

Kinetic Data from Nonisothermal Experiments: Thermal Decomposition of Ethane, Ethylene, and Acetylene

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A rigorous method was developed to account for nonuniform temperature distributions in the analysis of kinetic data. The rate constants cannot be determined directly since they are functions of temperature, so equations were derived and solutions developed for the substantially temperature independent kinetic parameters, activation energy, and pre-exponential factor. A digital computer was used to evaluate numerically various integrals involved in the solution of the equations. The method developed here will be useful in all laboratory kinetic studies where limitations of heat transfer do not permit an isothermal experiment and in the analysis of kinetic data obtained from commercial or pilot plant units where the temperature distribution is nearly always nonuniform.

Kinetic studies were made of the thermal decompositions of ethane, ethylene, and acetylene, all of which are high temperature fast reactions. The experimental conditions covered highly nonuniform temperature distributions with peaks from 730° to 1,330°C., a total pressure of 1 atm., varying amounts of nitrogen dilution, and residence times in the millisecond range.

When a kinetic study is undertaken, a highly desirable experimental condition is constant temperature throughout the reaction vessel. The processing of the data to obtain the kinetic rate constants is then a relatively simple procedure. Many kinetic experiments result in nonuniform temperature distributions, and the usual way to deal with this problem has been to assume some mean constant temperature for an estimated fraction of the reactor volume. These approximations lead to errors in the evaluation of the rate constants which are quite serious when the temperature distributions are highly nonuniform. These nonuniform temperature distributions result from laboratory experiments, where the heat transfer rate is not great enough to provide the flux necessary to maintain constant temperatures, as in the case of fast reactions at high temperatures or with considerable heat effects. Non-uniform temperature distributions are almost always encountered when data are obtained from plant-scale reactors.

A method is developed here for rigorously analyzing the kinetic data obtained from nonisothermal experiments for the order of reaction and the kinetic rate parameters, activation energy, and pre-exponential factor. The literature concerning kinetics in nonisothermal fields is almost exclusively concerned with the reactor design problem based on known kinetics. In a paper by Lee and Oliver (16) a

method was developed for measuring the order of reaction in a nonisothermal field. They also proposed a way of estimating reaction rates and determining the kinetic parameters, but their method was not rigorous as it required the matching of sections of the temperature profiles at different temperature levels and the averaging of the temperature around the peak of the distribution curve where the majority of the reaction occurred. Also, their method was restricted to differential rate measurements.

The reaction studied in this work was the homogeneous thermal decomposition of ethane to acetylene which proceeded by a series of consecutive steps from ethane to ethylene to acetylene and finally to carbon. Equilibrium considerations required temperatures of 900°C. and greater before appreciable amounts of acetylene were produced. The rates of reaction at these temperatures were very great so that the residence time has to be in the millisecond range to prevent complete degradation to carbon and hydrogen.

There is very little kinetic data for these reactions in the temperature range of this study. Most of it is for the thermal decomposition of ethane correlated by a first order disappearance model and is found in the work of Kinney and Crowley (14), plant-scale data by Schutt (24), Storch and Golden (33), Hague and Wheeler (10) Hepp et al. (12), and Eastwood and Potas (7). Some shock-tube work for ethane and ethylene decomposi-

tion was reported by Miller (18), Skinner and others (26, 27), and Greene (9) and for acetylene decomposition by Skinner (28) and Aten and Greene (3). Steacie (32) and Brooks et al. (6) contain reviews of a large amount of this literature data. There is some literature concerning commercial- and pilot-plant processes for the high-temperature pyrolysis of ethane and other saturated hydrocarbons to ethylene and acetylene. The significant authors here are Farnsworth et al. (8), Bogart et al. (5), Sittig (25), Bixler and Coberly (4), Hasche (11), Akin et al. (1), and Ried and Linden (21). These papers do not contain any kinetic data but only process descriptions and product distributions.

MATHEMATICAL ANALYSIS

Derivation of Kinetic Equations

The problem of nonuniform temperature distributions usually occurs in the case of fast reactions so that a steady state flow reactor experiment is convenient. The kinetic equations are written and integrated for a certain type of reaction and under certain assumptions, which represent the actual experimental conditions used in the experimental work. Later the equations are discussed for the more general case, and it is shown that the form of equations and the method of solution remain essentially the same.

A reaction of the general form



is selected and it is assumed to be n th order, homogeneous, and irreversible.

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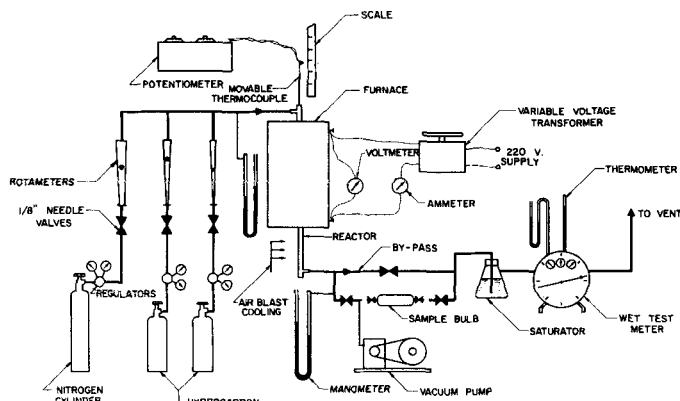


Fig. 1. Diagram of apparatus.

The equations are developed for a flow reactor with plug flow, no radial temperature distribution, and constant pressure. There is a considerable variation in longitudinal temperature distribution. The rate expression is then

$$\frac{dN_A}{dV} = -kC_A^n \quad (1)$$

dN_A can be replaced by $-Fdx$ and dV can be replaced by Sdl . The concentration of A is the molar flow rate of A divided by the total volumetric rate:

$$C_A = \frac{F(1-x)}{[F(1+x) + N_D]} \left(\frac{P}{RT} \right) \quad (2)$$

The rate constant is expressed as a function of temperature by the Arrhenius equation:

$$k = Ae^{-E/RT} \quad (3)$$

Substituting in Equation (1) one arrives at Equation (4):

$$\frac{Fdx}{Sdl} = Ae^{-E/RT} \left[\frac{F(1-x)P}{[F(1+x) + N_D]RT} \right]^n \quad (4)$$

Rearranging Equation (4) one obtains Equation (5):

$$\frac{F}{AS} \left[\frac{R[F(1+x) + N_D]}{PF(1-x)} \right]^n dx = \frac{e^{-E/RT}}{T^n} dl \quad (5)$$

Integrating Equation (5) along the length of the reactor with the temperature expressed as a function of length by $T(l)$ one arrives at

$$\left(\frac{R}{P} \right)^n \frac{F}{AS} \int_{x_i}^{x_o} \left[\frac{F(1+x) + N_D}{F(1-x)} \right]^n dx = \int_0^L \frac{e^{-E/RT(l)}}{T(l)^n} dl \quad (6)$$

The experimental data from a nonisothermal experiment will be values of x_i , x_o , F , N_D , P , and $T(l)$. $T(l)$ will

not usually be known in analytical form but only in tabular form, so that the right-hand integral in Equation (6) must be evaluated numerically. L and S are known geometry factors of the reactor. The problem now is to solve for three unknowns, n , A , and E in Equation (6).

Solution

A is explicit in Equation (6) but n and E are implicit, so in order to simplify the solution one of the implicit unknowns n will be determined by a separate set of experiments. This is done with a set of experiments in which the temperature distribution is held constant and the concentration varied by inert dilution. Quite large amounts of inert diluent are used so that the temperature profile is not altered when the concentration of the reactant is changed. The conversion is kept very small so that $1 \pm x$ is approximately equal to 1. Equation (6) can be rewritten for these special conditions as

$$\left(\frac{R}{P} \right)^n \frac{F}{AS} \int_{x_i}^{x_o} \left(\frac{F + N_D}{F} \right)^n dx = \int_0^L \frac{e^{-E/RT(l)}}{T(l)^n} dl \quad (7)$$

which, on integration of the left-hand side and rearranging, leads to

$$F(x_o - x_i) = \left(\frac{F}{F + N_D} \right)^n \left[AS \left(\frac{P}{R} \right)^n \int_0^L \frac{e^{-E/RT(l)}}{T(l)^n} dl \right] \quad (8)$$

$F(x_o - x_i)$ is the differential rate of reactions ΔN_A , and $F/(F + N_D)$ is the mole fraction X_A . If the temperature distribution $T(l)$ is held constant for a set of runs, then the terms inside the square brackets in Equation (8) remains a constant. Substituting into Equation (8) one gets

$$\Delta N_A = X_A^n (\text{constant}) \quad (9)$$

and taking logarithms one obtains

$$\log \Delta N_A = n \log X_A + \log (\text{constant}) \quad (10)$$

Equation (10) shows that $\log \Delta N_A$ plotted against $\log X_A$ will result in a straight line with a slope of n , the order of reaction. Lee and Oliver (16) also arrived at this result.

Equation (6) now contains only two unknowns, A and E . Equation (6) is rearranged to give Equation (11):

$$A = \frac{\left(\frac{R}{P} \right)^n \frac{F}{S} \int_{x_i}^{x_o} \left[\frac{F(1+x) + N_D}{F(1-x)} \right]^n dx}{\int_0^L \frac{e^{-E/RT(l)}}{T(l)^n} dl} \quad (11)$$

Since the lower integral in Equation (11) is implicit in the unknown E and cannot be integrated analytically as the function $T(l)$ is only known in tabular form, any method of solution will have to begin with an assumption of values of E . Clearly the solution for A and E from Equation (11) cannot be obtained from one experimental run, since for every E value assumed an A value can be calculated. Represent this relation between the assumed E values and the corresponding calculated A values in the functional form

$$A = f_1(E) \quad (12)$$

Now if the experimental data from a second run with different experimental conditions are substituted into Equation (11), a new set of A values corresponding to each assumed E value is obtained which can be expressed as

$$A = f_2(E) \quad (13)$$

Equations (12) and (13) can now be solved simultaneously for A and E . A was found to be almost a linear function of e^E so that linear interpolation was used in solving Equations (12) and (13). Considerable computation effort was required owing to the many numerical integrations, and these were readily handled by a digital computer.

This method of calculation of E and A is quite sensitive to experimental errors, since only two data points are used for each solution. It is pointed out that the experimental error is reduced considerably by the measurement and proper consideration of the temperature distributions in the reactor. However a method of smoothing the E and A values computed from each pair of experimental runs is needed. It is proposed that the conventional logarithm of the rate constant vs. reciprocal temperature plot be used. The k values are calculated from the Arrhenius equation with the E and A values obtained from each

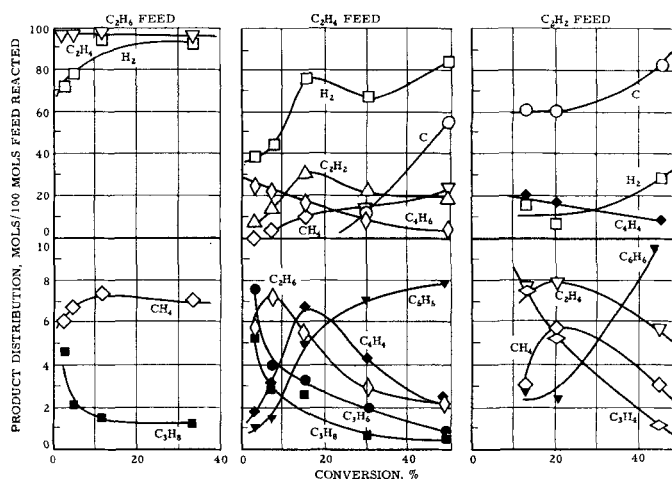
pair of runs and the peak temperatures of the two measured temperature profiles. The use of the peak temperature does not involve any approximation, since the k values are then plotted against the reciprocal of this temperature. The best line is drawn through the k vs. $1/T$ points and the smoothed values of E and A determined. It is important to note that the usual $\ln k$ vs. $1/T$ plot has been obtained without the requirement of an isothermal experiment. A sample calculation is presented in Table I.

The assumptions of constant pressure, negligible radial temperature distribution, and irreversible reaction were made in the derivation and fulfilled in the experiments. The equations and solutions resulting when these assumptions are not made are now discussed. If there is a considerable pressure drop in the reactor, then the pressure could be expressed as a function $P(l)$ of length (a linear function is a good approximation) which can be included in the right-hand integrand of Equation (6), and the solution will proceed as before. If there are significant radial temperature variations, then the temperature at each longitudinal position must be adjusted, and the solution will again proceed as before. If the stoichiometry of the reaction is different or if there are simultaneous reactions, the left-hand integrand in Equation (6) will have a different algebraic form which again will not alter the method of solution. A reversible reaction causes a little more complication, since the C_A term in Equation (1) is replaced by a $(C_A - C_R C_c/K_c)$ term. This leads to the inclusion of the temperature dependent K_c in the left-hand integrand of Equation (6). The solution now requires a number of iterations, since a relation between T and x must be assumed to evaluate the left-hand integral of Equation (6). The generalizations discussed here did not change the essential character of the equations or their method of solution and the additional calculations could be handled by changes in the digital computer program.

EQUIPMENT AND PROCEDURE

Equipment

A diagram of the apparatus is shown in Figure 1. The feed gases were obtained in high pressure cylinders. The ethane was 97.0 mole % purity (2% ethylene, 1% propylene), the ethylene and acetylene were 99.5 mole % purity, and the nitrogen diluent 99.996 mole % purity (8 p.p.m. oxygen). The flow rates were measured with glass rotameters with sapphire, glass, or stainless steel floats and controlled with $\frac{1}{8}$ -in. needle valves. The piping was $\frac{1}{4}$ - or $\frac{3}{8}$ -in. copper tubing with brass compression fittings. The gas passed into a vertical



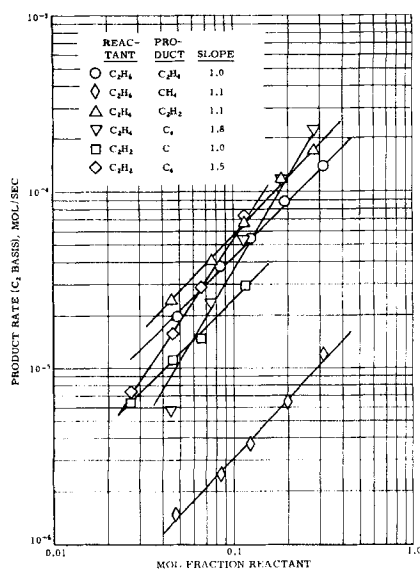


Fig. 4. Orders of reaction.

at a small pressure drop. Experiments were conducted in both of these reactors for the same reaction in the temperature range 1,000° to 1,100°K., and coincident results were obtained. The third reactor was the same design as the second except for an increased surface to volume ratio. It was concluded that in all three reactors the center thermocouple reads the gas temperature with a probable error of 10°C. and that the radial gradients were negligible.

Procedure

About 5 or 6 hr. were necessary to raise the furnace up to temperature as the heating rate was limited to 5°C./min. to prevent thermal shock damage to the alumina muffle. The furnace temperature was controlled manually with a variable voltage transformer connected to the 220-v. supply. The rates of the feed gases were observed with the rotameters and controlled manually with needle valves. The flow conditions were laminar as the Reynolds numbers were less than 500. The exit gas stream was diverted through a bypass line and an evacuated sample bulb inserted in the exit line. When the apparatus had reached steady state, a gas sample was obtained by closing the bypass and allowing the gas stream to flow into the sample bulb. The temperature distribution was then measured as quickly as possible with the movable thermocouples. The reactor inlet and exit manometers were read, and the volume of gas passing out through the wet test meter was recorded for a measured time. The temperature and pressure in the wet test meter were noted, and the atmospheric pressure was read and recorded. The experimental conditions were then changed to the next set of desired values, and the apparatus was left for ½ to 1½ hr. to attain steady state again. Air was passed through the hot reactor to burn off any carbon deposition. The chemical analysis of the feed gases and the reactor outlet samples were performed with a mass spectrometer.

The main steps in the over-all reaction were the decomposition of ethane to ethylene, ethylene to acetylene, and acetylene to carbon. Experiments conducted with all of these reactions occurring together would be very difficult to interpret, so separate kinetic studies were made of the thermal decomposition of ethane, ethylene, and acetylene.

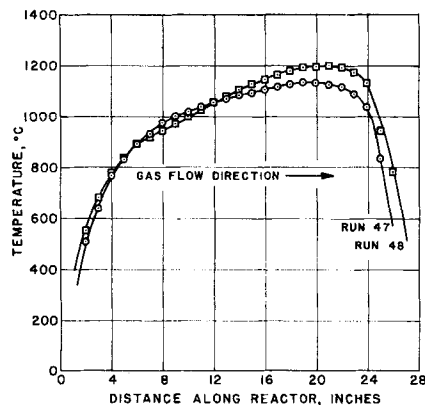


Fig. 5. Temperature profiles.

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EXPERIMENTAL RESULTS* AND DISCUSSION

Product Distributions

The product distributions were determined at various conversions at approximately the same temperature. The purpose of these experiments was to determine the major molecular products and to try and distinguish primary from secondary reactions. The data for ethane, ethylene, and acetylene decomposition are contained in Figure 3. Throughout this work only the major products were considered in the interest of having a tractable kinetic correlation model. The major primary products in ethane decomposition were hydrogen, ethylene, and methane, so that a reaction scheme of two parallel reactions to ethylene and methane was used. In the case of ethylene decomposition hydrogen, 1-3 butadiene, and acetylene were considered to be the major primary products. The reaction model adopted was parallel reaction to two products, the first acetylene and the second C, which was mainly butadiene, but also included the minor products on a C, basis. The data on acetylene decomposition showed that hydrogen, carbon, and vinylacetylene were the major primary products. Again parallel reaction to two products, carbon and C, which was mainly vinylacetylene, was adopted. Minor products were included on a C, basis. Hydrogen was evolved of course in the three decompositions studied, with the quantity being dictated by the stoichiometry of the hydrocarbon reactions.

Order of Reaction

The orders of the reactions in the

* A complete tabulation of original data and results and further details are available in the Ph.D. thesis of Gordon D. Towell, University of Michigan, Ann Arbor, Michigan (1960).

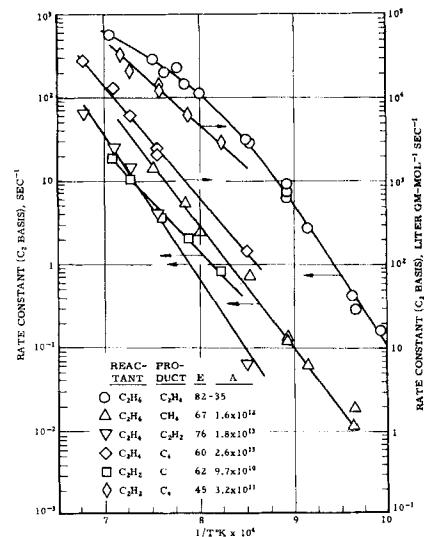


Fig. 6. Rate constants.

schemes proposed in the previous section were determined with a series of experiments in which the concentration of the reacting component was varied by nitrogen dilution with the temperature distribution held constant. Differential conversions were obtained, and the differential rate was plotted against the mole fraction of reactant in the form indicated by Equation (10). The slope of this plot on log-log coordinates is the order of reaction. The results are presented in Figure 4. The temperature distributions were identical for the points along any line on Figure 4, but the temperatures were not the same from line to line. The measured orders are presented on Figure 4, and these are interpreted as follows: first-order formation of methane and ethylene from ethane, acetylene from ethylene, carbon from acetylene, and second-order formation of C, from ethylene and acetylene. The major reactions and their orders have been established, and one can now proceed to the analysis for the rate constants for these reactions.

Rate Constants

The rate constant results were obtained from a set of experiments at spaced temperature intervals. The flow rates were increased at the higher temperatures in order to keep the conversion down to the point where the primary reactions would predominate. The experiments were planned so that the effect of the reverse reactions, hydrogenation of ethylene and acetylene, were negligible. This was achieved in part by nitrogen dilution. The temperature distributions were quite peaked as shown by Figure 5, and the shape and position of the peak temperatures was found to be dependent on the flow rate and temperature level. The data were analyzed for the kinetic rate parameters E and A by

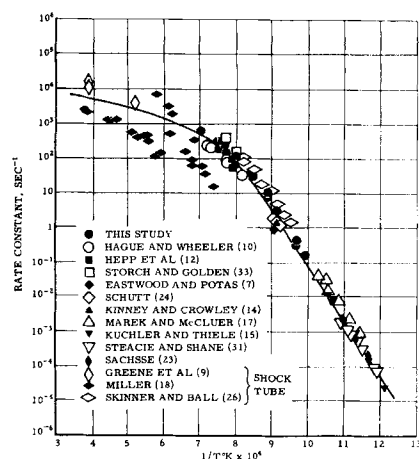


Fig. 7. First-order rate constants for ethane disappearance, a comparison with literature data.

solution of Equation (11) for pairs of experiments following the method developed in this paper. Representative data and calculations are presented in Table 1. The E and A values were used to calculate rate constants, and these were then plotted against reciprocal temperature as shown in Figure 6. These rate constants were all computed on a mole of C_2 basis. Identical results were obtained in reactors with different surface-to-volume ratios which indicated that the reactions were homogeneous which was in agreement with other work (20, 31, 34) at low temperatures. Reasonable

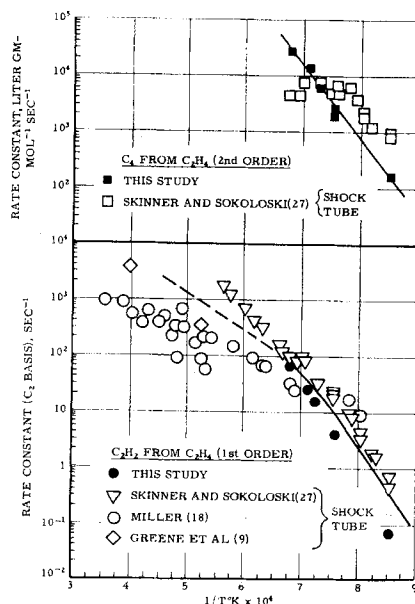


Fig. 8. Ethylene decomposition, a comparison with literature data.

straight lines could be drawn through all of the data on Figure 6 except for the ethylene formation from ethane. This is discussed further in the section on mechanisms.

The results of this work for first-order decomposition of ethane are compared with the data of a number of other workers in Figure 7. Good agreement was noted, and a best line was put through all of the available

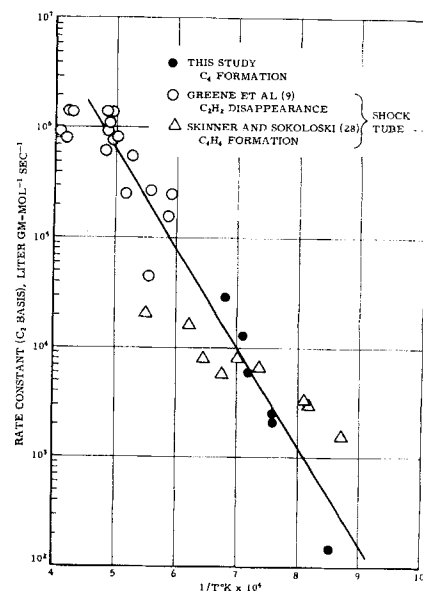
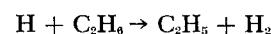
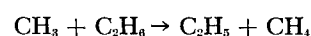
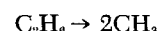


Fig. 9. Acetylene decomposition, a comparison with literature data.

data. There is very much less literature data for ethylene decomposition. A second-order polymerization with an activation energy of 40 kcal./g.-mole was reported (32) at low temperatures. Molera and Stubbs (19) reported 75 kcal./g.-mole for the decomposition and 35 kcal./g.-mole for the polymerization all at 700°C. The only literature data in the temperature range of this work are shock-tube data, and these are compared with the results of this work in Figure 8. The only literature acetylene data in the temperature range of this work are again shock-tube data, and these are compared with the results of this work in Figure 9. Some low-temperature data (22) was also reported which is correlated by a second-order model with an activation energy of 30 to 40 kcal./g.-mole.

Mechanism

The mechanism of the thermal decomposition of ethane at temperatures up to 800°C. has been shown by a number of workers to be a free radical chain process. These mechanisms were first proposed by Rice and Herzfeld (22), and a recent paper by Snow et al. (29) considered the mechanisms in detail and used them to correlate various other workers' data. A simplified picture of this mechanism follows:



It is reasonable to suppose that this mechanism will also occur at the higher temperatures of this work.

TABLE 1. REPRESENTATIVE DATA:

CALCULATION MODEL IS FIRST-ORDER FORMATION OF ACETYLENE FROM ETHYLENE

		Experimental Measurements				
	x_i	x_o	F g. mole/sec.	N_D	P , atm.	T (1), °C.
Run no. 47	0	0.181	5.34×10^{-4}	2.39×10^{-3}	1.009	Fig. 5
Run no. 48	0	0.249	8.53×10^{-4}	3.63×10^{-4}	1.020	Fig. 5
		Calculations				
Assumed E values, kcal./g.-mole			55.55	61.11	66.67	72.20
ln A values from Equation (11)	Run no. 47		31.215	32.248	35.278	37.306
	Run no. 48		31.315	33.261	35.203	37.141
By Linear interpolation ln $A = 33.548$		$E = 61.9$ kcal./g.-mole $A = 3.70 \times 10^{14}$ hr. ⁻¹				

Selecting the peak temperature from Figure 5, k is calculated from Equation (3).

	T_{max} , °C.	$1/T$ °K.	k sec. ⁻¹
Run 47	1132	7.12×10^4	24.2
Run 48	1197	6.80×10^4	65.2

These k values can be found on Figure 6.

Certain materials, particularly nitric oxide and propylene, react very readily with free radicals and have been used to study free radical reactions (30). The results of some experiments in which propylene was added to the ethane feed are presented in Figure 10. The ethylene formation rate was greatly reduced by small amounts of propylene which indicates a free radical chain mechanism. The methane rate was not affected, so that the ratio of the ethylene to the methane rate is an estimate of the chain length. The chain length was reduced from 24 to 1.5 which is in agreement with the results of Staveley (30) and Hobbs and Hinshelwood (13) who reported chain lengths reduced from 21 to 4 with nitric oxide inhibition. The ethane feed in this work contained 1% propylene impurity, so that the rate constant data for ethylene formation in Figure 6 was corrected to zero propylene impurity by the use of the results in Figure 10. Ethylene, acetylene, hydrogen, and butadiene were checked experimentally for inhibition effects, and only butadiene was found to be effective. The curvature of the ethylene formation rate constant data can possibly be explained by decreasing chain length due to the inhibiting effects of the secondary product butadiene.

Experiments were carried out with propylene added to the ethylene feed, and very little inhibiting effect was found which indicates no chain reaction. A possible free radical mechanism could begin with the formation of C_2H_3 and H radicals which then attack the ethylene molecule. Butadiene could result from combination of two C_2H_3 radicals and acetylene by H removal from C_2H_3 . A plausible radical scheme can be constructed which gives the correct order of reaction and approximately the right activation energies, but there is no direct evidence to support the scheme. A possible molecular mechanism would be initial dimerization of ethylene to butene and subsequent decomposition to butadiene, acetylene, ethylene, and hydrogen. However no butene was detected in the experiments. The acetylene decomposition mechanism probably contains a direct dimerization, since vinylacetylene was a primary product. The carbon formation probably results from direct hydrogen removal from the acetylene.

CONCLUSIONS

The method developed for analyzing kinetic data from nonisothermal experiments gave good results, and it is concluded that the method will be useful in obtaining rate constants from plant scale and many laboratory ki-

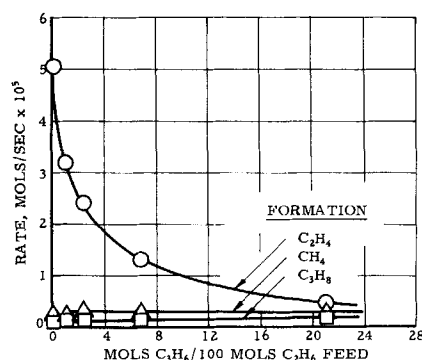


Fig. 10. Inhibition of ethane decomposition with propylene.

netic studies where nonuniform temperature distributions occur.

The ethane decomposition was correlated by two parallel first-order reactions to ethylene and methane. The ethylene formation was found to be strongly inhibited by propylene and the secondary product 1-3 butadiene. The ethylene decomposition was correlated by a first-order formation of acetylene and a second-order reaction to 1-3 butadiene. The acetylene decomposed by a first-order reaction to carbon and a second-order reaction to vinylacetylene.

NOTATION

A	= pre-exponential factor in Arrhenius equation (sec^{-1})*
C	= concentration (g.-mole/liter)
E	= activation energy in Arrhenius equation (kcal./g.-mole)
F	= feed rate of hydrocarbon (g.-mole/sec.)
K_e	= equilibrium constant, concentration units
k	= rate constant (sec^{-1})*
L	= total length of reactor (cm.)
l	= arbitrary length along reactor (cm.)
n	= order of reaction
N	= flow rate of any component (g.-mole/sec.)
N_D	= flow rate of inert diluent (g.-mole/sec.)
P	= pressure (atm.)
R	= gas constant
S	= cross sectional reactor flow area (sq. cm.)
T	= temperature ($^{\circ}\text{K.}$)
t	= time (sec.)
V	= reactor volume (liters)
$x_{i,0}$	= conversion inlet, outlet
X	= mole fraction

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Manuscript received December 29, 1960; revision received June 3, 1961; paper accepted June 12, 1961. Paper presented at A.I.Ch.E. New Orleans meeting.