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# Networks for Hydrogenolysis Reactions

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This paper describes a new scheme for deriving selectivity equations for a reaction network. Relatively simple equations can be obtained as long as the network has no reversible reaction steps. Isomerization reactions can be included in the network, provided that the isomerization can be regarded as being irreversible.

## INTRODUCTION

Workers in this laboratory have developed useful selectivity equations based on reaction networks for the hydrogenolysis of propane, butanes, isopentane, and hexanes (*1–4*) such as is given for isopentane in Fig. 1. These selectivity expressions plus the rate equation for the parent hydrocarbon provide a complete description of the course of the reaction. The network analysis provides considerably more pertinent information on the system than can be obtained in other ways.

The following assumptions, which do not unduly generalize the derivation, were made:

(a) Hydrocarbon molecule $C_x$ in the gas phase adsorbs reversibly on the surface of the catalyst to form adsorbed species $A_x$.

(b) Splitting of species $A_x$ is irreversible, no chain growth is possible, and no isomerization occurs.

(c) Adsorption of hydrocarbons is first order in the gaseous hydrocarbons; splitting and desorption are first order in the adsorbed species.

(d) Effects of the partial pressure of hydrogen on splitting and desorption are identical and the same for all $A_x$ species. Similarly, the $H_2$ dependencies for the rate of adsorption of hydrocarbons are the same for all species. Under these conditions, all the $H_2$ dependencies cancel, as will be shown in the next section.

(e) No rate-limiting step is assumed.

(f) Only one carbon–carbon bond is splitted at a time.

The rate constants used in the reaction network are $k_x$ for adsorption, $k'_x$ for de-

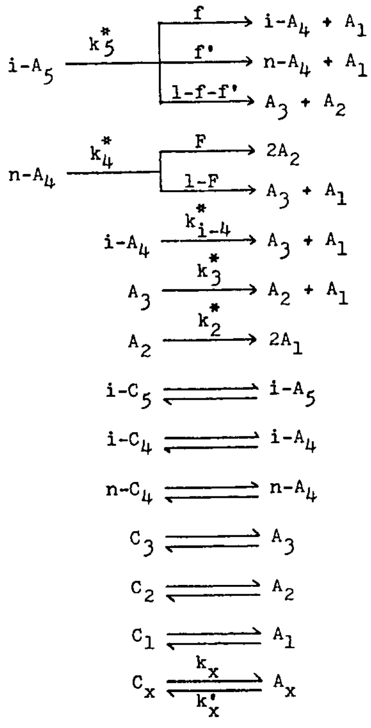

FIG. 1. Reaction network for hydrogenolysis of isopentane.

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$$Q_N = \sum_{\substack{\text{All paths}\\ \text{from R to } I_N}} \prod_{i=1}^{N} \left[ \begin{array}{l} \text{Probability factor in the } i^{\text{th}} \text{ reac-} \\ \text{tion of getting intermediate } I_i \\ \text{leading to product } I_N \end{array} \right]$$

$$- \sum_{\substack{\text{All paths}\\ \text{from } I_i \text{ to } I_N}} \left[ \begin{array}{l} \text{Selectivity of in-} \\ \text{termediate } I_i \text{ of} \\ \text{the } i^{\text{th}} \text{reaction} \end{array} \right] \prod_{j=i-1}^{N} \left[ \begin{array}{l} \text{Probability factor in the} \\ j^{\text{th}} \text{reaction of getting } I_j \\ \text{leading to product } I_N \end{array} \right]$$

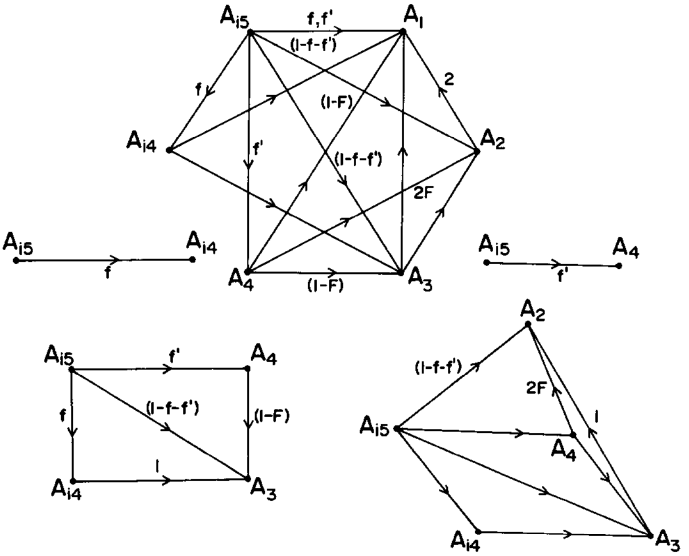
FIG. 2. Algorithm for the calculation of the $Q_N$ factor.

sorption, and $k_x^*$ for the irreversible breaking of C–C bonds. Splitting factors are probabilities of a molecule cracking at a particular C–C bond. As an example, iso-$A_5$ can be cracked into iso-$A_4$ and $A_1$ with probability $f$, into $n$-$A_4$ and $A_1$ with probability $f'$ or into $A_3$ and $A_2$ with probability $(1 - f' - f)$.

The selectivity equation for a given product is derived from rate and mass balance equations for a differential reactor, and the selectivities are differential quantities defined for product $P$ and reactant $R$ as

$$S_p = -R_p/R_R. \tag{1}$$

With this old-fashioned method, it is relatively easy to derive all the selectivity equations for the hydrogenolysis of propane or



$$Q_{i-4} = f \qquad Q_4 = f'$$

$$Q_3 = (1 - F)f' + f + 1 - f - f' - (1 - F)S_4 - S_{i-4}$$

$$Q_3 = 1 - Ff' - (1 - F)S_4 - S_{i-4}$$

$$Q_2 = (1 - F)f' + f + 1 - f - f' + 2Ff' + 1 - f - f' - S_3 - 2FS_4$$
$$- (1 - F)S_4 - S_{i-4}$$

$$Q_2 = 2 - f - f' + Ff' - S_3 - (1 + F)S_4 - S_{i-4}$$

FIG. 3. Pathways for the derivation of $Q$ factors for the hydrogenolysis of isopentane.

butane, but the derivation of networks for larger molecules is tedious and time consuming, and chances of mistakes are large.

## A NEW DERIVATION OF SELECTIVITY EQUATIONS

The purpose of this paper is to present a method for deriving selectivity equations. We will also consider its application to networks involving isomerization. Previous papers (*1–4*) show that the selectivity equation for product $P$ as defined in Eq. (1) has the form:

$$S_P = \frac{Q_P \dfrac{k'_p}{k'_p + k^*_p}}{\left[1 + \dfrac{k''_P}{k''_R}\dfrac{X_R}{1 - X_R}\right]}. \qquad (2)$$

The ratio $(k''_P/k''_R)$ compares the overall first-order rate constants for product $P$ and reactant $R$, respectively, which are defined the following way:

$$k''_x = k_x k^*_x/(k'_x + k^*_x). \qquad (3)$$

The term $Q_P$ represents the maximum amount of $P$ formed by cracking of higher molecular weight hydrocarbons. The ratio $(k'_P/(k'_P + k^*_P)) = j'_p$ measures the relative rates of cracking and desorption of adsorbed species $P$. If the rate-controlling step is the surface splitting reaction, this parameter will be close to unity.

Equation (3) shows that any dependency on $H_2$ for the overall rate constant $k''_x$ is due to the adsorption step. Effects of $H_2$ on splitting or desorption of $A_x$ cancel. Furthermore, in the selectivity equation, the dependency on $H_2$ cancels in terms like $k''_P/k''_R$ and $k'_P/(k'_P + k^*_P)$.

$$S_{i4} = M_{i4}f$$

$$S_{n4} = M_{n4}f'$$

$$S_3 = M_3(1-S_{i4}-(1-F)S_{n4}-Ff')$$

$$S_2 = M_2(2-S_{i4}-S_{n4}(1+F)-S_3-f-f'+Ff')$$

$$S_1 = 5-2S_2-3S_3-4S_{n4}-4S_{i4}$$

$$\text{where } M_h = \frac{\dfrac{k'_h}{(k'_h + k^*_h)}}{1 + \dfrac{k''_h}{k''_5}\,\dfrac{X_5}{(1 - X_5)}}$$

FIG. 4. Selectivity equations for the hydrogenolysis of isopentane.

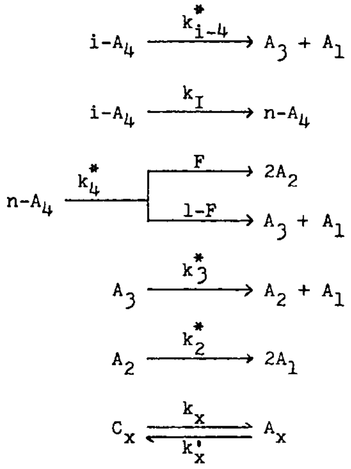


FIG. 5. Reaction network for hydrogenolysis and isomerization of isobutane over Pt catalyst.

The selectivity equation for $CH_4$ becomes $S_1 = Q_1$ since this molecule does not undergo cracking, and consequently, $k^*_1$ and $k'_1$ are equal to 0.0.

In Eq. (2), $Q_p$ is a summation of constants, the pertinent splitting factors, and of measurable variable quantities, the selectivities. $Q_p$ equals the moles of $P$ formed per mole of $R$ consumed following the reaction network minus the moles of $P$ produced if the observed intermediates react completely to $P$, as given by

$$Q_p = \begin{bmatrix}\text{moles of } P \text{ produced in} \\ R \to P \text{ for } X_{\text{int}} = 1\end{bmatrix} - \begin{bmatrix}\text{moles of } P \text{ produced in } J \to P \\ \text{for all } J\text{'s for } X_{\text{int}} = 1\end{bmatrix}$$

where $J$ denotes intermediates between $R$ and $P$, and $X_{\text{int}} = 1$ signifies that these intermediates react completely to $P$. The value of $Q$ for a product of the $N$th generation can be found by applying the algorithm of Fig. 2.

For example, isopentane can be split at three different bonds to give five products:

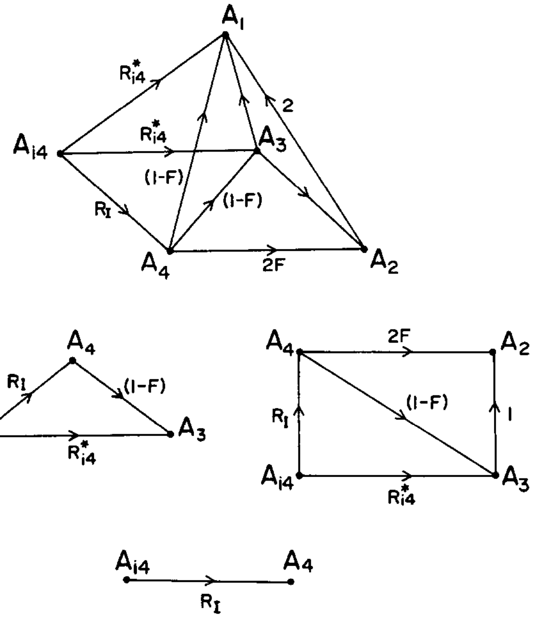


FIG. 6. Pathways for the reactions of isobutane over Pt catalyst.

iso-$C_4H_{10}$, $C_4H_{10}$, $C_3H_8$, $C_2H_6$, and $CH_4$. Figure 3 shows how to derive the $Q$ factor for each selectivity equation. The pathways in Fig. 3 represent all the possible ways of forming products, a genealogical tree for products. We find that $Q_{i4}$ is equal to the probability of cracking iso-$C_5$ to iso-$C_4$, $f$, and $Q_3$ is equal to the summation of probabilities of getting $C_3$ from reaction of iso-$C_5$ directly, $(1 - f - f')$, via $n$-$C_4$, $f'(1 - F)$, and via $i$-$C_4$, $f$.

Some correction terms are added to take account of the presence of $n$-$C_4$ and $i$-$C_4$ among the products, $-(1 - F)S_4 - S_{i4}$. The selectivity equations are given in Fig. 4. These formula are easily derived. Furthermore, the value of $Q$ can be explained physically as described with the algorithm.

Numerical values of the parameters can be found by nonlinear regression of experimental data. These parameters usually predict all the selectivity curves accurately. The splitting factors and the ratios of constants forming a given parameter sometimes cannot be separated and their values cannot be found. In all cases, the ratio $(k''_P/k''_R)$ is uniquely determined and values of $k'_x/(k'_x + k^*_x)$ are obtained very often (*4*).

This algorithm has also been used for deriving selectivity equations for reactions involving isomerization. For example, Fig. 5 shows the reaction network for the hydrogenolysis of isobutane with isomerization. We note that the reaction network can be solved only when all reaction steps are irreversible. In present case, the isomerization is assumed to be so slow relative to hydrogenolysis that the formation of $n$-butane may be considered irreversible. Actually, this approximation is valid for most isomer-

$$S_{n4} = M_{n4}R_I$$

$$S_3 = M_3(1-FR_I-(1-F)S_{n4})$$

$$S_2 = M_2(1-S_3-(1+F)S_{n4}+FR_I)$$

$$S_1 = 4-2S_2-3S_3-4S_{n4}$$

$$\text{where } M_h = \frac{\dfrac{k'_h}{(k'_h + k^*_h)}}{1 + \dfrac{k''_h}{k''_{i4}} \quad \dfrac{X_{i4}}{(1 - X_{i4})}}$$

FIG. 7. Selectivity equations for the reactions of isobutane over Pt catalyst.

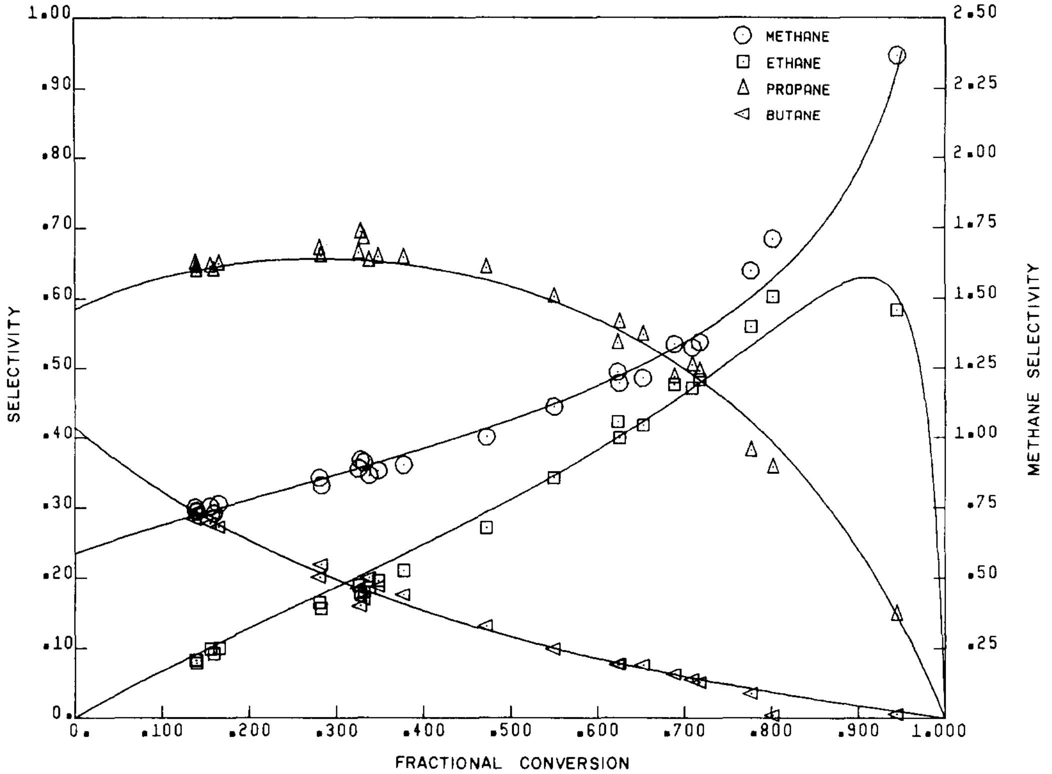


FIG. 8. Product selectivity curves for the hydrogenolysis and isomerization of isobutane over Pt on alumina at 426°C.

izations. All the other assumptions for the hydrogenolysis network are still used. Two new ratios have been defined:

$$R_I = k_I/(k^* + k_I) \text{ and } R^* = 1 - R_I$$

where $R^*$ represents the fraction of a converted reactant undergoing hydrogenolysis and $R_I$, the fraction being isomerized. By applying the algorithm, the selectivity equations can be derived for $n$-$C_4H_{10}$, $C_3H_8$, $C_2H_6$, and $CH_4$ (see Figs. 6 and 7).

## AN EXAMPLE OF HYDROGENOLYSIS WITH ISOMERIZATION

To test the network analysis, these equations have been applied to kinetic data for hydrogenolysis and isomerization of isobutane on Pt on alumina. Pellets of Houdry hydrogenation catalyst were crushed to 14 to 25 mesh. The catalyst was reduced *in situ* for 1 hr at 430°C.

The experiments were carried out in a differential reactor involving a recycle system with a metal bellows pump. Since this pump provides a large recycle, the rate and selectivities are differential quantities. Two gas chromatographs were used to analyze the exit gases for hydrocarbons and hydrogen. The reaction temperature was 426°C and the reactant ratio was 3 $H_2$:1 $i$-$C_4H_{10}$. The pressure was kept at around 125 kPa.

Figure 8 shows selectivities as functions of conversion of $i$-$C_4H_{10}$. The selectivity of $n$-$C_4H_{10}$ decreased monotonically as conversion increases. Initially, at zero-conversion, 41.5% of the converted $i$-$C_4H_{10}$ was isomerized into $n$-$C_4H_{10}$. The other primary products (58.5%) were $C_3H_8$ and $CH_4$. $C_2H_6$, being formed by hydrogenolysis of $n$-$C_4H_{10}$ and $C_3H_8$, was not initially found.

The selectivity equations (from Fig. 7) have been fitted to the experimental data using nonlinear regression methods (Marquardt's compromise (5)) and values for the

TABLE 1

Parameters for the Hydrogenolysis–Isomerization of Isobutane

| $h$ | $j'_h$ | $k''_h/k''_{i4}$ |
|---|---|---|
| $n$-$C_4H_{10}$ | 1.0 | 2.579 |
| $C_3H_8$ | 1.0 | 0.289 |
| $C_2H_6$ | 0.893 | 0.02514 |
| | $R_I = 0.4152$ | |
| | $F = 0.3$ | |

parameters were found. The splitting factor $F$ in hydrogenolysis reactions of $n$-$C_4H_{10}$ was assumed to be 0.3; the same as found for supported Ru. Furthermore, $j'_4$ and $j'_3$ were set equal to 1.0, which seemed reasonable for a Pt catalyst, i.e., the rate of cracking was much slower than the rate of desorption.

Table 1 gives values of the parameters. If $j'_4$ is taken as 1.0, we can calculate $R_I$ = 0.415, the fractions of reacted isobutane isomerized. The ratios of overall rates ($k''_x/k''_{i4}$) were also compared: $n$-$C_4H_{10}$ reacts 2.5 times faster than $i$-$C_4H_{10}$ over Pt while $C_3H_8$ cracks at about one-third the rate of $i$-$C_4H_{10}$. Ethane splits very much slower than the other hydrocarbons, and $j'_2$ is close to 1.0.

This paper has presented a scheme for deriving selectivity equations for networks involving irreversible reactions (either hydrogenolysis or isomerization). Experimental work has been done with a Pt catalyst and the method has been tested.

## ACKNOWLEDGMENTS

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## APPENDIX

| | |
|---|---|
| $A_x$ | Adsorbed hydrocarbon with $x$ carbon atoms |
| $C_x$ | Gaseous hydrocarbon with $x$ carbon atoms |
| $F, f, f'$ | Splitting factors |
| $R$ | Reactant |
| $P$ | Product |
| $J$ | Intermediate |
| $j'_x$ | $k'_x/(k'_x + k^*_x)$ |
| $k_x$ | Rate constant for adsorption |
| $k'_x$ | Rate constant for desorption |
| $k^*_x$ | Rate constant for splitting |
| $k_I$ | Rate constant for isomerization |
| $k''_x$ | Overall first-order rate constant |
| $Q_p$ | Factor for selectivity equations |
| $R_I$ | Fraction of converted reactant undergoing isomerization |
| $R^*_{i4}$ | $1 - R_I$ |
| $R_p$, $R_R$, $R_x$ | Differential reaction rates |
| $S_p$ | Selectivity of product $p$ |

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