Pyrolysis of Propane in a Shock Tube

A. M. BENSON

Shell Development Company, Emeryville, California

The pyrolysis of propane has been studied over the temperature range 830° to 1180°C. with a single-pulse shock tube employed to effect rapid heating and quenching. Both the uncatalyzed decomposition and the decomposition catalyzed by hydrogen sulfide were studied. First-order rate constants for the uncatalyzed reaction are in excellent agreement with published data obtained in nonisothermal, tubular reactors. The product distribution differs from that obtained in other studies. It is characterized by decomposition of propane via two routes at roughly equal rates, one route leading to propylene and hydrogen, the other to ethylene and methane or ethane. Propylene subsequently is converted, almost stoichiometrically, to ethylene and acetylene. Hydrogen sulfide accelerates the initial decomposition of propane, thus maintaining high propylene selectivity to high propane conversion. A free radical mechanism is used to explain the gross features of the pyrolysis.

The thermal decomposition of hydrocarbons has been the subject of numerous investigations in a variety of reactors. Generally, these reactors have been characterized by low temperature (500° to 800°C.), long residence times (1 sec. to 1 hr.), and nonisothermal conditions. The development of single-pulse, shock-tube technology has recently extended the temperature range to well beyond 1,000°C. with short residence times (0.1 to 1 msec.), isothermal conditions, almost instantaneous heating and rapid cooling. Thus far the number of systems studied by this means has been relatively small. In particular, no data have been published concerning propane. This paper presents data for propane which were gathered in the course of development and testing of a chemical shock-tube facility. The principal results of this investigation are (1) The Arrhenius parameters for the uncatalyzed decomposition are in excellent agreement wtih those obtained by more conventional techniques. (2) The distributions of products and their variations with the extent of reaction are explainable but are not consistent with the observations of previous workers. This paper is presented with the hope that it will elicit further investigations to rationalize the latter discrepancy.

EXPERIMENTAL PROCEDURE

The apparatus shown schematically in Figure 1 is a single-pulse or chemical shock tube. It consists of a smooth-bore, stainless steel pipe, 3 in. I.D. by 18 ft. long, connected at one end to a 200-gal. vacuum vessel. Two breakable, metallic diaphragms divide the apparatus into three sections. The reactant section holds the premixed gaseous reactants, customarily 1 to 5% in argon at 2 to 5 lb./sq.in.abs. The driver section holds a driver gas, customarily 0 to 25 mole % argon in helium at 100 to 200 lb./sq.in.abs. The vacuum tank is evacuated to 1 mm. Hg or less. Rupture of the diaphragm that separates the driver and reactant gases results in rapid expansion of the driver gas, producing a shock wave in the reactant gas which proceeds down the tube, accelerating, compressing, and heating the reactant gas. Reflection of the shock wave from the end of the tube decelerates and further compresses and heats the gas instantaneously to the desired reaction zone temperature. The absolute temperature behind the reflected wave will usually be somewhat less than twice that behind the incident wave. By appropriate adjustment of the composition of the driver gas, a "tailored" or "matched" interface can be achieved. Under these circumstances the reflected shock wave passes through the driver gas-reactant gas interface without producing secondary shocks or expansions. The reactant gas remains stationary, occupying a small volume at the end of the tube, until such time as the reaction is quenched by an expansion wave. The latter is generated by rupturing the diaphragm separating the driver gas and the vacuum tank. The time of reaction is controlled by the time interval between the rupturing of the two diaphragms. Following the method of Glick (*1*) this is accomplished by using an auxiliary shock tube to actuate the rupturing device. A shock wave generated by rupturing a third diaphragm in this tube travels down the auxiliary tube and through two hoses to the plungers used to rupture the metallic diaphragms in the main tube. By adjusting the relative lengths of the hoses and the bursting pressure (shock velocity) in the auxiliary tube, the desired delay between shock and quench is achieved.

The pressure history in the reaction zone is measured by a Kistler PZ-14 transducer with a sensitivity of 3.5$\mu\mu$ coulombs/lb.sq.in. and a natural frequency of 35 kc. A band reject filter at 140 kc. rejects the fourth harmonic of this frequency. A Transductron (manufactured by Elastronics, Inc.) following the filter is adjusted to the natural frequency and damping factor of the transducer to produce a response which is the inverse transform of the gauge. The resulting pressure trace is displayed on an oscilloscope; a typical one is shown in Figure 2. In this figure the sharp pressure rise at the left represents the arrival of the shock at the pressure transducer. The pressure rises from an initial value of 6 lb./sq.in.abs. to the value 127 lb./sq.in.abs. characteristic of the reflected shock. The slow rise following the shock results from slight mismatching of the driver and driven gases. The drop in pressure, commencing at about 1.2 msec., signals the arrival of the quench wave generated at the vacuum tank.

The temperature of the reaction zone is inferred from the velocity of the initial shock wave and the known thermodynamic properties of the reactant gas. The velocity of this wave is measured by a series of five platinum-film, resistance gauges spaced equally along the driven section. Through a complex of electronic instruments the arrival times of the shock wave at these gauges are displayed on an oscilloscope as pips on a television type of raster. Arrival at the last gauge also serves to actuate the pressure measuring system above. Some deceleration of the shock wave is noted as it proceeds down the tube, and the velocity at the end of the tube is obtained by extrapolation of the velocity data gathered above.

After the quenching of reaction, gas samples are removed from the end of the tube into a hydraulic compressor and are then compressed into stainless steel sample bulbs. This sampling is carried out within 30 sec. of the reaction to minimize longitudinal mixing. Experiments have shown that the fingering displacement of "heavy" reactant gas by "light" driver gas will result in helium reaching the far end of the tube in about 3 min.

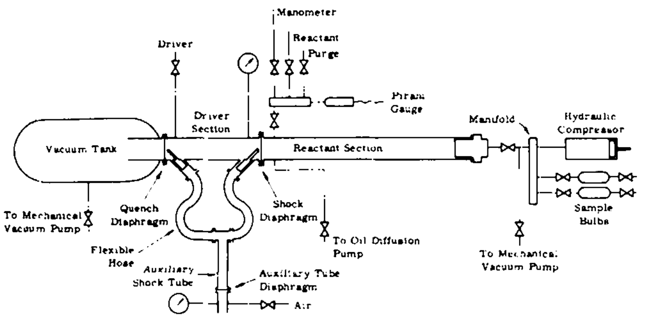

Fig. 1. Shock tube schematic.

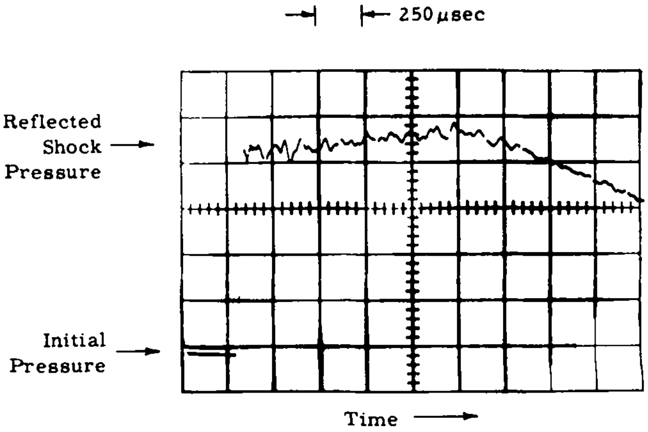

Fig. 2. Pressure trace from run 28-104.

Gas samples were analyzed on a modified Beckman GC-2 chromatograph employing silica gel, molecular sieve, and dimethylsulfolane: n-propyl sulfone columns. Initial calibrations showed that results were reproducible to within ± 0.01 percentage points at the 0.1% concentration level and ± 0.02 percentage points at the 2% concentration level. Analyses were made for methane, ethane, ethylene, acetylene, propane, propene, and nitrogen. Hydrogen sulfide in the reactant gas was measured by absorption in silver nitrate and titration of excess silver.

Reactant gases were generally prepared by filling ICC or stainless steel cylinders successively with appropriate partial pressures of reactants. Final compositions were determined by analysis. In the propane-oxygen-argon mixture the gases were metered through rotameters and mixed in-line, with a bleed stream introduced to the shock tube. The propane employed was Matheson CP grade (99.0% min.) and contained less than 0.1% oxygen by mass spectrometry. The argon was 99.998% min.

With the exception of one run at 5 atm., all pyrolyses were carried out at a nominal reaction zone pressure of 8 atm. Reaction zone temperatures ranged from 830° to 1,120°C. in the pyrolysis of propane and from 850° to 1,180°C. in the simultaneous pyrolysis of propane and hydrogen sulfide. Small quantities of nitrogen (~0.1%) were frequently found in the reactant and product gases, suggesting contamination by air. Although gas chromatographic analyses for oxygen were negative (<0.01%), a single run was made at low oxygen level to test the effects of air contamination.

TABLE 1. PYROLYSIS OF 0.8% PROPANE IN ARGON

Run No. 7513-	Temp.,* °K.	Pressure,† lb./sq.in.abs.	Time to quench point, μsec.	Conversion,† %	Selectivity, %†					Material closure error, %
					CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	
				No additive						
28-4	1,327	116.5	1,000	75.6	12.5	10.6	55.6	4.2	17.2	−14.4
28-5	1,392	126.1	400	75.9	10.0	8.7	59.7	3.9	17.3	−3.0
28-6	1,345	119.1	1,900	92.2	13.3	6.4	62.1	10.2	7.9	−4.0
28-7	1,372	123.2	450	77.4	9.8	9.5	59.6	4.0	17.2	+0.1
28-8	1,283	109.8	750	53.1	9.6	9.2	54.9	1.4	24.9	+1.0
28-10	1,339	118.5	500	56.2	10.4	10.4	52.8	1.8	24.5	−0.4
28-12	1,352	120.4	400	49.5	10.4	11.2	51.1	1.1	26.2	−3.6
28-13	1,387	125.7	800	76.4	11.9	10.2	56.5	4.5	16.8	−4.5
28-102	1,110	127.0	3,000	9.3	11.2	7.2	35.0	0	46.6	0.0
28-103	1,221	121.3	2,700	44.8	11.9	8.0	47.8	1.4	30.8	−6.3
28-104	1,256	127.4	1,200	41.5	11.2	8.6	46.1	0.8	33.3	−1.6
28-105	1,223	121.6	1,200	21.9	12.3	8.9	42.7	1.2	34.7	−5.3
32-1	1,350	120.1	700	57.1	11.2	10.7	53.2	2.1	22.9	−3.6
28-1	1,334	73.4	2,200	84.0	12.4	8.7	58.8	7.6	12.5	−6.0
				0.2% Oxygen added						
32-101	1,387	125.7	300	65.4	10.2	11.5	55.2	1.7	21.3	−3.5
				5% Hydrogen sulfide added						
32-6	1,390	125.6	750	98.7	20.4	35.5		4.2	15.8	−24.5
32-7	1,455	135.5	300	99.4	22.0	0.7	34.4	4.4	16.3	−22.1
32-8	1,295	111.0	300	92.2	16.4	1.7	29.4	0.7	34.9	−17.0
32-9	1,320	114.3	400	98.0	17.2	1.1	29.0	1.6	29.0	−22.1
32-201	1,123	124.2	1,000	16.6	15.5	1.4	36.4	0	46.6	+5.4
31-203	1,209	124.4	1,000	52.0	16.6	1.5	32.0	0.2	49.6	−3.1
32-204	1,207	124.3	700	35.0	16.5	0.8	34.6	0	48.1	−0.8
32-205	1,213	124.7	1,500	59.6	18.7	1.6	33.7	0.1	45.9	−2.6

* Values at the instant of shock reflection. Pressure computed from shock velocity.
† Based on carbon recovered except in runs 32-6 through 32-9.

RESULTS

Selectivities in Table 1 are based on moles of carbon in the compound in question per mole of carbon in the propane destroyed. Both selectivities and conversions were based on carbon recovered, with the exception of high conversion runs in the presence of hydrogen sulfide for which carbon fed was employed. In these runs the very poor closures of the material balances indicate the conversion of large quantities of propane to carbon, carbon disulfide, or alkyl sulfides. In earlier work in flames, sizable quantities of these compounds were formed. With the exception of these runs and run 28-4, material closures were good.

In analyzing the data the decomposition of propane was assumed to be a homogeneous, irreversible, first-order reaction:

$$\frac{dn}{dt} = nA \exp\left(-\frac{E}{RT}\right) \qquad (1)$$

Because of the small variations of temperature with time following the shock, and the larger but not instantaneous drop during the quench, it is not possible to integrate this equation directly. Rather, the variation of temperature was described by the differential equation for adiabatic expansion accompanied by chemical reaction:

$$CpdT = VdP - \Delta H_R dn \qquad (2)$$

The principal overall reactions are

$$C_3H_8 \rightarrow C_3H_6 + H_2 \quad \Delta H = -29.8 \text{ kcal./mole} \qquad (3)$$

$$C_3H_8 \rightarrow C_2H_4 + CH_4 \quad \Delta H = -19.5 \text{ kcal./mole} \qquad (4)$$

A value of -0.2 kcal./mole of gas mixture (0.8% propane) was used for ΔH_R.

For each experimental run the following procedure was adopted: For arbitrarily selected values of A and E, Equations (1) and (2) were integrated simultaneously from the time of the shock to the end of the pressure trace to obtain temperature and conversion as functions of time. The variation in pressure with time which is required to accomplish these integrations was obtained from the actual pressure trace for the run in question. The calculated conversion at the last point on the pressure trace was then compared with the experimentally determined conversion and the parameter A was adjusted to bring these into agreement. This resulted in a series of values for A as a function of E and the particular experiment. For each fixed value of E, the values of log A for the various experiments were averaged and the root-mean-square deviation was obtained. The activation energy was selected to be that value which yield the smallest root-mean-square deviation and the value of A to be antilog $(\overline{\log A})$. The results are

$$E = 56 \text{ kcal./mole.}$$

$$A = 1.272 \times 10^9 \text{ msec.}^{-1}$$

with a root-mean-square of 0.133 in log A. The Arrhenius expression employing these values is shown as the lower solid line in Figure 3. Also shown are the rate constants for the individual runs. In calculating these points, for each run that value of preexponential constant A was chosen which corresponded to the activation energy 56 kcal./mole. The reaction rate constant was then evaluated for the initial reaction zone temperature (reflected shock) for that run. Strictly speaking, the points do not represent the rate constants for the various runs, since these in fact vary as the run temperatures change. In effect they illustrate the degree of agreement between runs of the calculated values of the preexponential constant A for the fixed activation energy E.

A possibility of error in the above procedures arises from the need to terminate computations at the end of the measured pressure trace, before the gas has cooled completely. The errors in this approximation are estimated to be less than one percentage point in conversion.

Because of the limited number of experiments conducted with propane-hydrogen sulfide mixtures, estimates of Arrhenius parameters are less precise. Fortunately the rate constants are rather insensitive to the activation energy. Figure 3 shows the rate constants obtained by the same procedure as above for an assumed activation energy of 56 kcal./mole. They exceed those for sulfide-free pyrolysis by a factor of about 7.

Also shown for comparison are the results of Kershenbaum (4) obtained in a nonisothermal, flow reactor and an extrapolation of the results of Steacie and Puddington (3) obtained in a batch reactor. The latter were obtained at considerably lower temperatures and higher partial pressures of propane. The agreement between the best activation parameters obtained by these three investigations is quite good. The lack of sensitivity to propane pressure, illustrated by the comparison of the data of Steacie and Puddington with the other data, supports the picture of propane decomposition as a first-order reaction.

Figures 4 to 8 show productions of ethylene, propylene,

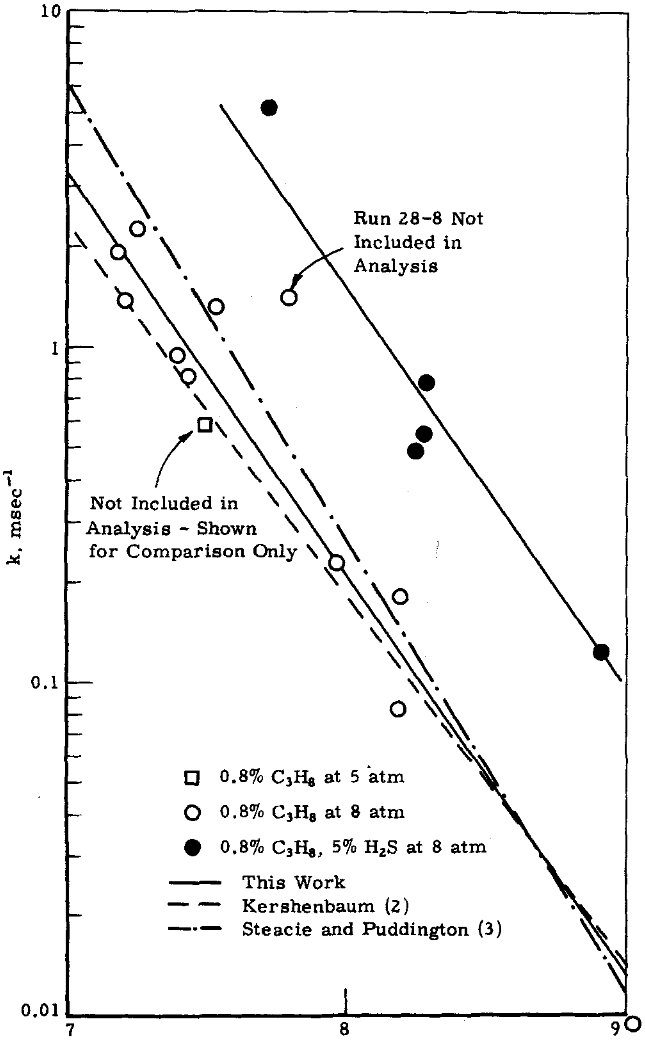

Fig. 3. First-order rate constants for the pyrolysis of propane.

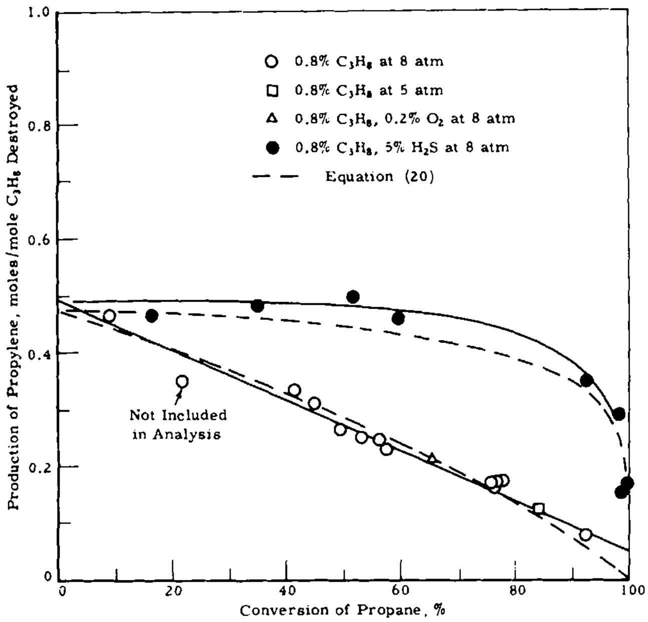

Fig. 4. Production of propylene.

ethane, and methane to be well correlated with conversion. Because higher conversions in these experiments were generally associated with high temperatures, we tried to test sensitivity with respect to both temperature and conversion in a regression analysis of the hydrogen sulfide-free data. The standard error was used as a criterion of fit on twelve data points for each component. Functions linear in conversion, quadratic in conversion, and linear in temperature and conversion were written about the average of the data (56.2% conversion, 1,300°K). Only in the case of ethane did the inclusion of temperature as a second variable produce a better fit than the inclusion of the quadratic term in conversion. Propylene and carbon unsaturates were fit satisfactorily by functions linear in conversion. No attempt was made to fit acetylene due to the small quantities obtained. Certain features of the data are notable:

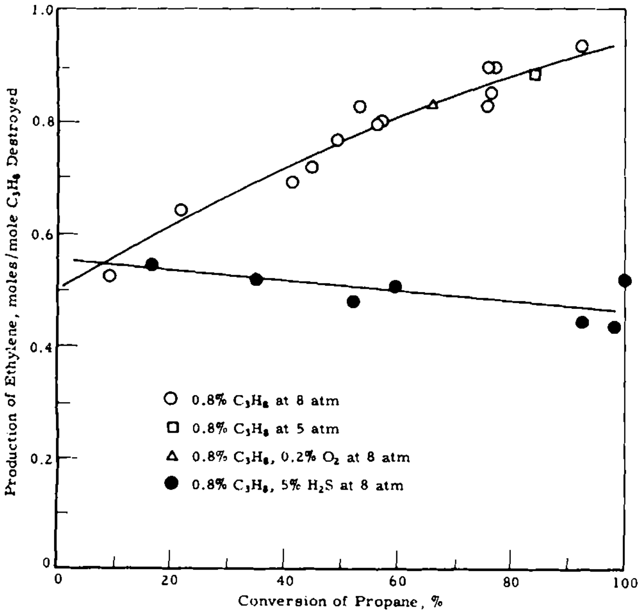

Fig. 5. Production of ethylene.

1. In the absence of hydrogen sulfide, propylene production falls with increased conversion. Production of ethylene and acetylene rises at the expense of propylene, while methane and ethane productions are substantially unchanged.

2. Hydrogen sulfide preserves the initial propylene-ethylene distribution to a fairly high conversion, that is, maintains a high propylene selectivity.

3. Hydrogen sulfide enhances methane formation at the expense of ethane, the combined production being lowered slightly (Figures 7 and 8).

4. Loss of material in the presence of hydrogen sulfide is accomplished almost entirely at the expense of propylene. No analyses were made for the lost material. On the basis of previous work in flames, it is likely that the carbon appears as alkyl sulfides, carbon disulfide, etc.

5. 0.2% oxygen in the argon (1:4 basis propane) has no effect on the selectivity pattern.

6. A change in pressure from 8 to 5 atm. has no effect on the selectivity pattern.

DISCUSSION

The gross features of the pyrolysis can be explained by a free radical mechanism of the type

$$\text{Initiation}\begin{cases} C_3H_8 \rightarrow CH_3\cdot + C_2H_5\cdot & (5)\\ C_3H_8 \rightarrow C_3H_7\cdot + H\cdot & (6)\end{cases}$$

$$R\cdot + C_3H_8 \rightarrow C_3H_7\cdot + RH \tag{7}$$

$$C_3H_7\cdot \rightarrow C_2H_4 + CH_3\cdot \tag{8}$$

$$C_3H_7\cdot \rightarrow C_3H_6 + H\cdot \tag{9}$$

$$R'\cdot + C_3H_6 \rightarrow C_2H_4 \text{ (many steps)} \tag{10}$$

$$C_3H_6 \rightarrow C_2H_4 \text{ (many steps)} \tag{11}$$

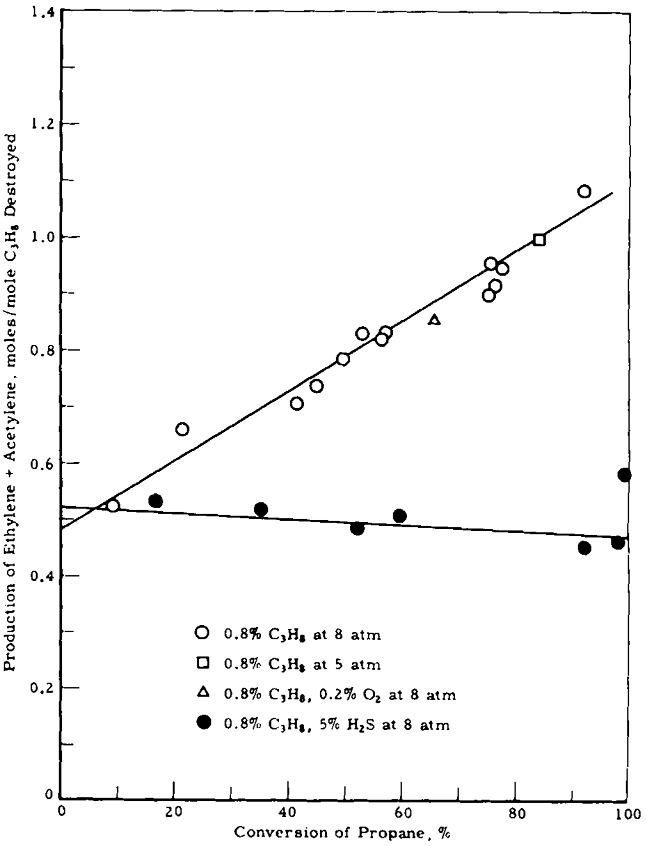

Fig. 6. Production of carbon unsaturates.

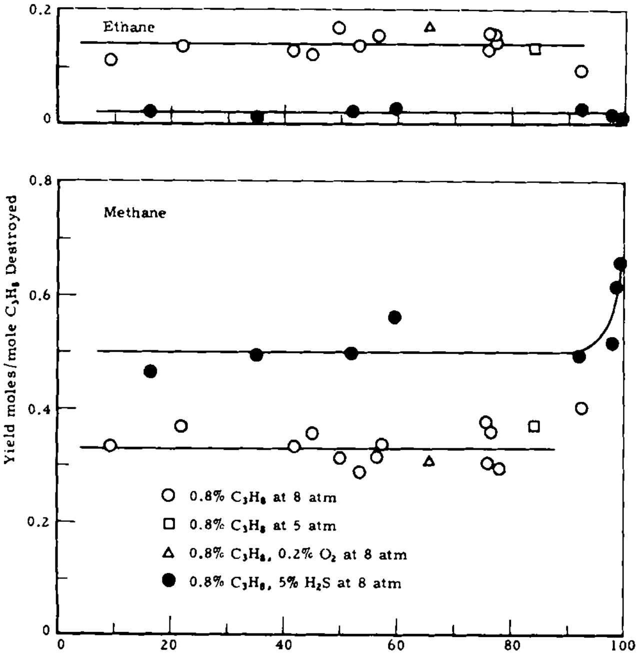

Fig. 7. Production of methane and ethane.

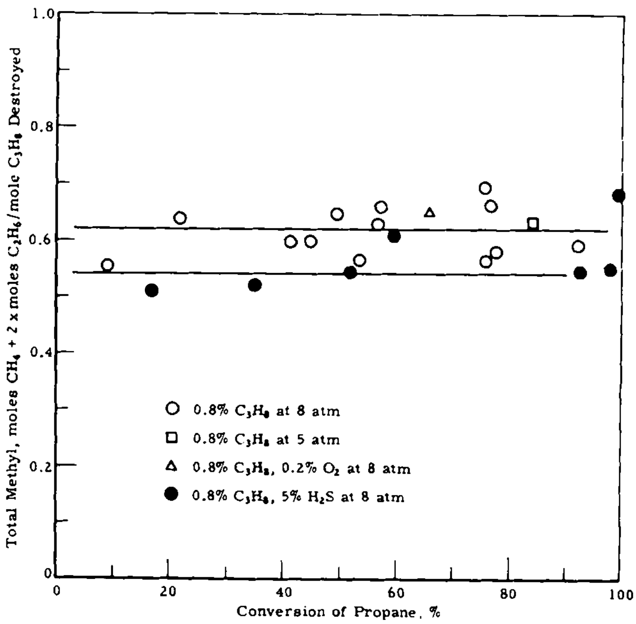

Fig. 8. Total methyl production.

where $R\cdot$ may be any of several radicals, namely, $CH_3\cdot$, $C_2H_5\cdot$, $H\cdot$. By extrapolation to zero conversion, other investigators have concluded that the initial products of the decomposition are hydrogen, methane, ethylene, and propylene in almost equal quantities, independent of temperature or pressure (3). This distribution is consistent with the bulk of the decomposition occurring via reactions (8) and (9) at roughly equal rates, the methyl radical being recovered entirely as methane. Present data for ethylene and propylene agree with these results. Methane selectivity is low, presumably due to the dimerization reaction:

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6 \qquad (12)$$

The sum total of methane and equivalent ethane is actually higher than that expected from ethylene production (compare Figures 5 and 8), perhaps because of the small contribution of the initiation reaction (5). Acetylene presumably arises from decomposition of ethylene in the latter stages of the reaction.

As the reaction proceeds to higher conversions, there is almost stoichiometric conversion of propylene to ethylene plus acetylene. This differs markedly from the behavior observed at lower temperatures (3) where decreased propylene selectivities were accompanied by sharp rises in selectivities for methane and ethane but not for ethylene. More recent data (2) also give an entirely different pattern for propylene decomposition, involving formation of considerable methane and methylacetylene. The details surrounding this discrepancy are not understood. Various free radical schemes for propylene decomposition have been considered but all would require very special relationships between various rate constants to conform to the data. The present data are not extensive enough to justify any one specific mechanism.

Hydrogen sulfide is thought to enter the reaction scheme in at least two places. By producing increased numbers of and/or more effective free radicals, namely, $H\cdot$ and $HS\cdot$, it accelerates the decomposition of propane to propyl. That the initial ethylene-propene ratio is unchanged implies that the sulfide does not enter into the decomposition of the propyl radical. It does apparently change the fate of the methyl radical. The enhancement of methane at the expense of ethane probably occurs as a result of siphoning off of the methyl radical via

$$CH_3\cdot + H_2S \rightarrow CH_4 + HS\cdot \quad \Delta H \sim -13\,\text{kcal.} \qquad (13)$$

The sum total of methane and equivalent ethane drops slightly in the presence of hydrogen sulfide (Figure 8) to a value in keeping with the initial production of ethylene (compare Figures 8 and 5). Presumably this results from decreased relative importance of initiation reaction (5) in the presence of hydrogen sulfide.

The ability of hydrogen sulfide to maintain the initial product distributions to high conversions can be explained largely from its enhancement of the rate of propyl radical formation relative to the other reactions. Returning to the gross scheme outlined in Equations (5) to (11), one may write

$$\frac{d(C_3H_8)}{dt} = -(k_5 + k_6)(C_3H_8) - k_7(R\cdot)(C_3H_8) \qquad (14)$$

$$\frac{d(C_3H_7\cdot)}{dt} = k_6(C_3H_8) + k_7(R\cdot)(C_3H_8) - (k_8 + k_9)(C_3H_7\cdot) \qquad (15)$$

$$\frac{d(C_3H_6)}{dt} = k_9(C_3H_7\cdot) - k_{10}(R'\cdot)(C_3H_6) - k_{11}(C_3H_6) \qquad (16)$$

In deriving Equation (15) the assumption is made that $R'\cdot$ does not include significant quantities of propyl radical. The usual steady state assumption concerning the propyl radical is

$$\frac{d(C_3H_7\cdot)}{dt} = 0$$

Equations (14) to (17) yield, after some manipulations

$$\frac{L(C_3H_6)}{d(C_3H_8)} = -\left(\frac{k_8}{k_8 + k_9}\right)\left[\frac{k_6 + k_7(R\cdot)}{k_5 + k_6 + k_7(R\cdot)}\right] + \left[\frac{k_{10}(R'\cdot) - k_{11}}{k_5 + k_6 + k_7(R\cdot)}\right]\frac{(C_3H_6)}{(C_3H_8)} \qquad (18)$$

$$\frac{d(C_3H_8)}{dt} = -[k_5 + k_6 + k_7(R\cdot)](C_3H_8) \qquad (19)$$

The chemistry is not defined well enough to allow us to make a definite statement as to the nature of the radicals $R\cdot$ and $R'\cdot$ which may be any or all of $H\cdot$, $CH_3\cdot$, $C_2H_5\cdot$, etc.

Note at this point that the use of first-order kinetics to describe the decomposition of propane implies that the concentration of $R\cdot$ remains constant throughout the decomposition. Steacie (*4*, pp. 101-105) has discussed the order of such decomposition schemes as they are affected by the natures of the initiation and termination reactions. For our purposes the employment of first-order kinetics leads to the conclusion that the first term of Eq. (18) is constant. As will be noted later, the value of k_5 is probably small compared with $k_6 + k_7(R\cdot)$, so that the argument is somewhat academic.

The behavior of the second term is less certain since, once again, the nature of $R'\cdot$ and its recombination scheme are not known. It seems likely from chemical arguments that the free radical decomposition of propylene is less important than its molecular decomposition. The most likely free radical obtained from propylene is the allyl radical which is resonance stabilized. It will probably not react further except by hydrogen abstraction to reform propylene for no net reaction of propylene via this path. This forms one basis on which to conclude tentatively that the coefficient of the second term of Eq. (18) is also constant. The resulting equation then becomes Bernoulli's equation and is readily integrated. In terms of selectivity for propylene and conversion, there results

$$S = \frac{1}{(1-\alpha)(1+\beta)}\left[\frac{(1-X)^{\alpha}-(1-X)}{X}\right](\alpha \neq 1) \tag{20}$$

The propylene data are compared with this expression in Figure 4. In preparing this figure a least-squares fit of the sulfide free data was used to obtain the values $\alpha = 1.45$ and $\beta = 1.09$.

The effect of hydrogen sulfide is to increase the numbers and kinds of free radicals so as to accelerate the decomposition of propane. In terms of Equations (18) and (19) this corresponds to

1. A sevenfold increase in $k_5 + k_6 + k_7(R\cdot)$.
2. No significant change in the first term of Equation (18) (k_5 is small).
3. A sevenfold decrease in the second term of Equation (18).

For the sulfide-accelerated decomposition the parameters in Equation (21) become $\alpha = 0.207$ and $\beta = 1.09$. This equation appears as well in Figure 4 and reproduces the sharp drop in propylene selectivity above 90% conversion. The failure of ethylene conversion to rise an equivalent amount implies that the heavy loss of material at high conversions (Table 1) occurs at the expense of ethylene rather than propylene.

Clearly other arguments and schemes may be advanced to explain the data, and the reasoning above is a consistency rather than a necessity type of argument. The principal points which are asserted are:

1. The apparent increase in propylene selectivity on sulfide addition is explainable solely in terms of the acceleration of the rate of propane decomposition.

2. On this basis the loss of light hydrocarbon material at high conversions occurs at the expense of ethylene rather than of propylene.

SUMMARY

1. The pyrolysis of propane in the temperature range 830° to 1,180°C. can be described as a first-order reaction.

2. The distribution of pyrolysis products can be described in a gross manner by a free radical mechanism involving parallel decompositions to propylene plus hydrogen and ethylene plus methane, followed by decomposition of propylene to ethylene. The product distribution is not consistent with the results of other workers.

3. Hydrogen sulfide accelerates the pyrolysis. The change in ethylene-propylene distribution can be explained solely on the basis of this accelerated rate.

NOTATION

A = preexponential Arrhenius parameter, sec.$^{-1}$
C_p = heat capacity, cal./(mole)(°K.)
E = Arrhenius activation energy, cal./mole
ΔH_R = enthalpy of reaction, cal./mole
k_i = rate constant in reaction *i*, sec.$^{-1}$
n = mole quantity of propane, moles
P = pressure, cal./liter
R = ideal gas constant, cal./mole
S = selectivity for propylene
t = time, sec.
T = absolute temperature, °K.
V = ideal gas volume, liter/mole
X = conversion of propane
α = coefficient of the second term in Equation (19)
β = k_8/k_9

LITERATURE CITED

1. Glick, H. S., W. Squire, and A. Hertzberg, "Fifth Symposium (International) on Combustion," pp. 393-402, Reinhold, New York (1955).
2. Kershenbaum, L. S., Ph.D. dissertation, Univ. Michigan, Ann Arbor (1964).
3. Steacie, E. W. R., and I. E. Puddington, *Can. J. Res.*, **B16**, 411-419 (1938).
4. Steacie, E. W. R., "Atomic and Free Radical Reactions," 2 ed., Reinhold, New York (1954).
5. "JANAF Thermochemical Data," Dow Chemical Co., Midland, Michigan.

APPENDIX

It is asserted that the initiation reaction (5) is unimportant relative to the sum of the initiation reaction (6) and the radical-induced decomposition (7). Some idea of its importance can be deduced from the relative production rates of methane, ethane, and ethylene. If we make the reasonable assumption that all the methyl radicals produced in (5) and (8) and up as methane or ethane, we can write the following relationships valid for the initial stages of the decomposition:

$$\frac{d\,(\text{total methyl})}{dt} = 3\,k_5\,(C_3H_8) + k_8\,(C_3H_7\cdot) \tag{21}$$

$$\frac{d\,(C_2H_4)}{dt} = k_8\,(C_3H_7\cdot) \tag{22}$$

$$\frac{d\,(\text{total methyl})}{d\,(C_2H_4)} = \frac{3k_5}{k_8}\,\frac{(C_3H_8)}{(C_3H_7\cdot)} + 1 \tag{23}$$

The ratio $(C_3H_8)/(C_3H_7\cdot)$ is obtained from Equation (15) and there results

$$\frac{d\,(\text{total methyl})}{d\,(C_2H_4)} = \frac{3k_5}{[k_6 + k_7\,(R\cdot)]}\,(1+\beta) + 1 = \gamma \tag{24}$$

From a comparison of Figures 4, 5, and 8 it is apparent that $\beta \sim 1.09$ and $\gamma \sim 1.24$, so that we obtain

$$\frac{k_5}{k_6 + k_7\,(R\cdot)} \sim 0.038 \tag{25}$$

Manuscript received May 5, 1966; revision received January 20, 1967; paper accepted January 23, 1967.