

MECHANISTIC AND MATHEMATICAL MODELING OF THE THERMAL DECOMPOSITION OF CYCLOHEXANE

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ABSTRACT

Molecular reaction schemes for the thermal decomposition of cyclohexane were proposed on the basis of observed product distribution, free radical mechanism and thermodynamic principles. The rate parameters were estimated systematically using a non-linear least squares technique (incorporating Marquardt algorithm) in minimizing a multi-response objective function.

Discrimination among rival models was based on the minimization of the sum of squares of the differences between the observed and predicted molar quantities of the cyclohexane pyrolysis products. The prediction of the product distributions was found to be reasonably good at the highest temperature of investigation.

INTRODUCTION

In mechanistic modeling, an intrinsic reaction network is determined on the basis of the most plausible set of elementary reactions. Rate constants are established individually for these elementary reactions through kinetic measurements. This type of model allows confident extrapolation outside the range of the data base in its development [18,20]. Mechanistic modeling has been useful in studying the kinetics of pyrolytic reactions at low conversions [14–16]. Few attempts have been reported at the high conversion levels of commercial cracking [7]. This stems from the large number of molecular species and free radicals with their associated reactions. The number of these reactive species increases substantially with conversion and leads to excessive computation time. Even the precise pyrolysis mechanism for a simple feedstock like propane is still a subject of dispute.

Simple molecular reaction schemes have often been employed for simulation and design purposes [2,4–6], even though pyrolyses reactions proceed via free radical mechanisms [3]. This is to forestall the complex mathematical problems often encountered in the integration of a system of stiff differential equations associated with the analysis of free radical reactions. Molecular reaction schemes not developed on the basis of free radical mechanisms would not account for the free radical reactions [7]. In addition, pyrolyses of hydrocarbons under industrial conditions occur at high conversions where secondary reactions of free radicals complicate the mathe-

matics even further. The sets of differential equations derived for a set of elementary reactions forming the desired products contain large numbers of kinetic parameters. These parameters are often determined by least squares estimation and/or trial and error techniques. Application of statistical tests determines the validity of the proposed molecular models and associated parameters [2].

In the present paper, a number of possible molecular reaction schemes are developed for cyclohexane pyrolysis on the basis of free radical mechanism, literature information and experimentally observed product distribution. The experimental data from previous work [24] are used in the modeling studies. The model kinetic parameters are estimated by non-linear regression technique using Marquardt's algorithm to minimize a multi-response objective function (sum of squares of residuals on the molar quantities of reaction products). Discrimination among rival models is based on physico-chemical constraints for the parameters and the closeness of fit of the model. This technique is similar to that used in the kinetic modeling of heterogeneous catalysis reactions by Hougen and Watson [11] and recently applied by Sundaram and Froment [2,4].

REACTION SCHEMES

Little work has been done to elucidate the mechanisms of pyrolyses of pure cycloalkanes or their mixtures [1,24]. There is no agreement among the few works available on the values of the kinetic parameters characterizing the pyrolyses of naphthenic molecules [9,10,24]. A detailed free radical mechanism proposed for cyclohexane pyrolysis on the basis of Rice-Kossia-koff free radical theory [17] is shown in Fig. 1 [8]. Molecular reaction schemes could be developed using this mechanism, experimentally observed

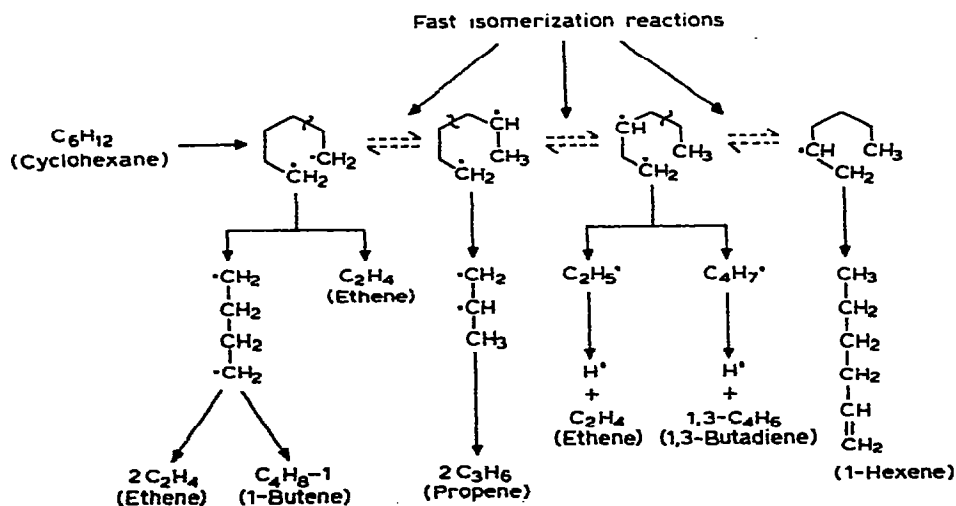


Fig. 1. The reaction path for cyclohexane pyrolysis. \sim = cleavage of the C—C bond at the beta position relative to the unsaturated valence bond.

product distribution, literature values of rate constants of free radical reactions and thermodynamic principles.

The main products of cyclohexane pyrolysis recently reported [24] were

TABLE 1

A series of plausible molecular reactions

1.	C_6H_{12}	$\xrightarrow{k_1}$	$3 C_2H_4$
2.	C_6H_{12}	$\xrightarrow{k_2}$	$2 C_3H_6$
3.	C_6H_{12}	$\xrightarrow{k_3}$	$C_2H_4 + C_4H_6 + H_2$
4.	C_2H_4	$\xrightleftharpoons[k_4]{k_4}$	$C_2H_2 + H_2$
5.	$C_2H_4 + H_2$	$\xrightleftharpoons[k_5]{k_5}$	C_2H_6
6.	$C_2H_4 + C_2H_2$	$\xrightarrow{k_6}$	C_4H_6
7.	$C_2H_4 + C_2H_6$	$\xrightarrow{k_7}$	$C_3H_6 + CH_4$
8.	$C_3H_6 + H_2$	$\xrightarrow{k_8}$	$C_2H_4 + CH_4$
9.	$C_3H_6 + C_2H_6$	$\xrightarrow{k_9}$	$C_4H_8 + CH_4$
10.	$C_3H_6 + 3 H_2$	$\xrightarrow{k_{10}}$	$3 CH_4$
11.	$2 C_3H_6$	$\xrightleftharpoons[k'_{11}]{k_{11}}$	$3 C_2H_4$
12.	C_3H_6	$\xrightleftharpoons[k'_{12}]{k_{12}}$	$C_2H_2 + CH_4$
13.	$2 C_2H_2 + H_2$	$\xrightarrow{k_{13}}$	C_4H_6
14.	$C_4H_8 + H_2$	$\xrightarrow{k_{14}}$	$C_3H_6 + CH_4$
15.	C_2H_2	$\xrightarrow{k_{15}}$	$2 C + H_2$
16.	$2 C_2H_6$	$\xrightarrow{k_{16}}$	$C_2H_4 + 2 CH_4$
17.	$C_4H_6 + H_2$	$\xrightleftharpoons[k'_{17}]{k_{17}}$	$2 C_2H_4$
18.	C_2H_4	$\xrightarrow{k_{18}}$	$2 C + 2 H_2$

TABLE 2

Proposed molecular models

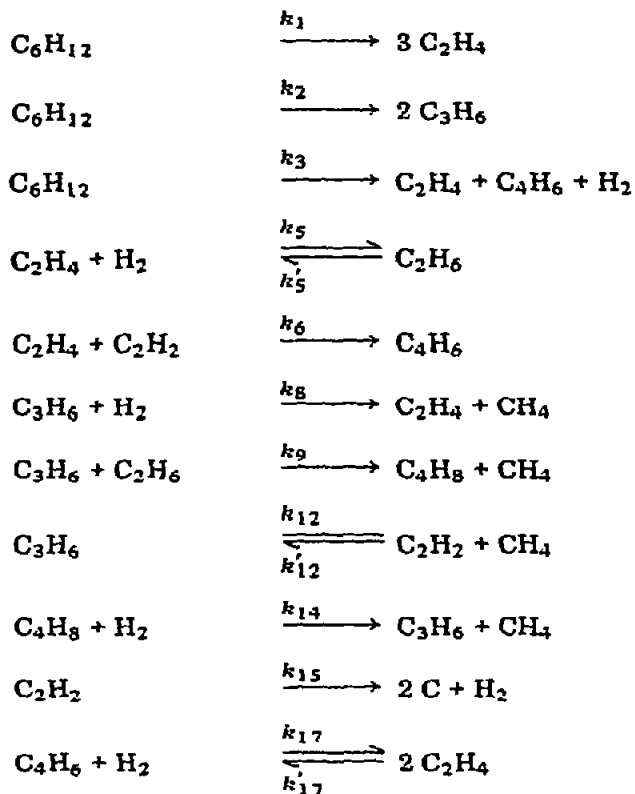
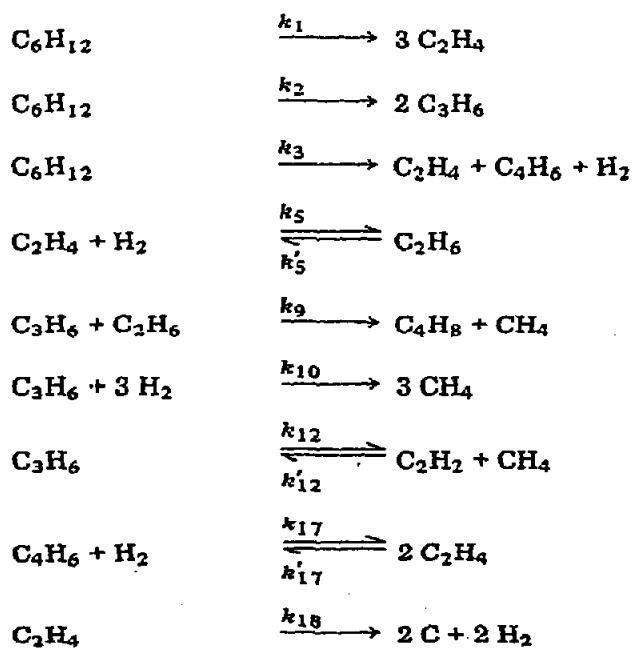
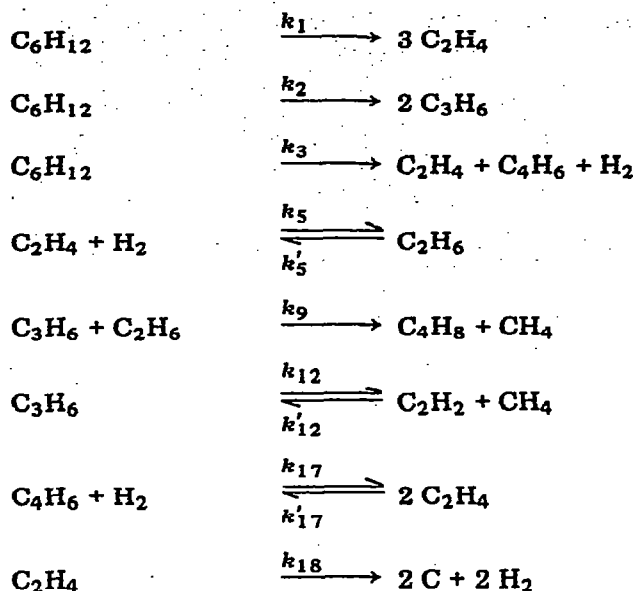
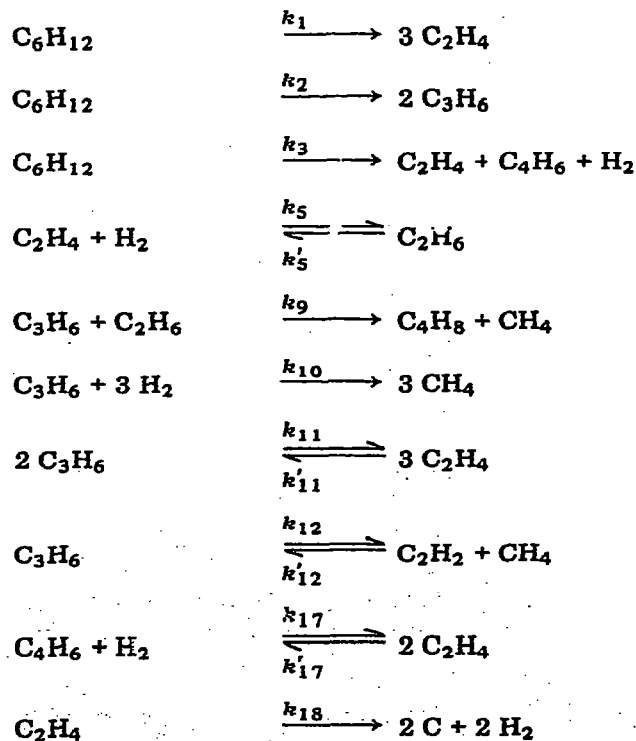
Model I*Model II*

Table 2 (continued)

Model III*Model IV*

ethene, propene, butadiene, methane and hydrogen. Small amounts of ethane, propane, ethyne, butene-1 and butene-2 were also observed. Other workers [9,12,13] reported the existence of propadiene, methylcyclop-

Table 3

Thermodynamic data at 1000 K for reactions of interest in cyclohexane pyrolysis

Reaction	Heat of reaction, ΔH_T° (kcal gmole ⁻¹)	Standard free energy change, ΔG_T° (kcal gmole ⁻¹)	Equilibrium constant, K
$C_6H_{12} \xrightarrow{1} 3 C_2H_4$	54.305	-9.839	1.414×10^3
$C_6H_{12} \xrightarrow{2} 2 C_3H_6$	26.777	-8.116	5.942×10
$C_6H_{12} \xrightarrow{3} C_2H_4 + C_4H_6 + H_2$	58.549	-3.628	6.208
$C_2H_4 \xrightarrow{4} C_2H_2 + H_2$	44.090	13.307	1.235×10^{-3}
$C_2H_4 + H_2 \xrightarrow{5} C_2H_6$	-34.463	-2.587	3.677
$C_2H_4 + C_2H_2 \xrightarrow{6} C_4H_6$	-39.845	-6.816	3.089×10
$C_2H_6 + C_2H_4 \xrightarrow{7} C_3H_6 + CH_4$	-5.274	-6.178	2.240×10
$C_3H_6 + H_2 \xrightarrow{8} C_2H_4 + CH_4$	-12.209	-10.908	2.422×10^2
$C_3H_6 + C_2H_6 \xrightarrow{9} C_4H_8 + CH_4$	-2.127	-2.046	2.800
$C_3H_6 + 3 H_2 \xrightarrow{10} 3 CH_4$	-54.396	-20.822	3.557×10^4
$2 C_3H_6 \xrightarrow{11} 3 C_2H_4$	-27.528	-2.143	2.940
$C_3H_6 \xrightarrow{12} C_2H_2 + CH_4$	31.881	2.399	2.990×10^{-1}
$2 C_2H_2 + H_2 \xrightarrow{13} C_4H_6$	-83.935	-20.123	2.502×10^4
$C_4H_8 + H_2 \xrightarrow{14} C_3H_6 + CH_4$	-15.356	-14.878	1.786×10^3
$C_2H_2 \xrightarrow{15} 2 C + H_2$	-53.193	-42.912	2.394×10^9
$2 C_2H_6 \xrightarrow{16} C_2H_4 + 2 CH_4$	16.981	-14.498	1.475×10^5
$C_4H_6 + H_2 \xrightarrow{17} 2 C_2H_4$	-4.244	-6.491	3.267
$C_2H_4 \xrightarrow{18} 2 C + 2 H_2$	-7.903	-28.405	1.616×10^6

tane, cyclohexadiene, cyclohexene, benzene and toluene in trace quantities in the product stream. A series of plausible molecular reactions developed on the basis of the above-mentioned considerations is contained in Table 1. These reactions are then used to set up four molecular schemes contained in Table 2. Thermodynamic calculations based on Rossini's tables [19] for free energies of formation were performed on the molecular reactions in Table 1

to determine their feasibility (see Table 3). Those reactions with negative standard free energy change (ΔG_T^0) are feasible while those with positive values of ΔG_T^0 are not (reactions 4 and 12).

MODEL DISCRIMINATION AND PARAMETER ESTIMATION

The kinetic equations of plausible molecular reactions of cyclohexane pyrolysis are listed in Table 4. All the reactions, except 11, 13, 16 and 17, were considered as elementary. Reactions 11, 16 and 17 are more complex and were assumed to be first order. Reaction 13 was assumed to be first order with respect to ethyne.

The kinetic parameters used for most of the individual steps were reviewed carefully from the literature and modified for our use. Parameters for reactions 1, 2 and 3 were selected from previous works [9,24] and used as initial values in the parameter estimation. More accurate rate parameters of some minor secondary reactions were obtained from processes in which they are significant [2,4] and used in the present studies. A coherent and precise set of kinetic data was developed in this way. The rate data were adjusted by altering only the pre-exponential parts of the parameters, with the activation energy remaining unchanged. The activation energy of a reaction can be estimated from thermochemical data with a certain degree of accuracy while, generally, a less accurate prediction can be made for the pre-exponential factor. Furthermore, the kinetic constant is more sensitive to changes in the pre-exponential factor, for most cases. The rate data so obtained were used in the continuity equations of the assumed models to predict the product distribution of cyclohexane pyrolysis. In this way, the suitability of each reaction scheme in predicting product distribution and the credibility of the selected rate parameters were determined. Table 5 contains the kinetic rate parameters of plausible reactions listed in Table 1.

Model parameters were determined by substituting the kinetic equations of the various models being considered into the appropriate continuity equations for the components involved in the cyclohexane pyrolysis reactions. The continuity equations were derived in a manner similar to that recently reported [2,4]. The general form of the continuity equations for pyrolysis in a tubular reactor with plug flow can be written as

$$\frac{dQ_j}{dV_r} = \frac{dF_j}{d\tau} = -\sum S_{ij}r_i \quad (1)$$

where S_{ij} = stoichiometric coefficient for j -th component in the i -th reaction; r_i = rate of i -th reaction; Q_j = molar flow rate of j -th component; F_j = molar mass of j -th component per unit reactor volume.

The set of continuity equations were numerically integrated by means of the Runge-Kutta-Gill routine. The computed molar quantities (F_j) obtained as solutions were compared to the experimental data (F_j^0).

The estimation of the rate parameters of the reactions in the molecular schemes is a critical stage in developing a model that adequately predicts the experimental results. The rate parameters were estimated by non-linear

TABLE 4

Kinetic equations of plausible molecular reactions

$$\begin{aligned}
 r_1 &= k_1 \left[\frac{F_1}{F_t} \left(\frac{P_t}{RT} \right) \right] \\
 r_2 &= k_2 \left[\frac{F_1}{F_t} \left(\frac{P_t}{RT} \right) \right] \\
 r_3 &= k_3 \left[\frac{F_1}{F_t} \left(\frac{P_t}{RT} \right) \right] \\
 r_4 &= \left[k_4 \frac{F_5}{F_t} \left(\frac{P_t}{RT} \right) - k'_4 \frac{F_2 F_4}{F_t^2} \left(\frac{P_t}{RT} \right)^2 \right] \\
 r_5 &= \left[k_5 \frac{F_2 F_5}{F_t^2} \left(\frac{P_t}{RT} \right)^2 - k'_5 \frac{F_6}{F_t} \left(\frac{P_t}{RT} \right) \right] \\
 r_6 &= \left[k_6 \frac{F_4 F_5}{F_t^2} \left(\frac{P_t}{RT} \right)^2 \right] \\
 r_7 &= \left[k_7 \frac{F_5 F_6}{F_t^2} \left(\frac{P_t}{RT} \right)^2 \right] \\
 r_8 &= \left[k_8 \frac{F_2 F_7}{F_t^2} \left(\frac{P_t}{RT} \right)^2 \right] \\
 r_9 &= \left[k_9 \frac{F_6 F_7}{F_t^2} \left(\frac{P_t}{RT} \right)^2 \right] \\
 r_{10} &= \left[k_{10} \frac{F_2 F_7}{F_t^2} \left(\frac{P_t}{RT} \right)^2 \right] \\
 r_{11} &= \left[k_{11} \frac{F_7}{F_t} \left(\frac{P_t}{RT} \right) - k'_{11} \frac{F_5}{F_t} \left(\frac{P_t}{RT} \right) \right] \\
 r_{12} &= \left[k_{12} \frac{F_7}{F_t} \left(\frac{P_t}{RT} \right) - k'_{12} \frac{F_3 F_4}{F_t^2} \left(\frac{P_t}{RT} \right)^2 \right] \\
 r_{13} &= \left[k_{13} \frac{F_2 F_4}{F_t^2} \left(\frac{P_t}{RT} \right)^2 \right] \\
 r_{14} &= \left[k_{14} \frac{F_2 F_9}{F_t^2} \left(\frac{P_t}{RT} \right)^2 \right] \\
 r_{15} &= \left[k_{15} \frac{F_4}{F_t} \left(\frac{P_t}{RT} \right) \right] \\
 r_{16} &= \left[k_{16} \frac{F_6}{F_t} \left(\frac{P_t}{RT} \right) \right] \\
 r_{17} &= \left[k_{17} \frac{F_2 F_8}{F_t^2} \left(\frac{P_t}{RT} \right)^2 - k'_{17} \frac{F_5}{F_t} \left(\frac{P_t}{RT} \right) \right] \\
 r_{18} &= \left[k_{18} \frac{F_5}{F_t} \left(\frac{P_t}{RT} \right) \right]
 \end{aligned}$$

$F_1 = F_{C_6H_{12}}$; $F_2 = F_{H_2}$; $F_3 = F_{CH_4}$; $F_4 = F_{C_2H_2}$; $F_5 = F_{C_2H_4}$; $F_6 = F_{C_2H_6}$;
 $F_7 = F_{C_3H_6}$; $F_8 = F_{C_4H_6}$; $F_9 = F_{C_4H_8}$; $F_{10} = F_C$.

F_t = total number of moles of reactants, products and diluent (nitrogen)

$$= \sum_{i=1}^9 F_i + F_{\text{nitrogen}}$$

TABLE 5
Kinetic parameters of plausible molecular reactions

	Pre-exponential factor, A	Activation energy, E (kcal mole ⁻¹)	Ref.
k_1	2.613×10^{14}	70.500	9
k_2	3.60×10^{13}	67.500	9
k_3	1.0×10^{14}	67.000	9
k_4	3.94×10^{16}	94.500	21
k_4'	4.54×10^9	49.400	21
k_5	1.98×10^7	38.500	21
k_5'	2.24×10^{14}	73.000	21
k_6	1.026×10^{12}	49.500	22
k_7	4.652×10^{13}	65.200	22
k_8	1.12×10^{12}	60.500	21
k_9	5.553×10^{11}	60.100	22
k_{10}	1.670×10^{11}	63.000	21
k_{11}	1.514×10^{11}	55.800	22
k_{11}'	1.300×10^{10}	50.000	22
k_{12}	3.794×10^{11}	59.390	22
$k_{12}' = k_{12}/K_c$	$K_c = 1.91 \times 10^4 \exp(-30.16/RT)$		22
k_{13}	6.00×10^{13}	45.000	23
k_{14}	4.743×10^{15}	67.000	11
k_{15}	5.00×10^{12}	62.000	7
k_{16}	3.900×10^{12}	67.000	23
k_{17}	1.5849×10^{11}	55.500	22
k_{17}'	$1.000 \times 10^{18.5}$	61.600	22
k_{18}	5.0×10^{14}	60.500	7

regression using Marquardt's algorithm. The multi-response nature of the problem was accounted for by the minimization of the sum of squares of the residuals (Φ) on the molar quantities of the pyrolysis reaction components at the reactor exit

$$\Phi = \sum (F_j^0 - F_j)^2 \quad (2)$$

where $i = 1 \dots L$ (L = number of experiments), $j = 1 \dots N$ (N = number of components), F_j^0 = experimental molar quantity, and F_j = predicted molar quantity.

In this procedure parametric corrections, δ , were evaluated by solving the following set of simultaneous algebraic equations

$$(A^T A + \lambda I) \delta = A^T e \quad (3)$$

where A = matrix of partial derivatives $\partial F_j / \partial K_m$, A^T = transpose of matrix A , δ = vector of parametric corrections Δk_m

$$\delta = \begin{bmatrix} \Delta k_1 \\ \vdots \\ \Delta k_m \end{bmatrix} \quad (4)$$

e = vector of differences between experimental and predicted molar quantities of components at reactor exit ($F_i^0 - F_i$)

$$e = \begin{bmatrix} F_1^0 - F_1 \\ \vdots \\ F_j^0 - F_j \end{bmatrix} \quad (5)$$

λ is an arbitrarily chosen scalar quantity, and I = identity matrix.

The partial derivatives ($\partial F_j / \partial k_m$), elements in matrix A , were evaluated by an expression similar to eqn. (6)

$$\frac{\partial F_1}{\partial k_1} = \frac{F_1(k_1, \dots, k_m) - F_1(k_1 + gk_1, \dots, k_m)}{gk_1} \quad (6)$$

where $g = 0.05$ is an arbitrary value.

Approximation of the partial derivatives by eqn. (6) makes the evaluation of the elements in matrix A easier and the parameter estimation procedure less tedious.

Algorithm for parameter estimation

- (1) Solve eqn. (1) simultaneously using initial rate parameters.
- (2) Estimate the vector of residuals (e) by eqn. (5).
- (3) Estimate the elements of matrix A using eqn. (6).

$$A = \begin{bmatrix} \frac{\partial F_1}{\partial k_1} & \dots & \frac{\partial F_1}{\partial k_m} \\ \vdots & & \vdots \\ \frac{\partial F_2}{\partial k_1} & \dots & \frac{\partial F_2}{\partial k_m} \\ \vdots & & \vdots \\ \frac{\partial F_N}{\partial k_1} & \dots & \frac{\partial F_N}{\partial k_m} \end{bmatrix} \quad (7)$$

- (4) Estimate the transpose of A (A^T).
- (5) Solve eqn. (3) for the parametric correction vector (δ).
- (6) Estimate Φ by eqn. (2).
- (7) Upgrade kinetic parameters according to eqn. (8) shown below

$$k_m = k_m + \Delta k_m \quad (8)$$

- (8) Repeat the whole procedure until the termination criterion is satisfied.

Computation is terminated each time the convergence criterion is satisfied. The criterion used initially was $\phi < 10^{-8}$; computation time for $\phi = 10^{-5}$ was so large (about 1 h) that the time to satisfy the initial termination criterion ($\phi < 10^{-8}$) would be prohibitive. This is due to the large number of function evaluations and iterations. To forestall this difficulty, the number of com-

plete iterations was limited and the new termination criterion (number of iterations = 10) was used to stop further computations. Computation time for the new termination criterion varied from 155 to 165 sec on IBM 370 Model 145.

A comparison between experimental and predicted product distributions is shown in Tables 6–10. Close examination of these tables reveals that the prediction of the product distribution was reasonably good at the highest temperature of this investigation (860°C). The discrepancies between measured and predicted values at lower temperatures (815, 795, 775 and 730°C) for all the molecular schemes considered cannot be disregarded. The estimated values of the sum of squares of residuals on the molar quantities are also shown in Tables 6–10. The residual for Model IV was much lower than those of other models at 860°C. At the lower cracking temperatures, the residuals of Models II, III and IV were almost the same and lower than those of Model I. The sum of squares of residuals and the closeness of fit reveal that Model IV was more plausible than Models I, II and III. The estimated rate parameters for Model IV are listed in Table 11.

The agreement between experimental and predicted product distributions using estimated rate parameters seems fairly good for all the reaction schemes considered at 860°C, the highest temperature of investigation. However, discrepancies exist between experimental and predicted values at lower temperatures (815, 795, 775 and 730°C). The fairly low performance of all the models in predicting experimental data at lower temperatures may be attributed to the non-availability of precise rate parameters for the reactions of interest in cyclohexane pyrolysis. Furthermore, the selected initial rate parameters used for parameter estimation had been determined at temperatures different from those of this work and for the pyrolyses reactions of

TABLE 6

Comparison of measured molar masses of cyclohexane pyrolysis products with predicted molar masses (temperature = 860°C)

Products	Experi- mental (measured) molar mass (gmole)	Predicted molar masses (gmole)			
		Model I	Model II	Model III	Model IV
C ₆ H ₁₂	0.02416	0.02521	0.02332	0.02332	0.02332
H ₂	0.01099	0.01590	0.01213	0.01499	0.01211
CH ₄	0.00320	0.00014	0.00473	0.00148	0.00440
C ₂ H ₂	0.00137	3.0 × 10 ⁻⁷	0.00030	0.00044	0.00031
C ₂ H ₄	0.02185	0.02808	0.02699	0.02687	0.02686
C ₂ H ₆	0.00142	0.00031	0.00204	0.00216	0.00203
C ₃ H ₆	0.00413	0.00379	0.00529	0.00610	0.00537
C ₄ H ₆	0.01523	0.01636	0.01473	0.01468	0.01472
C ₄ H ₈	0.00031	2.0 × 10 ⁻⁶	0.00095	0.00104	0.00095
C	0.00245	7.0 × 10 ⁻¹¹	0.00351	0.00351	0.00351
φ		0.8405 × 10 ⁻⁴	0.3541 × 10 ⁻⁴	0.5209 × 10 ⁻⁴	0.3335 × 10 ⁻⁴

TABLE 7

Comparison of measured molar masses of cyclohexane pyrolysis products with predicted molar masses (temperature = 815°C)

Products	Measured molar mass (gmole)	Predicted molar masses (gmole)			
		Model I	Model II	Model III	Model IV
C ₆ H ₁₂	0.02587	0.04033	0.03973	0.03973	0.03973
H ₂	0.02932	0.00545	0.00464	0.00475	0.00464
CH ₄	0.00387	5.0 × 10 ⁻⁶	0.00017	0.00006	0.00017
C ₂ H ₂	0.00031	3.0 × 10 ⁻⁸	0.00006	0.00006	0.00006
C ₂ H ₄	0.02032	0.00872	0.01023	0.01023	0.01021
C ₂ H ₆	0.00050	1.5 × 10 ⁻⁵	0.00015	0.00015	0.00015
C ₃ H ₆	0.00395	0.00123	0.00237	0.00240	0.00238
C ₄ H ₆	0.01450	0.00547	0.00452	0.00452	0.00452
C ₄ H ₈	0.00021	2.0 × 10 ⁻⁹	0.00001	6.0 × 10 ⁻⁶	0.00001
C	0.00040	2.0 × 10 ⁻¹²	0.00038	0.00038	0.00038
φ		0.1018 × 10 ⁻²	0.1019 × 10 ⁻²	0.1015 × 10 ⁻²	0.1020 × 10 ⁻²

TABLE 8

Comparison of measured molar masses of cyclohexane pyrolysis products with predicted molar masses (temperature = 795°C)

Products	Measured molar mass (gmole)	Predicted molar masses (gmole)			
		Model I	Model II	Model III	Model IV
C ₆ H ₁₂	0.02969	0.04338	0.04305	0.04305	0.04305
H ₂	0.01846	0.00317	0.00264	0.00266	0.00264
CH ₄	0.00349	9.0 × 10 ⁻⁷	0.00004	0.00002	0.00004
C ₂ H ₂	0.00017	1.0 × 10 ⁻⁸	0.00002	0.00002	0.00002
C ₂ H ₄	0.01748	0.00498	0.00599	0.00599	0.00598
C ₂ H ₆	0.00042	4.0 × 10 ⁻⁶	0.00004	0.00004	0.00004
C ₃ H ₆	0.00093	0.00070	0.00139	0.00140	0.00140
C ₄ H ₆	0.01213	0.00317	0.00257	0.00257	0.00257
C ₄ H ₈	0.00004	2.0 × 10 ⁻¹⁰	5.0 × 10 ⁻⁷	5.0 × 10 ⁻⁷	5.0 × 10 ⁻⁷
C	0.00102	4.0 × 10 ⁻¹³	0.00013	0.00013	0.00013
φ		0.6713 × 10 ⁻³	0.6653 × 10 ⁻³	0.6649 × 10 ⁻³	0.6655 × 10 ⁻³

TABLE 9

Comparison of measured molar masses of cyclohexane pyrolysis products with predicted molar masses (temperature = 775°C)

Products	Measured molar mass (gmole)	Predicted molar masses			
		Model I	Model II	Model III	Model IV
C ₆ H ₁₂	0.03392	0.04519	0.04502	0.04502	0.04502
H ₂	0.01868	0.00179	0.00146	0.00146	0.00146
CH ₄	0.00250	2.0 × 10 ⁻⁷	0.00001	7.0 × 10 ⁻⁶	0.00001
C ₂ H ₂	0.00051	3.0 × 10 ⁻⁹	0.00001	7.0 × 10 ⁻⁶	7.0 × 10 ⁻⁶
C ₂ H ₄	0.00949	0.00277	0.00337	0.00337	0.00336
C ₂ H ₆	0.00024	8.0 × 10 ⁻⁷	0.00001	8.0 × 10 ⁻⁶	8.0 × 10 ⁻⁶
C ₃ H ₆	0.00272	0.00039	0.00079	0.00079	0.00079
C ₄ H ₆	0.00792	0.00179	0.00143	0.00143	0.00143
C ₄ H ₈	0.00012	1.4 × 10 ⁻¹¹	4.0 × 10 ⁻⁸	4.0 × 10 ⁻⁸	4.0 × 10 ⁻⁸
C	0.00074	8.0 × 10 ⁻¹⁴	0.00004	0.00004	0.00004
φ		0.5079 × 10 ⁻³	0.5103 × 10 ⁻³	0.5102 × 10 ⁻³	0.5104 × 10 ⁻³

TABLE 10

Comparison of measured molar masses of cyclohexane pyrolysis products with predicted molar masses (temperature = 730°C)

Products	Measured molar mass (gmole)	Predicted molar masses (gmole)			
		Model I	Model II	Model III	Model IV
C ₆ H ₁₂	0.03637	0.04693	0.04690	0.04690	0.04690
H ₂	0.02160	0.00045	0.00035	0.00035	0.00035
CH ₄	0.00127	3.0 × 10 ⁻⁹	5.0 × 10 ⁻⁷	5.0 × 10 ⁻⁷	5.0 × 10 ⁻⁷
C ₂ H ₂	0.00021	2.0 × 10 ⁻¹⁰	5.0 × 10 ⁻⁷	5.0 × 10 ⁻⁷	5.0 × 10 ⁻⁷
C ₂ H ₄	0.00718	0.00067	0.00081	0.00081	0.00081
C ₂ H ₆	0.00178	2.0 × 10 ⁻⁸	2.0 × 10 ⁻⁷	0.2 × 10 ⁻⁶	2.0 × 10 ⁻⁷
C ₃ H ₆	0.00190	0.00009	0.00020	0.00020	0.00020
C ₄ H ₆	0.00608	0.00045	0.00035	0.00035	0.00035
C ₄ H ₈	0.00009	2.0 × 10 ⁻¹⁴	6.0 × 10 ⁻¹¹	6.0 × 10 ⁻¹¹	6.0 × 10 ⁻¹¹
C	0.00070	1.0 × 10 ⁻¹⁵	3.0 × 10 ⁻⁶	3.0 × 10 ⁻⁶	3.0 × 10 ⁻⁶
φ		6.417 × 10 ⁻³	0.6439 × 10 ⁻³	0.6439 × 10 ⁻³	0.6439 × 10 ⁻³

simple paraffins as opposed to cycloparaffins. This in effect means that the complexity of any pyrolysis reaction network (that is the type of product distribution) influences, to a large extent, the kinetic rate parameters of all reactions taking part in the pyrolysis. Alternatively, the main products (ethene, butadiene and propene) are formed by reaction paths which may be affected significantly by the estimated values of the rate parameters.

TABLE 11

Estimated rate parameters for model IV

	860°C	815°C	795°C	775°C	730°C
k ₁	0.6560 × 10 ³	0.1797 × 10 ³	0.9755 × 10 ²	0.5174 × 10 ²	0.1133 × 10 ³
k ₂	0.3426 × 10 ³	0.9914 × 10 ²	0.5525 × 10 ²	0.3011 × 10 ²	0.7032 × 10
k ₃	0.1189 × 10 ⁴	0.3471 × 10 ³	0.1942 × 10 ³	0.1063 × 10 ³	0.2511 × 10 ²
k ₅	0.7406 × 10	0.3651 × 10 ¹	0.2616 × 10	0.1850 × 10	0.8072
k ₅ '	0.1853 × 10	0.4839	0.2568	0.1330	0.2700 × 10 ⁻¹
k ₉	0.1847 × 10 ³	0.6189 × 10 ²	0.3696 × 10 ²	0.2165 × 10 ²	0.6007 × 10
k ₁₀	0.1173 × 10 ²	0.3687 × 10	0.2136 × 10	0.1212 × 10	0.3119
k ₁₁	0.2604 × 10	0.9340	0.5759	0.3486	0.1047
k ₁₁ '	0.2940 × 10 ²	0.1173 × 10 ²	0.7610 × 10	0.4854 × 10	0.1653 × 10
k ₁₂	0.1325 × 10 ⁴	0.4490 × 10 ³	0.2660 × 10 ³	0.1559 × 10 ³	0.4337 × 10 ²
k ₁₂ '	0.4563 × 10 ³	0.2667 × 10 ³	0.2071 × 10 ³	0.1592 × 10 ³	0.8481 × 10 ²
k ₁₇	0.3115 × 10 ¹	0.1123 × 10 ¹	0.6945	0.4216	0.1274
k ₁₇ '	0.1308 × 10 ⁴	0.4219 × 10 ³	0.2474 × 10 ³	0.1422 × 10 ³	0.3771 × 10 ²
k ₁₈	0.1066 × 10 ⁴	0.3509 × 10 ³	0.2078 × 10 ³	0.1206 × 10 ³	0.3275 × 10 ²
φ	0.3335 × 10 ⁻⁴	0.1020 × 10 ⁻²	0.6655 × 10 ⁻³	0.5104 × 10 ⁻³	0.6439 × 10 ⁻³

CONCLUSIONS

The mechanistic modeling performed in this work was successful. All the molecular reaction schemes considered predicted the increase in molar quantities of the pyrolysis products with temperature, although such values were often lower than the experimental results. This investigation has again brought to focus the significance of non-linear regression techniques in the analyses of homogeneous reactions. Finally, this work should provide some insight into the modeling of complex radical mechanisms of pure naphthenes or their mixtures.

NOMENCLATURE

k_i	rate constant for i th reaction (sec^{-1} , $1 \text{ mole}^{-1} \text{ sec}^{-1}$)
ΔH_T^0	standard heat of reaction (kcal mole^{-1})
ΔG_T^0	standard free energy change (kcal mole^{-1})
K	equilibrium constant
r_i	reaction rate for i th reaction ($\text{mole l}^{-1} \text{ sec}^{-1}$)
P_t	total pressure of system
A	pre-exponential factor (sec^{-1} or $1 \text{ mole}^{-1} \text{ sec}^{-1}$)
E	activation energy (kcal mole^{-1})
S_{ij}	stoichiometric coefficient for j th component in i th reaction
V_x	reactor volume (cm^3)
F_j	molar mass of component j per unit reactor volume (mole cm^{-3})
R	gas constant ($\text{kcal mole}^{-1} \text{ K}^{-1}$)
T	temperature ($^{\circ}\text{C}$, K).

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