[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

The Pyrolysis of Ethane[1]

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Introduction

Previous kinetic studies of the decomposition of ethane made by Pease[4] and by Marek and McCluer[5] have shown that the decomposition

$$C_2H_6 = C_2H_4 + H_2$$

is a homogeneous, first-order reaction in its early stages. The later stages of the reaction have not been studied by these workers, and the production of methane has not been investigated. The experiments of Travers and his associates[6-8] on these latter points seem to be distorted seriously by difficulties associated with solution of hydrogen in their quartz reaction vessels. The experiments to be reported here avoided such difficulties and therefore are able to give a more complete picture of the mechanism of ethane pyrolysis than has been available hitherto.

Experimental Method

Ethane was prepared by passing anesthesia-grade ethylene plus an excess of hydrogen through a palladium (on asbestos) catalyst at 100°. The resulting mixture was then passed through a copper–nickel–thorium oxide catalyst at room temperature. This procedure yielded a mixture of ethane and hydrogen containing about 0.02% C_2H_4. The ethylene determination was made by bromination using a 10-liter sample.

The remaining 0.02% of C_2H_4 in the $C_2H_6 + H_2$ mixture was removed by equilibrating the gas with a potassium bromide–bromine solution whose bromine vapor pressure was about 5 mm. at room temperature and subsequently exposing the gas for fifteen to twenty minutes to the illumination of a 900-watt lamp. The excess bromine was then removed by scrubbing with aqueous potassium iodide. The resulting gas was found to contain less than 0.0004% of ethylene. The ethane was then condensed by passage through two traps immersed in liquid nitrogen. Subsequent repeated melting and freezing of the ethane and pumping off the non-condensable gas, followed by a distillation at about 5 cm. pressure during which the first and last thirds of the ethane were rejected, yielded the pure ethane used in all of the experiments.

The ethane was stored in 5-liter flasks which had been evacuated and the walls degassed by heating. The ethane storage reservoirs were separated from the rest of the system by mercury valves.

The reaction vessel was a 500-cc. flask of 172AJ glass obtained through the courtesy of the Corning Glass Co. This flask could be used at temperatures of about 570° without any deformation upon evacuation. An alundum tube furnace 10 cm. in diameter and 60 cm. long insulated with a 25-cm. layer of infusorial earth was used as a thermostat. The reaction flask when placed in the center of the furnace, with the ends of the latter closed by tight-fitting refractory plugs, had a vertical temperature gradient of 2° and a horizontal gradient of 2.5°. A thermocouple was placed in a well centrally located in the reaction flask. It was possible to keep the temperature constant within ±0.5° during an experiment.

In order to fill the reaction vessel rapidly to a definite pressure, a 300-cc. calibrated bulb was sealed into one leg of the mercury valve which isolated the vessel from the rest of the system. A vacuum stopcock separated this bulb from the passage to the reaction vessel. The 300-cc. bulb was insulated by a 3-cm. layer of felt, and the temperature (to ±0.05°) and pressure (to ±0.1 mm.) of the gas in this bulb were measured before forcing the gas by displacement with mercury into the reaction vessel. The mercury valve on the reaction flask served as a manometer except that for pressures over 70 cm. a U-tube manometer was placed in series with it. Pressures were measured using a Gaertner cathetometer mounted on a concrete base.

Analysis of the reaction products for methane, hydrogen, and olefin content was made as follows. The sample was taken at a definite time by opening a vacuum stopcock which connected the reaction flask with two traps immersed in liquid nitrogen and a 1500-cc. evacuated space. The non-condensable gas was recirculated three times through the liquid nitrogen traps by means of a Töpler pump, and then it was collected and forced into a calibrated and evacuated pipet. A measurement of temperature and pressure in this pipet gave the $H_2 + CH_4$ volume. A stopcock connecting this pipet with a tube containing cupric oxide at 300° and magnesium perchlorate at room temperature was then opened and the gas periodically mixed by movement of a 75-cc. volume of mercury. The residual pressure in the pipet after contraction ceased was due to methane and having the calibration of the cupric oxide–magnesium perchlorate tube, a pressure and temperature measurement yielded the volume of methane. The volume of hydrogen was obtained by difference. Measurement of the volume of the ethane plus olefin fraction and subsequent olefin determination by bromination completed the analysis.

Pure ethylene (used for experiments on the pyrolysis of

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(4) Pease, THIS JOURNAL, **50**, 1779–1785 (1928).

(5) Marek and McCluer, *Ind. Eng. Chem.*, **23**, 878–881 (1931).

(6) Travers and Hockin, *Proc. Roy. Soc.* (London), **A136**, 1–27 (1932).

(7) Travers, *J. Indian Chem. Soc.*, Prafulla Chandra Rây Commemorative Vol., 17–26 (1933).

(8) Travers and Pearce, *J. Soc. Chem. Ind.*, **53**, 321–336T (1934).

$C_2H_4 + C_2H_6$ mixtures) was obtained by fractionation of anesthesia-grade ethylene.

The Production of Methane

It was found in our earlier experiments with pure ethane that the amount of methane formed increased more than linearly with the time, and also more than linearly with the initial pressure. Under conditions where the departures from linearity are most marked, the ethane–ethylene–hydrogen equilibrium is approximated during most of the reaction time. A reaction involving ethane alone could not account for the autocatalysis. A reaction involving only reaction products could not account for the high order, since (H_2) (C_2H_4) and $(C_2H_4)^2$ are both roughly proportional to $(C_2H_6)_{\text{initial}}$. A reaction between ethane and one of its reaction products would account for both of these effects. The following comparisons for one-hour runs at 565° show that hydrogen is not responsible for the production of methane.

Initial pressures, mm. C_2H_6	H_2	Final pressures, mm. CH_4
223.8	0	1.41
192.4	544.5	1.00
511.1	0	5.2
574.7	140.8	5.1

Similar comparisons with added ethylene show a very great increase in the rate of methane production.

Temp., °C.	Initial pressures, mm.		Final pressures, mm.		
	C_2H_6	C_2H_4	C_2H_6	C_2H_4	CH_4
565	716.3	0	642.8	64.9	6.51
565	616.8	75.4	571.9	107.7	16.32
565	1432.5	0	1306.0	108.4	21.7
565	1299.9	149.9	1215.8	178.2	49.6
541	650.8	0	620.2	31.9	1.36
541	627.9	73.8	601.2	96.9	4.35
541	1247.6	0	1196	55.9	2.26
541	1287.9	139.4	1255	163.3	11.5

The yields of methane can be at least approximately represented by the equation

$$d(CH_4)/dt = k_1(C_2H_6) + k_2(C_2H_6)(C_2H_4)$$

and there is little doubt that the stoichiometric equations leading to methane production are

$$C_2H_6 = CH_4 + 1/2C_2H_4$$
$$C_2H_6 + C_2H_4 = CH_4 + C_3H_6$$

Our experiments do not provide any direct test of whether or not butane is an intermediate product in the latter reaction. The rate of decomposition of *n*-butane at 565° may be calculated from the data of Paul and Marek[9] as 0.006 sec.$^{-1}$; approximately half of this goes to form methane and propylene. The largest yield of methane we obtained could thus have been produced from a steady-state butane pressure of 3–4 mm. This small quantity would not be detected readily at a total pressure of 2 atm. Some recent work of Frey and Hepp,[10] however, indicates that butane may have been an intermediate product for part, but not all, of the methane and propylene. These authors studied the reaction of low percentages of ethylene with propane and isobutane at 4500 pounds (300 atm.) total pressure and 500°, with a contact time of four minutes. A typical experiment with propane gave 4.59% pentanes and 2.09% methane. This methane cannot have been formed from pentane, since the rate constant[11] for isopentane decomposition at 500° is only 2.1×10^{-4} sec.$^{-1}$; the pentane found in this work could not have produced more than 0.2% methane. Decomposition of propane[9] could account for perhaps 0.3% methane. It seems likely, therefore, that both

$$C_2H_4 + C_3H_8 = C_5H_{12}$$

and

$$C_2H_4 + C_3H_8 = CH_4 + C_4H_8$$

occur, the former being 2 to 3 times more frequent. By analogy, it is likely that part of the methane and propylene found in our work is a product of butane decomposition.

Even though the decomposition of butane is so rapid that we could scarcely hope to detect the small amounts that might be present in our experiments, it is still slow enough to exert a very serious influence on our rate constants. The rate constant for *n*-butane decomposition is 5.70 hr.$^{-1}$ at 541° and 21.7 hr.$^{-1}$ at 565°. Then, in a simple case in which butane is formed at a uniform rate during a one-hour run, the total amount of butane formed is 1.21 times the amount decomposed at 541° and 1.05 times that decomposed at 565°. A determination of the temperature coefficient of butane formation from the observed quantity of methane would then be too high by 7800 cal. Extrapolation to 650°, which will later be needed, would give a value too high by 49%. The actual situation with which we have to deal is more complex. The runs in which the initial reactant is pure ethane are of principal importance in determining k_1. In these runs, however, most of the butane is formed in the

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[9] Paul and Marek, *Ind. Eng. Chem.*, **26**, 454–457 (1934).

[10] Frey and Hepp, *ibid.*, **28**, 1439–1445 (1936).

[11] Frey and Hepp, *ibid.*, **25**, 441–449 (1933).

latter portion of the experiment. The ratio of butane decomposed to butane formed is therefore smaller than for runs made with ethane–ethylene mixtures.

We have found that the most reasonable values for activation energies are obtained by assuming *n*-butane as an intermediate for all the second-order methane. The fraction of the butane decomposed is calculated on the assumption of a uniform rate of formation for ethane–ethylene runs, and a rate proportional to the time for pure ethane runs. The mean olefin pressure during a run can be determined rather accurately from the pressure–time curve, but it is necessary to assume that propylene is about as efficient as ethylene in forming methane. The best values for the rate constants of

$$C_2H_6 = CH_4 + 1/2C_2H_4 \qquad k_1$$
$$C_2H_6 + C_2H_4 = C_4H_{10} \qquad k_2$$

are

Temp., °C.	k_1, sec.$^{-1}$	k_2, mm.$^{-1}$ sec.$^{-1}$
541	2.62×10^{-7}	1.85×10^{-8}
565	1.00×10^{-6}	6.28×10^{-8}
600	6.14×10^{-6}	3.31×10^{-7}
650	6.44×10^{-5}	2.83×10^{-6}

The rates at 600 and 650° are calculated by extrapolation, using $E_1 = 75.4$ kcal., $E_2 = 69.0$ kcal. The mechanism of these reactions is discussed in a subsequent section.

The Rate of Dehydrogenation

We had hoped to be able to measure $d(H_2)/dt$ as a function of time and thus to determine a rate equation applicable to all stages of the reaction. Such an equation would provide a test of various possible reaction mechanisms. The system is so complex, however, that the best we have been able to do is to establish the approximate relation

$$d(H_2)/dt = k(C_2H_6) - k'(H_2)(C_2H_4) \qquad (1)$$

Deviations from this simple rate equation of a magnitude that might exist if the reaction had a free radical mechanism are not observable by our methods.

The data at our disposal consisted of pressure-time curves supplemented by gas analyses at the end of thirty, sixty or one hundred and twenty minutes. When these curves are smoothed by fitting to third or fourth degree polynomials in t, it is found that $d\,\Delta P/dt$ is approximately a linear function of ΔP, where ΔP is the total pressure increase from zero time to time t; if the only reaction products are hydrogen, ethylene and methane, ΔP is equal to the partial pressure of ethylene. If

$$d\Delta P/dt = A - B\Delta P \qquad (2)$$

it follows that

$$-\log(1 - B\Delta P/A) = Bt \qquad (3)$$

The constants A and B are very conveniently found by seeking the value of B/A that will make the logarithmic plot suggested by (3) a straight line. It is found that the values of A are proportional to the initial pressure of ethane. Equation (2) fails for values of ΔP near A/B, and values greater than this limit may be obtained. It is curious to note, however, that these pseudo-limiting ΔP values, when interpreted as representing the pressures of hydrogen and ethylene, give a false "equilibrium" constant, which is actually almost constant for initial pressures from 100 to 1400 mm.

Equations (1) and (2) might appear to be contradictory. We have found, however, that the ideal system

$$C_2H_6 = C_2H_4 + H_2$$
$$H_2 + C_2H_4 = C_2H_6$$
$$C_2H_6 = CH_4 + 1/2C_2H_4$$

with differential equations

$$d(C_2H_6)/dt = -(k_1 + k_3)(C_2H_6) + k_2(H_2)(C_2H_4)$$
$$d\Delta P/dt = d(C_2H_4)/dt = (k_1 + 1/2k_3)(C_2H_6) - k_2(H_2)(C_2H_4)$$
$$d(H_2)/dt = k_1(C_2H_6) - k_2(H_2)(C_2H_4)$$

when solved by numerical methods gives values of ΔP which fit (2) about as well as the experimental values do. We take this to be evidence that (1) is at least approximately correct.

The accuracy with which a first-order law has been established for the initial rate is shown by the following figures.

INITIAL RATE OF DECOMPOSITION AT 565°

Initial pressure, mm.	k, sec.$^{-1}$	Initial pressure, mm.	k, sec.$^{-1}$
99.0	9.2×10^{-5}	423.8	5.5×10^{-5}
104.0	7.9	512.6	6.0
107.7	7.7	716.3	5.5
223.8	6.0	1093.4	5.6
224.1	6.0	1432.5	6.5
420.6	6.6	1517.0	6.9

There is apparently an appreciable amount of wall reaction at 100 mm., but for 200 mm. and higher the first-order law is obeyed within the experimental error. The agreement with the first-order constant $k = 11.6 \times 10^{-5}$ sec.$^{-1}$ extrapolated from the original equation given by Marek and McCluer[6] is not good. Paul and Marek[9] have recalculated Marek and McCluer's data, and give an equation from which $k = 6.2 \times 10^{-5}$ sec.$^{-1}$ in excellent agreement with our result.

The Equilibrium Constant

Many of our runs were of sufficient length to establish the ethane–ethylene–hydrogen equilibrium as exactly as is possible in a system where other reactions are still in progress. The perturbation of the equilibrium by these side reactions, while not negligible, is probably less serious than the error introduced by assuming that all olefins present are ethylene. This error can be at least partially eliminated by subtracting the calculated propylene from the experimental value for total olefins. The results at 565° are as follows.

Time, min.	Initial pressures, mm. C_2H_6	Initial pressures, mm. C_2H_4	Final pressures, mm. H_2	Final pressures, mm. C_nH_{2n}	Final pressures, mm. C_2H_4	Final pressures, mm. C_2H_6	K, atm.$^{-1}$ uncorr.	K, atm.$^{-1}$ corr.
60	1299.9	149.9	65.0	178.2	132.4	1215.8	0.0125	0.0093
60	616.8	75.4	41.6	107.7	95.1	571.9	.0103	.0091
60	716.3	0	64.7	64.9	58.7	642.8	.0086	.0078
60	1432.5	0	108.7	108.4	85.3	1306.0	.0119	.0093
120	1472.3	0	121.2	115.1	58.4	1295.5	.0142	.0072
120	377.5	0	53.6	49.8	42.7	318.1	.0110	.0095
							Average	0.0087

It is clear that correction for propylene gives much better constants. Figure 1 shows our value for the equilibrium constant and also the values of Pease and Durgan[12] and of Frey and Huppke[13] as recalculated by Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan.[14] Our result appears at first to be decidedly out of line with the other values. Pease and Durgan, however, determined ethylene by absorption in bromine water, and it is thus necessary to apply a correction for propylene to their results similar to that used in our own calculation. Their experiments do not extend over an appreciable range of pressure and hence do not permit calculation of k_1 and k_2. This correction, therefore, can only be made by the rough method of using our extrapolated values of k_1 and k_2. Pease and Durgan obtained the following results.

Temp., °C.	Time, sec.	Initial pressures, mm. C_2H_4	Initial pressures, mm. H_2	Initial pressures, mm. C_2H_6	Final pressures, mm. C_2H_4	Final pressures, mm. H_2	Final pressures, mm. C_2H_6	Final pressures, mm. CH_4
600	1800	99.4	111.2	470.7	102.4	103.8	442.0	43.3
650	360	153.6	168.3	440.1	153.2	162.4	402.6	63.0

For the experiment at 600°, the calculated methane production is 5.0 mm. from k_1 and 27.4 mm. from k_2, a total of 32.4 mm., in fair agreement with experiment. At 650° the calculated values are 9.8 mm. and 66.1 mm., a total of 75.9 mm. For the purpose of correcting Pease and Durgan's equilibrium constants we assume 36.5 mm. of propylene at 600° and 54.9 mm. at 650°. These figures are obtained by dividing the actual CH_4 in the proportion of our calculated values. Then $K = 0.020$ at 600°, and 0.052 at 650°. It is evident from Fig. 1 that these recalculated values are in good agreement with our value at 565°. The agreement with the calculations of Smith and Vaughan[15] based on spectroscopic and thermochemical data is very much better than it had been before, the previous very disturbing discrepancy now being only about 17% or 0.3 e. u.

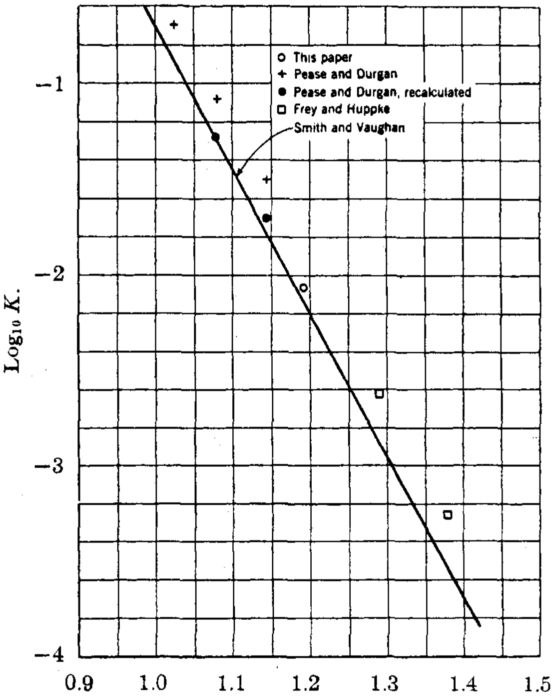

Fig. 1.—Equilibrium constant for $C_2H_6 = C_2H_4 + H_2$.

It has been proposed very recently by Kemp and Pitzer[16] that this same discrepancy is to be removed by invoking a potential barrier of 3150 cal. opposing free rotation in ethane. Such a barrier leads to a statistical mechanical entropy for ethane in agreement with an experimentally accurate third-law value.[16a] A barrier of this magnitude is difficult if not impossible to account for by present valence-theory methods; our value for

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(12) Pease and Durgan, THIS JOURNAL, **50**, 2715–2718 (1928).

(13) Frey and Huppke, *Ind. Eng. Chem.*, **25**, 54–59 (1933).

(14) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65–75 (1935).

(15) Smith and Vaughan, *J. Chem. Phys.*, **3**, 341–343 (1935).

(16) Kemp and Pitzer, THIS JOURNAL, **59**, 276–279 (1937).

(16a) Witt and Kemp, *ibid.*, **59**, 273–276 (1937).

the equilibrium constant constitutes a second objection to so large a barrier. It is clear that final solution of this problem will depend upon an unimpeachable experimental value for the equilibrium constant; ethane and ethylene must be determined by low-temperature fractionation, and the experiments must cover a wide enough range of pressure to guarantee that the value found is a true constant.

The Reaction Mechanism

A definite free radical mechanism for ethane pyrolysis has been proposed by Rice and Herzfeld.[17] It is necessary to generalize their scheme somewhat to take account of our new results on methane formation. The resulting mechanism is

$$\begin{aligned}
C_2H_6 &= 2CH_3 && (1)\\
C_2H_6 &= C_2H_5 + H && (2)\\
H_2 + C_2H_4 &= H + C_2H_5 && (3)\\
H + C_2H_6 &= H_2 + C_2H_5 && (4)\\
H + C_2H_4 &= C_2H_5 && (5)\\
H + C_2H_6 &= CH_4 + CH_3 && (6)\\
CH_3 + H_2 &= CH_4 + H && (7)\\
CH_3 + C_2H_6 &= CH_4 + C_2H_5 && (8)\\
C_2H_5 &= C_2H_4 + H && (9)\\
C_2H_5 + H_2 &= C_2H_6 + H && (10)\\
C_2H_5 + H_2 &= CH_4 + CH_3 && (11)\\
H + C_2H_5 &= C_2H_6 && (12)\\
H + C_2H_5 &= C_2H_4 + H_2 && (13)\\
C_2H_5 + C_2H_4 &= CH_3 + C_3H_6 && (14)
\end{aligned}$$

Using the customary steady-state treatment based on the assumption of long chains, one finds

$$d(\mathrm{En} + \mathrm{Pn})/dt = \sqrt{[(k_1 + k_2)\mathrm{E} + k_3\mathrm{HmEn}]/(k_{12} + k_{13})} \times \frac{(k_7\mathrm{Hm} + k_8\mathrm{E})(k_4k_9\mathrm{E} - k_5k_{10}\mathrm{HmEn}) + k_6k_8k_9\mathrm{E}^2 - k_5k_7\mathrm{HmEn}(k_{11}\mathrm{Hm} + k_{14}\mathrm{En})}{\sqrt{[(k_7\mathrm{Hm} + k_8\mathrm{E})(k_9 + k_{10}\mathrm{Hm}) + k_7\mathrm{Hm}(k_{11}\mathrm{Hm} + k_{14}\mathrm{En})]\,[(k_7\mathrm{Hm} + k_8\mathrm{E})(k_4\mathrm{E} + k_5\mathrm{En}) + k_6k_8\mathrm{E}^2]}}$$

where

$[C_2H_6] = \mathrm{E}$ $[CH_4] = \mathrm{M}$ $[H_2] = \mathrm{Hm}$ $[C_3H_6] = \mathrm{Pn}$
$[C_2H_5] = \mathrm{Et}$ $[CH_3] = \mathrm{Me}$ $[H] = \mathrm{Ha}$
$[C_2H_4] = \mathrm{En}$

Since it is an experimental fact that the rates of the methane-forming reactions are ordinarily small compared with the actual rates of hydrogenation and dehydrogenation,[18] the inequalities

$$k_6 \ll k_4 \qquad \begin{cases} k_{14}\mathrm{En} \ll k_{10}\,\mathrm{Hm}, \text{ or} \\ k_{14}\,\mathrm{En} \ll k_9 \end{cases}$$
$$k_{11} \ll k_{10}$$

must be assumed. It then follows, for conditions not too close to equilibrium, that

$$d(\mathrm{En} + \mathrm{Pn})/dt = \sqrt{\frac{(k_1 + k_2)\mathrm{E} + k_3\,\mathrm{HmEn}}{k_{12} + k_{13}}} \times \frac{k_4k_9\mathrm{E} - k_5k_{10}\mathrm{HmEn}}{\sqrt{(k_9 + k_{10}\mathrm{Hm})(k_4\mathrm{E} + k_5\mathrm{En})}}$$

When Hm = En = 0, the initial rate of dehydrogenation is

$$d\mathrm{En}/dt = \sqrt{(k_1 + k_2)\,k_4k_9/(k_{12} + k_{13})}\,\mathrm{E}$$

and when E = 0, the initial rate of hydrogenation is

$$-d\mathrm{En}/dt = \sqrt{\frac{k_3k_5k_{10}}{k_{12} + k_{13}}}\,\mathrm{HmEn}\,\sqrt{\frac{k_{10}\mathrm{Hm}}{k_9 + k_{10}\mathrm{Hm}}}$$

It follows that for hydrogen pressures not less than those for which the hydrogenation has been proved second order

$$k_9 \ll k_{10}\mathrm{Hm}$$

The rate of formation of methane associated with ethylene is approximately

$$2k_1\mathrm{E} + 2\sqrt{\frac{(k_1 + k_2)\mathrm{E} + k_3\mathrm{HmEn}}{k_{12} + k_{13}}} \times \frac{k_6\mathrm{E}(k_9 + k_{10}\mathrm{Hm}) + k_{11}\mathrm{Hm}(k_4\mathrm{E} + k_5\mathrm{En})}{\sqrt{(k_4\mathrm{E} + k_5\mathrm{En})(k_9 + k_{10}\mathrm{Hm})}}$$

Our results which show no increase of the rate of methane formation by added hydrogen must be interpreted by assuming that the term $2k_1\mathrm{E}$ is dominant in this expression. The constants k_6 and k_{11} are thus discarded everywhere, and the corresponding reactions may be dropped from the mechanism. The rate of formation of methane associated with propylene is approximately

$$k_{14}\mathrm{En}\sqrt{\frac{(k_1 + k_2)\mathrm{E} + k_3\mathrm{HmEn}}{k_{12} + k_{13}}}\sqrt{\frac{k_4\mathrm{E} + k_5\mathrm{En}}{k_9 + k_{10}\mathrm{Hm}}}$$

When

$$(k_1 + k_2)\mathrm{E} \gg k_3\mathrm{HmEn}$$
$$k_4\mathrm{E} \gg k_5\mathrm{En}$$
$$k_9 \gg k_{10}\mathrm{Hm}$$

this reduces to

$$k_{14}\sqrt{(k_1 + k_2)k_4/(k_{12} + k_{13})k_9}\,\mathrm{EEn}$$

which is of the correct form to agree with experiment. The formation of butane seems to offer more difficulties to a free radical theory than the direct formation of methane and propylene, and in the absence of direct evidence that it occurs, we have omitted the former reaction from this discussion.

By requiring the results of the free radical mechanism to agree with experiment we have thus obtained the following conditions

$k_9 \ll k_{10}\,\mathrm{Hm}$ for Hm $\geqq$ 300 mm.
$k_9 \gg k_{10}\,\mathrm{Hm}$ for Hm $\leqq$ 50 mm.
$k_4\mathrm{E} \gg k_5\,\mathrm{En}$ for E $\sim$ 10 En
$(k_1 + k_2)\,\mathrm{E} \gg k_3\mathrm{HmEn}$ for HmEn/E $\leqq K$

The first two conditions are incompatible as they stand; the contradiction could be removed if the reactions of $H_2 + C_2H_4$ and $C_2H_6 + C_2H_4$

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(17) Rice and Herzfeld, THIS JOURNAL, 56, 284–289 (1934).

(18) These rates may be estimated from measured initial rates. The *net* rate of hydrogenation or dehydrogenation is easily made less than the rate of methane formation.

departed more widely from simple second-order laws than Pease's experiments and our own work indicate. The condition $k_4/k_5 \gg 0.1$ is in poor agreement with the Rice and Herzfeld assumptions of activation energies, $E_4 = 17$ kcal., $E_5 = 10$ kcal. The evidence that a lower value of E_4 must be used is now almost overwhelming.[19] On one hand, Sachsse and Patat[20] have shown that the concentration of atomic hydrogen in decomposing ethane is 1000-fold less than would be the case if E_4 were 17 kcal. On the other, Steacie and Phillips[21] have found by direct experiment with high concentrations of atomic hydrogen at low temperatures that the reaction rate is incompatible with a value of E_4 greater than 6 kcal. The use of this lower value, however, leads to new difficulties, as Steacie and Phillips already have pointed out. We are now able to exhibit these difficulties in a very direct way. The rate of dehydrogenation is[22]

$$k_1 = \sqrt{(k_1 + k_2)k_4k_9/(k_{12} + k_{13})} = 6 \times 10^{-5} \text{ sec.}^{-1} \text{ at } 838\text{°K.}$$

The rate of first-order methane formation is

$$k_m = 2k_1 = 10^{-6} \text{ sec.}^{-1} \text{ at } 838\text{°K.}$$

The value of k_4, calculated from an activation energy of 6 kcal., is

$$k_4 = 10^{11} \text{ cc. mole}^{-1} \text{ sec.}^{-1} \text{ at } 838\text{°K.}$$

To exclude the chain-breaking reaction

$$2C_2H_5 = C_4H_{10} \qquad (15)$$

which would give the wrong order, we must have

$$k_{15}/(k_{12} + k_{13}) < k_9/k_4E$$

for E up to 2 atm. Then, since

$$k_4k_9/(k_{12} + k_{13}) \leqq 2k_f^2/\text{km}$$

we must have

$$k_{15}/(k_{12} + k_{13}) < 2 \times 10^{-20} (k_{12} + k_{13}) \text{ mole sec. cc.}^{-1}$$

Then, even if $k_{12} + k_{13}$ has its largest possible value, 10^{14} cc. mole^{-1} sec.$^{-1}$

$$k_{15}/(k_{12} + k_{13}) < 2 \times 10^{-6}$$

It seems highly improbable that the rates of two recombination reactions would differ so widely.

The fourth condition in the preceding list requires that in the hydrogenation of ethylene the second-order constants, corrected for back reaction, should increase considerably with the extent of reaction. There are no good data available for testing this point.

Our analysis has developed two serious objections to the free radical mechanism. The first of these, arising from the order of the reactions

$$H_2 + C_2H_4 = C_2H_6$$
$$C_2H_6 + C_2H_4 = CH_4 + C_3H_6$$

consists of contradictory conditions upon the ratio k_9/k_{10}. The second, depending upon experimental values for the rates of

$$C_2H_6 = C_2H_4 + H_2$$
$$C_2H_6 = CH_4 + 1/2C_2H_4$$

and upon Steacie and Phillips' determination of k_4, relates to the very arbitrary and unlikely assumption necessary to exclude undesired chain-breaking reactions. It seems probable to us, therefore, that the relatively simple classical mechanism

$$\begin{aligned} C_2H_6 &\rightleftarrows C_2H_4 + H_2 \\ C_2H_6 &\longrightarrow CH_4 + CH_2 \\ CH_2 + C_2H_6 &\longrightarrow CH_4 + C_2H_4 \quad \text{(rapid)} \\ C_2H_4 + C_2H_6 &\rightleftarrows C_4H_{10} \\ C_4H_{10} &\longrightarrow CH_4 + C_3H_6 \\ C_4H_{10} &\longrightarrow H_2 + C_4H_8 \\ C_2H_4 + C_2H_6 &\longrightarrow CH_4 + C_3H_6 \end{aligned}$$

accounts for the major part of the observed reaction. There are undoubtedly a few free radicals present, and a certain amount of chain reaction. The foregoing objections to a chain mechanism do not apply when the classical contribution is dominant, since the orders and relative rates of the chain contributions to the various stoichiometric reactions are then unknown.

Summary

1. The production of methane in the pyrolysis of ethane has been traced to two reactions

$$C_2H_6 = CH_4 + 1/2C_2H_4$$

and

$$C_2H_6 + C_2H_4 (= C_4H_{10}) = CH_4 + C_3H_6$$

The rates of these reactions have been determined. There is no measurable production of methane by the reaction $H_2 + C_2H_6 = 2CH_4$.

2. The initial rate of dehydrogenation of ethane is first order from 200 mm. to 1500 mm. The rate during a run does not deviate measurably from

$$d(H_2)/dt = k(C_2H_6) - k'(H_2)(C_2H_4)$$

The presence of side reactions makes an exact test of this relation impossible.

3. The applicability of a free radical chain mechanism to these experimental results has been

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[19] Various thermochemical objections to so large a value were stated in a letter from one of us (L. S. K.) to Dr. Rice on August 7, 1933, before the Rice and Herzfeld paper was submitted to THIS JOURNAL.

[20] Sachsse and Patat, *Z. Elektrochem.*, **41**, 493–494 (1935).

[21] Steacie and Phillips, *J. Chem. Phys.*, **4**, 461–468 (1936).

[22] k_f is the rate constant k of the section on "Rate of Dehydrogenation," and k_m is k_1 of the section on "Production of Methane."

investigated. There are two serious objections to such a mechanism for the entire reaction, but it is possible for chain reactions to contribute a few per cent. to the total.

4. Our own experiments, and recalculation of Pease and Durgan's data in the light of our work on methane production, suggest a lower value for the equilibrium constant of the dehydrogenation reaction than has been obtained in previous experimental work. This new value is in far better agreement with statistical mechanical calculations than were the earlier values.

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Two-Step Oxidation of Benzoin to Benzil

BY L. MICHAELIS AND E. S. FETCHER, JR.

The purple color which arises during the oxidation of benzoin to benzil has been known for many years, and the various conditions under which it can be produced have been studied by a number of authors.[1–4] It may be best observed on addition of sodium hydroxide to an alcoholic solution of a mixture of benzil and benzoin. The colored substance arising under this condition has been fully shown to be on an oxidation level between benzil and benzoin.[1,2,5,6] As far as an attempt to interpret its structure has been made, it usually has been considered as a bimolecular compound[4,7] supposedly comparable to the quinhydrones, which also had been considered to be bimolecular. Another interpretation adopted, but without reliable proof, by some authors[3–5] is that of a unimolecular radical. Since many quinhydrones have now been proved to be semiquinone radicals[8] it was suggestive to investigate the nature of the purple substance with those methods developed for the study of the quinhydrones.

$C_6H_5COCOC_6H_5$ (I) $C_6H_5COCOHC_6H_5$ (II) $C_6H_5COCHOHC_6H_5$ (III)

If this purple substance be a radical such as II, it would have the same molecular size as benzoin (III) or benzil (I). If it be a molecular compound of benzil and benzoin the molecular size would be a multiple. The customary procedures for the determination of molecular weights are of no avail in this case. But there are at least two methods that might be used. One is the potentiometric method which has been applied successfully to the solution of the problem for many organic dyestuffs.[8] A number of unfavorable circumstances obviate its use in the present case. Another method, referred to in a previous paper[9] as the dilution test, is readily applicable under the requisite experimental conditions, and is just as reliable.

To carry out this test, equivalent weights of the oxidized and the reduced forms of the system, *i. e.*, benzil and benzoin, are dissolved in a solvent in which the intermediate purple compound is formed spontaneously. Two experiments are carried out in which nothing but the volume of the solvent is varied. A color comparison of the two solutions is made in tubes of the same diameter by examination through the whole length of the tubes, thus comparing the total amounts of the colored substance. If the substance be a radical this amount will be independent of the volume; if it be a bimolecular compound the color intensity will be inversely proportional to the volume.

This statement, however, is true[9] only if the amount of the colored substance, in equilibrium with the two parent substances, is but a small fraction of that which can arise *in maximo*. This amount is dependent on the concentration of alkali, increasing with it. This influence of the alkalinity can be accounted for by the same argument that has been presented for anionic semiquinones.[9] The alkali concentration should be

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(1) More recent papers are: A. Weissberger, H. Mainz, and E. Strasser, *Ber.*, **62B**, 1942 (1929).

(2) A. Weissberger, E. Strasser and H. Mainz, *Ann.*, **478**, 112 (1930).

(3) Ben B. Corson and R. W. McAllister, THIS JOURNAL, **51**, 2822 (1929).

(4) A. Weissberger, *Ber.*, **65B**, 1815 (1932).

(5) W. E. Bachmann, THIS JOURNAL, **53**, 2758 (1931).

(6) A. Weissberger, W. Schwarze and H. Mainz, *Ann.*, **481**, 68 (1930).

(7) E. Beckmann and T. Paul, *ibid.*, **266**, 6 (1891).

(8) L. Michaelis, *Chem. Reviews*, **16**, 243 (1935).

(9) L. Michaelis, THIS JOURNAL, **58**, 873 (1936).