Thermal Cracking of Ethane and Ethylene in a Stock Tube

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The rates of decomposition of ethane and ethylene were measured at temperatures between 1,250° and 2,800°K. and pressures between 0.25 and 2.0 atm. by exposing the gases to high temperature during the interval between the arrival of a compression wave and a reflected rarefaction wave in a shock tube. As contrasted with cracking at lower temperatures the ethane apparently reacted to hydrogen, ethylene, and acetylene and the ethylene to hydrogen and acetylene with negligible side reactions or polymerization. The over-all decomposition rates at high temperature fall off sharply from those extrapolated from low temperature, indicating a change in mechanism. Additions of air, oxygen, carbon monoxide, and chlorine in amounts up to 17% did not effect the rate constants significantly.

The pyrolysis of ethane has been investigated extensively at temperatures below 1400°K. The early work has been thoroughly reviewed by Steacie (*1*) and subsequent work by Snow, Peck, and Von Fredersdorf (*2*). The work on the pyrolysis of ethylene is less extensive. Burk, Baldwin, and Whitacre (*3*) have summarized the early work and Dahlgren and Douglas (*4*) the more recent.

The objective of this investigation was to obtain rate data above 1,400°K. with a shock tube. Since this investigation was undertaken, shock tube data in the range from 1,000° to 1,750°K. have been reported by Skinner and co-workers (*5*, *6*) and in the range from 1,900° to 2,500°K. by Greene, Taylor, and Patterson (*7*). Additional data in the range from 1,000° to 1,400°K. have also since been obtained by Towell and Martin (*8*) in a nonisothermal reactor.

Snow, Peck, and Von Fredersdorf (*2*) postulated a set of free-radical mechanisms for the pyrolysis of ethane and determined values of the rate constants which best fit previous experimental compositions. The reactions which they conclude to be important at 900°K. are

$$C_2H_6 \xrightarrow{k_1} 2CH_3 \qquad (1)$$

$$CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5 \qquad (2)$$

$$C_2H_5 \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} C_2H_4 + H \qquad (3)$$

$$H + C_2H_6 \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} H_2 + C_2H_5 \qquad (4)$$

$$2C_2H_5 \xrightarrow{k_5} C_2H_4 + C_2H_6 \qquad (5)$$

If the net rate of production of each of the free radicals is assumed to be zero, the following expression can be derived for the disappearance of ethane:

$$r = 2k_1[C_2H_6] + k_3\sqrt{\frac{k_1}{k_5}[C_2H_6]}\left[\frac{1 - \frac{k_4'k_3'}{k_4k_3}\frac{[C_2H_4][H_2]}{[C_2H_6]}}{1 + \frac{k_3'}{k_4}\frac{[C_2H_4]}{[C_2H_6]}}\right] \qquad (6)$$

Equation (6) suggests that the disappearance of ethane may be approximately first order or half order depending on the values of the concentrations and coefficients. Numerical calculations indicate that both terms may be significant within the range of conditions of interest herein.

At temperatures above 1,400°K. Snow, Peck, and Von Fredersdorf conclude that all of the above reactions except (5) plus

$$CH_3 + H_2 \xrightarrow{k_7} CH_4 + H \qquad (7)$$

$$CH_3 + C_2H_5 \xrightarrow{k_8} C_3H_8 \qquad (8)$$

and the reverse of (1) are important. The expression obtained by elimination of the free radicals from this set of reaction steps is far too complicated to serve as a guide to correlation.

EXPERIMENTAL APPARATUS AND PROCEDURE

The shock tube constructed by Gluckstein and Churchill (*9*) was utilized in this work with only minor modifications. It consisted of a 1.0 in. long driver section and a 48 in. long test section, both with a square cross section ½ in. on a side. Gluckstein and Churchill used a longer driver section and quenched the reaction by allowing the shock wave to rupture a diaphragm separating the test section from a vacuum chamber. In this investigation no surge tank was used, and the reaction was instead quenched by the rarefaction wave reflected from the upstream end of the driver section.

The shock wave was initiated by adding gas to the driver section until the brass diaphragm separating the driver and test sections ruptured. Except as noted, undiluted ethane and ethylene were used in the test section. The wave velocity was measured by two quartz pressure transducers actuating an interval timer. After sufficient time was allowed for the mixed driver and product gas to reach uniformity, a sample was withdrawn and analyzed on a mass spectrometer. In order to determine the minor components more accurately, the hydrocarbons were first separated from the driver gas and hydrogen by condensation in a liquid nitrogen bath.

The temperature and pressure behind the wave and the reaction time for each element of gas were computed from the measured wave velocity with the well-known equations for the conservation of energy, mass, and momentum across the

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wave. The results of Roshko (*10*) indicate that the reduction in the reaction time due to the boundary layer behind the shock wave was not appreciable in these experiments. Special experiments were run to test the measurements of wave velocity, the computed point of intersection of the rarefaction and shock waves, and the spectrographic analysis. By limiting the conversion to about 30% or less, as was done in most runs, the temperature drop due to reaction is limited to 5% or less of the absolute temperature immediately behind the shock wave. The reciprocals of the temperatures at the beginning and end of the reaction zone were averaged to obtain the mean temperature used in the correlation of the data. The calculation and effect of the unknown rate of quenching have been discussed by Kervorkian, Heath, and Boudart (*11*). An instantaneous rate of quenching was assumed in the calculations herein.

The experimental conditions and results are summarized in Table 1. Additional details concerning the apparatus, procedures, and calculations are given in reference *12*.

EXPERIMENTAL RESULTS

Ethane Pyrolysis

The analysis of free radical mechanisms in the previous section indicates that the rate data cannot be expected to follow any simple rate expression over an extended range of concentrations and temperature. The data obtained in this investigation did not encompass a sufficient range of conversion to test critically the apparent order of ethane disappearance even for a narrow range of conditions. Accordingly, the precedent of previous investigators was followed, and the data were arbitrarily correlated in terms of the equation for a first-order, irreversible reaction.

Each element of gas along the length of the tube was exposed to high temperature during the interval between the arrival of the compression and rarefraction waves. For a first-order, irreversible, isothermal reaction the fractional decomposition of ethane in an element of gas is related to the reaction time for that element as follows:

$$Z = 1 - e^{-kt} \tag{9}$$

If the waves and the gas particles behind the shock wave have a constant velocity, the reaction time for the elements of gas varies from a maximum adjacent to the diaphragm to zero at the point where the reflected rarefaction wave overtakes the shock wave. The conversion for an element of gas at a distance x from the diaphragm is

$$Z = 1 - \exp\left[-kt_{\max}\left(1 - \frac{x}{L}\right)\right] \tag{10}$$

Table 1. Summary of Experimental Conditions and Results

M_s	P_o, atm. × 10^4	Product, % C_2H_4	P, atm.	T, °K.	t_{max}, μsec.	$\log_{10} k$, $(sec.)^{-1}$
		(Reactants: 96.3% C_2H_6, 3.7% C_2H_4)				
7.33	100	38.7	0.470	1,620	340	3.46
7.87	90	65.2	0.495	1,720	378	3.82
8.46	167	27.7	1.05	2,260	415	3.16
6.70	525	28.7	2.06	1,600	344	3.26
6.50	591	11.7	2.19	1,610	338	2.70
		(Reactants: 97.3% C_2H_6, 2.7% C_2H_4)				
6.01	268	4.7	0.847	1,680	304	2.12
5.32	344	3.6	0.843	1,410	330	1.74
6.55	194	4.9	0.728	1,510	307	2.17
6.40	214	3.9	0.768	1,470	300	1.91
6.79	164	4.5	0.658	1,730	318	2.06
7.43	124	10.2	0.600	1,840	356	2.64
8.29	74	24.0	0.448	2,410	409	3.09
6.03	191	3.2	0.604	1,400	299	1.54
7.29	64	9.8	0.295	1,780	345	2.63
7.52	127	8.9	0.629	1,890	359	2.56
8.41	87	24.0	0.544	2,220	412	3.09
†9.40	33	32.9	0.2541	2,610	485	3.33
†9.55	37	34.6	0.296	2,690	498	3.39
6.39	217	3.6	0.779	1,470	300	1.78
6.26	256	3.5	0.876	1,420	293	1.75
*6.45	120	9.4	0.542	1,460	452	2.50
*6.07	114	3.0	0.465	1,350	400	1.17
7.68	160	11.8	1.06	1,940	368	2.72
7.34	208	9.8	1.23	1,810	350	2.64
		(Reactants: 97.3% C_2H_6, 2.7% C_2H_4 plus 5% O_2)				
6.86	204	6.8	0.840	1,620	324	2.36
7.17	157	11.7	0.711	1,740	339	2.76
6.22	274	3.4	0.918	1,400	291	1.69
7.73	120	15.4	0.630	1,950	372	2.88
		(Reactants: 97.3% C_2H_6, 2.7% C_2H_4 plus 5% air)				
8.19	104	16.8	0.614	2,140	398	2.90
7.34	147	8.9	0.691	1,820	349	2.56
6.69	211	4.2	0.829	1,570	313	1.99
6.26	291	3.1	0.992	1,410	293	1.44
		(Reactants: 97.3% C_2H_6, 2.7% C_2H_4 plus 5% CO)				
6.18	154	12.8	0.645	1,330	288	2.87
8.15	140	15.6	1.02	2,130	396	2.86
7.65	181	10.6	1.16	1,930	367	2.66
6.92	218	6.3	1.14	1,660	327	2.34

The conversion of the mixed product is then

$$Z_m = \frac{1}{L}\int_o^L Z dx = 1 - \frac{1}{kt_{\max}}\left[1 - e^{-kt_{\max}}\right] \tag{11}$$

The rate constant was determined from Equation (11) with the measured compositions of the feed and product and the value of t_{max} computed from the measured shock wave velocity.

The resulting values of the first-order rate constant are plotted vs. the average reciprocal temperature in the reaction zone in Figure 1. The data of recent investigations and a line representing the earlier low-temperature work (*1*) are included for comparison. Rate constants were not presented by Greene, Taylor, and Patterson, and the indicated points were computed from other information in their paper (*7*). Skinner and Ball (*5*) did not include in their own plot of rate constants vs. temperature the set of data which was obtained at high temperatures and high conversions, but these points are included in Figure 1. The scatter in the data of the authors' investigation is somewhat greater than that in the lower temperature work as might be expected owing to uncertainties in composition, temperature, and reaction time inherent in the shock-tube technique. The rate constants agree in trend with the results of the other investigators but are generally lower. This discrepancy may be due to the presence of ethylene in the feed gas, the high concentration of the undiluted reactant gas, and/or the relatively low reaction pressure, rather than to the experimental technique.

M_o	P_o, atm. $\times 10^4$	Product % C_2H_4	P, atm.	T, °K.	t_{max}, μsec.	$\log_{10} k$, $(sec.)^{-1}$
		(Reactants: 97.3% C_2H_6, 2.7% C_2H_4 plus 17% CO)				
7.27	217	14.9	1.26	1,810	346	2.90
7.89	150	23.6	1.03	2,060	380	3.12
		(Reactants: 97.3% C_2H_6, 2.7% C_2H_4 plus 4% Cl_2)				
8.72	134	17.8	1.01	2,240	404	2.92
7.06	227	5.6	1.25	1,710	334	2.25
		(Reactant: 100% C_2H_4)				
7.21	151	94.9	0.761	2,010	342	2.49
8.17	94	89.7	0.611	2,470	397	2.72
8.90	80	82.7	0.618	2,810	447	2.94
8.47	60	84.5	0.420	2,570	417	2.92
7.38	144	94.5	0.763	2,080	350	2.48
7.90	104	89.8	0.634	2,320	381	2.75
6.80	184	97.0	0.828	1,840	320	2.27
6.90	194	96.8	1.02	1,880	325	2.28
6.50	221	98.0	1.03	1,720	304	2.12
6.28	244	98.7	1.05	1,620	293	1.94
6.15	264	99.1	1.11	1,580	287	1.79
6.15	277	99.1	1.16	1,580	287	1.79
5.82	377	99.7	1.41	1,440	272	1.34
5.88	334	99.6	1.27	1,470	273	1.47
5.41	421	99.8	1.35	1,280	253	1.20
5.59	382	99.7	1.30	1,340	260	1.36
5.32	435	99.9	1.35	1,240	249	0.90
7.59	137	92.2	0.863	2,170	362	2.65
7.00	211	97.5	1.14	1,940	330	2.18
*6.15	137	98.6	0.575	1,570	444	1.79
		(Reactant: 100% C_2H_4 plus 5% CO)				
7.94	134	93.6	0.931	2,370	384	2.54
7.29	187	98.4	1.10	2,070	346	1.92
6.85	234	99.1	1.21	1,880	323	1.72
		(Reactant: 100% C_2H_4 plus 17% CO)				
6.81	207	97.0	1.07	1,840	321	2.27
7.32	147	93.8	1.37	2,210	349	2.56
		(Reactant: 100% C_2H_4 plus 6% Cl_2)				
7.39	144	89.6	0.871	2,040	351	2.79
7.36	187	96.2	1.13	2,100	350	2.33
6.92	227	98.7	1.20	1,910	327	1.90

Compositions are given on the basis of hydrocarbons only.
In all runs with ethane feed except those two noted with a dagger the ethane in the product can be found by subtracting the ethylene percentage from 100. In those two cases the acetylene percentage was 7.6 and 10.4 respectively.
In all runs with ethylene feed the acetylene in the product can be found by subtracting the ethylene percentage from 100.
In the three runs noted with an asterisk helium was used as the driver gas.

The striking decrease in the slope of the curve in Figure 1 is the most significant effect observed for the pyrolysis of ethane at high temperatures. This decrease corresponds to a reduction in the apparent energy of activation from about 74 kcal./g. mole at low temperatures to about 11 kcal./g. mole at 2,500°K. The reduction must be due to a change in the reaction mechanism. It is worth considering how erroneous would be extrapolation in the coordinates of Figure 1 of the line representing low-temperature data to high temperatures. Skinner and Ball (5) also noted this fall off in their runs at higher temperatures, but attributed the effect to the corresponding higher conversions. In the authors' work higher temperatures were also associated with higher conversions, but the fall off occurred at all conversions.

Because of the high pressure ratios used in this work mixing of the driver gas and the test gas during the reaction period might be expected. To determine the effect this mixing might have on the measured reaction rate a few runs were carried out substituting helium for hydrogen as the driver. The effect of mixing of hydrogen with the reactants would presumably be to decrease the rate constant. As indicated in Figure 1 the data for helium are within the scatter of the data, indicating that the effect, if any, of mixing was indeterminate.

Greene, Taylor, and Patterson suggested that carbon monoxide may suppress the formation of ethylene. To investigate such effects additions of 5% oxygen, 5% air, 4% chlorine, 5% carbon monoxide, and 17% carbon monoxide to the feed gas were made in some runs. The effects, if any, of these additives were also within the scatter of the data.

The decomposition of ethane appeared to be almost wholly to ethylene and hydrogen, but up to 10% acetylene was found in the products at the highest temperatures. Hydrogen and carbon balances for the runs with a helium driver indicated that little or no carbon was formed by side reactions.

Ethylene Pyrolysis

The conversion in all runs was 17% or less, and the first-order rate constant for the disappearance of ethylene was computed as for ethane. The computed values are plotted vs. reciprocal temperature in Figure 2. The rate constants determined by Towell and Martin (8) and by Skinner and Sokoloski (6) and the constants computed from the two runs of Greene, Taylor, and Patterson (7) are included in Figure 2. Again the data of this investigation fell well below the straight line which might be drawn through the low-temperature data. There is some disagreement between the different sets of data, but again it is evident that the apparent energy of activation decreases with temperature. The curve drawn as a compromise for all of the data corresponds to a decrease from about 65 to about 20 kcal./g. mole. The reason for the discrepancy between the data of this investigation and the data of Skinner and Sokoloski for a feed gas containing 0.466% ethylene in argon is unknown.

Hydrogen and acetylene were the principal products of decomposition of ethylene. Carbon and hydrogen balances suggested the formation of side products in some runs, but higher hydrocarbons were detected even after concentration of the products by condensation with a liquid nitrogen bath. Polymerization of the acetylene was observed by Towell and Martin and the investigators at low temperature (3, 4), and Skinner and Sokoloski obtained significant fractions of methane, propylene, and butadiene under some conditions. Polymerization is favored by high pressure, low temperature, and large conversions. Apparently both polymerization and side reactions can be avoided by using high temperatures, moderate pressures and low conversions, and quenching rapidly.

Again some runs were carried out with helium as the driver gas and with additions of chlorine and carbon monoxide. The scatter in these runs is somewhat greater, but no significant effects are apparent.

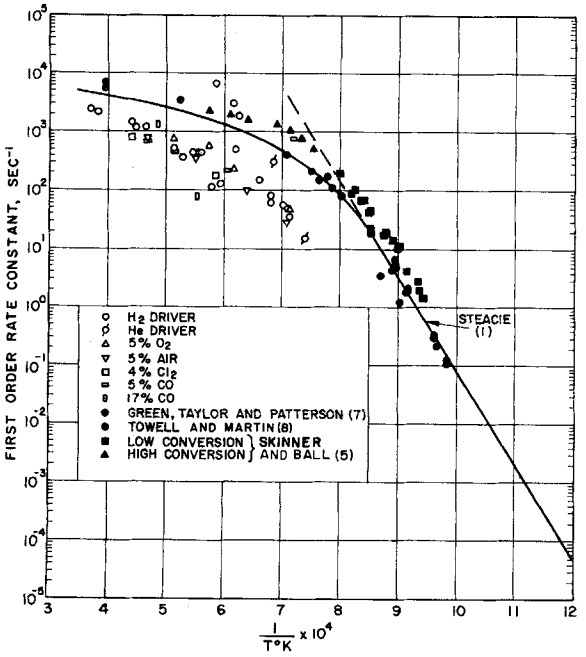

Fig. 1. First-order reaction rate constants for ethane pyrolysis.

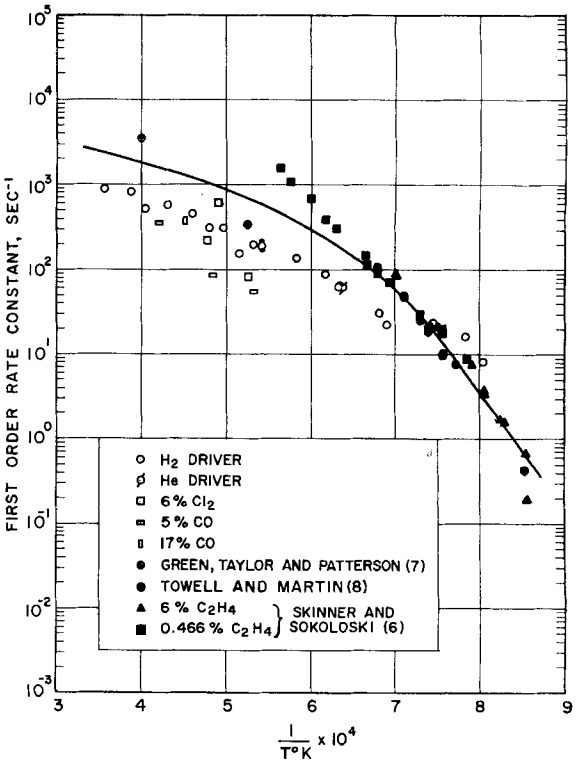

Fig. 2. First-order reaction rate constants for ethylene pyrolysis.

DISCUSSION

The data of this investigation are less precise than those obtained at lower temperatures in conventional reactors but serve to indicate the trends with increasing temperature. The principal products of decomposition of ethane were found to be hydrogen, ethylene, and acetylene and of ethylene to be hydrogen and acetylene. By contrast previous investigators have reported a wide spectrum of products with little or no acetylene. The difference may be due to the higher temperatures, lower pressures, lower conversions, and more rapid quenching which were obtained in this investigation. However in view of the inherent uncertainties in the analysis of the diluted product gases and the fact that the observed rates were generally lower than those of previous investigators, the observed product distribution should be considered tentative.

The apparent energies of activation for first-order decomposition of ethane and ethylene were both found to decrease with increasing temperature, indicating a change in reaction mechanism.

The investigation tentatively suggests that acetylene can be produced from ethane or ethylene without excessive side products at a sufficiently high temperature. The mass of gas reacted per mass of equipment is too small to allow commercial processing in a shock tube of the type utilized in this investigation. The reactants might be passed continuously through a standing shock wave at the exit of a converging-diverging nozzle. However the heat flux density which would be required to maintain the gas at near-isothermal conditions during the expansion through the nozzle would probably be prohibitively high.

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NOTATION

k = rate constant for forward reaction

k' = rate constant for reverse reaction

L = distance from diaphragm to point of interaction of shock wave and reflected rarefaction wave

M_o = Mach number of shock wave based on initial conditions

P = pressure behind shock wave, atm.

P_o = initial pressure in test section, atm.

r = reaction rate, moles/(time)(volume)

t = reaction time for an element of gas

t_{max} = reaction time for an element of gas adjacent to the diaphragm

T = temperature behind shock wave, °K.

x = distance down test section from diaphragm

Z = fractional conversion of ethane in an element of gas

Z_m = fractional conversion of ethane in all of test gas

[ ] = concentration, moles/volume

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