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Kinetics of Simultaneous Isomerization and Cracking of *n*-Hexane over Pt/Al_2O_3

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Simultaneous isomerization and cracking of *n*-hexane has been studied over a commercial 0.35 wt% Pt/Al_2O_3 catalyst at 420 to 450°C, a total pressure of 10.5 bar and a hydrogen/hydrocarbon partial pressure ratio of 20 in a fixed-bed reactor. Under these reaction conditions the individual reactions were assumed to be pseudomonomolecular and the method of Wei and Prater was used to obtain isomerization and cracking rate constants. The proposed reaction scheme consisted of a reversible three-component system, namely isomerization of *n*-hexane to 2-methylpentane and 3-methylpentane, and three irreversible steps, namely C–C bond rupture of *n*-hexane, 2- and 3-methylpentane yielding C_1–C_5 alkanes, and isomerization to 2,2- and 2,3-dimethylbutane. From measurements of the equilibrium composition, an artificial straight line reaction path, and a curved reaction path, the pseudomonomolecular reaction rate constant matrix was obtained.

INTRODUCTION

Isomerization and C–C bond cleavage of hydrocarbons take place on metals, acidic metal oxides, and bifunctional supported metal catalysts. While the mechanisms of these reactions over various types of catalyst have been widely studied (*1–6*), there is little literature concerning the kinetics of simultaneous isomerization and cracking of hydrocarbons. De Pauw and Froment (*7*) investigated the isomerization and hydrocracking of *n*-pentane over a commercial Pt/Al_2O_3 reforming catalyst. They reported that the isomerization rate was independent of total pressure whereas the hydrogenolysis rate increased linearly with increasing total pressure. Kinetic parameters for the individual reactions were obtained by curve fitting techniques. Simultaneous hydroisomerization and hydrocracking of cyclohexane in the presence of a Pd–H faujasite was modelled by Luzarraga and Voorhies (*8*) with a system of ordinary first-order differential equations, the rate constants being calculated by an iterative trial and error procedure. The pseudomonomolecular reaction model was found to be in close agreement with the experimental data.

From the experimental results of the above-mentioned studies and other investigations on either the isomerization or the C–C bond rupture of hydrocarbons (10–16, 24) it is clear that isomerization and cracking rates over various types of catalysts are first order with respect to the hydrocarbon partial pressure and zero to minus third order with respect to the hydrogen partial pressure.

In the present study kinetic parameters for the simultaneous isomerization and hydrocracking of *n*-hexane in the presence

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of a commercial Pt/Al_2O_3 reforming catalyst were obtained. For evaluation of the rate constants the method introduced by Wei and Prater (*9*) was used; this method can be applied to monomolecular and pseudomonomolecular reaction systems. We have shown elsewhere (*16*) that the assumption of pseudomonomolecular reactions for the reaction system under consideration is justified in the case of constant hydrogen partial pressure and high hydrogen/hydrocarbon partial pressure ratios, which are the reaction conditions usually applied in industrial reforming and isomerization plants.

EXPERIMENTAL

(*a*) *Materials.* 0.35 wt% Pt/Al_2O_3 catalyst (RD 150°C) was provided from Kalichemie Engelhard. The pure grade reactions *n*-hexane (Fa. Merck AG), 2-methylpentane, and 3-methylpentane (Fluka AG) were further purified by drying and distillation. Hydrogen was dried over molecular sieves to a content of less than 0.5 vpm.

(*b*) *Apparatus and operation conditions.* The experiments were carried out in an isothermally operated fixed-bed reactor (i.d. 30 mm, length 150 mm). Catalyst, 1 to 10 g, was packed between two layers of inert material. At the end of the reaction zone a small product gas flow was withdrawn and fed directly into a gas chromatograph with a squalane capillary column for analysis.

The operation conditions were selected in such a manner that the measured chemical reaction rates were not influenced by catalyst deactivation or limited by mass transfer rates. Activity and selectivity of the catalyst depend to a large extent on the water content of the reactants and on the history of the catalyst during the operation. By accomplishing a large number of preliminary experiments an activity level of the catalyst which was constant during a series of measurements and the same for different catalyst charges could be attained by the following procedure. The catalyst was heated up to the highest temperature of the series of tests, normally to a temperature of 450°C in the presence of dried hydrogen, followed by conversion of *n*-hexane at this temperature for 1 h at a total pressure of 10.5 bar, hydrogen/hydrocarbon partial pressure ratio of 20, and space velocities of 6 to 24 h^{-1}. Thereafter the required set of experiments was started, during which the activity and selectivity of the catalyst was further checked under standard conditions. All experimental results were rejected if the deviation of the measured conversion under standard conditions exceeded 7%.

The criterion of Chilton and Colburn (*17*) was used to estimate film diffusion rates, and then experimental gas velocities were applied at which film diffusion rates far exceeded the chemical reaction rates. The limitation of the chemical reaction rates by pore diffusion rate was examined experimentally. As a result catalyst particle diameters of 0.4 to 0.5 mm were selected to prevent the chemical reaction rates being influenced by mass transfer rates in the catalyst. Following the above preliminary tests the kinetic experiments were performed at 420 to 450°C, a total pressure of 10.5 bar, a hydrogen/hydrocarbon molar ratio of 20, and space velocities of 6 to 60 h^{-1}.

RESULTS AND DISCUSSION

(*A*) *General*

The kinetic experiments were performed at constant hydrogen partial pressure and excess hydrogen in the reaction vessel, i.e., conditions similar to those in reforming plants. The dehydrocyclization activity of the catalyst was small because of the relatively low temperature of 420 to 450°C and could be neglected. Isomerization of the methylpentanes yielding 2,2- and 2,3-dimethylbutane gave small conversions, too. However, in the course of the experimental work it turned out that in the methylpentane-rich part of the reaction simplex experimental and theoretical reaction paths deviated up to 12%, whereas the deviations remained within a few percent if the isomerization to dimethylbutanes was taken into consideration as irreversible pseudomonomolecular reaction steps included in the cracking steps.

This yielded a reaction scheme consisting of a reversible three-component system and of three irreversible reaction steps proceeding at different rates. As has been demonstrated by Silvestri *et al.* (*19*, *20*), the difficulty in the kinetic evaluation of reaction systems like this one originates in the fact that the principle of detailed balancing is not available for the total system. The characteristic decay constant of the equilibrium composition vector will not be zero, which implies that the other two characteristic vectors will not in general be located in a plane parallel to the reaction simplex. This is demonstrated in Fig. 1. The lower triangle plane represents the reaction simplex of the reversible three-component system *n*-hexane, 2-methylpentane, 3-methylpentane in the coordinate system of the pure components.

Whereas in the case of a reversible reaction system the end point of the composition vector is fixed to this triangle plane, the plane is shifted towards the origin in the case of simultaneous irreversible reaction steps, with decaying mass of the three-component system. All reaction paths are moving towards the origin, forming thereby a set of curves which envelops the only straight line reaction path located in the positive octant, which has been called the ray vector, x_r, by Prater *et al.* (*18*). As the irreversible reaction steps will proceed at different rates the characteristic vectors x_1 and x_2 are not located in a plane parallel to the reaction simplex, i.e., these vectors will not directly correspond to observable straight line reaction paths. Composition vectors $\alpha_x(t)$, however, located in a plane stretched by one characteristic vector and the ray vector will remain in this plane while decaying to zero according to the following equation (*20*):

$$\alpha_x(t) = b_r(t)x_r + b_i(t)x_i.$$

In this equation b_i and b_r are amounts of the characteristic species B_i in the transformed coordinate system. A projection of this composition vector into the triangle plane yields an "artificial straight line reaction path" (*18*) which can be measured experimentally.

Thus the experimental and mathematical procedure for evaluating the rate constant matrix results in the following. First the end point of the ray vector on the "reversible" reaction simplex and the end point of an artificial straight line reaction path located on an edge of the reaction simplex are determined experimentally. By linear

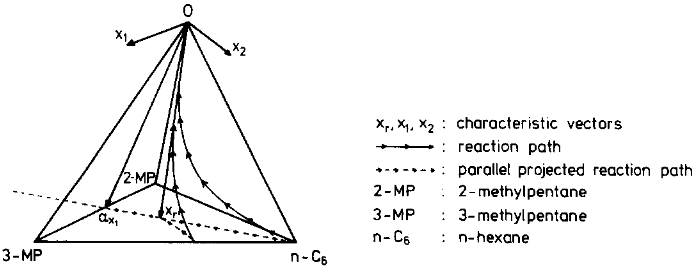


FIG. 1. Reaction simplex of a three-component system containing reversible and irreversible reaction steps.

combination of this composition vector and the ray vector

$$x_1 = \alpha_{x_1}(0) - \gamma x_r$$

and the orthogonality relation between the two characteristic vectors

$$x_r^T D^{-1} x_1 = 0$$

a second eigenvector is obtained (*20*). In this equation x_r^T is the transposed ray vector, D^{-1} a diagonal matrix from the reciprocal equilibrium concentrations (without irreversible steps), and γ is a scalar. The third characteristic direction will be obtained from an orthogonality relation, too. Following the evaluation of the eigenvectors the rate constants for the reactions of the hypothetical species are determined from any curved reaction path and from these and the eigenvectors the rate constant matrix can be calculated.

(*B*) *Results and Discussion*

The equilibrium composition for the reversible three-component system *n*-hexane, 2-methylpentane, and 3-methylpentane, which is needed for the transformation of the rate constant matrix into an orthogonally similar matrix, was calculated from free energy data (*21*) to be

$$\bar{a}_{\text{calc.}} = \begin{bmatrix} 0.271 \\ 0.405 \\ 0.324 \end{bmatrix}, \quad \text{at } 450°\text{C}.$$

The order of the components in the column is

$$\begin{bmatrix} n\text{-hexane} \\ 2\text{-methylpentane} \\ 3\text{-methylpentane} \end{bmatrix}.$$

The experimentally obtained ray vector is given by the following column matrix

$$x_r = \begin{bmatrix} 0.299 \\ 0.406 \\ 0.295 \end{bmatrix}.$$

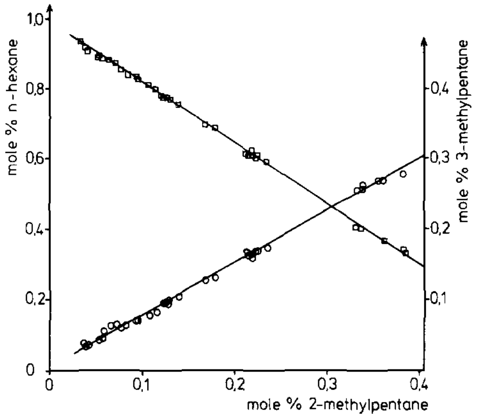


FIG. 2. Composition points on the artificial straight line reaction path; solid lines were obtained by a least-squares fit.

The artificial straight line reaction path is shown in Fig. 2, where the concentrations of *n*-hexane and 3-methylpentane are plotted against the concentration of 2-methylpentane.

The initial composition vector $\alpha_{x_1}(0)$ obtained from the linear regression is (regression coefficient for the least-square fit: 0.999)

$$\alpha_{x_1}(0) = \begin{bmatrix} 0.9942 \\ 0.0 \\ 0.0058 \end{bmatrix}.$$

Solving the equations of the linear combination of $\alpha_{x_1}(0)$ and the ray vector (Eq. (2)) and the orthogonality relation (Eq. (3)) for γ yields (*20*)

$$\gamma = \frac{x_r^T D^{-1} \alpha_{x_1}(0)}{x_r^T D^{-1} x_r} = 0.958,$$

where D^{-1} is the diagonal matrix of the reciprocal equilibrium concentrations and x_r^T the transposed ray vector.

Introducing the value of γ into Eq. (2) the second eigenvector x_1 is obtained and from the ray vector and x_1 the third eigenvector x_2 can be computed by use of orthogonality relations (*19*).

Combining the characteristic vectors the matrix X will be

$$X = [x_r \quad x_1 \quad x_2]$$

$$= \begin{bmatrix} 0.200 & -7.048 & -0.052 \\ 0.406 & 4.697 & -9.918 \\ 0.295 & 3.351 & 10.970 \end{bmatrix}.$$

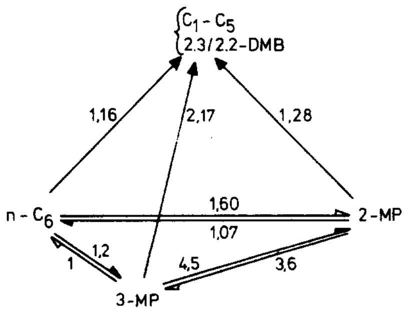
The relative rate constant matrix Λ' for the characteristic system can be determined by any reaction path, corresponding to an artificial curved reaction path on the reaction simplex of the reversible system. Measured compositions $\alpha(t)$ of such a reaction path are transformed into compositions $\beta(t)$ of the hypothetical system by $\beta = X^{-1}\alpha$, where X^{-1}, the inverse of the matrix X, has been computed by conventional methods, and β is the vector of concentrations of the hypothetical species

$$\beta = \begin{bmatrix} b_r \\ b_1 \\ b_2 \end{bmatrix}.$$

From the graphs $\ln|b_1|$ and $\ln|b_2|$ vs $\ln|b_r|$ (Fig. 3) the ratios of the rate constants λ_1/λ_r and λ_2/λ_r are obtained. The relative rate constant matrix is then calculated by (20)

$$K = X\Lambda'X^{-1}.$$

Hence, for simultaneous isomerization and cracking of *n*-hexane at 450°C the relative rate constants are



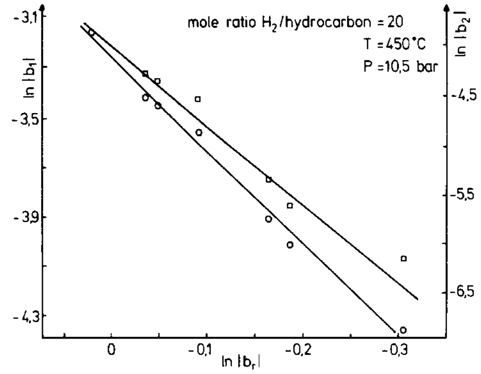


FIG. 3. Plots of $\ln|b_1|$ and $\ln|b_2|$ versus $\ln|b_r|$. The slopes of the straight lines are λ_1/λ_2 and λ_2/λ_r.

Calculated and experimental reaction paths are shown in Fig. 4. The curved reaction path with the initial composition

$$\begin{bmatrix} 0.602 \\ 0.015 \\ 0.383 \end{bmatrix}$$

was used to evaluate the characteristic rate constant matrix. As Fig. 4 reveals, there is good agreement between calculated and measured reaction paths in all parts of the reaction simplex, which signifies the applicability of the Wei and Prater method for the reaction system under discussion.

A very interesting feature of the reaction

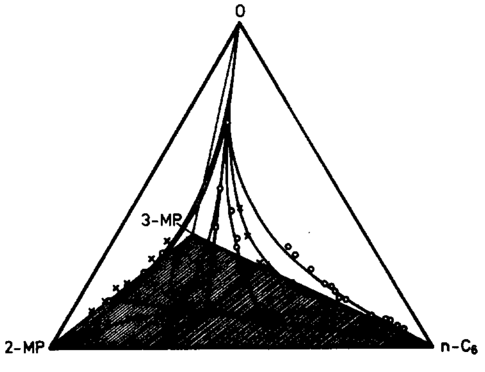


FIG. 4. Comparison of calculated (solid lines) and experimental reaction paths in the reaction simplex and their projection on the [111] plane in the composition space of the three-component system 2-methylpentane, 3-methylpentane, and *n*-hexane.

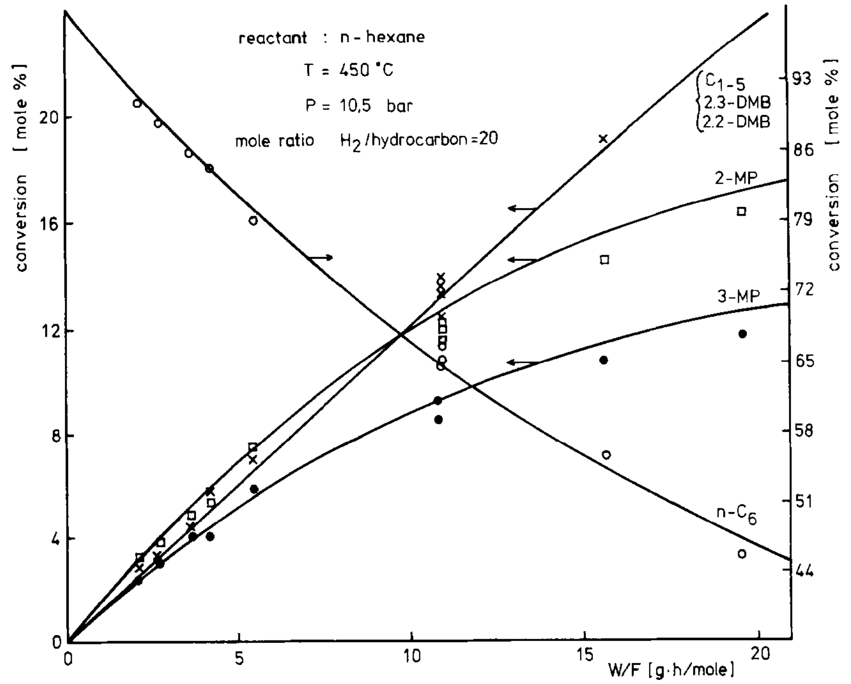


Fig. 5. Comparison of calculated (solid lines) and experimental conversion of *n*-hexane vs space time plots.

system is the location of the measurable artificial straight line reaction path, with the starting composition of nearly pure *n*-hexane intersecting the 2-methylpentane, 3-methylpentane edge of the reaction plane nearly at the equilibrium concentrations of the methylpentanes. There are two possible explanations for this behavior. Either the isomerization between the methylpentanes is fast compared with the isomerization of *n*-hexane to methylpentanes, or both methylpentanes are formed simultaneously by a mechanism involving equilibrium concentrations of intermediate products, the ratio of which is similar to the ratio of the equilibrium concentrations of 2- and 3-methylpentane. Evidence that the isomerization of the methylpentanes into one another may be fast compared with the isomerization of *n*-hexane was reported by Evering (*22*) and by Cull and Brenner (*23*). The ratio of rate constants of 3-methylpentane–*2*-methylpentane and *n*-hexane–3-methylpentane isomerization was shown to be 50.4 (*23*) and 65 (*22*), respectively. In case of our results, however, the ratio of the rate constants of 2-methylpentane–3-methylpentane and *n*-hexane–2-methylpentane isomerization is approximately 2.2, which is similar to the experimental results of Chevalier *et al.* (*6*) who report a value of 7.5 for the same ratio for

TABLE 1

Temperature Dependences of the Reaction Rate Constants θ_{ij}

	Temperature (°C)			E_a [kJ/mole]	$\theta_{ij,0}$ [1/s]
	420	435	450		
θ_{11}	0.110	0.164	0.318	147.1	1.29×10^{10}
θ_{12}	0.088	0.184	0.293	167.2	3.71×10^{11}
θ_{13}	0.084	0.165	0.274	164.3	2.09×10^{11}
θ_{21}	0.136	0.280	0.438	162.6	2.58×10^{11}
θ_{22}	0.151	0.204	0.352	117.3	9.98×10^{7}
θ_{23}	0.295	0.583	1.248	200.2	3.55×10^{14}
θ_{31}	0.104	0.202	0.328	159.6	1.15×10^{11}
θ_{32}	0.236	0.469	0.997	200.0	2.75×10^{14}
θ_{33}	0.181	0.344	0.595	165.3	5.30×10^{11}

hexane isomerization over a bifunctional Pt/Al_2O_3–SiO_2 catalyst. The ratio of the rate constants for 2-methylpentane and 3-methylpentane formation amounts to 1.3, a value which is in accordance with the one given by Chevalier *et al.* (*6*) and which corresponds to the ratio of the equilibrium concentrations of 2-methylpentane and 3-methylpentane. Therefore, the second explanation given above will be more likely in the interpretation of our results.

In order to determine the temperature dependence of the rate constants, experiments similar to those above were performed at 420 and 435°C. The results are given in Table 1. The apparent activation energies amount to 160 to 200 kJ/mole for isomerization reactions and 117 to 165 kJ/mole for the irreversible reaction steps.

Absolute reaction rate constants are obtained from a plot of $\ln|b_i|$ versus the reaction time. Using these constants actual conversion versus time factor graphs can be computed. A comparison between experimentally observed *n*-hexane conversions at different space velocities and theoretical graphs (solid lines) is shown in Fig. 5. The agreement is quite good, indicating that the basic assumption of pseudomonomolecularity incorporated into the applied method for evaluating the rate constants is justified.

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