A Computer Study of a Free-Radical Mechanism of Ethane Pyrolysis

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The pyrolysis of ethane (including the equilibrium behavior and the tendency to form secondary products) has been reproduced by calculations based on a reaction mechanism which includes the reverse of the chain propagating reactions as well as other hitherto neglected elementary reactions. Reverse reactions are important even at low conversion (1%); hence previous investigations of initial reaction rate have doubtful fundamental significance. Values of rate constants used in the calculations were taken mostly from the literature. Consideration was limited to reactions of methyl, ethyl, and hydrogen free radicals with ethane and its primary pyrolysis products. The results can be incorporated into reactor performance calculations to replace empirical reaction rate correlations and thus widen the range of conditions over which the calculations are reliable.

There is much evidence that the pyrolysis of hydrocarbons occurs in steps and that most of the elementary reactions involve free-radical intermediaries. The rate constants of these elementary reactions are fundamental constants in the sense that they have the same value even when the elementary reaction occurs in different systems, for example in the pyrolysis of ethane and of propane. A goal for the technology of pyrolysis of hydrocarbons is the development of the theory to permit making design and performance calculations of reactors based on experimentally determined free-radical reaction-rate constants. The present work represents a step toward that goal.

Means of calculating performance of pyrolysis reactors have been presented by Myers and Watson (*22*), Schutt (*33*), and Snow and Schutt, (*38*). The reaction rates were expressed by means of empirical correlations, and the other aspects of the calculations were based on firm theoretical concepts. In the present work the essential features of the mechanism of ethane pyrolysis have been established, and product distributions have been calculated from theoretically sound expressions. These results can be incorporated into reactor performance calculations to make such calculations valid over a wider range of conditions. The results are also of theoretical interest because they demonstrate certain important but hitherto not understood features of the mechanism of ethane pyrolysis. An understanding of the mechanism even more detailed than that given here is still needed to predict the formation of individual higher hydrocarbons and especially of carbon, which is important because it limits reactor performance.

To include in the study a number of hitherto neglected reactions which proved to be important, it was necessary to apply numerical techniques rather than to solve the equations explicitly. The use of a digital computer was essential for this work, and several computer techniques applicable to such kinetic studies were developed.

EXPERIMENTS ON ETHANE PYROLYSIS

A thorough review of studies of ethane pyrolysis up to 1955 is contained in Steacie's (*41*) monograph, which also reviews investigations of the free-radical reactions involved.

Early workers (*5, 9, 18, 24, 30*) found that the over-all decomposition is approximately of first order. By extrapolating product distributions to zero conversion Schneider and Frolich (*32*), Hinshelwood and co-workers (*3*), and Silcocks (*36*) showed that the primary products of the pyrolysis are hydrogen, ethylene, and methane. Secondary products are small amounts of acetylene, three- and four-carbon hydrocarbons, higher olefins, aromatic compounds, and carbon. Several investigators have recently determined relatively complete product distributions These studies are listed below:

Reference	Temperature, °K.	Pressure, atm.
36	863	0.7 to 1.2
2a	1023 to 1143	1.0
14	1089	1.0
11	1255	1.0
46	1373	0.04
25	998 to 1148	1.0

Hinshelwood and co-workers (*3*), Travers and Hawkes (*45*), and Silcocks (*36*) have studied the tendency of the pyrolysis to approach the equilibrium

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \qquad (1)$$

The equilibrium constant for this reaction has been calculated by Kilpatrick and co-workers (*13*), and it appears that the system does tend to approach the equilibrium state defined by this constant. However true equilibrium is never attained because of the occurrence of secondary reactions.

Dintses and Frost (*5, 6*) derived an empirical expression for the over-all rate as a function of reaction time. The complicated form of this expression suggests that the mechanism must be complex.

Investigations of the pyrolysis of pure samples of secondary products (*14, 20, 21, 31, 34, 37*) and of secondary reactions in ethane pyrolysis (*18, 48*) demonstrate that the primary products, ethylene, hydrogen, and methane, are relatively stable compared with the secondary products, which are three- and four-carbon hydrocarbons. The same conclusion may be reached on thermochemical grounds since hydrogen, ethylene, and methane have bond dissociation energies of over 100 kcal. according to Steacie (*41*), while butene splits into radicals with a dissociation energy of only 60 kcal.

MECHANISM OF ETHANE PYROLYSIS

A free-radical mechanism for ethane pyrolysis was first proposed by Rice and Herzfeld (*28*), who showed that the existence of a free-radical chain can

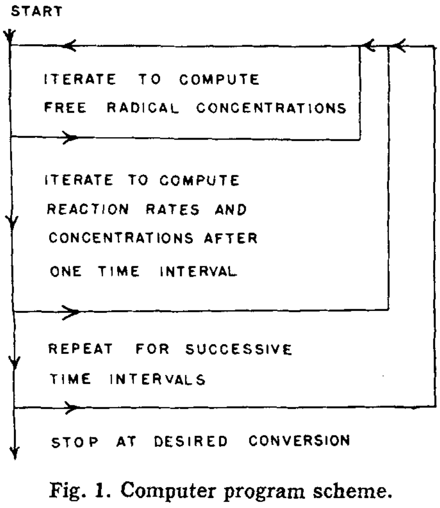

Fig. 1. Computer program scheme.

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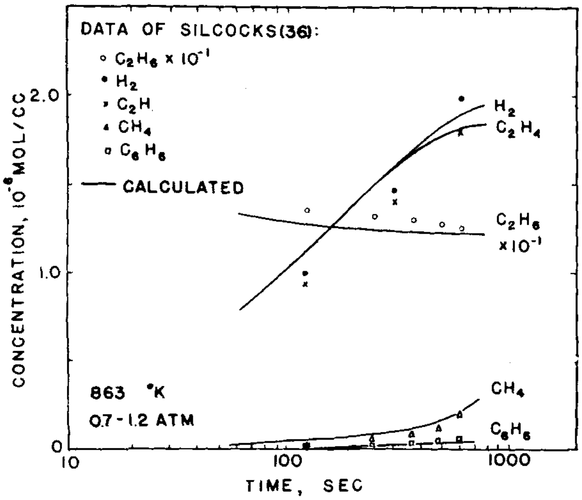

Fig. 2. Calculated and experimental products from ethane pyrolysis.

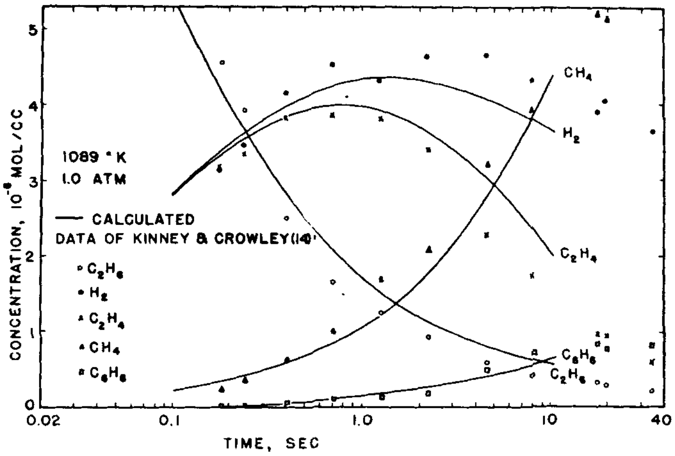

Fig. 3. Calculated and experimental products from ethane pyrolysis.

result in an over-all rate having a lower activation energy than the energy of scisson of ethane into radicals, and they thus succeeded in explaining a puzzling experimental fact. The best estimate of the carbon-carbon bond dissociation energy in ethane is 86 kcal., according to Steacie (*41*), and the activation energy for the scission reaction (2) cannot be less than this value,

$$C_2H_6 \rightleftharpoons 2\,CH_3 \qquad (2)$$

An Arrhenius plot of the reported values of the over-all rate constants for ethane pyrolysis is consistent with a value between 70 and 72 kcal. (*42*, *38*). Hence it is necessary to postulate the existence of such a chain mechanism or alternatively to assume the occurrence of some radical initiating reaction with a lower activation energy.

Free-radical mechanisms for ethane pyrolysis have also been proposed by Küchler and Thiele (*15*), Storch and Kassel (43), and Steacie (*41*). None of these mechanisms fit the experimental data quantitatively, although they explain certain trends in the data. The qualitative agreement of these mechanisms, together with certain other evidence, indicates that the true mechanism does involve free radicals and is complex. Other evidence that ethane pyrolysis involves free radicals is provided by experiments in which the pyrolysis is inhibited by nitric oxide and olefins (*37*, *39*, *45*). Rice and Dooley (*26*) detected methyl radicals in the pyrolysis of ethane by means of chemical detectors. Eltenton (*8*) detected both methyl and ethyl radicals, with a mass spectrometer. The ortho-para hydrogen conversion measurements of Patat and Sachsse (*30*, *31*) indicate that atomic hydrogen is involved.

Radicals other than ethyl, methyl, and hydrogen have not been directly detected in pyrolyzing ethane (*41*). Hinshelwood and co-workers (*3*) have proposed that the methylene radical may be an intermediary. Methylene radical has been detected from decomposing diazomethane (*26*, *27*) and from ketene (*23*) but not from pyrolyzing hydrocarbons (*26*). Pearson, Purcel, and Saigh (*23*) suggested that methylene radicals may form and may react too rapidly to be detected, but this is merely speculation. Although unsaturated radicals may play a role in ethane pyrolysis, it is not feasible to analyze a mechanism including their reactions since there are insufficient data concerning the pertinent reaction rates. The results of the present work indicate that for a first approximation they may be neglected.

Hinshelwood and co-workers (*40*, *44*) have shown that large amounts of nitric oxide do not produce as great an inhibitory effect as would be predicted on the basis of any reasonable free-radical mechanism. They (*44*) concluded that a direct molecular split of ethane by reaction (1) is involved in addition to a free-radical chain. But Rice and Varnerin (*29*) studied the products of isotope-exchange reactions in ethane pyrolysis and concluded that the molecular split does not occur. Steacie (*41*) has reviewed other conflicting evidence. The only safe conclusion to be drawn from this controversy is that the mechanism of inhibition by nitric oxide is not fully understood.

Silcocks (*36*) has proposed molecular reactions to account for the formation of secondary products in ethane pyrolysis and has cited experimental attempts to inhibit the formation of secondary products as evidence that the secondary reactions are essentially molecular. In view of the lack of understanding of the role of nitric oxide in the secondary reactions this evidence is questionable. Nor does his own kinetic analysis of the secondary reactions answer the question, since his results are based on the assumption that free radicals play only a minor role.

ANALYSIS OF A FREE-RADICAL MECHANISM OF ETHANE PYROLYSIS

This analysis was limited to reactions of ethyl, methyl, and hydrogen radicals and of ethane, ethylene, hydrogen, and methane. The reactions to be considered were selected in a systematic way by means of Steacie's (*41*) classification, which includes molecule scission, radical transfer, addition of radicals and molecules, and radical recombination.

Of the reactions included in the above categories those requiring three-body collisions, such as the recombination of hydrogen atoms or hydrogen and methyl radicals, were neglected. Scission of ethane to give hydrogen atoms was neglected, since the activation energy for this reaction is at least 98 kcal., while that of the competing reaction (2) is only 86 kcal. (*41*). The dissociation reactions of methane, ethylene, and hydrogen were neglected, since the bond dissociation energies for these compounds appear to be much higher than the dissociation energy for ethane, according to Steacie (*41*). The remaining reactions considered in the mechanism are

$$C_2H_6 \rightleftharpoons 2\,CH_3 \qquad (2)$$

$$CH_3 + C_2H_6 \rightleftharpoons CH_4 + C_2H_5 \qquad (3)$$

$$H_2 + CH_3 \rightleftharpoons H + CH_4 \qquad (4)$$

$$C_2H_5 \rightleftharpoons C_2H_4 + H \qquad (5)$$

$$H + C_2H_6 \rightleftharpoons H_2 + C_2H_5 \qquad (6)$$

$$H + C_2H_5 \rightarrow C_2H_6 \qquad (7)$$

$$CH_3 + C_2H_5 \rightarrow C_3H_8 \qquad (8)$$

$$\left.\begin{aligned} 2C_2H_5 &\rightarrow C_4H_{10} \\ &\rightarrow C_2H_4 + C_2H_6 \end{aligned}\right\} \qquad (9)$$

This mechanism is similar to that of Rice and Herzfeld (*28*) but includes additional important reactions, especially the reverse ones.

Two other reactions, (10) and (11), were included but later had to be eliminated to make calculated product distributions agree with experimental ones. This subject is discussed later.

$$CH_3 + C_2H_4 \rightarrow C_3H_7 \qquad (10)$$

$$C_2H_5 + C_2H_4 \rightarrow C_4H_9 \qquad (11)$$

The secondary products C_3H_8 and C_4H_{10} result from reactions (8) and (9). These substances actually react further

Table 1. Rate Constants as Functions of Temperature

$$k_i = A_i e^{-E_i/RT}$$

	Reaction	Rate constants from literature		Literature source of		Rate constants used in calculations	
		Frequency factor, A_i	Activation energy, E_i	Activation energy	Frequency factor	Frequency factor, A_i	Activation energy, E_i
2	$C_2H_6 \rightleftharpoons 2CH_3$	1×10^{17}	86,000	Bond strength(*41*)	Entropy calculation(*47*)	6.3×10^{16}	86,000
2′		7×10^{13}	0	Experiment(*10*)	Experiment(*10*)	7×10^{13}	0
3	$CH_3 + C_2H_6 \rightleftharpoons CH_4 + C_2H_5$	2×10^{11}	10,400	Experiment(*48*)	Experiment(*48*)	2.5×10^{11}	10,800
3′		1×10^{13}	13,000	Thermochemical(*41*)	Assumed	1×10^{11}	13,200
4	$CH_3 + H_2 \rightleftharpoons CH_4 + H$	2×10^{11}	9,200	Experiment(*47*)	Experiment(*16*)	1.9×10^{11}	9,500
4′		1×10^{9}	4,500	Experiment(*41*)	Experiment(*41*)	1.1×10^{9}	4,700
5	$C_2H_5 \rightleftharpoons C_2H_4 + H$	3×10^{14}	39,500	Experiment(*2*)	Entropy calculation(*47*)	5.3×10^{14}	40,800
5′		2×10^{13}	4,000	Experiment(*4*)	Experiment(*4, 19*)	5.4×10^{13}	5,400
6	$H + C_2H_6 \rightleftharpoons H_2 + C_2H_5$	3.4×10^{12}	7,000	Experiment(*1*)	Experiment(*1*)	3.8×10^{12}	7,000
6′		1×10^{11}	11,400	Experiment(*41*)	Estimate(*41*)	1.8×10^{12}	11,400
7	$H + C_2H_5 \rightarrow C_2H_6$	7×10^{13}	0	Analogy with 2′	Analogy with 2′	7×10^{13}	0
8	$CH_3 + C_2H_5 \rightarrow C_3H_8$	7×10^{13}	0	Analogy with 2′	Analogy with 2′	7×10^{13}	0
9	$2C_2H_5 \rightarrow C_4H_{10}$	6×10^{13}	0	Experiment(*12*)	Experiment(*12*)	7×10^{13}	0
	$\rightarrow C_2H_4 + C_2H_6$	1×10^{13}	0	Experiment(*35*)	Experiment(*35*)		

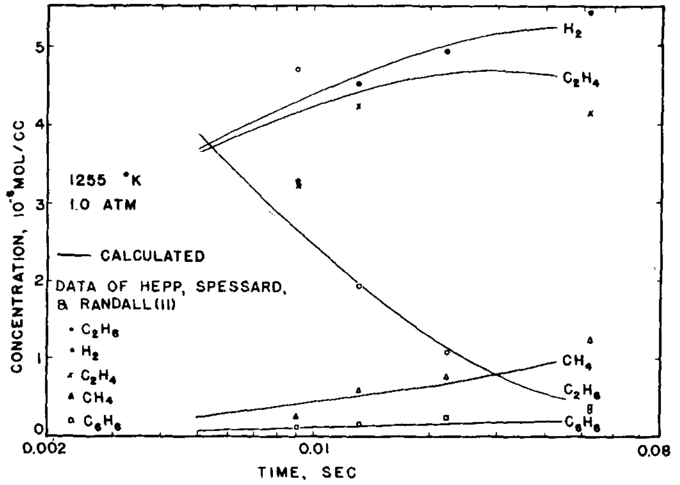

Fig. 4. Calculated and experimental products from ethane pyrolysis.

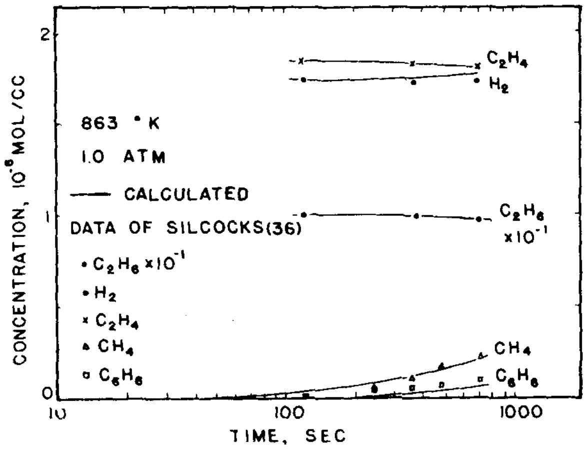

Fig. 5. Calculated and experimental products from an equilibrium mixture of ethane, ethylene, and hydrogen.

to give methane, higher hydrocarbons, and perhaps hydrogen. The amount of methane formed by secondary reactions was made to depend on a parameter which could be varied to fit the pyrolysis data. The mechanism does not predict the individual higher hydrocarbons formed. The average molecular weight and carbon-hydrogen ratio of the higher hydrocarbons depend on the conversion and the temperature and pressure, but as a crude approximation their average properties are like benzene (*33*). The formation of methane, higher hydrocarbons expressed as benzene, and hydrogen is given by the stoichiometric reactions (8*a*) and (9*a*):

$$CH_3 + C_2H_5 \rightarrow C_3H_8 \rightarrow X\, CH_4 + (1/2 - X/6)\, C_6H_6 + (5/2 - 3X/2)\, H_2 \tag{8a}$$

$$2C_2H_5 \rightarrow C_4H_{10} \rightarrow 2X\, CH_4 + (2/3 - X/3)\, C_6H_6 + (1 - X)\, H_2 \tag{9a}$$

To calculate the rates of reactions and hence the product distributions expressions giving the free-radical concentrations are needed. It is known and was confirmed by later calculations that the concentrations of free radicals are small compared with the concentrations of molecular species and that therefore the net rate of formation of radicals is small compared with the rate of formation of other compounds. Therefore the usual procedure was used, in which the net rate of formation from reactions (2) to (9) of each radical was equated to zero, and the resulting expressions were solved for the free radical concentrations. The following expressions were obtained:

$$(CH_3) = \frac{D}{4k_2'}\left[-1 + \sqrt{1 + \frac{8k_2'[2k_2\,(C_2H_6) + k_3'\,(C_2H_5)(CH_4) + k_4'\,(H)(CH_4)]}{D^2}}\right] \tag{a}$$

where

$$D = k_3\,(C_2H_6) + k_8\,(C_2H_5) + k_4\,(H_2)$$

$$(C_2H_5) = \frac{E}{4k_9}\left[-1 + \sqrt{1 + \frac{8k_9[k_3\,(CH_3)(C_2H_6) + k_4\,(H_2)(CH_3) - k_4'\,(H)(CH_4)]}{E^2}}\right] \tag{b}$$

where

$$E = k_3'\,(CH_4) + k_8\,(CH_3) + 2k_7\,(H)$$

$$(H) = \frac{k_5 + k_6'\,(H_2)(C_2H_5) + k_4\,(H_2)(CH_3)}{k_5'\,(C_2H_4) + k_6\,(C_2H_6) + k_4'\,(CH_4) + k_7\,(C_2H_5)} \tag{c}$$

At this point in the derivation the values of free-radical concentrations are usually substituted into the expressions for the formation rates of the products; these rate expressions are then solved explicitly. In some cases drastic simplifying assumptions were formerly made to solve the rate expressions. The simplifications required for ethane pyrolysis have been discussed by Steacie (*41*); they destroy essential features of the mechanism. Simplifying assumptions were not made in this work. Instead the rate expressions were solved numerically by a trial procedure, with a digital computer.

This change of method dictated by the inherent complexity of ethane pyrolysis required some change in conventional ways of thought. For example order of reaction with respect to pressure or concentration of a reactant is ordinarily defined by the form of an explicit rate expression. With simple systems experimental evidence that the rate is of a certain order has been used to establish that the rate expression has the corresponding form; with systems as complicated as ethane pyrolysis an accurate rate expression cannot be written in explicit form, and therefore the order of reaction cannot be predicted in the usual way. In the case of ethane experimental evidence indicates that the over-all reaction is approximately of first order, but on the other hand the complexity of the proposed mechanism suggests that the order may vary with conditions. Instead of using the order of reaction concept in cases as complicated as ethane one can always compute incremental changes in reaction rates with respect to any variable at point values of temperature, pressure, and conversion.

CALCULATION OF PRODUCT DISTRIBUTIONS

To calculate a product distribution a step-by-step trial-and-error integration is carried out. An IBM 650 digital computer was programed for these calculations. Figure 1 is a simplified block diagram showing the steps in the calculation. In the first loop Equations (a), (b), and (c) are solved for (CH_3), (C_2H_5), and (H), iterating until the results converge to within six significant figures.

With the free-radical concentrations obtained in this way, the rates of the individual reactions are calculated in the second loop. The over-all rates of formation of each product due to all the reactions in the mechanism are calculated from stoichiometric relations. By multiplying these over-all rates by a small interval of time one obtains the change in concentration of each component. Then new arithmetic averages of the values of (C_2H_6), (C_2H_4), (H_2), and (CH_4) at either end of the time interval are computed. The free-radical concentrations and the reaction rates are then calculated anew, and this procedure is repeated until it is determined that that the first six significant figures of successive values of (C_2H_6) are the same.

The concentrations of all components are computed at the end of the time interval for a static system. For a flow system at essentially constant pressure these results are corrected for the stoichiometric expansion of the gases by the multiplication of the concentrations by the ratio $\sum_i C_{0i}/C_i$. The computer then proceeds to the third loop, where a new interval of time is taken for the next step in the calculation. The whole procedure is repeated until the desired conversion is reached. The calculation of each product distribution by the computer requires from 2 to 4 hr.

FITTING RATE CONSTANTS TO EXPERIMENTAL DATA

The main objective of this work was to establish that the proposed mechanism is consistent with experimental data and with the results of other investigators. For this purpose product distributions were calculated based on the kinetics of this mechanism and compared with experimental product distributions. The rate constants used in these calculations were chosen to lie within the uncertainties of values previously determined by other investigators from studies of numerous reacting systems. These values and their literature sources are listed in Table 1. Considerable uncertainty exists concerning the true values of some of these rate constants. It was therefore necessary to establish some of the rate constants more exactly by finding the values which resulted in the best fit of calculated and experimental product distributions. Since product distributions were available at a number of widely spaced temperatures, these experimental data provided more than enough quantitative restrictions to fix the values of certain rate constants.

Special experiments are often designed to test selectively the form of the rate expressions when the rate expressions can be solved explicitly. For example the concentrations of the reactants are varied separately or in other special ways. The value of each rate constant is then found by a least-squares fit of the data from such experiments.

This procedure cannot be used in the present case because separate terms in the rate expressions cannot be identified solely with particular variables. Therefore an unconventional treatment is necessary. In this work the rate constants were established by the following trial procedure: A trial set of rate constants for a particular temperature is chosen based on the work of previous investigators. A product distribution is then calculated as described above. The calculated product distribution is compared with an experimental product distribution from the literature. If it does not agree, the rate constants are changed in a systematic way, and a new product distribution is calculated. The process is repeated until the calculated product distribution agrees with the experimental one. To aid in selecting new trial values of rate constants, provision is made in the computer program to calculate at several levels of conversion the incremental changes in product distribution resulting from incremental changes in rate constants. New trial values of rate constants are then estimated based on the incremental changes in product distributions, and a new product distribution is computed.

To determine rate constants as functions of temperature, separate sets of such constants are determined for experimental product distributions corresponding to different temperatures. An additional requirement imposed is that the temperature dependence of the rate constants conform to Arrhenius functions.

This trial-and-error procedure for determining rate constants is as rigorous as the conventional procedures, since in both procedures the results are based on measurements of product distribution or on measurements of special aspects of product distributions.

The results are listed in Table 1. Some calculated product distributions are shown in Figures 2 to 5. The solid lines represent computed product distributions, while the points represent experimental data from the literature. Each figure corresponds to a particular temperature and pressure. It may be seen that no trend exists over different temperatures in the deviations of calculated results from experimental results. The temperatures range from 863° to 1,255°K. at about 1 atm. A calculated product distribution also agrees with an incomplete product distribution determined by Tropsch and Egloff (*46*) at 1,373°K. and 0.04 atm.

Certain inconsistencies are evident within each set of experimental data. Pyrolysis product distributions at these temperatures are extremely difficult to measure, the greatest uncertainty resulting from uncertainty of true gas temperature. A simple calculation shows that an error of a factor of 2 in the primary reaction rate could for example result from an error of 25°K. in the

TABLE 2. LIST OF REACTIONS WHICH ARE IMPORTANT UNDER VARIOUS CONDITIONS

Data, Ref.	Temperature, °K.	Pressure, atm.	Reactions					
(*36*)	863	1	2	3 (4)	5 5′	6 6′		9
(*25*)	998	1	2	3 (4)	5 5′	6 6′		8 9
(*14*)	1089	1	2(2′)	(3) 4	5 5′	6 6′		8 9
(*11*)	1255	1	2 2′	(3) 4	5 5′	6 6′	(7)	8 (9)
(*46*)	1373	0.04	2 2′	3 4	5 5′	6 6′	7	8

measurement of the true-average pyrolysis temperature. The calculated results agree with the data within 10 %. The experimental data are a little more precise than this but not more accurate. To use the present results as the basis for design of pyrolysis-reactor coils it would be necessary to compare data from a commercial pyrolysis coil with a product distribution computed from the proposed mechanism for the varying temperatures and pressures of such a coil. Snow and Schutt (*38*) have described a method for making such a comparison. Any slight discrepancy could then be corrected by correcting the frequency factors of the pertinent rate constants.

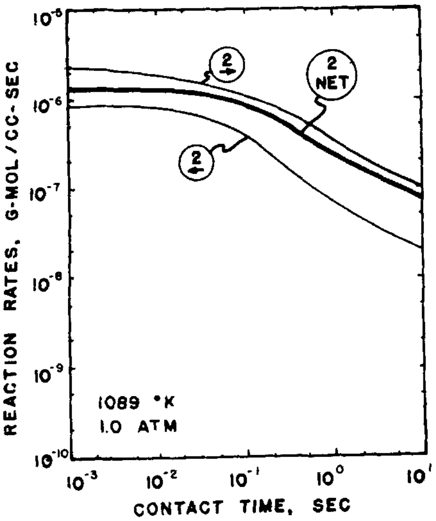

Fig. 6. Forward, reverse, and net rates of initiating reaction.

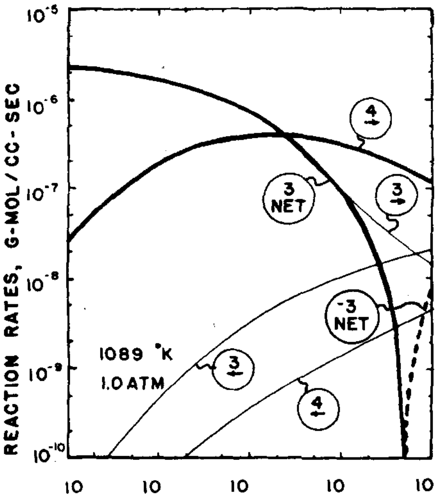

Fig. 7. Forward, reverse, and net rates of radical transfer reactions.

The rate constants given in the last column of Table 1 are those which resulted in the best fit of calculated product distributions with the laboraroty pyrolysis data shown in Figures 2 to 5. Some of these rate constants are believed to be more accurate than previously determined values, especially the frequency factors for reactions 2, 3′, 5, and 6′ and the activation energy for reaction 2.

DISCUSSION OF KINETICS OF ETHANE PYROLYSIS

The mechanism includes a number of competing reactions; those found to be important under various conditions of temperature and pressure are listed in Table 2. The exact relationships depend of course on the conversion. The reactions listed in parentheses are of minor importance. Reactions 3′ and 4′ are not important under any of these conditions. The rates are compared in detail for one set of conditions in Figures 6 to 9.

Of particular importance is the finding that reactions 5′ and 6′ are important at very low conversions. These are the reverse of the chain-carrying reactions. The following are approximate results for all conditions studied:

Conversion, %	Rate of 6′/rate of 6, %
0.5	10
1	20
5	55

Hinshelwood and co-workers (*3*) and Steacie and Shane (*42*) measured the rate of ethane disappearance at 5 to 10 % conversion, extrapolated the rate to zero conversion, and identified the result with the forward rate alone. It now appears that the reverse rate was high at these conversions, and the extrapolation was of doubtful validity*.

The net reactions 5 − 5′ and 6 − 6′ actually reverse at higher conversions for the conditions of Figures 3 and 4, and ethylene and hydrogen begin to disappear to form secondary products. The calculations quantitatively account for this interplay of equilibrium behavior with continual occurrence of secondary reactions. They reproduce even a product distribution for an equilibrium mixture of ethane, ethylene, and hydrogen given in Figure 5. This mechanism is valid for such mixtures due to higher stability of ethylene and hydrogen than that of ethane. Even when present in larger amounts than ethane they do not split as much and do not produce appreciable amounts of free radicals, which would affect the pyrolysis rate. The same would not be true of the pyrolysis of higher hydrocarbons, whose primary reaction products are not highly stable.

An attempt was made to include reactions (10) and (11) in the mechanism It was assumed that the C_3H_7 and C_4H_9 react further to give a mixture of higher hydrocarbons and methane. Rate constants for these reactions were assumed to equal $10^{11} \exp(-7{,}000/RT)$. This is a reasonable value, since Mandelcorn and Steacie (*17*) found the activation energy of (10) to be 7 kcal., and similar reactions are known to have similar activation energies. With these assumptions it was found that the rates of Reactions (10) and (11) are too high, and calculated product distributions did not agree with experiment. The rate constants would have to be smaller by several orders of magnitude, but it is not reasonable to expect this to be true. It is believed that this difficulty arises because Reactions (10) and (11) may not be included without also including other important reactions of the radicals C_3H_7 and C_4H_9. In particular, calculations based on values of the rate constants (*2, 7, 47*) indicate that the reverse of reactions (10) and (11) are more important than other reactions of these radicals; hence the net rates could be much less than the forward rates.

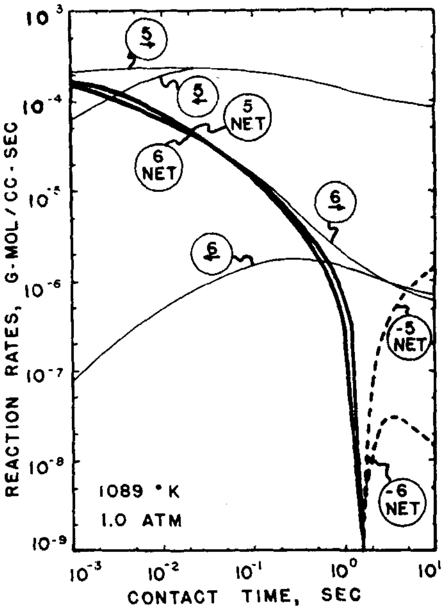

Fig. 8. Forward, reverse, and net rates of chain-propagating reactions.

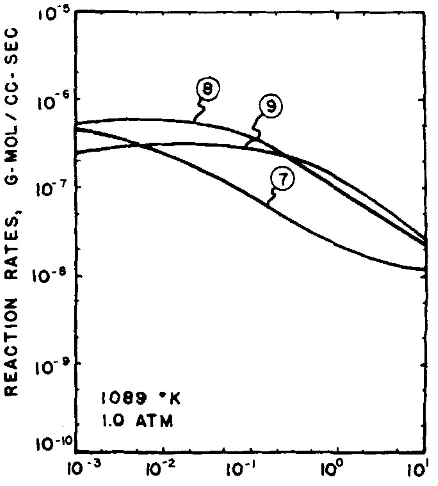

Fig. 9. Rates of terminating reactions.

These reactions and other reactions of secondary products could affect the concentrations of methyl, ethyl, and hydrogen free radicals and thus affect

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*Two possible approaches to investigations of reaction kinetics are designing experiments for simplicity of interpretation, by attempting, for example, to measure a reaction rate at zero conversion, and carrying out the most complete mathematical analysis permitted by available knowledge for a given experiment. This example indicates that many kinetic problems, including some which were once thought simple, are actually so complicated that both methods should be used insofar as is feasible. One objective of the present work was to further develop the second method.

the primary pyrolysis rate. No reasonable number of elementary reactions can completely characterize a hydrocarbon pyrolysis mechanism, since the number of secondary products and radicals which can react is large. However the mechanism studied fits the available pyrolysis data from 863° to 1,373°K. up to relatively high conversions (20 to 85%), for which the concentrations of secondary products become equal to the concentration of unreacted ethane, and exhibits rate constants which agree with previously determined values. It is therefore believed that if all important reactions of secondary products are included, the rate constants needed to fit the pyrolysis data would differ from those given here by not more than twofold. For example in this work it was found that about half the methane is produced direct from ethane by reactions (3) and (4). The other half therefore results from secondary reactions, and probably exclusively from scissions of molecules or radicals to produce methyl radical. This additional methyl radical may again react via (3) or (4) to give methane and at the same time initiate primary reaction chains. If the amount of methane measures this effect, then it may be expected that rate constants for the primary part of the pyrolysis should be lower by a factor of 2.

As was previously explained, the production of methane from secondary products was empirically accounted for by means of a stoichiometric factor, X. The required variation of X with temperature to best fit the pyrolysis data is given in Table 3.

TABLE 3. VARIATION OF STOICHIOMETRIC FACTOR WITH TEMPERATURE

Temperature, °K.	Data identification	Stoichiometric factor, X
863	*L*—Fig. 2	0.5
1089	*D*—Fig. 3	0.85
1255	*E*—Fig. 4	0.95

It would be desirable to include more reactions in order to calculate the amounts of individual higher hydrocarbons formed and eventually to calculate the amount of coke formed, since this is a problem of major industrial importance. It is not at present feasible to make a more complete study because the rate constants of the additional reactions are not known. They cannot be determined solely by fitting pyrolysis data because there are so many possible reactions that pyrolysis data alone would not provide enough quantitative restrictions. Further experimental work on simpler hydrocarbon reaction systems needs to be done to determine these rate constants.

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NOTATION

A_i = frequency factor, same units as k_i
(A) = concentration of substance A, g-mole/cc.
C = concentration, *g*.-mole/cc.
C_i = concentration of component in product
C_{0i} = concentration in feed
E_i = activation energy, cal./g.-mole
k_i = rate constant of the ith reaction, 1/sec. for a first-order reaction or cc./g. mole-sec. for a second-order reaction
k_i' = rate constant of the reverse of the ith reaction, 1/sec. or cc./g. mole-sec.
X = parameter, stoichiometric factor

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An appendix to this paper has been deposited as Document No. 5970 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C. and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm. It contains calculated product-distribution tables including rates of individual reactions at various conversions, a discussion of the mathematics of the computations, and a description of the computer program.

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