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# NOTE

# The Cracking of Isobutane Interpreted as a Chain Mechanism

Recently we reported a methodology for quantifying the details of cracking mechanisms of light hydrocarbons using the selectivity pattern for the *initial* products. Our interpretation is based on the suggestion that such reactions proceed via a chain reaction mechanism (1). In light of this proposal we have examined experimental data for the cracking of isobutane reported by Lombardo and Hall (2). Here we present our findings regarding these data using this new methodology and the mechanistic postulates of the original authors. Based on their proposed mechanism we write the reaction scheme for the conversion of isobutane as shown in Table 1.

In order to determine the reaction pathway probabilities (RPPs), our methods require that we only consider the results obtained under initial conditions. Consequently, from the data available in (2) we have selected data at low conversions (Table 2 in Ref. (2)), conditions which are often taken to yield initial selectivities.

The equations shown in Table 2 come from mass balance considerations based on the mechanism shown in Table 1. For example, propane is formed by processes identified as 21 and 30 in Table 1. The molar selectivity for propane is therefore equal to the sum of two RPPs, $X_{21} + X_{30}$. Similar mass balancing applies to other initial products as for example to the production of propylene. To determine the selectivity for this olefin we have to account for all the possible reactions of propyl carbenium ions, the sole source of propylene formation under initial conditions. As a result, the molar selectivity for propylene is equal to the difference between the sum of probabilities for the formation of propyl carbenium ions and the sum of probabilities for their consumption to give products other than propylene. Accordingly, the molar selectivity for propylene is equal to $X_{01} + X_{41} + X_{21} - X_{30}$. When all the observed initial products are treated in this way we obtain the equations in Table 2. Experimental values of molar selectivities used in Table 2 were taken from (2) from the "molecules formed/100 molecules reacted" column.

As in our previous work (1), GAMS software was used to solve the equations in Table 2. However, in this case the system of equations which results from the proposed mechanism and the reported selectivities from (2) has no feasible solution for any of the four cases reported there. The problem may lie with the experimental data or the reaction mechanism suggested by the authors in (2). There is certainly a problem with the accuracy in the reported experimental data, as moles of product (presumably the primary data) are reported to only one place of decimals. There may also be a problem with just how "initial" the selectivities at the reported conversions are. We have previously recommended the estimation of initial selectivities from the slope at zero conversion on plots of *optimum performance envelopes* for each product (3) in order to avoid inaccuracies introduced by the presence of secondary products at finite conversions and by the presence of error in the chemical analysis. Lombardo and Hall (2) in their Table 2 report single point evaluations of yields at low, but finite, conversions. This is not to say the work of Lombardo and Hall is in error but rather that it is not suited for quantitative interpretation of the sort we are undertaking.

The data are also put into question by inconsistencies between the reported "number of molecules formed/100 molecules converted" and the number of "molecules formed." For example, in the case of the H-Y catalyst these two values are not in agreement with each other for *n*-butane, the butenes, and the pentanes. In the case of $Al_2O_3$–$SiO_2$ isobutene data is similarly inconsistent and in the case of H-ZSM-5 there is a problem with data for

**TABLE 1**

**Elementary Reactions in Isobutane Cracking**

| Reactions | Reaction pathway probability |
|---|---|
| Initiation | |
| $iC_4H_{10} + HS \rightarrow H_2 + C_4H_9S$ | $X_{00}$ |
| $iC_4H_{10} + HS \rightarrow CH_4 + C_3H_7S$ | $X_{01}$ |
| Propagation | |
| $iC_4H_{10} + C_2H_5S \rightarrow C_2H_6 + C_4H_9S$ | $X_{20}$ |
| $iC_4H_{10} + C_2H_5S \rightarrow C_3H_8 + C_3H_7S$ | $X_{21}$ |
| $iC_4H_{10} + C_3H_7S \rightarrow C_3H_8 + C_4H_9S$ | $X_{30}$ |
| $iC_4H_{10} + C_4H_9S \rightarrow nC_4H_{10} + C_4H_9S$ | $X_{40}$ |
| $iC_4H_{10} + C_4H_9S \rightarrow C_5H_{12} + C_3H_7S$ | $X_{41}$ |
| Chain transfer ($\beta$-cracking) | |
| $C_4H_9S \rightarrow C_2H_4 + C_2H_5S$ | $X_{B42}$ |

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### TABLE 2

**Equations for Calculating the RPPs for Isobutane Cracking over H-Y Catalyst[a]**

$$
\begin{aligned}
X_{01} &= 0.17\\
2{*}X_{B42} - X_{21} &= 0.06\\
X_{21} + X_{30} &= 0.14\\
X_{40} &= 0.15\\
X_{41} &= 0.10\\
X_{01} + X_{21} + X_{41} - X_{30} &= 0.19\\
X_{00} + X_{20} + X_{30} - X_{B42} - X_{41} &= 0.40\\
X_{00} + X_{01} + X_{20} + X_{21} + X_{30} + X_{40} + X_{41} &= 1.00
\end{aligned}
$$

[a] Values of selectivity used here are from Table 3 for HY catalyst and lead to "infeasibility" problems.

### TABLE 4

**RPP Values for the Cracking of Isobutane[a]**

| | H-Y | H-ZSM | $SiO_2$–$Al_2O_3$ |
|---|---|---|---|
| $X_{00}$ | 0.417 | 0.733 | 0.916 |
| $X_{01}$ | 0.180 | 0.266 | 0.000 |
| $X_{20}$ | 0.000 | 0.000 | 0.000 |
| $X_{21}$ | 0.014 | 0.000 | 0.083 |
| $X_{30}$ | 0.139 | 0.000 | 0.000 |
| $X_{40}$ | 0.097 | 0.030 | 0.000 |
| $X_{41}$ | 0.153 | 0.000 | 0.000 |
| $X_{B42}$ | 0.028 | 0.400 | 0.083 |

[a] Obtained using "reconstructed" data from Table 3 in the equations of Table 2.

$C_3 + C_4$. In the case of H-M, there is no possible solution of the data as it is reported. We believe that this system merits re-examination. We have therefore assumed the values of "molecules formed" are in general the most likely to be correct and then have "reconstructed" these values as follows.

Noting that the primary data in (2) are reported to an accuracy of only one figure of decimals, we were able in the case of H-Y to find a feasible solution for the system of equations by correcting the inconsistencies and changing some of the reported values of "molecules formed," keeping within the margin of uncertainty implied by the accuracy of the reported data. Table 3 shows the "reconstructed" data. The solution, i.e., the RPPs obtained using these "reconstructed" results, is reported in Table 4. For $SiO_2$–$Al_2O_3$ and H-ZSM we had to exceed these error bounds to some extent before a solution could be found. These results are also shown in Tables 3 and 4. The experimental results for the H-M catalyst reported in (2) cannot be amended to give a feasible solution using this procedure.

Initial molar selectivities can be calculated from the "reconstructed" results and then used to examine the mass balance for C and H. Results for the case of H-Y are shown in Table 5. We note that, using the "reconstructed" data, the calculated H/C value for the products is in good agreement with this ratio in the feed. This implies that any coke formed had the same H/C ratio as the feed or that coke was produced in insignificant amounts. If significant amounts of coke, with an altered H/C ratio, were produced at these low conversions one would have to add coking processes to the reaction mechanism.

If we examine Table 4 in greater detail we can also extract information about the contribution of the various chain processes to the formation of each product. For example, all the propane formed over H-Y comes from two alternate forms of chain propagation in the following proportions:

$$iC_4H_{10} + C_3H_7S \rightarrow C_3H_8 + C_4H_9S \text{ gives } X_{30}/(X_{30} + X_{21}) = 91\%.$$

$$iC_4H_{10} + C_2H_5S \rightarrow C_3H_8 + C_3H_7S \text{ gives } X_{21}/(X_{30} + X_{21}) = 9\%.$$

### TABLE 3

**"Reconstructed" Values[a]**

| | H-Y | H-ZSM-5 | $SiO_2$–$Al_2O_3$ |
|---|---|---|---|
| Methane | 0.648(18.0) | 0.400(26.6) | 0.0(0.0) |
| Total $C_2$ | 0.152(4.22) | 1.200(80.0) | 0.100(8.3) |
| Propane | 0.551(15.3) | 0.0(0.0) | 0.100(8.3) |
| Propylene | 0.749(20.8) | 0.400(26.6) | 0.100(8.3) |
| *n*-Butane | 0.351(9.75) | 0.000(0.00) | 0.0(0.0) |
| Total $C_4$ olefins | 1.350(37.5) | 0.500(33.3) | 1.000(83.3) |
| Pentanes | 0.551(15.3) | 0.000(0.00) | 0.0(0.0) |

[a] See the text for explanation of the reconstruction procedure.

### TABLE 5

**Mol Balances for the Initial Cracking of Isobutane over H-Y**

| | Molar selectivity[a] | Carbon | Hydrogen |
|---|---|---|---|
| $H_2$ | 0.417 | — | 0.834 |
| $CH_4$ | 0.180 | 0.180 | 0.720 |
| $C_2H_6$ | 0.0 | 0.0 | 0.0 |
| $C_3H_8$ | 0.153 | 0.459 | 1.224 |
| $n$-$C_4H_{10}$ | 0.0975 | 0.390 | 0.975 |
| $C_5H_{12}$ | 0.153 | 0.765 | 1.836 |
| $C_2H_4$ | 0.0419 | 0.838 | 0.1676 |
| $C_3H_6$ | 0.2081 | 0.6243 | 1.2486 |
| $C_4H_8$ | 0.3747 | 1.4988 | 2.9976 |
| Total | 1.6248 | 4.0015 | 10.0028[b] |

[a] Molar selectivities are the *reconstructed* values from Table 3 for all reported products and the *calculated* value from Table 4 for hydrogen.

[b] Calculated H/C ratio is 2.4998.

Other such quantities can be calculated as described in (1), yielding interesting insights into the process of cracking in short-chain paraffins. For example, from Table 4 we can conclude that initially there is no ethane formed on any of the catalysts and all the $C_2$ produced was in the form of ethylene. We also note that the RPP of hydrogen formation is high in all cases, a feature which may have had an influence on the precision of the rather difficult product analysis procedure reported in (2).

Although the data in Ref. (2) are not amenable to quantitative interpretation using our procedures and mechanism suggested by the authors, relatively minor "reconstruction" of the reported data does lead to solvable equations for all catalysts except H-M. This leads to some important and informative insights into the cracking of isobutane though, in view of the procedures used to reconstruct the data, there is some uncertainty as to the accuracy of the RPPs obtained. Since the mechanism proposed by Lombardo and Hall is reasonable and the mathematical procedures we have used are well defined, we believe the problems we encountered must lie with the precision of the data, not with the proposed mechanism or the mathematical procedures.

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