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NOTES

Hydrocracking Product Distributions from *n*-Alkanes and iso-Alkanes

Coonradt and Garwood (*1*) have found that the rate of C—C bond splitting in *n*-hexadecane hydrocracking over platinum is at its maximum in the center of the molecule and decreases toward the ends. We have studied the hydrocracking of *n*-decane over nickel–molybdenum/alumina catalyst (*2*) and the hydrocracking of C_{10}–C_{12} *n*-alkanes over Pt/Al_2O_3 (*3*). Weitkamp (*4*) has investigated the hydrocracking of *n*-tetradecane on Pt/Ca-Y-zeolite, and Steijns *et al.* (*5*) have determined the product composition resulting from the hydrocracking of *n*-dodecane on an ultrastable zeolite having a Pt content of 0.5% by weight. All these latter papers (*2–5*) provide data on the hydrocarbon product decomposition under conditions such that the secondary alkane cracking reactions may be ignored. Qualitatively, all the data are in agreement with those obtained by Coonradt and Garwood (*1*).

These results pose the question as to whether there are any quantitative laws of hydrocarbon decomposition which would hold true for different catalysts. In an earlier paper (*2*), we made an attempt to define such laws based on the composition of the products from *n*-decane hydrocracking on $NiMo/Al_2O_3$. The hydrocracking products were analyzed using a chromatograph employing a flame-ionization detector which supplied a signal proportional to the number of carbon atoms in the hydrocarbon molecule. It was found that the relative rates of the reactions

$$C_{10} \rightarrow C_1 + C_9 \qquad (1)$$

$$C_{10} \rightarrow C_2 + C_8, \qquad (2)$$

depended upon the conditions of catalyst pretreatment. On the other hand, the relative peak areas for the C_7, C_6, and C_5 alkanes stayed nearly constant in all of our experiments. Further experiments (*3*) showed that the peak areas for C_7, C_6, and C_5 alkanes were constant in *n*-decane hydrocracking on Pt/Al_2O_3. Moreover, peaks of equal area were found for C_6, C_7, and C_8 components in the products from decomposition of $C_{11}H_{24}$, and for C_6, C_7, C_8, and C_9 components in the products from decomposition of $C_{12}H_{26}$.

Let us define by Z_N the number of moles of the higher fragment C_NH_{2N+2} which is formed during the decomposition of C_MH_{2M+2} in the reaction

$$C_M \rightarrow C_N + C_{M-N}. \qquad (3)$$

The fact that peak areas are constant for cracking products leads to the equation:

$$N \cdot Z_N = \text{const.}, \quad \frac{M}{2} \leqq N \leqq M - 3, \quad M \geqq 10. \qquad (4)$$

Equation (4) enables one to forecast the yields of various hydrocarbons in the decomposition of alkanes.

It is interesting to compare the calculations based on Eq. (4) with the published data. The comparison shows that Eq. (4) does not hold not only for the reactions (1) and (2) which proceed through elimination of C_1 and C_2 groups from alkane molecules, but also for the reaction

$$C_M \rightarrow C_3 + C_{M-3}. \qquad (5)$$

Thus, in Eq. (4), $N \leqq M - 4$. Furthermore, the differences in splitting rates for adjacent C—C bonds in accordance with Eq. (4) increase toward the center of the molecule;

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for instance, if $M = 12$ then $(Z_6 - Z_7) > (Z_7 - Z_8)$, while the experimental data indicate that the trend is opposite. Nevertheless, the results of the calculations are in good agreement with the experimental data.

Thus, Coonradt and Garwood (*1*) have found that hydrocarbon yields in *n*-hexadecane hydrocracking on $Pt/SiO_2–Al_2O_3$ at the conversion level of 53% are as follows:

Hydrocarbon:	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{11}H_{24}$	$C_{12}H_{26}$
$Z_N\left(\frac{\text{moles}}{\text{100 moles cracked}}\right)$	24	22	19	18	13
$N \cdot Z_N$	192	198	190	198	156

It is evident that $N \cdot Z_N$ is practically the same for C_8–C_{11} hydrocarbons and equal to 190–198 in agreement with Eq. (4). For C_{12} there is a small deviation from the results calculated using Eq. (4). The comparison shows that Eq. (4) may be used, with satisfactory accuracy, to describe the data obtained by Weitkamp (*4*) for the yield of C_7, C_8, C_9, and C_{10} hydrocarbons during the hydrocracking of *n*-tetradecane, and the data obtained by Steijns *et al.* (*5*) for the yields of C_6, C_7, and C_8 during the hydrocracking of *n*-dodecane. Thus, estimations using the plots presented in Ref. (*4*) give (in moles/100 moles cracked) $Z_7 = 30$, $Z_8 = 29$, $Z_9 = 26$, $Z_{10} = 21$ and $N \cdot Z_N = 210–230$. Similar estimations using the data of Ref. (*5*) give $Z_6 = 40$, $Z_7 = 40$, $Z_8 = 30$, and $N \cdot Z_N = 240–280$.

A comparison of the results of studies of the decomposition products with kinetic analyses of hydrocarbon cracking reactions leads one to interesting conclusions. The kinetic analysis of the experimental data on *n*-decane hydrocracking on $NiMo/Al_2O_3$ (*2*) shows that the cracking products were predominantly formed by decomposition of the initial hydrocarbon; hence, Eq. (4) proved to be valid for *n*-alkane. On the other hand, the experiments with C_{10}, C_{11}, and C_{12} *n*-alkanes on Pt/Al_2O_3 catalyst (*3*) show that the major part of the cracking products was formed by the decomposition of mono- and dimethyl-substituted isomers of the initial *n*-alkane. Thus, Eq. (4) is applicable for *n*-alkane and also for its methyl- and dimethyl-substituted isomers. In the same manner, Steijns *et al.* (*5*) showed that over their catalyst the decomposition products are formed predominantly by iso-alkane cracking.

Hence, the analysis of the various experimental data leads to an unexpected claim: the same equation, namely Eq. (4), holds true both for normal alkanes and their methyl- and dimethyl-substituted isomers. In other words, the decomposition of *n*-alkanes and their isomers produce the same cracking product distribution. The distribution is not sensitive or only marginally sensitive to changes in the structure of the alkanes.

In conclusion, the applicability of the same relationship [Eq. (4)] both for normal and for branched alkanes is of practical as well as theoretical interest. The product distribution can depend on the catalyst used, but if Eq. (4) holds true, it will enable one to predict the composition of cracking products for complex alkane mixtures, which, due to their complexity, seemed hitherto to be unpredictable and there appeared to be no way to approach them.

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