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Kinetics of the polymerization of alkenes on zeolites

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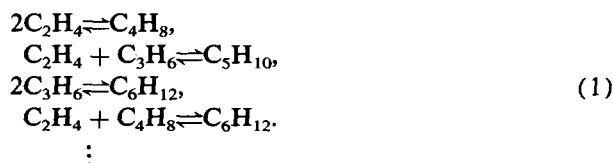
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The polymerization of alkenes at temperatures in the neighborhood of 600 K on a zeolite catalyst can be described in terms of a mechanism with bimolecular polymerization reactions and cracking reactions of isomer groups. The rate equations for the formation of isomer groups up to $C_{13}H_{26}$ have been integrated using the fourth-order Runge-Kutta method for polymerizations at constant temperature and pressure. In the absence of data on rate constants, calculations have been made on the basis of the assumption that all the bimolecular rate constants are equal or all the cracking constants are equal. In each case the rate constants for the reverse reactions have been calculated using the equilibrium constants for the steps in the mechanism. Under some circumstances the plots of weight fractions of isomer groups vs time have nearly the same shape for the two assumptions. However, it is possible to distinguish between the two assumptions by using experiments at sufficiently high pressures. The calculations show that it is of interest to examine the compositions arising from different starting materials, even though the equilibrium composition depends only upon temperature and pressure.

INTRODUCTION

Propylene and butylene can be polymerized to gasoline (C_5 to C_{10}) and diesel fuel (C_{10} to C_{20}) using zeolite ZSM-5 catalyst at temperatures in the range 450–600 K.¹ Equilibrium distributions of alkene isomer groups in the ideal gas phase have been calculated over a range of temperatures and pressures.^{1,2} The use of isomer groups in thermodynamics greatly reduces the number of species that have to be considered in complicated organic systems and provides a means for extrapolating thermodynamic properties to higher carbon numbers where data are not available on all individual species.^{3,4} The kinetics of the polymerization of propylene is interesting in that it oligomerizes to C_6 , C_9 , C_{12} , etc., oligomers early in the reaction.⁵ These products then crack and polymerize to an almost continuous distribution of isomer groups at an equilibrium that depends on temperature, pressure, and selectivity of the catalyst. The isomerization reactions occur more rapidly on ZSM-5 than the polymerization and cracking reactions.⁵ Thus the kinetics can be described in terms of isomer groups. The study of the kinetics of alkene polymerization provides an opportunity to learn about the rates of cracking and polymerization reactions of isomer groups.

This paper presents numerical integrations of the rate equations for the following 30-step mechanism that provides for all possible bimolecular reactions of isomer groups up to $C_{13}H_{26}$. The first several steps in this mechanism of 30 steps are as follows:



All thirty steps are represented later in the first three columns of Table I. When reactants or products have isomers, the rate constants in this mechanism are weighted averages.

The first order rate constants are of the type

$$k = \sum_{i=1}^{N_i} k_i y_i, \quad (2)$$

where the y_i are equilibrium mole fractions of the N_i species in the isomer group. The second order rate constants are more complicated weighted averages. If the reacting molecules A and B each have two isomers,

$$k = k_{11}y_{A1}y_{B1} + k_{12}y_{A1}y_{B2} + k_{21}y_{A2}y_{B1} + k_{22}y_{A2}y_{B2}. \quad (3)$$

Since the equilibrium constants for the steps in the mechanism can readily be calculated from Gibbs energies of formation of isomer groups,⁴ there are only half as many unknown rate constants as it appears.

This mechanism is too simple in the sense that the polymerization occurs in the pores of ZSM-5 and not in the gas phase. However, polymerization involves bringing molecules together, and this mechanism involving bimolecular reactions is the simplest way of formulating that. Even when mechanisms incorporate Langmuir-Hinshelwood adsorption, steps may behave in a bimolecular way under certain experimental conditions, and in any case the rate equations must yield the correct equilibrium composition in the gas phase.

In the absence of data on the individual rate constants, calculations have been made on the basis of either of two assumptions: (1) the bimolecular rate constants can all be assumed to be equal, and the cracking constant for each step is calculated using the Gibbs energies of formation of the isomer groups involved in that step, or (2) the cracking rate constants are assumed to be equal, and the bimolecular rate constant for each step is calculated from the Gibbs energies of formation. In the absence of detailed data, both assumptions are plausible. In support of assumption (1) the biomolecular reactions are all very similar; in each step two alkene molecules come together to form a single alkene molecule. In support of assumption (2) the cracking reactions are all very

TABLE I. Effective rate constants at 600 K for the steps in the mechanism.

			Pressure $P/P^0 = 0.1$				Pressure $P/P^0 = 5$			
			Assumption (1)		Assumption (2)		Assumption (1)		Assumption (2)	
Reactants			k'_f	k'_b	k'_f	k'_b	k'_f	k'_b	k'_f	k'_b
2	2	4	1	0.005	1887.56	10	1	0.0001	1887.56	0.2
2	3	5	1	0.029	346.27	10	1	0.0006	346.27	0.2
3	3	6	1	0.140	71.64	10	1	0.0028	71.64	0.2
2	4	6	1	0.070	143.34	10	1	0.0014	143.34	0.2
2	5	7	1	0.224	44.64	10	1	0.0045	44.64	0.2
3	4	7	1	1.221	8.19	10	1	0.0244	8.19	0.2
4	4	8	1	5.372	1.86	10	1	0.1074	1.86	0.2
2	6	8	1	0.408	24.51	10	1	0.0082	24.51	0.2
3	5	8	1	1.972	5.07	10	1	0.0394	5.07	0.2
2	7	9	1	0.212	47.21	10	1	0.0042	47.21	0.2
3	6	9	1	3.707	2.70	10	1	0.0741	2.70	0.2
4	5	9	1	8.956	1.12	10	1	0.1791	1.12	0.2
5	5	10	1	14.932	0.67	10	1	0.2986	0.67	0.2
2	8	10	1	0.219	45.72	10	1	0.0044	45.72	0.2
3	7	10	1	1.925	5.20	10	1	0.0385	5.20	0.2
4	6	10	1	16.840	0.59	10	1	0.3368	0.59	0.2
2	9	11	1	0.219	45.72	10	1	0.0044	45.72	0.2
3	8	11	1	1.988	5.03	10	1	0.0398	5.03	0.2
4	7	11	1	8.743	1.14	10	1	0.1749	1.14	0.2
5	6	11	1	28.076	0.36	10	1	0.5615	0.36	0.2
6	6	12	1	52.791	0.19	10	1	1.0558	0.19	0.2
2	10	12	1	0.219	45.72	10	1	0.0044	45.72	0.2
3	9	12	1	1.988	5.03	10	1	0.0398	5.03	0.2
4	8	12	1	9.028	1.11	10	1	0.1806	1.11	0.2
5	7	12	1	14.577	0.69	10	1	0.2915	0.69	0.2
2	11	13	1	0.219	45.72	10	1	0.0044	45.72	0.2
3	10	13	1	1.988	5.03	10	1	0.0398	5.03	0.2
4	9	13	1	9.028	1.11	10	1	0.1806	1.11	0.2
5	8	13	1	15.052	0.66	10	1	0.3010	0.66	0.2
6	7	13	1	27.409	0.36	10	1	0.5482	0.36	0.2

similar, each involving breaking an alkene molecule into two alkene molecules. Therefore, calculations have been made here with each assumption. We will see that if assumption (1) is reasonably accurate, comparison of experimental data with the calculated plots will yield a value for the common bimolecular rate constant. If assumption (2) is reasonably accurate, comparison of experimental data with plots calculated using this assumption will yield a value for the common cracking rate constant.

NUMERICAL INTEGRATIONS OF RATE EQUATIONS FOR MECHANISMS

This subject has a long history and so only several recent references emphasizing the use of matrices are given here.⁶⁻⁹ Since rate equations for ideal gases must reduce to equilibrium expressions for ideal gases at long times, the symbols used in kinetics should be consistent with those used in thermodynamics. Therefore, thermodynamic symbols used by Smith and Missen¹⁰ for multicomponent systems have been largely followed. The use of matrix notation simplifies both the theory and computer programming involved in the numerical integration of the differential equations corresponding with a mechanism. A mechanism involving N species A_i (in this case isomer groups) and R steps is represented by

$$\sum_{i=1}^N \nu_{ij} A_i = 0 \quad j = 1, \dots, R. \quad (4)$$

The stoichiometric coefficients ν_{ij} are integers that are positive for products and negative for reactants. In calculating equilibrium compositions, all that is required is a set of independent reactions that can represent all possible chemical changes in the system, but in treating kinetics the mechanism as a whole is taken as a given. Of course, the number N of steps in the mechanism must be equal to or greater than the number of independent reactions R . The calculation of the amounts n_i of the species involved in the mechanism as a function of time is based on the use of the equation

$$n_i = n_i^0 + \sum_{j=1}^R \nu_{ij} \xi_j \quad i = 1, 2, \dots, N, \quad (5)$$

where n_i^0 is the initial amount of species i and ξ_j is the extent of reaction j . This is a linear transformation from the N variables n_i to the R variables ξ_j . The stoichiometric coefficients are defined in Eq. (4). Extents of reaction are zero at $t = 0$ and are expressed in moles. The use of Eq. (5) ensures that atom balances will be maintained throughout the course of the approach to equilibrium. This equation is readily converted to matrix form. The amounts of the various species at a given time are represented by a column vector \mathbf{n} :

$$\begin{bmatrix} n_1 \\ n_2 \\ \vdots \\ n_N \end{bmatrix} = \begin{bmatrix} n_1^0 \\ n_2^0 \\ \vdots \\ n_N^0 \end{bmatrix} + \begin{bmatrix} \nu_{11} \\ \nu_{21} \\ \vdots \\ \nu_{N1} \end{bmatrix} \xi_1 + \begin{bmatrix} \nu_{12} \\ \nu_{22} \\ \vdots \\ \nu_{N2} \end{bmatrix} \xi_2 + \cdots + \begin{bmatrix} \nu_{1R} \\ \nu_{2R} \\ \vdots \\ \nu_{NR} \end{bmatrix} \xi_R. \quad (6)$$

Thus

$$\mathbf{n} = \mathbf{n}^0 + \mathbf{v}\boldsymbol{\xi}, \quad (7)$$

where \mathbf{n}^0 is the initial amount of substance matrix and

$$\mathbf{v} = \begin{bmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1R} \\ \nu_{21} & \nu_{22} & \cdots & \nu_{2R} \\ \vdots & \vdots & & \vdots \\ \nu_{N1} & \nu_{N2} & \cdots & \nu_{NR} \end{bmatrix}, \quad (8)$$

$$\boldsymbol{\xi} = \begin{bmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_R \end{bmatrix}. \quad (9)$$

The matrix \mathbf{v} is referred to as the complete stoichiometric coefficient matrix by Smith and Missen,¹⁰ who use the symbol \mathbf{N} for this matrix.

The basic kinetic equation for a mechanism is obtained by differentiating Eq. (7):

$$\frac{d\mathbf{n}}{dt} = \mathbf{v} \frac{d\boldsymbol{\xi}}{dt} = \mathbf{v}\mathbf{r}. \quad (10)$$

The matrix $d\boldsymbol{\xi}/dt = \mathbf{r}$ can be referred to as the rate of conversion matrix, following the IUPAC recommendation¹¹ that $d\xi_j/dt$ is the rate of conversion for a single reaction. It is useful to refer to r_j as the net rate of a step to emphasize that it is the difference between the forward and backward rates of step j at a particular composition. Thus $d\boldsymbol{\xi}/dt = \mathbf{r}$ will be referred to here as the net rate matrix. The amount rate matrix $d\mathbf{n}/dt$ is $N \times 1$, the stoichiometric coefficient matrix \mathbf{v} is $N \times R$, and the net rate matrix \mathbf{r} is $R \times 1$.

Polymerization of a gas with a heterogeneous catalyst is most conveniently carried out at constant pressure using a flow system. The calculations presented here apply to an isothermal-isobaric process. The forms of the equations for the net rates r_j need to be derived for constant pressure and for the two assumptions stated in the Introduction.

NET RATES ASSUMING THE BIOMOLECULAR RATE CONSTANTS ARE EQUAL

Since it is customary to define rate constants on the concentration scale, the net rate $d\xi_1/dt$ of the first step is given by

$$\frac{1}{V} \frac{d\xi_1}{dt} = k_f [\text{C}_2\text{H}_4]^2 - k_b [\text{C}_4\text{H}_8]. \quad (11)$$

If the concentrations are in moles per ℓ , k_f has the unit $\ell \text{ mol}^{-1} \text{ s}^{-1}$ and k_b has the unit s^{-1} .

The rate constant for the backward reaction can be expressed in terms of that for the forward reaction by using the

equilibrium constant K_c written in terms of concentration:

$$K_c = \frac{[\text{C}_4\text{H}_8]}{[\text{C}_2\text{H}_4]^2} = \frac{k_f}{k_b}. \quad (12)$$

Note that K_c has the units of $\ell \text{ mol}^{-1}$. Since thermodynamic data are available for these isomer groups for a standard state pressure of 1 bar, the value of K_c can be calculated from the dimensionless K_p written in terms of P/P^0 , where P^0 is the standard state pressure. Ideal mixtures of perfect gases are assumed throughout. For each step in this mechanism, K_c and K_p are related by

$$K_c = (RT/P^0)K_p. \quad (13)$$

Thus

$$k_b = k_f P^0 / RT K_p. \quad (14)$$

The equilibrium constant K_p was calculated from tabulated values of standard Gibbs energies of formation of alkene isomer groups up to C_8H_{16} ,⁴ and linear extrapolations of $\Delta_f G^0(I)$ were used for higher isomer groups. If the catalyst excludes certain bulky isomers, standard Gibbs energies of formation of restricted isomer groups can be used.²

Rate Eq. (11) can be written in the following form:

$$\begin{aligned} \frac{1}{V} \frac{d\xi_1}{dt} &= k_f \{ [\text{C}_2\text{H}_4]^2 - (P^0/RTK_p) [\text{C}_4\text{H}_8] \} \\ &= k_f \left[\frac{n_2^2}{V^2} - \left(\frac{P^0}{RTK_p} \right) \frac{n_4}{V} \right]. \end{aligned} \quad (15)$$

Since the polymerization is carried on at constant pressure, the volume is not constant, but it is readily calculated from the total number of moles of gas,

$$V = (RT/P) \sum n_i. \quad (16)$$

When Eq. (15) is multiplied by V and then V is eliminated by use of Eq. (16) we obtain

$$r_1 = \frac{d\xi_1}{dt} = k_f \left[\frac{n_2^2}{(RT/P) \sum n_i} - \left(\frac{P^0}{RTK_p} \right) n_4 \right]. \quad (17)$$

Since k_f is unknown, but is assumed to be the same for each step, and RT/P is constant, these quantities can be moved to the left side of the equation:

$$r'_1 = \frac{d\xi_1}{d\tau} = \frac{RT}{f_f P} \frac{d\xi_1}{dt} = \frac{n_2^2}{\sum n_i} - \left(\frac{P^0}{PK_p} \right) n_4, \quad (18)$$

where τ is a dimensionless time defined by

$$\tau = (k_f P / RT) t. \quad (19)$$

The value of the common bimolecular rate constant can be calculated using this equation by comparing experimental data with calculated plots of n_i or weight function vs τ . In the figures in this paper weight percentages of various isomer groups are plotted vs τ .

Since the expressions for net rates of the steps each incorporate the equilibrium expression for that step, the correct equilibrium expression is necessarily obtained at long times. When the net rate of the first step is zero, Eq. (18) yields the equilibrium expression

$$K_y = K_P P / P^0 = \frac{n_4 \sum n_i}{n_2^2}, \quad (20)$$

where y_i is the equilibrium mole fraction and K_y is the mole fraction equilibrium constant at pressure P . If the mole fractions are calculated on the basis of C_2H_4 and C_4H_8 only, $P = P_2 + P_4$. If the mole fractions are calculated on the basis of all gases present, P is the total pressure. Thus it is the mole fraction equilibrium constant at the applied pressure that is important in kinetics at constant pressure.

NET RATES ASSUMING THE CRACKING RATE CONSTANTS ARE EQUAL

If the cracking rate constants are assumed to be equal, k_f can be eliminated between Eqs. (11) and (14) to obtain

$$r_1 = \frac{d\xi_1}{dt} = k_b \left(\frac{PK_P}{P^0} \frac{n_2^2}{\sum n_i} - n_4 \right). \quad (21)$$

Since k_b is assumed to be the same for each step, both sides of the equation can be divided by k_b . Since the pressure is constant, it is also convenient to divide both sides of the equation by P/P^0 to obtain

$$r'_1 = \frac{d\xi_1}{d\tau} = \frac{P^0}{Pk_b} \frac{d\xi_1}{d\tau} = \frac{K_P n_2^2}{\sum n_i} - \frac{P^0 n_4}{P}, \quad (22)$$

where τ is a dimensionless time defined by

$$\tau = (P/P^0) k_b t. \quad (23)$$

This way of writing the net rate has the advantage that the first term in the net rate for each step is not affected by the pressure. Thus a change in scale of the time axis is not required for calculations at a series of pressures. When the net rate of a step is zero, the rate expression for that step reduces to the equilibrium constant expression for that step, as it must. If the plots of n_i vs τ follow the values calculated using Eq. (22), and similar equations for the other steps, then the time scale can be interpreted using Eq. (23) to obtain the value k_b for the cracking reactions.

EFFECTIVE RATE CONSTANTS

Equations (18) and (22) are the most suitable forms for numerical integrations to show the characteristics of the kinetics of the polymerization under the two assumptions. When Eq. (18) is integrated at different pressures, the plots start out in the same way because the pressure affects only the reverse reactions. Thus when the pressure is changed by a small factor it is not necessary to change the time scale. When different starting materials are used, the plots start out with the same slope since all the bimolecular rate constants are assumed to be equal. When Eq. (22) is integrated there is no avoiding the fact that the K_P in the first term causes the plots to start with different slopes when different starting materials are used. However, the fact that the pressure only affects the second term means that it is not necessary to change the time range considered when the pressure is changed by a small factor.

The shapes of plots presented in this article are dependent only on the effective rate constants shown in Table I. The effective rate constants k'_f and k'_b for the first step in the

mechanism are defined by the following representation of Eqs. (18) and (22):

$$r'_1 = \frac{k'_f n_2^2}{\sum n_i} - k'_b n_4. \quad (24)$$

The effective rate constants are dimensionless.

When assumption (1) is used the effective rate constant for each bimolecular reaction is unity. The effective rate constants for the cracking reactions are given by P^0/PK_P . The ratio of the effective bimolecular constant to the effective cracking constant is equal to K_y [Eq. (20)], just as the ratio of the actual rate constants is equal to K_c [Eq. (12)].

When assumption (2) is used, the effective bimolecular rate constant is equal to K_P , and the effective rate constant for the cracking reaction is P^0/P , as shown in Eq. (22). Again the ratio of the effective bimolecular rate constant to the effective cracking constant is equal to the mole fraction equilibrium constant K_y . In Table I the reactants in each step of the mechanism are indicated schematically in the first three columns; the first step $2C_2H_4=C_4H_8$ is represented by 2 2 4. This matrix is more than a simple way of labeling the rows in this table. A computer program was written to convert this 30×3 matrix to the 12×30 v matrix. The integers 2 2 4 give the addresses in the first column of the v matrix of -1 for each reactant and +1 for the product.

When a single isomer group is used as the starting material, the initial slope is due to the bimolecular reaction. However, as soon as C_6H_{12} is formed from propylene it can crack to form C_2H_4 and C_4H_8 . Since according to assumption (2) ethylene reacts rapidly with C_3H_6 , it immediately contributes to the reduction in the weight fraction of C_3H_6 . As soon as C_8H_{16} is formed from butylene, it can crack to $C_2H_4 + C_6H_{12}$ and $C_3H_6 + C_3H_{10}$. Since C_2H_4 and C_3H_6 react so rapidly with C_4H_8 according to assumption (2), the weight fraction of C_4H_8 is reduced more rapidly than it otherwise would be.

NUMERICAL INTEGRATION OF RATE EQUATIONS

Numerical integrations of the set of 12 simultaneous rate equations represented by

$$\frac{dn}{d\tau} = \mathbf{v} \mathbf{r}' \quad (25)$$

were carried out using the fourth order Runge-Kutta method.¹² The species abundance matrix after a short time interval h is given by

$$\mathbf{n}_{k+1} = \mathbf{n}_k + h \mathbf{v} \mathbf{r}', \quad (26)$$

where the net rate matrix is evaluated with \mathbf{n} . The first calculations were carried out with APL programs using a constant step size, and a sufficiently small step size was used so that different results were not obtained by reducing the step size. Later calculations were made with APL program RUNGE with variable step size written by Fred Krambeck of Mobil Research and Development.

The programs utilized the vector formulation of the Runge-Kutta method.¹³ In order to use the usual symbols for the Runge-Kutta method, it is convenient to represent $dn/d\tau$ by $f(y_n)$, where y_n represents the amounts of the

TABLE II. Equilibrium weight percentages of isomer groups at 600 K.

P/bar	0.1	5
C ₂ H ₄	1.8	.1
C ₃ H ₆	10.4	1.0
C ₄ H ₈	27.2	5.5
C ₅ H ₁₀	24.5	9.8
C ₆ H ₁₂	23.9	19.1
C ₇ H ₁₄	6.2	10.0
C ₈ H ₁₆	3.2	10.1
C ₉ H ₁₈	1.5	9.8
C ₁₀ H ₂₀	0.7	9.4
C ₁₁ H ₂₂	0.4	8.9
C ₁₂ H ₂₄	0.2	8.4
C ₁₃ H ₂₆	0.1	7.8

In all cases the correct equilibrium composition was approached as closely as desired at long times. As a check the equilibrium composition for the pressure and temperature used was calculated using EQUICALC, written in APL by Krambeck.¹⁴ Table II gives the equilibrium weight percentages of the 12 isomer groups under the conditions used in the kinetic calculations.

WEIGHT DISTRIBUTIONS AS A FUNCTION OF DIMENSIONLESS TIME FOR THE TWO ASSUMPTIONS

Figure 1 shows the weight percentages of the isomer groups as a function of the dimensionless time τ at 600 K and 0.1 bar starting with C₃H₆ and C₄H₈ and assuming that the bimolecular rate constants are all equal. When C₃H₆ is polymerized, C₆H₁₂ is formed rapidly, and then the C₆H₁₂ cracks to give, in addition to C₃H₆, the products C₂H₄ and C₄H₈ that can react with the initial reactant. When C₄H₈ is the initial reactant C₈H₁₆ is formed, but it cracks rapidly, especially to C₃H₆ + C₅H₁₀ as shown in Table I. When the pressure is raised to 5 bar and C₃H₆ is the initial reactant, C₆, C₉, and C₁₂ all go through maxima, as shown in Fig. 2. The effective cracking constants are small at 5 bar, and so the other isomer groups grow in slowly. When C₄H₈ is the initial reactant, C₈H₁₆ and C₁₂H₂₄ go through maxima. The difference between Figs. 1 and 2 is simply that the reverse rate constants have all been reduced by a factor of 50.

Figure 3 shows that significantly different results are obtained when the cracking constants are all assumed to be equal. Figure 3 may be compared with Fig. 1 since the pressure is 0.1 bar in both cases and the same equilibrium composition is obtained. The change in scale is not significant be-

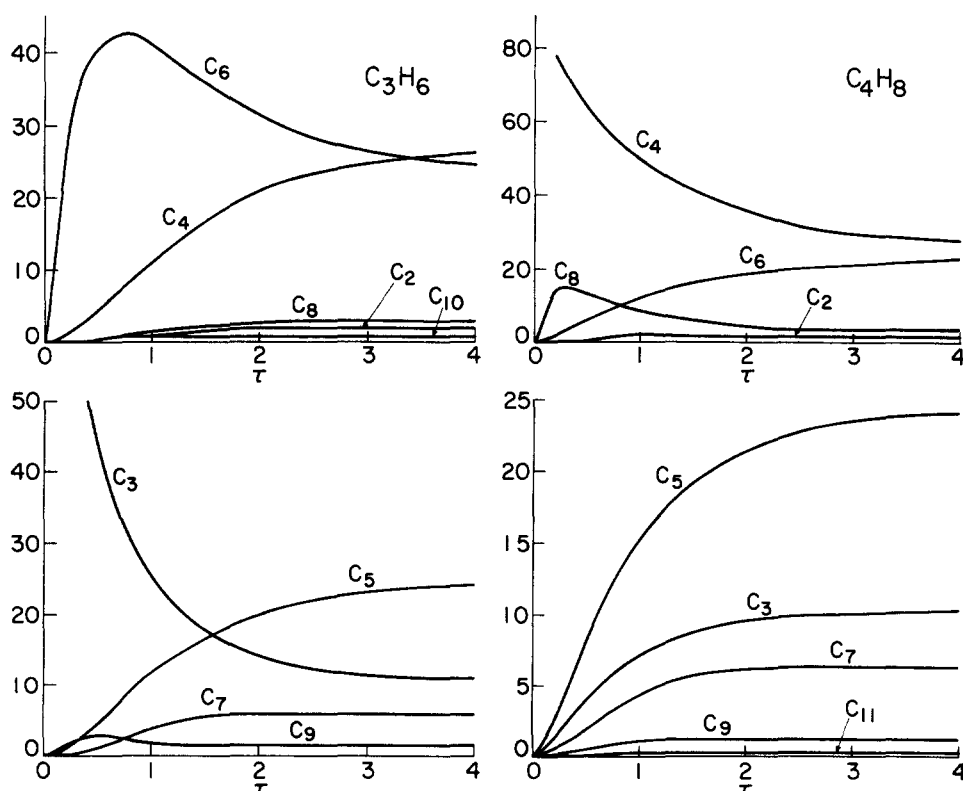


FIG. 1. Weight percentages of isomer groups as a function of time at 600 K and 0.1 bar starting with C₃H₆ and C₄H₈ and assuming the bimolecular rate constants are equal.

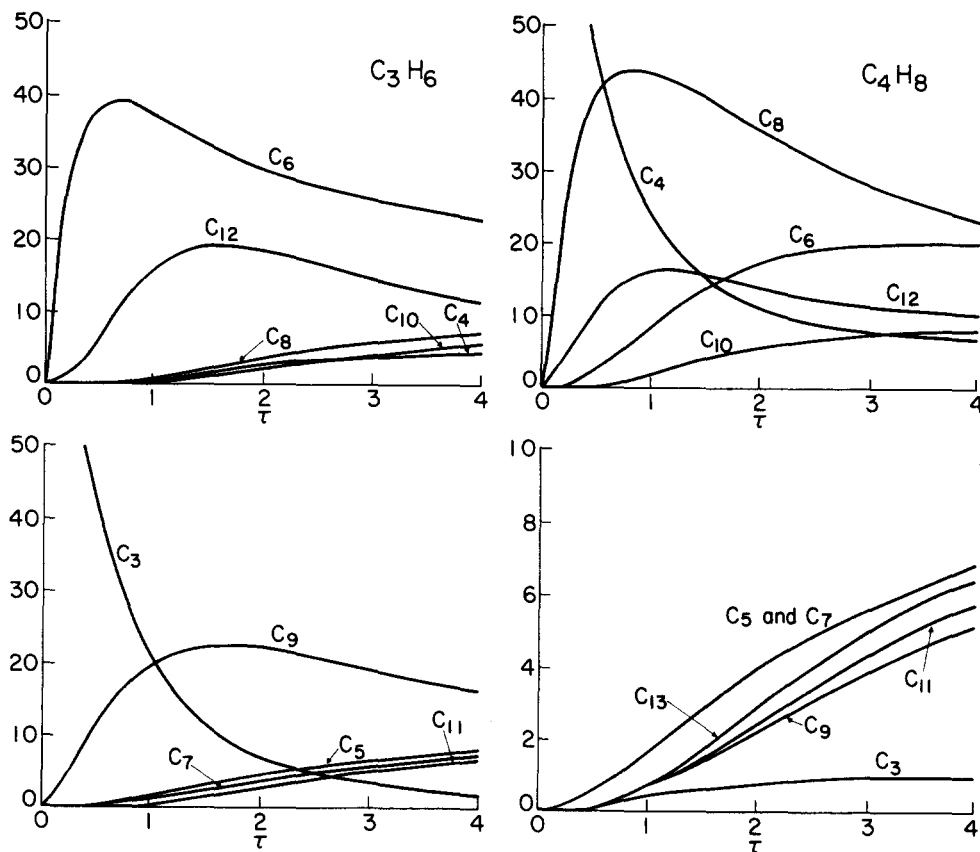


FIG. 2. Weight percentages of isomer groups as a function of time at 600 K and 5 bar starting with C_3H_6 and C_4H_8 and assuming the bimolecular rate constants are equal.

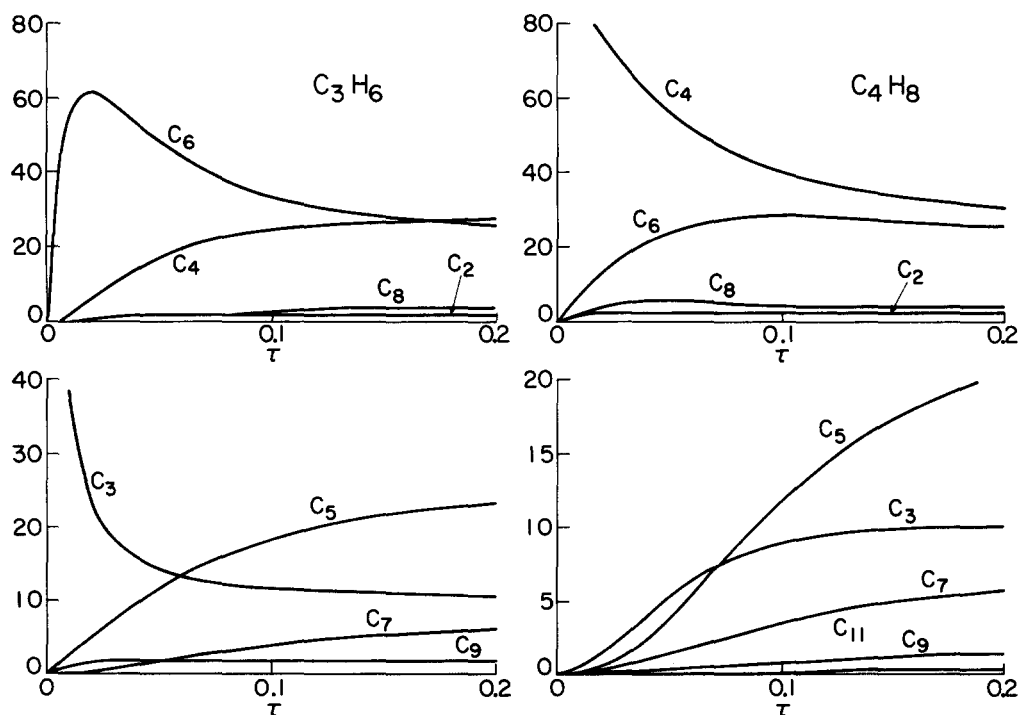


FIG. 3. Weight percentages of isomer groups as a function of time at 600 K and 0.1 bar starting with C_3H_6 and C_4H_8 and assuming the cracking constants are equal. Note the dimensionless time is $1/20$ as great as in the other figures.

cause the interpretation of the dimensionless time is different in Fig. 1 [Eq. (19)] and in Fig. 3 [Eq. (23)]. The relationships between the time courses for the various reactants are important for distinguishing between the two assumptions. In Fig. 3 the weight fraction of C_3H_6 drops much more rapidly, compared with other changes, than in Fig. 1. That is because the effective second order rate constant is faster compared with other bimolecular rate constants, as indicated in Table I. This effect is even more striking when C_2H_4 is used as the starting material.

The difference between Figs. 1 and 3 is not striking when the starting material is C_4H_8 because the rate with which it reacts with itself is only about twice as great under assumption (2). However, the C_8H_{16} that is formed can crack relatively rapidly, especially into $C_2H_4 + C_6H_{12}$, and the C_2H_4 and C_3H_6 formed can react rapidly with various species.

When the pressure is raised to 5 bar and C_3H_6 is the initial reactant, it is even clearer that the C_3H_6 disappears rapidly, compared with other polymerization reactions, as shown in Fig. 4. When C_4H_8 is the initial reactant, C_8H_{16} does not go through a maximum, as it does under assumption (1) (Fig. 2) because the cracking reactions to $C_2H_4 + C_6H_{12}$ and to $C_3H_6 + C_3H_{10}$ are relatively faster compared with cracking to C_4H_8 .

The calculations that show that C_6H_{12} cracks so slowly raise a question about the accuracy of standard Gibbs energies of formation of the hexenes that were used to calculate the Gibbs energy of the isomer group. This question has already been raised² on the basis of equilibrium calculations

since they indicate more C_6H_{12} compared with C_5H_{10} and C_7H_{14} than would be expected.

DISCUSSION

If the standard Gibbs energies of formation of the alkene isomer groups were a linear function of the carbon number, the equilibrium constants for the successive steps in the mechanism would be equal. The standard Gibbs energies of formation of the alkene isomer groups are very nearly linear in carbon number at higher carbon numbers, but ethylene and propylene are less stable—that is their standard Gibbs energies of formation are above the straight line that represents the data for C_4H_8 to C_8H_{16} isomer groups. If the equilibrium constants were the same for all of the alkene polymerization reactions of the form of those in mechanism (1), this would not mean that the bimolecular rate constants for the successive steps were all equal and that the cracking constants for the successive steps were equal. But it would mean that the bimolecular rate constants would have to be the same function of the sum of the carbon numbers of the alkenes coming together in the bimolecular reaction.

The actual polymerization using a zeolite catalyst is considerably more complicated than mechanism (1) indicates because the catalytic activity occurs in pores, but a simple mechanism such as that used here represents some of the larger effects. Although taking the bimolecular rate constants in mechanism (1) to be equal [assumption (1)] or the cracking rate constants to be equal [assumption (2)] are

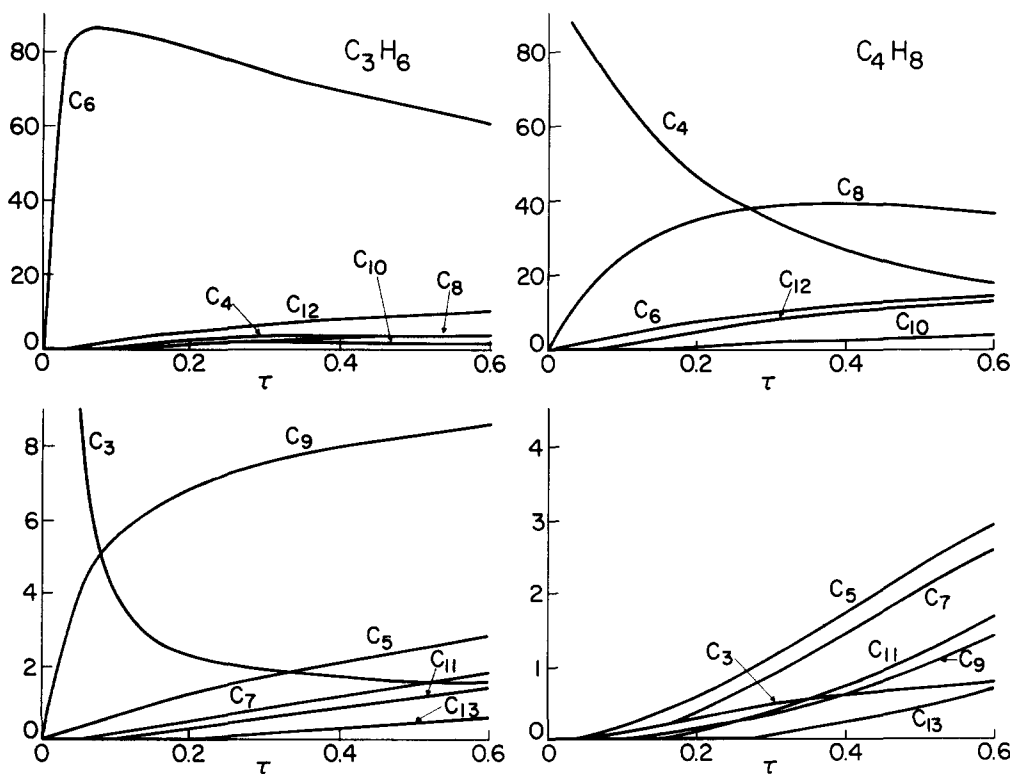


FIG. 4. Weight percentages of isomer groups as a function of time at 600 K and 5 bar starting with C_3H_6 and C_4H_8 and assuming the cracking constants are equal.

rather different starting points, the time course of the polymerization reaction is not greatly affected in some cases. Nevertheless, it is possible to distinguish between these two cases without making initial velocity measurements.

Calculated results at other temperatures in the range 450–800 K are not very different from 600 K, although considerably different pressures have to be used. If the pressure is too low, polymerization does not occur to an appreciable extent, and if it is too high it will exceed the critical pressure at which the average molar mass goes to infinity if a constant slope of $\Delta_f G^0(I)$ vs carbon number is used at high carbon numbers.¹⁵ To investigate the kinetics at higher pressures than those used here, the mechanism would have to be extended to higher carbon numbers.

The effect of the selectivity of ZSM-5 on the kinetics of the restricted isomer groups for C_6H_{12} and higher carbon numbers can be calculated. The effects of the exclusion of various types of species on the equilibrium amounts at 500, 550, and 600 K has been investigated.²

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¹S. A. Tabak, F. J. Krambeck, and W. E. Garwood, *AIChE J.* **32**, 1526 (1986).

²R. A. Alberty, *J. Chem. Eng. Sci.* (in press).

³R. A. Alberty, *J. Phys. Chem.* **87**, 4999 (1983).

⁴R. A. Alberty and C. A. Gehrig, *J. Phys. Chem. Ref. Data* **14**, 803 (1985).

⁵W. E. Garwood, *Am. Chem. Soc. Symp. Ser.* **218**, 383 (1983).

⁶H. G. Othmer, *Chem. Eng. Sci.* **31**, 993 (1976).

⁷G. M. Côme, *Comput. Chem. Eng.* **3**, 603 (1979).

⁸H. G. Othmer, in *Modeling of Chemical Reaction Systems*, edited by K. H. Ebert, P. Deufhard, and W. Jäger (Springer, New York, 1981), pp. 2–19.

⁹W. C. Gardiner Jr., *Combustion Chemistry* (Springer, New York, 1984).

¹⁰W. R. Smith and R. W. Missen, *Chemical Reaction Equilibrium Analysis* (Wiley, New York, 1982).

¹¹K. J. Laidler, *Pure Appl. Chem.* **53**, 753 (1981).

¹²W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University, New York, 1986).

¹³P. Henrici, *Essentials of Numerical Analysis with Pocket Calculator Demonstrations* (Wiley, New York, 1982).

¹⁴F. J. Krambeck, presented at the Annual AIChE Meeting, Miami Beach, November 16, 1978 (unpublished).

¹⁵R. A. Alberty and I. Oppenheim, *J. Chem. Phys.* **84**, 917 (1986).