

Kinetics of the Nonisothermal Pyrolysis of Propane

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A method was devised to yield chemical reaction kinetic parameters from nonisothermal, non-isobaric flow experiments. The system studied was the pyrolysis of propane at high temperatures (800° to 1,000°C.). At these temperatures the rates of the various reactions are so high that a batch or even an isothermal flow experiment is impossible. To keep the conversions low so that the initial stages of decomposition could be studied, the feed gas was diluted with varying amounts of nitrogen. Residence times in the reactor were in the millisecond range. The reactor exit gas was analyzed by mass spectrometry. The method developed in this work is not limited to simple kinetic studies, but can be useful in complicated series and parallel reactions which often require nonisothermal conditions.

As reaction temperatures are raised, it becomes increasingly difficult to measure kinetic rate constants experimentally. In this work, the pyrolysis of propane was studied at 800° to 1,000°C. where the reactions are extremely rapid. Furthermore, the products of reaction themselves decompose under these conditions, tending to mask the primary kinetics. Conversions, therefore, were kept low through the use of a steady state flow system, where residence times can be shorter than in batch systems; the concentration of the reaction products was minimized by diluting the feed gas with nitrogen to about 5% propane. The extent of this dilution was limited however, because the higher the concentration of diluent and the lower the conversion, the more difficult becomes the exit gas analysis.

Since rate constants are strongly dependent upon temperature, it would be most convenient to conduct kinetic experiments isothermally. However, because of the low residence times required and the physical limitations on heat transfer rates, a nonisothermal experiment results. Some previous workers have chosen an equivalent, average temperature for all or a fraction of the reactor, but this procedure leads to only partially satisfactory results. An alternative is to measure the gas temperature profile throughout the reactor and to devise some method of treating the data to yield the desired rate constants. Such was the method used in this study.

Once the rate constants are obtained as functions of temperature, the kinetic model can be programmed on an analog computer; it is then possible to test the consistency of the data and to predict product distributions, conversions, etc., for any arbitrary set of conditions. This is extremely valuable if similar studies are made for the other low hydrocarbons which are products of propane pyrolysis. Then the entire series could be studied simultaneously; that is, product distributions could be predicted not only for the simple case of low conversions but also for the more complicated cases of consecutive reactions where reaction products themselves react further.

There is much published information in the literature dealing with the thermal decomposition of hydrocarbons in general and propane in particular. While much kinetic work has been done with propane at lower temperatures (500° to 600°C.), none has been done in the temperature range of this study (800° to 1,000°C.). The data avail-

able on product distributions over a wide range of temperatures (500° to 900°C.) all agree that the main reaction products are methane, ethylene, propylene, and hydrogen. Most of these data are from commercial and pilot plant processes for producing ethylene, acetylene, and/or aromatics from paraffins. High-temperature, noncatalytic processes are described by Akin, Reid, and Schrader (1), Farnsworth et al. (5), Linden and Peck (12), Schutt (20), Bixler and Coberly (2), Eastwood and Potas (4), and Reid and Linden (18).

There has been, however, considerable work done on the kinetics of propane pyrolysis at lower temperatures (500° to 600°C.). Most workers have found the reactions to be homogeneous and first order, although recent mechanism studies seem to indicate otherwise. Arrhenius rate constants have been obtained in this temperature range for the overall decomposition of propane by Hepp and Frey (6), Marek and McClellan (13), Paul and Marek (16), Peard et al. (17), Laidler et al. (8), and Steacie and Puddington (21).

THEORY

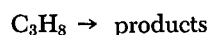
General Introduction

When hydrocarbons are thermally decomposed at high temperatures, they usually split into lower hydrocarbons, carbon and/or hydrogen; there is also a tendency toward polymerization into higher hydrocarbons, especially if the starting material is an olefin. Past work has shown that over a wide range of conditions, the main reaction products of propane pyrolysis are methane, ethylene, propylene, and hydrogen.

Although isothermal kinetic experiments are convenient (obtaining the kinetic parameters becomes relatively simple), it is possible to obtain similar results, but not as easily, from nonisothermal experiments. In this work, no attempt was made to alter the shape of the temperature profile; rather, the existing profile was accurately measured and used in the determination of rate constants as outlined below.

Determination of Orders of Reaction

For an irreversible reaction



which takes place in a flow reactor, the overall rate can be expressed as

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$$-\frac{dm}{dV} = kC^n \quad (1)$$

By using the Arrhenius form of the rate constant, expressing the concentration in terms of the ideal gas law, and replacing dV by sdl , Equation (1) becomes

$$-\frac{dm}{sdl} = Ae^{-E/RT(l)} \left[\frac{xP(l)}{RT(l)} \right]^n \quad (2)$$

For small conversions of propane, the mole fraction x will not change appreciably throughout the reactor; the arithmetic average $\bar{x}$ can be used upon integration to yield

$$-\Delta m = \bar{x}^n \left[\frac{sA}{R^n} \int_0^L e^{-E/RT(l)} \left(\frac{P(l)}{T(l)} \right)^n dl \right] \quad (3)$$

For a set of runs at identical temperature profiles and flow rates (and hence pressure profiles) the entire term within the brackets in Equation (3) is a constant. A logarithmic plot of $-\Delta m$ (which is the rate of propane disappearance) vs. the average propane mole fraction should yield a straight line of slope n :

$$\log(-\Delta m) = n \log(\bar{x}) + \log(\text{const.})$$

Such a procedure for obtaining reaction orders corresponds *exactly* to the procedure in an isothermal experiment, where (for a series of runs at the same temperature) the logarithm of the reactant concentration is plotted against the logarithm of differential rate of reaction.

Evaluation of Rate Constants in Nonisothermal Experiments

In an irreversible decomposition



the rate of decomposition of A has been expressed by Equation (2). The term dm can be replaced by $-Fdz$ and from the stoichiometry of the reaction, the mole fraction x of propane is

$$x = \frac{F(1-z)}{F(1+z) + N_o}$$

Substituting in Equation (2) and integrating along the length of the reactor from 0 to L and from conversion 0 to z_e , we obtain

$$\frac{F}{s} \int_0^{z_e} \left[\frac{1 + (N_o/F) + z}{1-z} \right]^n dz = \frac{A}{R^n} \int_0^L e^{-E/RT(l)} \left[\frac{P(l)}{T(l)} \right]^n dl$$

or

$$A = \frac{\frac{FR^n}{s} \int_0^{z_e} \left[\frac{1 + (N_o/F) + z}{1-z} \right]^n dz}{\int_0^L e^{-E/RT(l)} \left[\frac{P(l)}{T(l)} \right]^n dl} = \phi(E) \quad (4)$$

Similar derivations have been illustrated in greater detail by Towell and Martin (24) and Lee and Oliver (10).

From Equation (4) it is noted that L and s are the dimensions of the reactor and F , N_o , z , $T(l)$, and $P(l)$ are experimental data. Therefore, once the order of reaction n has been determined as outlined above, the frequency factor A is merely a function of the activation energy E .

It is obvious that no single set of data will be sufficient to solve Equation (4) for the kinetic parameters A and E . One possibility is to use the data of two distinct experi-

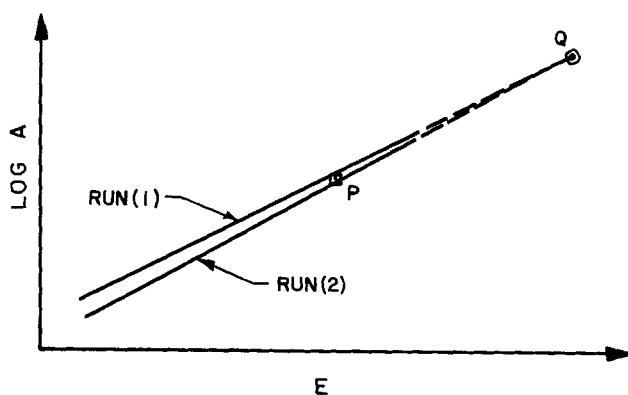


Fig. 1. Errors introduced by the pairing method.

mental runs to solve the two resulting equations simultaneously for A and E . Since the equations are explicit in A , it is relatively simple to select a series of values for E and solve for A in each of the cases, although the numerical integration requires the use of a digital computer. The solution is obtained when for a certain E , the value of A for both runs is identical. Conveniently, the functional relationship is such that a plot of $\log A$ vs. E is a fairly good straight line.

Unfortunately, when two other runs are paired, substantially different values of A and E result. Towell and Martin (24) developed the following method for treating the data. A pair of runs is used to calculate the kinetic parameters for that pair. Then, for every run, the maximum rate constant

$$k_{\max} = Ae^{-E/RT_{\max}}$$

is calculated. The calculated values of $k_{\max}$ for each run are used in an Arrhenius plot of $\log k_{\max}$ vs. $1/T_{\max}$ to yield, from the slope and intercept, the smoothed values of E and A .

However, there is a serious drawback to this method; depending upon how the points (data runs) are paired, different values of the kinetic parameters can result. Suppose a pairing between two runs which were made under similar conditions of temperature and pressure. If one attempts to solve Equation (4) simultaneously for two runs which do not differ greatly, the resulting functions should be quite similar. Thus, in Figure 1, if the point P represents the true value of E and A , the functions obtained from runs 1 and 2 are both satisfied (within the limits of experimental error) by the true value. However, if the two are paired, the intersection point Q is considerably in error. Thus, depending upon how the paired runs are chosen, there can be much variation in the final average values of E and A .

Several alternate methods were used to determine the best values of the parameters E and A by a statistical treatment of *all* the data in a single step. These methods have been outlined in great detail (7) and can be used with varying degrees of success in solving the problem at hand. An overall least squares method of treating the data was found to be the easiest and most reliable averaging technique. It was noted above that the results of every data run could be placed in the form

$$\log A = u_i + v_i E \quad (i = 1, 2, \dots, N)$$

or

$$u_i = \log A + (-E) v_i \quad (5)$$

by a least squares fit of Equation (4). An equation similar to (5) can be written for each run. A second least squares analysis can now be performed on $u = \psi(v)$ to yield the

best fit by choosing constants $\log A$ and $(-E)$ which minimize the sum of deviations $\Delta^2 = [u_i - (\log A - Ev_i)]^2$.

EXPERIMENTAL APPARATUS AND TECHNIQUES

Apparatus

A schematic diagram of the experimental apparatus is shown in Figure 2. The reactant gases and nitrogen diluent were metered from cylinders into a ceramic reactor which was contained inside the electrically heated furnace. Power input to the furnace was controlled manually with a variac connected to a 220-v. supply. Temperature was measured with a thermocouple which was continuously driven along the length of the reactor. Pressures were measured with mercury and water manometers. Upon leaving the furnace, the gas was quickly cooled to room temperature with an air blast. For each run, a sample of the reactor exit gas stream was taken. The gas then passed through a saturator and wet-test meter (for overall volumetric measurement) before being vented.

The gases used were obtained from the Matheson Company, Inc. Prepurified grade nitrogen (99.996% minimum purity, with a typical oxygen content of 8 p.p.m.) was used as the diluent; the oxygen content had to be kept low because it is a known accelerator of hydrocarbon pyrolysis. The propane used was instrument grade (99.5% minimum purity) and the propylene, C.P. grade (99.0% minimum purity); both hydrocarbons were products of the Phillips Petroleum Company.

The electric furnace, built by G. D. Towell for his work at the University of Michigan, was wound with platinum over its 26-in. heated length, and was designed to operate up to 1,600°C. The alundum muffle was 1½-in. bore with ¼-in. walls. Further details of construction may be found elsewhere (23).

The reactor used was an annular one, with both surfaces made from Vitreous Refractory Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). The I.D. of the outer tube was ¼ in. and the O.D. of the inner tube was 7/32 in. as shown in Figure 3. Several runs were made with an inner tube O.D. of 3/16 in. to test the homogeneity of the reactions. The gas flowed through the annulus and the thermocouple traveled up and down the reactor's central tube.

The driving mechanism continuously moved the thermocouple up and down the reactor. It consisted of a ½ rev./min. reversible, synchronous motor and a set of gears which were used to change the thermocouple drive speed. Depending upon the steepness of the temperature profile of any particular run, the drive speed could be increased or decreased to give easily readable temperature profiles on the recorder chart. The thermocouple measured the gas temperature from the inlet to the reactor (at room temperature) down to the point where the exit gas has been cooled close to room temperature by the air blast. Thus, there was no need to assume an instantaneous or linear heating and cooling.

Experimental Procedure

The furnace was allowed to heat slowly overnight to prevent damage caused by thermal shock. The feed rates of the hydrocarbons and nitrogen diluent were adjusted manually and measured with the rotameters. The maximum temper-

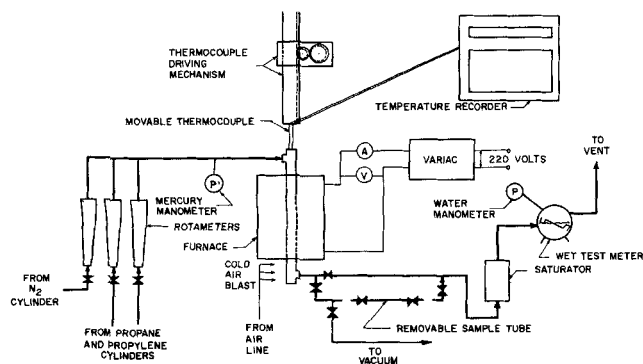


Fig. 2. Schematic diagram of apparatus.

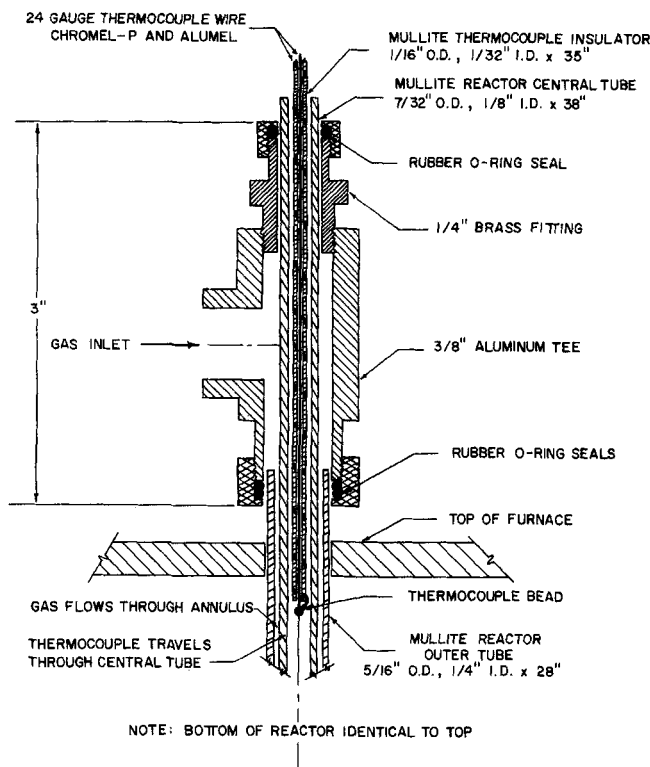


Fig. 3. Details of reactor and thermocouple.

ature could be controlled crudely by changing the power input through the variac. The thermocouple drive mechanism was started and the temperature profiles recorded. Steady state conditions were achieved when successive temperature profiles (representing approximately 45 min. total traversing time for most runs) were identical. At that time, the experimental conditions were recorded and a gas sample was taken for analysis.

The experimental parameters which were recorded were: nitrogen and hydrocarbon feed rates, reactor inlet pressure, reactor exit pressure, atmospheric pressure, reactor temperature profile, room temperature, furnace power input (voltage, current, and variac setting), total exit gas volumetric flow rate, thermocouple drive speed, and exit gas composition (by mass spec analysis).

The experimental conditions (namely, nitrogen and hydrocarbon feed rates, and the furnace power input) were then changed for the next run and the parameters were allowed to reach the steady state again. After an entire series of runs, the power was turned off and air was passed through to burn any carbon deposits.

Some Preliminary Problems Solved

A major problem that had to be solved before any useful data could be obtained was whether the thermocouple (located at the center of the reactor) was reading the true temperature of the gas (flowing through the annulus). Theoretical considerations of fluid dynamics and heat transfer might have been used to settle the question but instead the problem was solved experimentally.

A thin thermocouple was cemented in a fixed position through the rubber seals into the annulus of the reactor. The depth of the thermocouple into the reactor was noted and the movable thermocouple was placed in the corresponding position of the central tube.

Over a wide range of conditions of temperatures and flow rates, the two thermocouples agreed to within 3°C. It was thereby concluded that the central thermocouple could indeed be used to give the true gas temperature.

A second problem was the effect of any longitudinal diffusion as the gas flowed through the reactor. A flow reactor in which a first-order reaction with longitudinal diffusion is taking place can be described (11) by the differential equation

$$D \frac{d^2 z}{dl^2} - u_1 \frac{dz}{dl} + k(1 - z) = 0$$

Since the effect of longitudinal diffusion is represented by the first term alone in this equation, the fractional error introduced by neglecting diffusion is approximately equal to the ratio

$$\frac{D(d^2 z/dl^2)}{u_1(dz/dl)}$$

At the conclusion of this study, the rate constants were fed, along with the experimental data, into an analog computer and the expressions (dz/dl) and $(d^2 z/dl^2)$ were easily calculated along the length of the reactor. For a typical run, the value of the above ratio was approximately 1%, so the diffusional effects were indeed negligible.

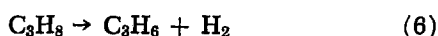
DISCUSSION OF EXPERIMENTAL RESULTS*

Product Distribution

The first experimental step in this program was to determine which were the primary molecular products of reaction in the decomposition of propane, that is, those which are present at the lowest overall conversions. A series of runs was made at approximately identical temperature profiles. The conversion for each run could be changed by altering either the total flow rate (and hence the residence time) or the inlet propane mole fraction, or both.

For this series of runs, the conversion to each of the reaction products (as moles of that product per mole of propane reacted) was plotted against the total conversion of propane. Any carbon formed was determined by material balance.

The results of the product distribution runs are shown in Figure 4. It is seen that the primary products of reaction are methane, ethylene, propylene, and hydrogen. Some of the minor or secondary products of reaction were ethane, methylacetylene, acetylene, carbon, and butane. The overall stoichiometry of these major reactions may be set forth as follows (although the mechanism is in fact, free radical):



Orders of Reaction

Once the stoichiometric reactions are determined, it is possible to find the orders of reaction for the overall decomposition and for each of the individual reactions. From the theory developed it is seen that a series of runs is needed in which the total flow rate and temperature profile are kept constant. Conversions were varied by changing the mole fraction of the propane in the feed. The runs were designed to hold conversions at a minimum by keeping the residence times low. A differential reaction rate could then be calculated and plotted against the average mole fraction of propane on logarithmic coordinates.

As was shown above, the slope of such a graph is the order of reaction. Figure 5 shows the results for each of the individual reactions and for the overall decomposition. The slope for the overall decomposition is 1.11 and for propylene and methane formation, 1.13 and 1.17, respectively.

It appears, therefore, that both the overall decomposition reaction and the individual reactions are first order, within the limits of experimental uncertainty. Most previous workers (3, 13, 15, 16, 21) have found the reaction to be first order, although a few (8, 22) have found evidence of 1.5 order kinetics, at least under certain condi-

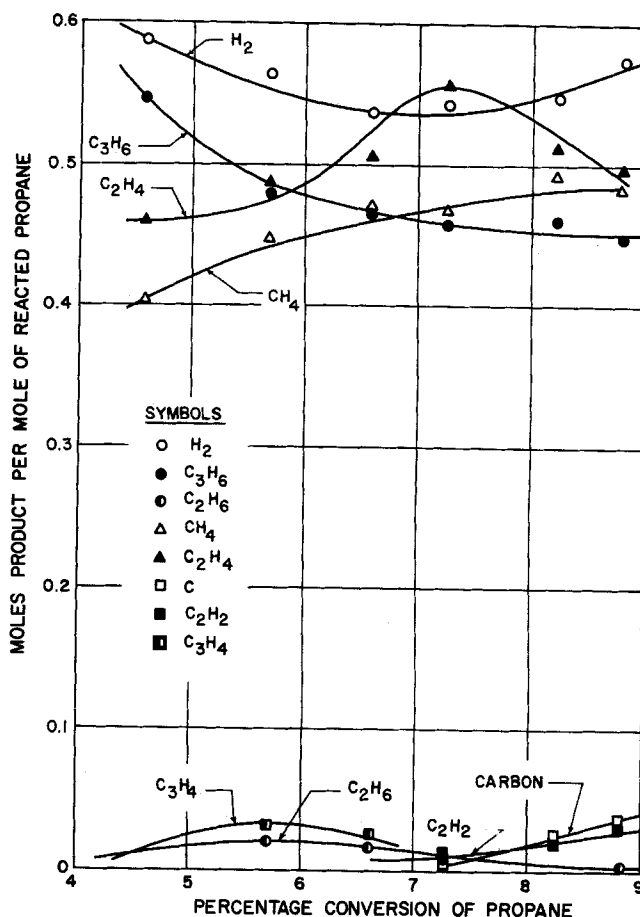


Fig. 4. Propane product distribution; $T_{\max} = 1,514^\circ\text{F}$.

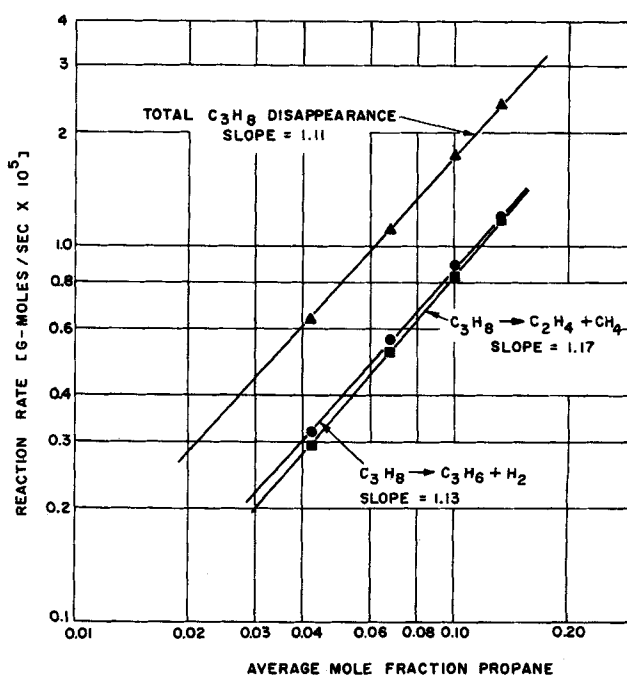


Fig. 5. Order of reaction determination for propane decomposition; $T_{\max} = 1,514^\circ\text{F}$.

* See reference 7 for complete tabulation of results.

tions of temperature and pressure. Martin et al. (14) have empirically found the order to be between 1.2 and 1.3.

Rate Constant Determination

Once the primary reactions have been determined and a reaction order has been postulated, one can conduct experiments to determine the rate constants. In actuality, since no runs were made at constant temperature, it is the parameters A and E which are determined and not the rate constants themselves.

The functional relationship between A and E for any run was given in Equation (4). Although the pairing of two runs was found to be an unsatisfactory method of obtaining A and E , this method can be used, for comparison with the overall correlation, if the paired runs were made at greatly different temperatures; then the errors introduced under these conditions are usually at a minimum. Thus, values of $k_{\max} = Ae^{-E/RT_{\max}}$ can be calculated and plotted against $1/T_{\max}$ in the usual Arrhenius graph.

Figure 6 shows the results for the overall propane decomposition. The straight line represents the best fit of all the data by least squares methods; the points, on the other hand, are judiciously chosen results obtained by the pairing method. Only runs made under widely differing experimental conditions are paired here; inclusion of other pairs would have scattered the points considerably.

A similar method of calculation is used in obtaining the kinetic parameters for each of the first-order reactions in Equations (6) and (7). The differences between the calculations here and for the overall decomposition reaction are slight, and these results are also shown in Figure 6. The values of the preexponential factors and activation energies for the reactions are listed in Table 1.

Figure 7 compares all the published kinetic data for first-order propane pyrolysis. While it is true that the other

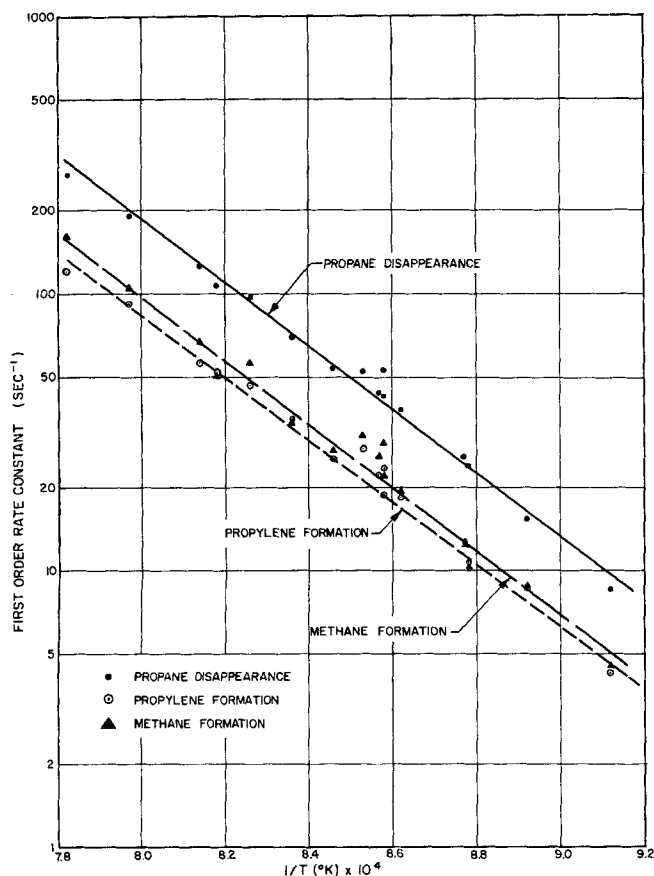


Fig. 6. Arrhenius plot for propane pyrolysis.

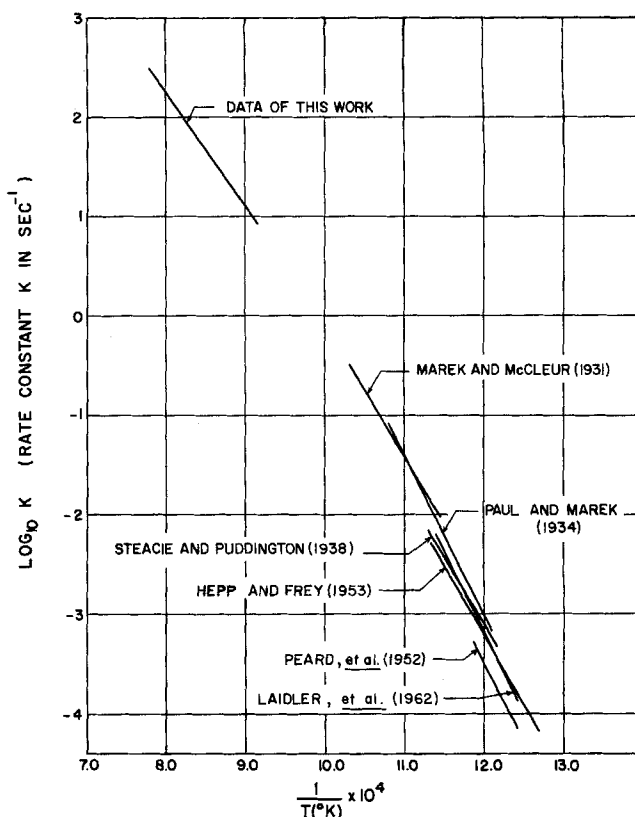


Fig. 7. A comparison with literature values of first-order rate constants for propane decomposition.

studies have indicated higher activation energies, usually between 60 and 70 kcal./g.-mole, the discrepancies can be explained by the great temperature difference.

Several workers (8, 14, 15, 23) have noted that as the temperature of hydrocarbon pyrolysis is increased, the activation energy for the reaction appears to decrease rather than remain constant. This effect can be noted even in the short temperature range of this work; Figure 6 shows that the data might have been fitted more closely by curves (concave downward) than by straight lines. A possible cause is the rapid formation at higher temperatures of olefins, which are reaction inhibitors.

Since the individual decomposition reactions had not been studied previously, no comparison could be made for those results. However, all earlier workers had found the primary product distribution in propane pyrolysis to be approximately equal amounts of propylene, hydrogen, methane, and ethylene; this study confirms those results at higher temperatures.

A series of runs with a feed of propylene diluted with nitrogen was made to study the product distribution of propylene pyrolysis for use in the analysis of the mixed feed (propane plus propylene) runs. The primary products of decomposition are methane, hydrogen, and methylacetylene, with smaller quantities of acetylene, ethylene, 1-butene, and 1, 3-butadiene. These results are basically in agreement with those of previous workers.

TABLE 1. EXPERIMENTAL VALUES OF PRE-EXPONENTIAL FACTORS AND ACTIVATION ENERGIES IN PROPANE PYROLYSIS

	A , sec. ⁻¹	E , kcal./g.-mole
Decomposition of propane	2.40×10^{11}	52.1
Formation of methane	1.52×10^{11}	52.5
Formation of propylene	9.26×10^{10}	51.7

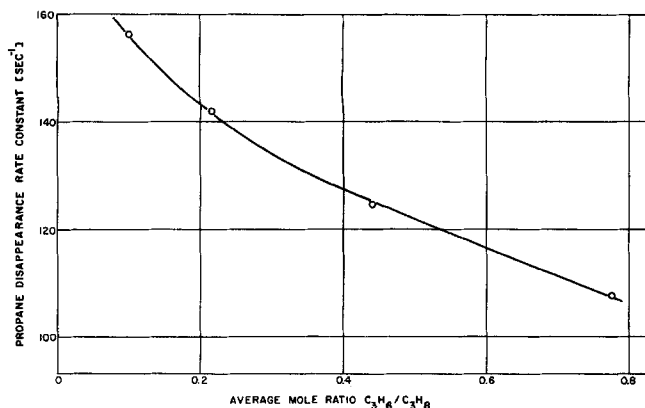
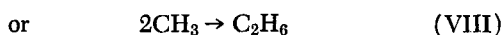
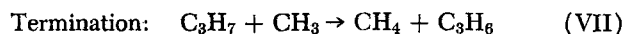
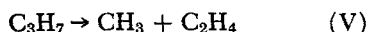
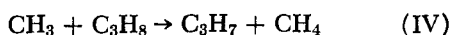
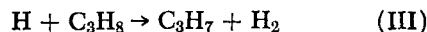
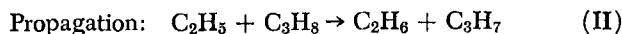
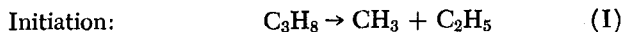


Fig. 8. The effect of propylene on propane decomposition rate constants; $T_{\max} = 1,800^{\circ}\text{F}$.

Mechanism

Much work has been done on possible mechanisms for the pyrolysis of propane and hydrocarbons in general. Indeed, so many problems and inconsistencies remain that present-day chemists are still in conflict over the true mechanisms involved. All of the experimental work has been done at moderately low temperatures (500° to 600°C .), to facilitate observation of the initial stages of reaction.

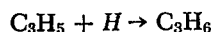
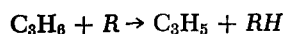
Rice and Herzfeld (19) proposed the currently accepted mechanisms for hydrocarbon pyrolysis, which is essentially a chain reaction mechanism consisting of chain initiation, chain propagation, and chain termination steps. However, because of its complex mechanisms, the decomposition of propane has not been studied extensively. It is only very recently (1962) that Laidler, Sagert, and Wojciechowski (8) have formulated the free radical steps as follows:



Their experimental work shows that the overall reaction is first order at high pressures and low temperatures and 1.5 order at low pressures and high temperatures. The most recent mechanism studies predict orders of reaction between 1.0 and 1.5, and the older and more empirical work seems to agree in general.

When free radical inhibitors such as nitric oxide and propylene are added to the reacting hydrocarbon, the rate of reaction diminishes to some finite, nonzero level. Many theories were proposed to explain this behavior and the inhibition was found to be a free radical mechanism also.

For the inhibition of hydrocarbon decomposition by propylene, in general, Laidler and Wojciechowski (9) propose that if R is any of the free radicals of the hydrocarbon pyrolysis, the inhibition is represented by



The final experimental phase of this study consisted of feeding propane with small amounts of propylene and diluted with nitrogen. A series of runs was made at con-

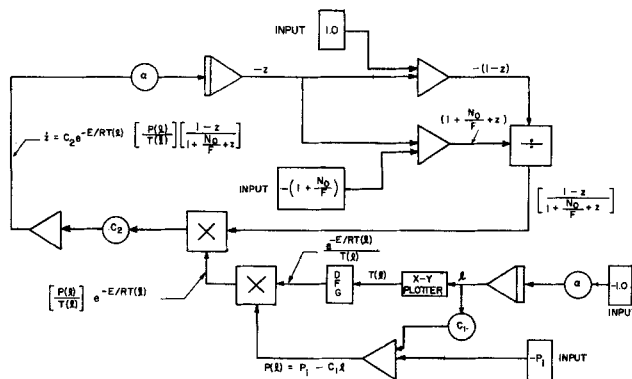


Fig. 9. Analog computer flow diagram.

stant total flow rate, temperature profile, and mole fraction propane, with varying amounts of propylene in the feed. The purpose of these runs was to note the effect of propylene, if any, on the pyrolysis of propane.

While these runs were not designed to demonstrate the validity of mechanism hypotheses, they do point out quite clearly the extent to which propylene does inhibit propane pyrolysis. Figure 8 shows that the rate constant for propane decomposition falls off very rapidly as the average ratio of propylene-to-propane in the reactor is increased.

TEST OF THE KINETIC MODEL

When the experimental phase of this work was completed, the main results (the kinetic parameters for propane decomposition) were programmed on an analog computer. The decomposition of propane was shown to follow the equation

$$\frac{F}{s} \left[\frac{1 + (N_0/F) + z}{1 - z} \right]^n dz = \frac{A}{R^n} e^{-E/RT(l)} \left[\frac{P(l)}{T(l)} \right]^n dl$$

or, for a first-order reaction

$$\frac{dz}{dl} = \frac{sA}{FR} e^{-E/RT(l)} \left[\frac{P(l)}{T(l)} \right] \left[\frac{1 - z}{1 + (N_0/F) + z} \right] \quad (8)$$

Equation (8) readily lends itself to solution on an analog computer, and a flow diagram for one solution is shown in Figure 9.

The general input to the computer consists of the overall kinetic constants and the reactor cross section and

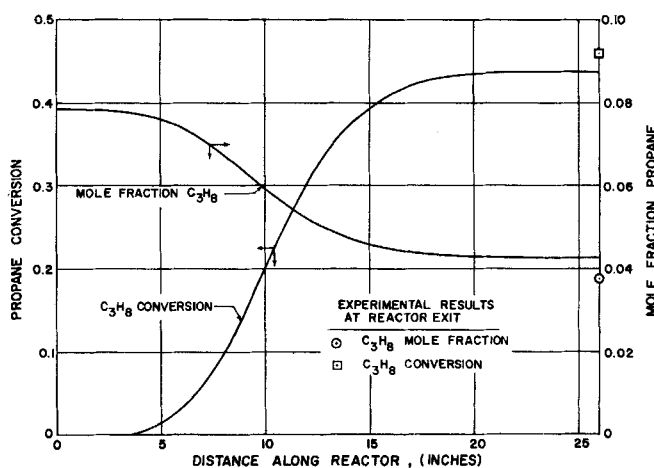


Fig. 10. Calculated propane conversion and mole fraction profiles; analog computer results, run 47.

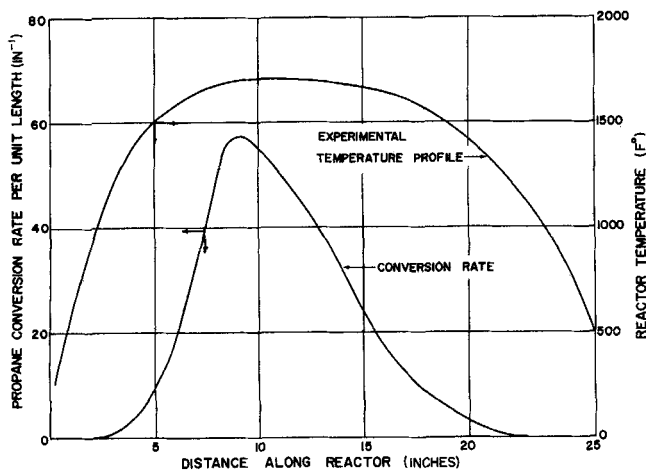


Fig. 11. Temperature and calculated propane conversion rate profiles; analog computer results, run 47.

length; in addition, for each run, the temperature and pressure profiles plus the inlet gas feed rates must be supplied.

The computer output consists of profiles along the length of the reactor of any of the parameters of the reaction. Among these are the reaction rate, conversion rate, percentage conversion, product distribution, and, indirectly, the rate of change of the reaction rate. At the reactor exit, the percentage conversion and the mole fraction of propane can be checked against the experimental data points.

The results for one set of experimental conditions (run 47) are shown in Figures 10 and 11. Figure 10 shows profiles of the percentage conversion and mole fraction of propane. The experimental values of these parameters at the reactor exit are plotted for comparison. In Figure 11, the propane conversion rate throughout the reactor is plotted together with the experimental temperature profile.

Programming the experimental results on the analog computer is valuable for several reasons. It can serve as a check on any of the individual data points. It also serves to show the progress of the reaction in the reactor; this information is often useful and of interest. For example, it was used above to show that longitudinal diffusion effects in this study were negligible. Finally, the program can be used to extrapolate easily beyond the present experimental conditions of temperature, pressure, reactor dimensions, etc. With further study, it might be possible to introduce mixed hydrocarbon feeds and simulate nonisothermal industrial cracking operation.

CONCLUSIONS

In this study a method of treating nonisothermal kinetic data in a complex reaction system was developed. The technique required extensive numerical calculation, but well within the capabilities of a digital computer. Nonisothermal conditions prevailed because the reactions involved were too fast to neglect the heating up and cooling down times. Such a method is applicable, in general, to many kinds of complicated, nonisothermal, nonisobaric experiments. In analyzing the data, several methods were developed for finding the best solution in a set of functional relationships between the variables.

Pyrolysis of propane was found to yield as primary products ethylene, methane, propylene, and hydrogen. All reactions were found experimentally to be first-order and the rate constants were temperature dependent as follows: for propane decomposition, $k = 2.40 \times 10^{11} \exp(-52.1/RT)$; for propylene and hydrogen formation, $k_1 = 9.26 \times$

$10^{10} \exp(-51.7/RT)$; for ethylene and methane formation, $k_2 = 1.52 \times 10^{11} \exp(-52.5/RT)$. These rate constants are expressed in units of sec^{-1} , temperatures in $^{\circ}\text{K}$., and R in $\text{kcal./g.-mole } (^{\circ}\text{K.})$.

The experimental results were used to design a kinetic model for the pyrolysis of propane. This model was used with an analog computer to check results of any individual experiment and to predict product distribution and conversions beyond the experimental range of this study.

NOTATION

- A = pre-exponential factor, $(\text{cc.})^{n-1}/(\text{g.-mole}^{n-1})$ (sec.) where n is the order of reaction
- C = concentration, g.-moles/cc.
- D = diffusion coefficient, sq.cm./sec.
- E = activation energy, kcal./g.-mole
- F = hydrocarbon feed rate, g.-moles/sec.
- k = rate constant (same units as A)
- $k_{\max}$ = rate constant at maximum temperature (same units as A)
- L = total reactor length, cm.
- l = reactor length, cm.
- m = flow rate of any component, g.-moles/sec.
- N = number of experimental runs
- N_o = feed rate of diluent, g.-moles/sec.
- n = order of reaction
- P = pressure, mm. Hg
- R = gas constant, $(\text{cc.}) (\text{mm. Hg})/\text{g.-mole } (^{\circ}\text{K.})$ or $\text{kcal./g.-mole } (^{\circ}\text{K.})$
- s = reactor cross-sectional area, sq.cm.
- T = temperature, $^{\circ}\text{K}$.
- $T_{\max}$ = maximum temperature, $^{\circ}\text{K}$.
- u_i = linear velocity, cm./sec.
- u_i = empirical constant
- V = reactor volume, cc.
- v_i = empirical constant
- x = mole fraction
- $\bar{x}$ = average mole fraction
- z = fractional conversion
- z_e = reactor exit fractional conversion
- Δ = deviation
- ϕ, ψ = arbitrary functions

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Manuscript received October 25, 1965; revision received July 14, 1966; paper accepted July 14, 1961. Paper presented at A.I.Ch.E. Minneapolis meeting.

Isobaric Integral Heats of Vaporization for Methane-Ethylene System

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An isobaric calorimeter has been built for measuring the integral heat of vaporization at high pressures and low temperatures simultaneously with vapor-liquid equilibria data. The methane-ethylene system was studied at 20 and 40 atm., with data obtained on three mixtures and the two pure components. The experimental results are compared with three different calculation methods.

The industrial and theoretical importance of the heats of vaporization of mixtures is well established. The most useful form of these data is the isobaric integral heat of vaporization. Dana (2) built the first calorimeter for determining these enthalpy differences experimentally at atmospheric pressure and cryogenic temperatures.

Schroeder (16, 20) modified the Dana calorimeter to operate above room temperature for his investigation of methanol-benzene mixtures. Tallmadge (18 to 20) improved Schroeder's apparatus by adding a heater to compensate for heat lost to the surroundings. By calibrating this heater, he was able to obtain reproducible results on acetone-chloroform, acetone-benzene, and benzene-methanol mixtures. Schnelle (14, 15) rebuilt the Tallmadge apparatus by utilizing ground-glass joints throughout. He also added a hypodermic probe to sample the acetone-

chloroform mixtures without opening the calorimeter. Recently, Kumar (7) modified the Schnelle apparatus by adding a bubble cap above the heater for improved vapor-liquid contact of benzene-chloroform mixtures. More thermowells and sampling probes were also added.

Concurrent with the work of Schroeder and Tallmadge, Plewes et al. (10 to 12) were working on their own version of the Dana calorimeter to operate under vacuum. The calorimeter heater was encapsulated to study corrosive mixtures. Data were obtained on water binaries of methanol, ethanol, *n*-propanol, acetone, and formic acid.

Stein and Martin (17) made a glass, adiabatic flow, Dana calorimeter with a unique modification to eliminate the heat-leak problem. Instead of immersing the vacuum-jacketed bulb in the bubble point mixture as was done by the other investigators, they placed it in a large volume of the dew point mixture, which underwent vaporization simultaneously with the liquid in the bulb. With both

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