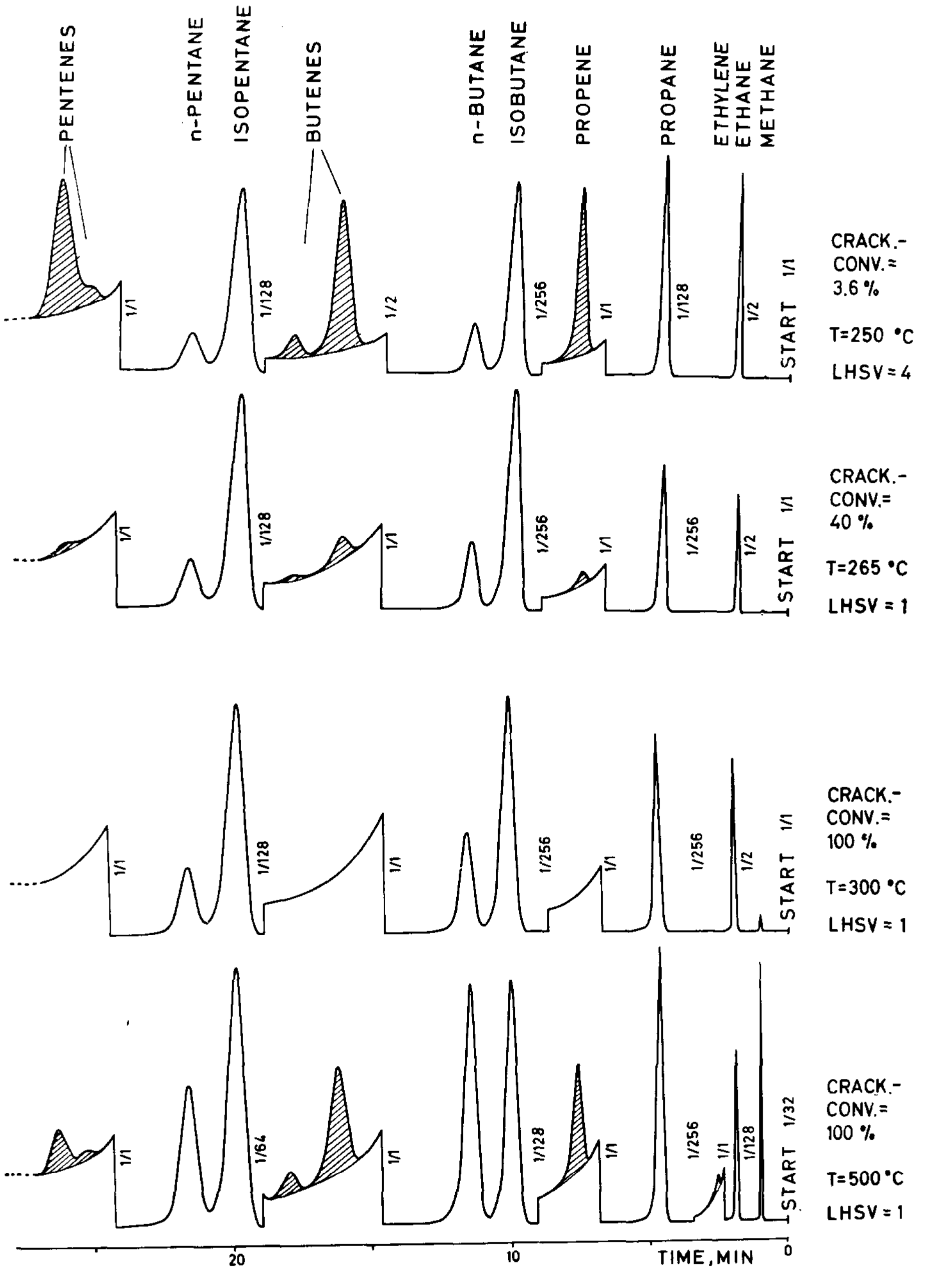

FIG. 1. Chromatograms of the gaseous reaction products (C_1–C_5) from *n*-dodecane hydrocracking. Column: Reoplex modified Al_2O_3, length, 2 m; D_i, 3 mm; temperature program: 2.5°C/min starting at 60°C.

consumed by secondary cracking as well as by dehydrogenation to aromatics. A remarkable variation of the absolute olefin content with reaction conditions may be noticed.

At cracking conversions below 100% (250–285°C) its value is about 0.01–0.02 wt %. But in the range of 300–350°C corresponding to a total C_{12}-consumption and ample secondary cracking, no olefins at all may be detected in the products whereas at higher temperatures ($>400°C$) the absolute olefin content increases again.

It is of greater significance, however, to compare the ratios of olefins to paraffins of the same carbon number. In Fig. 1 chromatograms of the gaseous fractions of four characteristic products are shown which demonstrate the principal interdependences as well as the quantitative reliability of olefin determination.

At low cracking conversions (e.g., 3.6% at 250°C, LHSV = 4 hr^{-1}) relatively large olefin peaks are detected which sharply decrease when the cracking conversion is enhanced (e.g., 40% at 265°C, LHSV = 1 hr^{-1}). No olefins at all are found when a complete C_{12}-consumption is achieved (300°C) whereas at high reaction temperatures (500°C) again appreciable olefin peaks appear. Due to the increase of the C_2-fraction, traces of ethylene are found under these reaction conditions.

The molar ratios of olefinic to paraffinic crackproducts with the same carbon number calculated from the amounts and analyses of the gaseous and liquid fractions are presented in Fig. 2 and Table 2 in dependence of reaction temperature and space velocity, respectively. In Table 2 additional values of thermodynamic equilibrium are listed which were calculated from thermodynamic data (*10*) and the analytically determined ratios of branched to straight chain paraffins in the reaction products.

At high reaction temperature (Fig. 2, 500°C) the experimental ratios of olefins to paraffins in the order of $1–3 \times 10^{-3}$ are mainly controlled by thermodynamics and thus no conclusions concerning the mechanistic importance of olefinic crackproducts can be derived under these conditions. However, in contrast to the thermodynamic

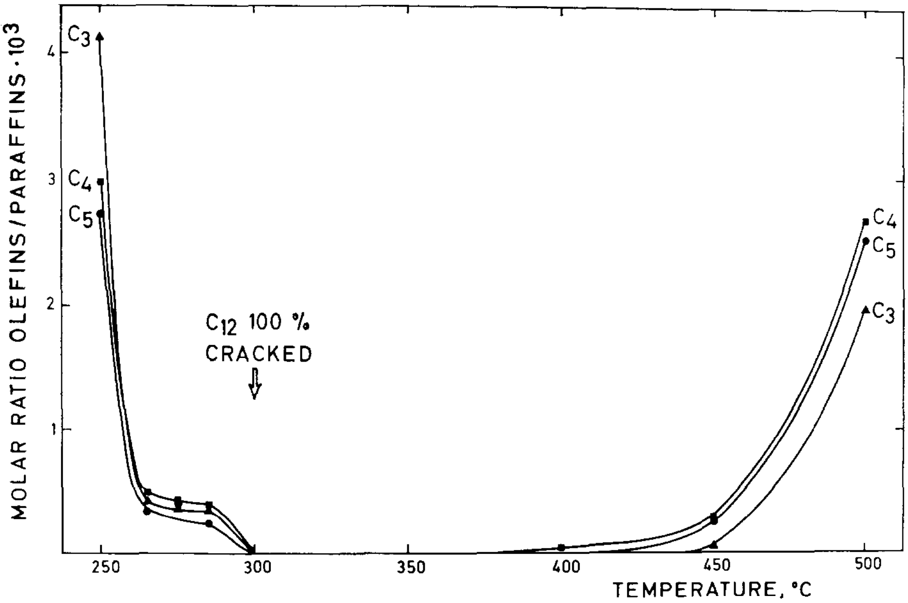

FIG. 2. Molar ratio olefins/paraffins in products from *n*-dodecane hydrocracking. Dependence on reaction temperature.

TABLE 2
MOLAR RATIOS OLEFINS/PARAFFINS[a]

Temp (°C):	250	250	250	500
LHSV (hr^{-1}):	1.13	4.01	Thermodynamic equilibrium	
C_{12}-Cracking conversion (%):	14.8	3.6		
Propene/propane	4.14×10^{-3}	9.02×10^{-3}	0.5×10^{-7}	1.0×10^{-3}
Butenes/butanes	2.99×10^{-3}	7.56×10^{-3}	3.7×10^{-7}	2.8×10^{-3}
Pentenes/pentanes	2.74×10^{-3}	6.63×10^{-3}	10.0×10^{-7}	6.1×10^{-3}

[a] Influence of space velocity and thermodynamic values.

behavior of decreasing olefin to paraffin ratios with decreasing temperatures, a considerable increase in the olefin/paraffin ratios occurs at lower temperatures (<300°C). At 250°C and a space velocity of 1 hr^{-1}, for instance, the experimental propene/propane ratio exceeds the equilibrium value by a factor of 10^5. An increase of space velocity from 1.1 to 4.0 hr^{-1} (Table 2) increases the olefin/paraffin ratios by a factor of ca. 2.5. These results are consistent with the primary formation of olefinic crackproducts.

A further remarkable result is that whereas in thermodynamic equilibrium the sequence of olefin/paraffin ratios is $C_5 > C_4 > C_3$, the opposite sequence $C_3 > C_4 > C_5$ is observed when these values are controlled by kinetics.

According to the theory of bifunctional catalysis, dodecenes should be present in the products from *n*-dodecane hydrocracking in concentrations up to those of thermodynamic equilibrium. However, an estimation of these upper limits gives very low concentrations in the order of magnitude of the detection level. At reaction conditions less severe than necessary for 100% cracking conversion (<300°C) two very small dodecene peaks were detected with areas of ca. $1/10^5$ compared with that of *n*-dodecane.

CONCLUSIONS

The present results concerning the first observation and determination of olefinic crackproducts as intermediates in paraffin hydrocracking are consistent with the widely accepted theory of bifunctional catalysis. According to this mechanism, paraffins are converted to olefins at hydrogenation/dehydrogenation sites. The olefins are adsorbed and cracked at the acidic sites and the resulting olefinic crackproducts are again hydrogenated at the hydrogenation/dehydrogenation sites.

The question arises as to why the relatively high olefin concentrations occur at low cracking conversions of the feed hydrocarbon. Diffusion of the olefins as the rate controlling step can be ruled out, because in this case the olefin/paraffin ratios should not follow the observed sequence $C_3 > C_4 > C_5$. It is our opinion that competition of molecules of different size at the hydrogenation/dehydrogenation centers plays a predominant role, as similarly found to be decisive for the selectivity of reactions at the acidic sites (*4–7*).

Additional investigations of the kinetics of competitive olefin hydrogenation are necessary for further conclusions and have been started in this laboratory.

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