THE THERMAL DECOMPOSITION OF ETHANE PART I. INITIATION AND TERMINATION STEPS

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ABSTRACT

The rates of production of methane and butane in the pyrolysis of ethane have been measured over the temperature range 550-620 °C and at pressures of 40-600 mm. At high pressure the rates of formation of both products were first order in ethane, but below 200 mm the first-order rate coefficients decreased. The ratio of methane to butane was consistent with the interpretation that methane is a measure of the initiation reaction and that the combination and disproportionation of ethyl radicals is the main termination step. The order of the decomposition of the ethyl radical with respect to ethane varied between 0.38 and 0.59. The results are discussed in terms of the mechanism of the overall process.

INTRODUCTION

The initiation and termination steps in the chain decomposition of ethane have been the subject of much controversy. There is general agreement that the rate is first order with respect to ethane and that hydrogen atoms and ethyl radicals are the chain carriers. The mechanisms proposed generally include the following reactions.

[1]	$C_2H_6 \rightarrow 2CH_3$
[2]	$\mathrm{CH}_3 + \mathrm{C}_2\mathrm{H}_6 \rightarrow \mathrm{CH}_4 + \mathrm{C}_2\mathrm{H}_5$
[3]	$\mathrm{C_2H_5}\rightarrow\mathrm{C_2H_4}+\mathrm{H}$
[4]	$\mathrm{H} + \mathrm{C_2H_6} \rightarrow \mathrm{H_2} + \mathrm{C_2H_5}$
[5 <i>a</i>]	$C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$
[5 <i>b</i>]	$\rightarrow C_2H_4 + C_2H_6$
[6]	$H + C_2 H_5 \rightarrow C_2 H_6$
[7]	$CH_3 + C_2H_5 \rightarrow C_3H_8$

Rice and Herzfeld (1) pointed out that termination by reaction [6] would lead to firstorder kinetics, as observed. Küchler and Theile (2), however, showed that the rate was increased on addition of inert gases and suggested that the initiation step was a secondorder process and that termination occurred by the combination of ethyl radicals. This mechanism also gave first-order kinetics. In an experimental and theoretical examination of the problem, Laidler and Wojciechowski (3) concluded that the Küchler-Theile mechanism was more consistent with the evidence then available. For example, the concentration of ethyl radicals was shown to be much greater than that of hydrogen atoms (4) so that termination by combination of ethyl radicals should predominate. Also, the Küchler-Theile mechanism predicted an activation energy for the decomposition close to that observed, and a change in the order of the decomposition to 3/2 in the regions of temperature and pressure in which this change was found.

More recently, however, several investigations of the initial rate of formation of methane (5-8) have shown that this reaction is first order with respect to ethane, indicating that the initiation step is a first-order process. This fact has been reconciled with the other evidence in various ways. Davis and Williamson (6), whose experiments were done in a flow system at high temperatures (676–775 °C), found that the rate of formation

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of methane was slightly pressure-dependent. They favored the combination of ethyl radicals as the chain-ending step and suggested that the pressure sensitivity of both the initiation step and the decomposition of the ethyl radical combined to give first-order kinetics, which were, at any rate, only roughly obeyed under their conditions. Quinn (7) made this suggestion more specific by proposing that when the overall rate and the rate of production of methane were exactly first order, the rate constant for decomposition of the ethyl radical should be proportional to the square root of the pressure. Evidence from a previous study of the pyrolysis of n-butane (9) supported this view. Gordon (8) found a considerable surface dependence of the rate and suggested that one of the termination reactions was heterogeneous. This probably involved hydrogen atoms, because of their high diffusion coefficient.

The present experiments were undertaken to measure the rate of production of butane and, by a comparison with the rate of production of methane, to establish whether this is the main termination product.

EXPERIMENTAL

Apparatus The decome

The decomposition was studied in a conventional static system. The reaction vessel was a quartz sphere of 511.5 cc with S/V ratio of 0.6 cm⁻¹ enclosed in an electrically heated steel cylinder about 2 cm thick. The temperature of the vessel was controlled with a Thermoelectric thermoregulator. When evacuated the temperature could be maintained within 0.2° but because of fluctuations in temperature on admission of reactant, especially at high pressures, the temperature during an experiment was precise only to 0.5°. A reaction vessel packed with silica tubes was used to increase the S/V ratio to 9.4 cm⁻¹, an increase of 15 times that of the unpacked vessel. Both vessels were treated with hot nitric acid followed by several washings with distilled water. Gases to be mixed prior to decomposition were condensed into a large flask on an inner-sealed cold finger. When the finger was warmed rapidly the gases were mixed by convection.

Reagents

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Phillips Research Grade ethane was distilled from trap-to-trap several times and finally degassed at -160 °C.

Procedure and Analysis

Before each experiment the system was evacuated to a pressure lower than 10^{-4} mm. At the end of an experiment the products and reactant were removed through a series of traps, which were, in order, a spiral trap, a Le Roy still, a conventional trap, and a final spiral trap, followed by a Toepler pump and gas burette. A mercury diffusion pump between the last two traps aided collection of the non-condensable gases. Initially all traps were cooled with liquid nitrogen. When most of the non-condensable gases had been collected in the gas burette, the first spiral trap was warmed to room temperature and the Le Roy still was warmed to -162 °C. Final traces of occluded non-condensable gases were then collected while most of the ethane distilled into the conventional trap. Butane remained in the Le Roy still and was analyzed by gas chromatography on a 12 ft column of hexanedione on Firebrick maintained at 0 °C. Careful checks of the distillation showed that losses of butane were never more than 10% and could be reliably corrected for. In experiments with carbon dioxide, an additional trap filled with ascarite removed the carbon dioxide before condensation in the Le Roy still.

The mixture of methane and hydrogen collected in the gas burette was analyzed by combustion of hydrogen in a copper oxide furnace maintained at 280 °C. Attempts to separate ethylene from the noncondensable gases by using a trap packed with copper filings maintained at -196 °C resulted in loss of methane, and the packing was finally abandoned. Instead, traces of ethylene were collected in the Toepler pump with the hydrogen and methane, but the gases were admitted to the combustion furnace through a liquid nitrogen trap. The concentration of ethylene in the furnace was then negligible. When combustion of hydrogen was complete the gases were expanded into the large bulb of the Toepler pump, isolated from the combustion furnace, and measured in the gas burette. An amount of ethylene equivalent to the saturated vapor pressure at -196 °C in the Toepler bulb was thus collected in the gas burette, and correction for this amount was made to the final measurement of methane. This correction was not more than 10% of the amount of methane. The yield of hydrogen was obtained by subtracting the yield of methane from the total non-condensable gases.

RESULTS

The yields of hydrogen, methane, and butane were measured as a function of reaction time over the temperature range 550–620 °C and the pressure range 40–600 mm. The

measurements of hydrogen and methane were extended to the range 640-726 °C over a lower pressure range. Initial rates of hydrogen production were obtained by extrapolation of plots of the rate against time. From 400 to 150 mm the order of hydrogen production was 1.0. At higher pressures a slight decrease in order was observed, while at lower pressures the order increased. This continuous change in order of the hydrogen production is shown in Fig. 1, in which the complete temperature range is represented. The first-order rate constant could be represented by the following expression.

$$\log k (s^{-1}) = (16.22 \pm 0.11) - \frac{77\ 600 \pm 600}{2.303RT}$$

Typical plots of methane yield as a function of time are shown in Fig. 2. The rate of production of methane was constant only in the initial stages of the decomposition and increased at all temperatures as secondary reactions became important. The initial rate was not obtained directly from plots such as Fig. 2, but from an extrapolation to



FIG. 1. Log rate of hydrogen production against log ethane pressure: O, for unpacked vessel; +, for packed vessel. FIG. 2. Yield of methane as a function of time at 584.7 °C.

zero time of the rate as a function of time. This procedure, which is described in Part III (23), was particularly important at high temperatures where secondary reactions occur at very low conversions. The order of the rate of production of methane with respect to ethane was 1.0 above $\sim 200 \text{ mm}$ and is illustrated in Fig. 3. The falloff in the first-order rate coefficient is discussed in detail in Part II (23). First-order rate constants were calculated from the equation

$$k_1 = \frac{\frac{1}{2}R^0_{\text{CH4}}}{[\text{C}_2\text{H}_6]}$$

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FIG. 3. Log rate of methane production against log ethane pressure: O, for unpacked vessel; +, for packed vessel. FIG. 4. Arrhenius plot of first-order rate constant, k_1^{∞} , for rate of methane production: \times , ref. 8; \triangle , ref. 9; O, present results.

and are listed in Table I. The Arrhenius plot of the first-order constants is shown in Fig. 4 together with the measurements of Quinn (7) and Gordon (8). The following relation was found.

$$\log k_1 (s^{-1}) = (16.00 \pm 0.066) - \frac{86\,000 \pm 370}{2.303RT}$$

At low temperatures the kinetics of butane production followed a similar pattern to that of methane production, the rate increasing from the initial value at about the same conversion. At 585 °C and above the rate decreased as the reaction time increased. Typical plots of yield as a function of time are shown in Fig. 5. Again, initial yields were obtained by extrapolation of rate vs. time curves. The order of butane production was 1.0 at high pressures but increased as the pressure was lowered. The double logarithmic plot is shown in Fig. 6. The Arrhenius plot of the first-order rate constants gave an activation energy of 89.8 kcal/mole.

The ratio $\frac{1}{2}R^{0}_{CH_{4}}/R^{0}_{C_{4H_{10}}}$ varied from 1.3 to 1.8 and is included in Table I. If methane is a measure of the initiation step and butane of the termination step and if the ratio of disproportionation to combination for ethyl radicals is 0.15 (10), then the ratio $\frac{1}{2}R^{0}_{CH_{4}}/R^{0}_{C_{4H_{10}}}$ is 1.15.

If hydrogen is formed only by reactions [3] and [4] and butane only by combination of ethyl radicals then

$$\frac{R^{0}_{H_{2}}}{(R^{0}_{C_{4}H_{10}})^{1/2}} = \frac{k_{3}}{k_{5a}^{1/2}} \cdot$$

A plot of log $\{R^{0}_{H_{2}}/(R^{0}_{C_{4}H_{10}})^{\frac{1}{2}}\}$ against log $[C_{2}H_{6}]$ is shown in Fig. 7. If it is assumed that k_{5a} is independent of pressure, the slopes of these curves give the order of reaction

<i>T</i> (°C)	<i>Р</i> ⁰ с _{2Н6} (mm Hg)	$\frac{R^0_{\rm CH_4}}{2[\rm C_2H_6]_0}$	$\frac{\underline{R^{0}_{CH_{4}}}}{2R^{0}_{C_{4}H_{10}}}$
549.7	592.8401.5299.7164.797.467.3	1.43 1.44 1.41 1.34 1.28 1.15	1.351.591.531.571.721.55
570.5	590.5 400.0 236.0 199.7 153.4 96.0 78.3 59.4 40.1	5.48 5.19 5.12 5.13 4.92 4.63 4.50 3.96	1.67 1.55 1.73 1.61 1.62 1.80 1.68 1.68 1.63
584.7	$594.1 \\ 498.8 \\ 341.8 \\ 257.5 \\ 168.2 \\ 92.4 \\ 62.4$	$12.7 \\ 12.7 \\ 12.5 \\ 12.3 \\ 12.5 \\ 11.4 \\ 10.4$	$1.44 \\ 1.44 \\ 1.46 \\ 1.46 \\ 1.51 \\ 1.48 \\ 1.63$
599.7	500.6402.1298.9203.199.968.441.0	$29.5 \\ 29.3 \\ 29.6 \\ 29.1 \\ 26.7 \\ 24.6 \\ 22.4$	$1.40 \\ 1.40 \\ 1.49 \\ 1.59 \\ 1.69 \\ 1.76 \\ 2.15$
620,3	$\begin{array}{c} 448.3\\ 335.6\\ 236.1\\ 209.8\\ 124.5\\ 87.6\\ 57.9\\ 40.7\end{array}$	$\begin{array}{c} 88.8\\ 89.7\\ 89.9\\ 84.3\\ 83.9\\ 78.2\\ 73.1\\ 66.5\end{array}$	$1.18 \\ 1.23 \\ 1.27 \\ 1.20 \\ 1.47 \\ 1.43 \\ 1.63 \\ 1.76$

TABLE I First-order rate coefficients for rate of methane production in units of s^{-1}

[3] with respect to ethane. This varied from 0.38 at low temperatures and high pressures to 0.59 at high temperatures and low pressures. The activation energy for the decomposition of the ethyl radical, if the combination of ethyl radicals involves no activation energy, is 32.7 ± 1.5 kcal/mole. No trend was observed with pressure.

Rates of hydrogen, methane, and butane production were measured at 585 °C in the presence of various pressures of carbon dioxide. On addition of 100 mm of carbon dioxide to 100 mm of ethane, the rates of methane and butane production were unchanged but the rate of hydrogen production increased by about 20%.

Rates of formation of products measured using the packed reaction vessel are compared with those from the unpacked vessel in Figs. 1, 3, 6, and 7. The rate of methane production was unaffected by the increase in S/V ratio, but the yields of both butane and hydrogen decreased. The effect was greatest at the lower temperatures and pressures, as would be expected for a surface reaction. The order of both butane and hydrogen production increased slightly.

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Yield of butane as a function of time at 585 °C. Log rate of butane production against log ethane pressure: O, for unpacked vessel; +, for FIG. 5. Yie FIG. 6. Lo packed vessel.

DISCUSSION

The present results largely confirm the mechanism of the decomposition proposed by Davis and Williamson (6) and by Quinn (7). In particular, the measurement of the production of butane supports the combination of ethyl radicals as the main termination step.

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We have assumed that the initial decomposition of the ethane molecule occurs by the rupture of the C—C bond to give two methyl radicals. An alternative mode of initiation to give methane and a methylene radical has been suggested (11)

[1a]

$$C_2H_6 \rightarrow CH_4 + CH_2$$

but from the present results this appears less likely than reaction [1]. In the subsequent reaction of the methylene radical with ethane, the excited molecule of propane formed would either be stabilized or dissociate into radical fragments, probably $CH_3 + C_2H_5$. By comparison with the reaction of methylene radicals with methane (12), it may be deduced that stabilization would be dependent on pressure in the range of the present experiments. If some of the "hot" propane formed is stabilized, then methane is formed without the production of an ethyl radical and hence without the formation of butane. This would give a high ratio of methane to butane, as actually found, but would show a marked increase with increasing pressure, whereas the observed ratio decreased as the pressure increased. It is very unlikely that formation of propane by reaction of methylene with ethane would be independent of pressure in the range covered by the present experiments. Reaction [1*a*] must therefore be at most only a minor mode of dissociation of the ethane molecule.

The rate of production of methane is a measure of the rate of reaction [1] only if all methyl radicals react with ethane and none are lost by termination. The most likely termination step involving methyl radicals is reaction [7] and the relative rates of reaction [2] and [7] may be calculated from the following equation.

$$\frac{\text{Rate [7]}}{\text{Rate [2]}} = \frac{k_7 (R^0_{C_4 \text{H}_{10}})^{1/2}}{k_{52}^{1/2} k_2 [C_2 \text{H}_6]}$$

Inserting the values $k_2 = 10^{11.20} e^{-10400/RT}$ (13), $k_{5a} = 2.0 \times 10^{13}$ (14), and $k_7 = 4 \times 10^{13}$ in the units cc mole⁻¹ s⁻¹, we obtain for 100 mm ethane $R_7/R_2 = 5.0 \times 10^{-3}$ at 550 °C and 2.8×10^{-2} at 620 °C. The temperature coefficient of k_5 has been ignored in these and later calculations because of the uncertainty involved in the long extrapolation. These ratios are therefore upper limits since an activation energy of 2 kcal/mole causes an increase in k_5 of almost a factor of 10 at 550 °C. In the present experiments it is thus unlikely that methyl radicals are involved in termination, and the first-order production of methane shows that the dissociation of ethane into two methyl radicals is a firstorder process above about 200 mm in the temperature range 550–620 °C.

In Fig. 4 the Arrhenius plot of k_1 is compared with two recent measurements in the same temperature range. The absolute values for k_1 agree very well at temperatures in the neighborhood of 570 °C, but some divergence at the higher and lower ranges caused a considerable deviation in the activation energies. We feel that the method of extrapolation which was used in the present experiments at each pressure and temperature to obtain the initial rate of methane production gives rate constants more reliable than those obtained by Quinn, and that his activation energy is consequently too high.

The errors quoted in the present results are the probable errors obtained by a leastsquares analysis of the data. The systematic errors are undoubtedly much larger, but because of the difficulty in estimating these quantitatively we have not attempted to state the total error limits. Recent measurements of the Arrhenius parameters of k_1 are summarized in Table II.

Arrhonius parameters of h

Reference	Temp. range (°C)	$\log A$ (s ⁻¹)	E (kcal/mole)		
(5) (6) (7) (8) Present results	$766-836 \\ 675-770 \\ 564-608 \\ 475-600 \\ 550-620 \\$	$\begin{array}{r} 14.85 - 15.7 \\ 16.29 \\ 17.45 \pm 0.82 \\ 14.5 \\ 16.00 \pm 0.066 \end{array}$	$\begin{array}{c} 85{-}89\\ 86{.}0\\ 91{.}7\\ 81{.}0\\ 86{.}0 \end{array}$		

For a reaction which involves the rupture of one bond and for which the reverse combination of radicals has no activation energy, the activation energy may be related to the bond dissociation energy in the following general way (15).

$$D \leqslant E \leqslant D + RT$$

From the present results and from the values (16) for ΔH_t at 0 °K given in the first column below, one may calculate the values given in the second column.

$\Delta H_{\rm f}({\rm C_2H_6}) = -16.517 \text{ kcal/mole}$	$D(CH_3 - CH_3) = 85.0 \pm 0.5 \text{ kcal/mole}$
$\Delta H_{\rm f}({\rm CH_4}) = -15.987 \text{ kcal/mole}$	$\Delta H_{\rm f}({\rm CH}_3) = 34.2 {\rm kcal/mole}$
$\Delta H_{\rm f}({\rm H}) = 51.620 {\rm kcal/mole}$	$D(CH_3-H) = 102 \text{ kcal/mole}$

The observed order with respect to total pressure of the decomposition of the ethyl radical confirms previous suggestions (6, 7) that in this range of temperature and pressure the ethyl radical is roughly halfway into its second-order region. The activation energy for decomposition is in agreement with that found by Purnell and Quinn (9) if an activation energy of 10.4 kcal/mole (17) is taken for the abstraction of hydrogen from butane by the ethyl radical, instead of 15.2 kcal/mole as used by these authors. As expected, the activation energy of 32.7 ± 1.5 kcal/mole is lower than the activation energy of 39.5 kcal/mole (18) for the first-order decomposition. The relation of this decrease to the number of effective oscillators in the ethyl radical is discussed in Part II (23).

In agreement with previous results (7, 8), the rate of methane production was unchanged by increasing the S/V ratio by a factor of about 15. It seems well substantiated that the initiation reaction is the homogeneous dissociation of ethane. The decrease in the rate of hydrogen production, however, would suggest an increased rate constant for the termination process in the packed vessel. This would lower the radical concentration, thus decreasing the overall rate, while the rate of removal of radicals would still equal the rate of initiation. Since butane production was not enhanced, but was in fact decreased, this heterogeneous termination does not yield butane and thus probably does not involve an adsorbed ethyl radical. The adsorbed species must therefore be a hydrogen atom which may become attached to the surface by reaction with an ethyl radical as well as by direct adsorption.

[8]
$$H + S \rightleftharpoons H - S$$

[9] $C_2H_5 + S \rightarrow C_2H_4 + H - S$

Termination may then take place as follows.

The surface reaction becomes more predominant at low pressures and its rate is thus probably dependent in some way on the homogeneous concentration of hydrogen atoms.

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Although in the present experiments the concentration of hydrogen atoms is always lower than that of ethyl radicals, the rate of reaction [8] may be faster than that of [9] if an appreciable activation energy is required for the latter. This is quite reasonable in view of the strength of the bond broken. Termination may occur by either reaction [10] or [11], since the rate constant of reaction [10] may be much larger than that of reaction [11] and may outweigh the difference in concentration of H atoms and ethyl radicals. Our results therefore favor the occurrence of reaction [8] followed by reactions [10] or [11].

The magnitude of the effect of the surface on the rate was smaller than that observed by Gordon (8). The heterogeneous reaction may be very sensitive to the nature of the surface, which in turn may be a function of the treatment of the vessel prior to the experiments or even of the purity of the quartz of which the vessel is made. For these reasons it may be difficult to obtain quantitative agreement for the surface reaction from one laboratory to another.

The fact that in both vessels the ratio of methane to but ane is higher than that expected on the basis of reactions [1] to [5] suggests that a second termination reaction, which does not produce butane, makes a minor contribution. The most probable reaction is reaction [6], but this interpretation is unlikely for two reasons. Calculation of the relative concentrations of hydrogen atoms and ethyl radicals indicates that the concentration of the former is too low to make a significant contribution to the termination, unless the rate constant for reaction [6] is much greater than for reaction [5]. The ratio of hydrogen atoms to ethyl radicals is given by $k_3/k_4[C_2H_6]$, and values for k_3 may be taken from Fig. 7 with $k_{5a} = 2.0 \times 10^{13}$ cc mole⁻¹ s⁻¹ (14). Using Berlie and Le Roy's measurement of $k_4 = 10^{12.53} e^{-6800/RT}$ cc mole⁻¹ s⁻¹ (19) at 100 mm ethane $k_3/k_4[C_2H_6] =$ 7.0×10^{-3} at 550 °C and 3.0×10^{-2} at 620 °C. With a recent measurement of $k_4 =$ $10^{14 \cdot 12} e^{-9700/RT} \text{cc} \text{ mole}^{-1} \text{s}^{-1}$ (20) these ratios are slightly lower. To account for the ratios of methane/butane of 1.7, however, the percentage termination by a reaction other than [5] may be shown to be 33% and for a ratio of 1.4, 20%. Furthermore, even if the calculated values were in error to the extent that at 550 °C reaction [6] could account for about 25% of the termination, the relative temperature coefficients of k_3 and k_4 are such that at 620 °C hydrogen atoms should be the predominant radical and termination should be largely by [6]. The trend, however, in the ratio of methane/butane is in the reverse direction and at 620 °C and high pressures the ratio is exactly as predicted.

Another possible explanation may be that the ratio of disproportionation/combination of 0.15 for ethyl radicals, measured in a temperature region lower than the present experiments, is not the correct ratio under the conditions of these experiments. It seems unlikely, however, that the activation energy difference between the combination and disproportionation reactions would be more than 1 kcal/mole. This was the upper limit suggested by Ivin and Steacie (21). This difference raises the ratio k_{5b}/k_{5a} to 0.27 at 550 °C, which is not sufficient to account for the ratios in Table I.

It seems probable that a heterogeneous termination may contribute to a sufficient extent in the unpacked vessel to account for the ratios of methane/butane. This would necessitate a non-linear extrapolation of the rate of butane production as a function of S/V ratio, the rate rising steeply towards zero S/V ratio to give the required rate of butane production. Such a curve was found by Voevodsky (22) in a study of the decomposition of propane in vessels packed with various amounts of tubing. The heterogeneous reaction would be consistent with the trend of less participation at high temperatures

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and high pressures. It is worth noting that this discrepancy between the rates of production of methane and butane affects neither the calculation of k_3 nor the conclusions regarding the order of reaction [3] with respect to ethane, provided only that the yield of butane gives a measure of the concentration of ethyl radicals and that production of hydrogen from possible termination steps is negligible compared to that from reaction [4].

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REFERENCES

 F. O. RICE and K. F. HERZFELD. J. Am. Chem. Soc. 56, 284 (1934).
 L. KÜCHLER and H. THEILE. Z. Physik. Chem. B, 42, 359 (1939).
 K. J. LAIDLER and B. W. WOJCIECHOWSKI. Proc. Roy. Soc. London, Ser. A, 260, 91 (1961).
 E. W. R. STEACIE. Atomic and free radical reactions. Reinhold Publishing Corp., New York. 1954.
 C. H. LEIGH, M. SZWARC, and J. BIGELEISEN. J. Am. Chem. Soc. 77, 2193 (1955).
 H. G. DAVIS and K. D. WILLIAMSON. Fifth World Petroleum Congress, 1959. Section IV, p. 37.
 C. P. QUINN. Proc. Roy. Soc. London, Ser. A, 275, 190 (1963).
 A. S. GORDON. C.I.C. Symposium on the Kinetics of Pyrolytic Reactions, Ottawa, September 1964.
 J. H. PURNELL and C. P. QUINN. Proc. Roy. Soc. London, Ser. A, 270, 267 (1962).
 A. F. TROTMAN-DICKENSON and J. A. KERR. Progress in reaction kinetics. Vol. I. Pergamon Press, Ltd., London. 1961. A. F. TROTMAN-DICKENSON and J. A. NERK. Frogress in feaction kinetics. vol. 1. regument reas, Ltd., London. 1961.
 C. J. DANBY, B. C. SPALL, F. J. STUBBS, and C. N. HINSHELWOOD. Proc. Roy. Soc. London, Ser. A, 218, 450 (1953).
 J. A. BELL and G. B. KISTIAKOWSKY. J. Am. Chem. Soc. 84, 3417 (1962).
 A. F. TROTMAN-DICKENSON and E. W. R. STEACHE. J. Chem. Phys. 19, 329 (1951).
 A. SHEPP and K. O. KUTSCHKE. J. Chem. Phys. 26, 1020 (1957).
 Swarc. Chem. Rev. 47, 75 (1950).
 Selected values of physical and thermodynamic properties of hydrocarbons. American Petroleum In-

M. SZWARC. Chem. Rev. 47, 75 (1950).
 Selected values of physical and thermodynamic properties of hydrocarbons. American Petroleum Institute of Research Project, Carnegie Press. 1953.
 P. J. BODDY and E. W. R. STEACIE. Can. J. Chem. 38, 1576 (1960).
 S. BYWATER and E. W. R. STEACIE. J. Chem. Phys. 19, 326 (1951).
 M. R. BERLIE and D. J. LE ROY. Discussions Faraday Soc. 14, 50 (1953).
 R. R. BALDWIN and A. MELVIN. J. Chem. Soc. 1785 (1964).
 K. J. IVIN and E. W. R. STEACIE. Proc. Roy. Soc. London, Ser. A, 208, 25 (1951).
 V. V. VOEVODSKY. Trans. Faraday Soc. 55, 65 (1959).
 M. C. LIN and M. H. BACK. The thermal decomposition of ethane. Parts II and III. To be published.

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