

## The Mercury Photosensitized Decomposition of Ethane

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Citation: [The Journal of Chemical Physics](#) **6**, 179 (1938); doi: 10.1063/1.1750223

View online: <http://dx.doi.org/10.1063/1.1750223>

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# THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 6

APRIL, 1938

NUMBER 4

## The Mercury Photosensitized Decomposition of Ethane\*

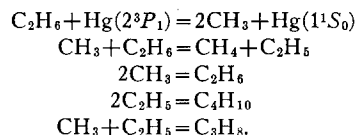
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(Received January 10, 1938)

An investigation of the mercury photosensitized decomposition of ethane has been made, the products of the reaction being analyzed by low temperature fractional distillation. It is found that by improved trapping methods it is possible to remove butane from the system as formed, and thus the formation of secondary products is entirely inhibited. Under these circumstances the products of the reaction consist exclusively of methane, propane, and butane, the hydrogen and higher hydrocarbons found in

previous investigations being secondary products of the propane and butane decompositions. The quantum yield (in terms of ethane disappearing) is approximately 0.2. The suggested mechanism of the reaction is:



### INTRODUCTION

A GREAT many papers have been published on the decomposition reactions of the simple hydrocarbons, thermal, photochemical, photosensitized, free radical sensitized, etc.<sup>1</sup> The mercury photosensitization method has certain marked advantages, since the input of energy to the reactant molecule is a very definite process. With the development of improved light sources and analytical methods it has become possible to obtain much more detailed and definite information, and a re-investigation of the photosensitized decomposition reactions of the simple paraffins has therefore been commenced in this laboratory.

The present paper deals with the mercury photosensitized decomposition of ethane. This reaction was first studied by Taylor and his

collaborators in the course of their classical investigations of mercury photosensitized reactions. Taylor and Hill<sup>2</sup> observed that in ethylene-hydrogen mixtures ethane and higher hydrocarbons were formed. After the pressure change accompanying this reaction was over, other changes occurred which led them to suspect that the ethane formed was being attacked both by hydrogen atoms and by excited mercury. They verified this, and suggested that radicals were undoubtedly involved in the process.

Kemula<sup>3</sup> also showed that ethane could be decomposed by excited mercury atoms. A more thorough investigation of the reaction was made by Kemula, Mrazek and Tolloczko<sup>4</sup> following on earlier work by Tolloczko.<sup>5</sup> In their investigation the reaction mixture was circulated through a trap at  $-80^\circ\text{C}$  to remove the products

\* The work described in this paper was done with financial assistance from the National Research Council of Canada, which is hereby gratefully acknowledged.

<sup>1</sup> See Steacie, *Chem. Revs.* April (1938) for references.

<sup>2</sup> Taylor and Hill, *J. Am. Chem. Soc.* **51**, 2922 (1929).

<sup>3</sup> *Rocz. Chem.* **10**, 273 (1930).

<sup>4</sup> Kemula, Mrazek and Tolloczko, *Coll. Czech. Chem. Comm.* **5**, 263 (1933).

<sup>5</sup> Tolloczko, *Przemysl Chem.* **11**, 245 (1927).

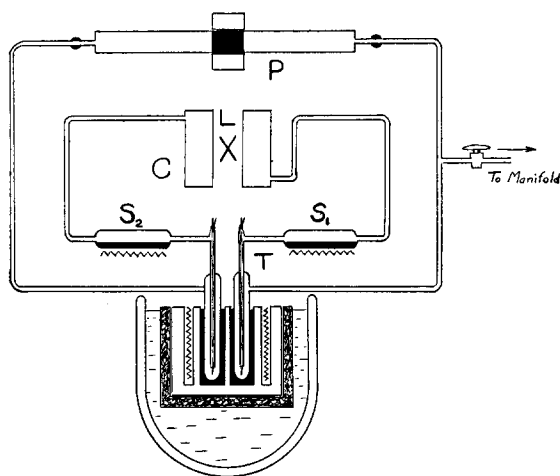
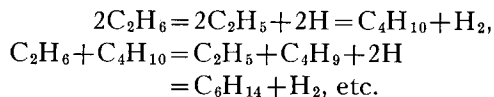


FIG. 1.

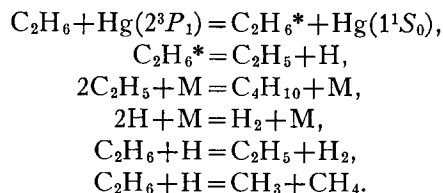
of higher molecular weight as fast as formed, and thus prevent secondary processes. (This is not a sufficiently low temperature to remove butane efficiently, since its vapor pressure is 11 mm at  $-80^{\circ}\text{C}$ , and the prevention of secondary changes was thus only partially successful.) They found that the decrease in pressure as the reaction progressed was accompanied by an exactly parallel increase in the volume of the liquid condensate. The rate was independent of the ethane pressure, but at high pressures a higher percentage of condensate was formed. The gaseous products consisted entirely of hydrogen and methane, the ratio of hydrogen to methane being considerably greater than unity, and approaching infinity if the trap were kept at  $-20^{\circ}\text{C}$  instead of  $-80^{\circ}\text{C}$ . The condensable products were analyzed by a rough fractional distillation, and were found to consist mainly of butane and octane, with a small amount of hexane and no propane or pentane.

Tolloczko had previously suggested that the mechanism of the process was

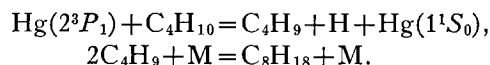


This assumes only a C-H rupture and leads obviously to hydrocarbons with an even number of carbon atoms only. It gives, however, no explanation of the formation of methane.

Kemula, Mrazek and Tolloczko therefore suggested



The higher hydrocarbons then result from secondary reactions of butane, etc. The fact that octane is the main higher product suggests that the chief reaction of butane is



As we shall see, however, the efficient removal of butane from the system causes a pronounced change in the products of the reaction.

## EXPERIMENTAL

### Apparatus and procedure

A dynamic method was employed. The apparatus is shown diagrammatically in Fig. 1.

The light source *L* was a Hanovia Sc2537 mercury resonance lamp. The lamp was in the form of a double U, and was run at 100 milliamperes with a 5000-volt sign transformer. (The actual potential across the lamp after it had warmed up was about 370 volts.) The radiation from the lamp was used directly without filtering, since blank experiments showed that no reaction occurred when ethane was illuminated in the absence of mercury. The fused quartz reaction vessel *C* was annular in form, being 10 cm long, 8 cm in diameter, with a hole 4 cm in diameter through the middle. Its volume was 320 cc. A well in the side of the vessel was provided to accommodate a thermocouple.

The pump *P* consisted of a brass tube 40 cm long and 4 cm diameter inside which was a close-fitting steel cylinder. A solenoid of about 1000 ampere-turns was arranged to slide on the outside of the tube, and a reciprocating motion was applied to the solenoid by means of a wheel and crank. The displacement of the pump was 350 cc, so that the entire contents of the reaction vessel were displaced each half-cycle.

The saturation of the gas with mercury vapor

was accomplished by means of the vessels  $S_1$  and  $S_2$ , each of which provided a mercury surface of about 30 cm<sup>2</sup>. The saturators were heated electrically to about 60°C.

As mentioned above, one of the main objects of the present work was the elimination of secondary processes by the removal of hydrocarbons of higher molecular weight from the system as fast as formed. With this end in view the gases were circulated through the traps  $T$ . The method by which these traps were maintained at definite low temperatures for long periods of time was as follows. The traps were immersed in mercury contained in two holes drilled in a steel block. Small electric heaters were inserted in other holes in the same block. The block was surrounded by an insulating layer of cotton encased in a sheet metal container, and the container was immersed in liquid oxygen. By keeping the liquid oxygen level constant and varying the electrical input, it was possible to maintain the traps at any desired temperature in the range to be studied. The temperature could thus be controlled to within 1–2°. The temperature of the traps was measured by means of copper-constantan thermocouples situated inside the traps themselves. These were calibrated at the boiling points of oxygen and ethylene, at the sublimation point of carbon dioxide, and from –50° to 0°C by means of standard thermometers.

The main portion of the apparatus had a total volume of about 1200 cc. It was connected to a manifold which led to the pumping system, a McLeod gauge, gas reservoirs, a Toepler pump, gas holders, etc.

In later runs mercury valves were used so that circulation occurred in the same direction during both strokes of the pump, and only one trap and saturator were used. The total volume of the altered system was 1500 cc. No changes in the optical system were made.

In making a run, a suitable amount of gas was introduced into the reaction system, and the traps  $T$  were brought to the desired temperature. The pump  $P$  was started, and the saturators were heated to 60°C. The gas was then illuminated for a definite period of time. At the conclusion of this period, the traps were brought to room temperature and the products of reaction

were completely pumped by the Toepler pump into a portable gas holder. The gas was then analyzed by low temperature fractional distillation in an apparatus of the Podbielniak type. A 500 cc sample could thus be analyzed for the gaseous constituents (i.e., those with boiling points below room temperature) with an accuracy of about 0.5 percent. In the analysis methane and hydrogen were taken off together, and this fraction was analyzed by combustion in the usual way. The distillation apparatus available was not suitable for the analysis of high boiling products. However, as will be shown later, such products were only present when secondary reactions occurred, and were entirely absent during the more significant experiments.

### Materials

Ethane and butane were obtained in cylinders from the Ohio Chemical and Manufacturing Company. The gases were stated to be not less than 97 and 99 percent pure, respectively. Analysis of the cylinder ethane showed it to contain 1.3 percent ethylene, less than 0.3 percent of  $H_2 + CH_4$ , and less than 0.3 percent of higher hydrocarbons. This gas was passed over hot copper oxide, through a 40 percent KOH solution and a trap at –80°C, and was then condensed and fractionally distilled. Butane was purified merely by fractional distillation. Hydrogen was taken from cylinders and passed over platinized asbestos at 600°C, and then through a liquid-air trap.

TABLE I. Absorption of the resonance line under various conditions. Arc current, 0.100 amp. Cell temperature, 35°C. Mercury saturation at 35°C =  $4 \times 10^{-3}$  mm.

FOREIGN GAS	PRESSURE, MM	RESONANCE RADIATION ABSORBED, ERG CM <sup>-3</sup>	FRACTION OF RESONANCE RADIATION ABSORBED
$H_2$	180	$8.0 \times 10^{15}$	1.00
	87	7.7	0.96
	72	7.6	0.95
	51	7.4	0.92
	10	5.2	0.65
$C_2H_6$	680	$7.8 \times 10^{15}$	0.97
	420	7.8	0.97
	330	7.8	0.97
	210	7.7	0.96
	171	7.7	0.96
	151	7.6	0.95
	136	7.5	0.94
	75	7.0	0.87
	40	6.3	0.79
	10	4.3	0.54

TABLE II. The mercury photosensitized decomposition of ethane. Volume of system = 1200 cc (1500 cc in runs 7 and 8). Resonance radiation absorbed =  $4.0 \times 10^{-6}$  einsteins per sec. Volume of cell = 320 cc. Cell temperature = 35°C. Arc current = 0.100 amp. Arc voltage = 370. Mercury vapor pressure =  $4 \times 10^{-3}$  mm.

RUN NO.	TIME, HR.	INITIAL PRES-SURE, CM	FINAL PRES-SURE, CM	TRAP TEM-PERA-TURE, °C	CIRCULATION RATE, LITERS PER MIN.	PARTIAL PRESSURE OF C <sub>2</sub> H <sub>6</sub> DURING RUN	FRACTION OF C <sub>2</sub> H <sub>6</sub> DECOM-POSED	DECOM-POSITION RATE, MOLE PER SEC. $\times 10^6$	QUANTUM YIELD (ETHANE REACTING)	PRODUCTS, MOLE PERCENT				
										H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	HIGHER HYDROCARBONS (AS C <sub>8</sub> )
1	10	44.1	42.0	- 70	6	40 to 15	0.67	0.53	0.13	47	16	none	23	14
2	8	43.1	41.8	- 70	6	40 to 15	0.60	0.58	0.14	43	23	none	20	14
3	8.5	42.2	41.9	-100	1.3	40 to 20	0.50	0.44	0.11	—	—	—	25	present
4	8	75.0	75.0	-108	1.2	25	0.23	0.38	0.095	19.6	44.7	none	35.7	trace
5	15	73.2	73.2	-115	4	15	0.45	0.39	0.098	—	—	—	—	none
6	20	69.9	69.9	-116	6	15	0.58	0.36	0.090	6.1	59.3	<1.0	34.6	none
7	8.75	39.0	39.0	-125	3	7	0.55	0.54	0.15 <sup>a</sup>	0.0	59.5	21.5	19.0	none
8	6.75	39.0	39.0	-131	3	4	0.45	0.61	0.18 <sup>b</sup>	0.0	58.8	23.5	17.7	none

<sup>a</sup> The ethane partial pressure was too low for complete absorption of the incident resonance radiation. Hence in this run the absorbed resonance radiation was only  $3.7 \times 10^{-6}$  einsteins per sec.

<sup>b</sup> Resonance radiation absorbed =  $3.4 \times 10^{-6}$  einsteins per sec.

### The intensity of the light source

The intensity of the mercury resonance radiation was determined by measuring the rate of hydrolysis of monochloroacetic acid.<sup>6</sup> Two concentrations of the acid were employed, 0.5*N* and 0.25*N*. These gave identical results, showing that absorption was complete. The solution after irradiation was neutralized with NaHCO<sub>3</sub> and titrated with AgNO<sub>3</sub>, using K<sub>2</sub>CrO<sub>4</sub> as an indicator. The mean of a number of concordant measurements made at different times gave for the total resonance radiation entering the cell  $4.2 \times 10^{-6}$  einsteins per second.

The light intensity was also measured by means of a Moll thermopile in conjunction with a galvanometer. The thermopile was placed outside the reaction vessel, and the intensity of resonance radiation was determined by taking the difference in thermopile readings with the cell evacuated, and with it filled with mercury vapor at 35°C in the presence of a high hydrogen pressure. This method gave a value of  $3 \times 10^{-6}$  einsteins per second. Considering the uncertainty in this method due to the geometry of the cell, etc., the agreement of this result with that obtained actinometrically is better than could be expected.

### The absorption of resonance radiation

By means of the galvanometer-thermopile system, measurements were made of the absorption of resonance radiation by mercury vapor

in the presence of ethane and hydrogen. During these experiments the gases were circulated over the mercury saturators as in a normal run, the mercury vapor pressure thus being maintained at approximately  $4 \times 10^{-3}$  mm. With this precaution the amount of absorbed resonance radiation became constant in less than one minute after admitting the gas to the system. Measurements were made rapidly in the case of ethane in order to avoid appreciable decomposition. The results of these measurements are given in Table I.

Measurements of the efficiency of the absorption were also made by observing the rate of the mercury photosensitized hydrogen-oxygen reaction in an auxiliary quartz cell placed close to the outside of the reaction cell. The ratio of the rates of combination of hydrogen and oxygen with the reaction cell empty, and with it filled with ethane at 650 mm pressure in the presence of mercury at its vapor pressure at 35°C was 40. This is an excellent check on the absorption at

TABLE III. The mercury photosensitized decomposition of butane.

Operating conditions	as in Table II
Time, hours	4.5
Initial pressure, cm	59.5
Final pressure, cm	40.25
Trap temperature, °C	0.0
Fraction decomposed	0.88
Hydrogen produced, cm	30.0
Mole decomposed per second	$2.2 \times 10^{-6}$
Quantum yield	0.55
Mole hydrogen formed per second	$1.3 \times 10^{-6}$

<sup>6</sup> Rudberg, Zeits. f. Physik **24**, 247 (1924).

high ethane pressures as determined by thermopile measurements.

### RESULTS

The results are given in Table II. One run was also made with butane, for reasons to be discussed later, and the data for this are given in Table III. Several runs were also made with  $C_2H_6-H_2$  mixtures, the results of which are given in Table IV. The "initial" and "final" pressures given in columns 3 and 4 of Table II are those with the traps at room temperature before and after the run. The values of the initial partial pressure of ethane in column 7 are lower than the values in column 3 for the later runs, since the initial ethane pressure was higher than the vapor pressure of ethane at the trapping temperature, and some ethane condensed in the traps. Column 5 gives the temperature of the traps, and thus expresses qualitatively the degree of removal of high boiling products. In runs (4), (5), (6), (7), and (8) the vapor pressures of propane and butane should be less than those inferred from the temperature of the traps, because of their solubility in the condensed ethane in the traps. The vapor pressures of propane and butane at a few temperatures are given in Table V to show the extent to which they were removed at the various trapping temperatures employed. Still lower trapping temperatures were, of course, not feasible on account of the diminution in the vapor pressure of ethane.

It is apparent from the analytical data that the circulation rates employed were sufficiently high to insure complete absence of secondary decomposition products when sufficiently low trapping temperatures were employed.

As pointed out previously, the analytical

TABLE V.\*

TEMPERATURE, °C	VAPOR PRESSURES, MM	
	PROPANE	BUTANE
-70	209	19
-100	30	2
-110	13	0.7
-120	5	0.3
-130	2	0.07

\* Values taken from *International Critical Tables*.

apparatus available was not satisfactory for the determination of higher hydrocarbons. In runs in which such products were present, they are reported as  $C_8H_x$ , calculated from a carbon balance, since the boiling point of the residue corresponded with that of octane. Actually, the higher fraction was by no means pure octane, since it had an aromatic odor, and since qualitative tests showed the presence of some unsaturation. In the later, and more important runs, however, no higher hydrocarbons were present and the analyses are therefore complete. In these runs perfect material balances were obtained.

Before entering on a discussion of the mechanism of the reactions it will be convenient to summarize the main conclusions to be drawn from the data of Tables II, III, and IV.

#### (1) The decomposition of ethane

(a) At high trapping temperatures, in agreement with the results of previous investigators, much hydrogen is produced, the  $H_2/CH_4$  ratio being approximately 3. Considerable butane and higher hydrocarbons are formed, but no propane.

(b) When the trapping temperature is reduced to about  $-115^\circ C$ , the formation of higher hydrocarbons is entirely inhibited, and much butane is produced. At the same time the production of hydrogen decreases greatly, the  $H_2/CH_4$  ratio falling to about  $\frac{1}{3}$ .

TABLE IV. *Experiments with added hydrogen. Volume of system = 1500 cc. Volume of cell = 320 cc. Cell temperature =  $35^\circ C$ . Trap temperature =  $-123$  to  $-125^\circ C$ . Resonance radiation absorbed =  $4.0 \times 10^{-6}$  einstein per sec. Arc current = 0.100 amp. Arc voltage = 370. Circulation rate = 3 liters per min. Partial ethane pressure = 8 cm. Mercury vapor pressure =  $4 \times 10^{-3}$  mm.*

RUN No.	TIME, HR.	INITIAL PRES-SURE, CM	FINAL PRES-SURE, CM	PERCENT HYDRO-GEN IN MIXTURE	FRACTION OF $C_2H_6$ REACTED	RATE OF DISAP-PEARANCE OF $C_2H_6$ , MOLE PER SEC. $\times 10^6$	QUANTUM YIELD (ETHANE REACTING)	PRODUCTS, MOLS PER MOLE OF ETHANE REACTING				
								$H_2$ CON-SUMED	$CH_4$ FORMED	$C_2H_6$ FORMED	$C_4H_{10}$ FORMED	HIGHER HYDROCARBONS FORMED
1	5.5	47.7	47.7	40.0	0.39	0.45	0.11	0.48	1.32	0.07	0.12	none
2	6.0	45.7	45.7	39.3	0.44	0.46	0.12	0.46	1.30	0.08	0.11	none
3	6.0	45.4	45.4	40.0	0.44	0.45	0.11	0.50	1.34	0.05	0.13	none

(c) At very low trapping temperatures where butane has a negligible vapor pressure, and that of propane is also low, hydrogen formation ceases entirely. Propane now makes its appearance in large quantities. This is a striking result, inasmuch as previous investigators have found only hydrocarbons with an even number of carbon atoms (with the exception of methane), and previous mechanisms have been designed primarily for the purpose of explaining this.

(d) It should be observed that, especially at low trapping temperatures where the partial pressure of ethane is low while the methane formed is all in the gas phase, there will be a competition for the incident energy. Under these circumstances the methane present may absorb up to 25 percent of the incident energy. It has been shown by Morikawa, Benedict, and Taylor<sup>7</sup> that the quantum yield in the mercury photosensitized methane decomposition is very low at low temperatures. Thus they obtained values of about 0.2 at 196°C, and only 0.008 at 98°C. It appears, therefore, that the decomposition of methane is negligible at 35°C, and the methane merely quenches the resonance radiation without being chemically affected. On account of this effect the quantum yields obtained will be somewhat low, and a value of about 0.20 for the ethane decomposition at 35°C appears the most probable.

## (2) Experiments in the presence of added hydrogen

(a) Hydrogen is consumed, not produced.  
 (b) The production of methane is very large compared with that of higher hydrocarbons.  
 (c) No hydrocarbons higher than butane are formed at low trapping temperatures.

## (3) The decomposition of butane

(a) Much hydrogen is produced. The decomposition of butane (and perhaps also that of propane) is thus the source of most of the hydrogen formed in the ethane decomposition at higher trapping temperatures. Higher hydrocarbons are also produced in large quantity. As in the case of ethane, these correspond roughly to octane, but are to some extent unsaturated.

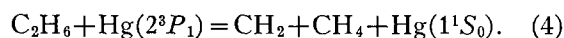
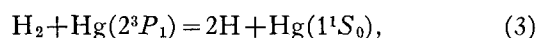
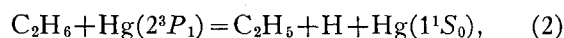
<sup>7</sup> Morikawa, Benedict and Taylor, J. Chem. Phys. 5, 212 (1937).

(b) The quantum yield of the butane decomposition is definitely higher than that of the ethane decomposition.

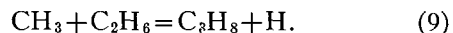
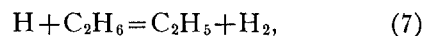
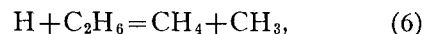
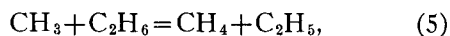
## DISCUSSION

The following reactions may be considered in discussing the decomposition of ethane and its reaction with hydrogen atoms:

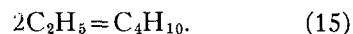
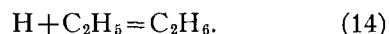
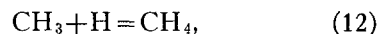
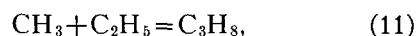
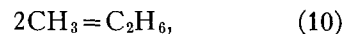
### Primary reactions



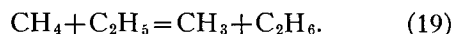
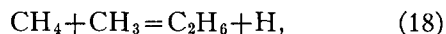
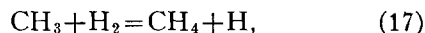
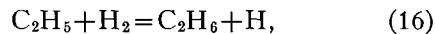
### Secondary reactions of radicals or atoms with ethane



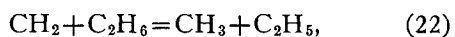
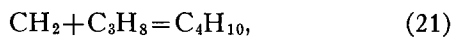
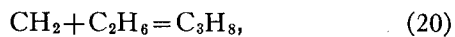
### Radical and atom recombination reactions



### Other secondary reactions of radicals



### Reactions involving the methyldene radical



### The ethane decomposition

There are three fundamentally different possibilities for the primary reaction, a C—C bond split (1), a C—H bond split (2), and the elimination of a methylidene radical (4). These will be discussed separately.

(a) *The elimination of a methylidene radical.*—This is intrinsically not a very likely mechanism. If (4) were the primary step, it would be possible to account for the products obtained by assuming secondary reactions of the methylidene radical such as (20) and (21). On this basis we would expect the amount of methane to be equal to  $(C_3H_8 + 2C_4H_{10})$ , in exact agreement with runs 7 and 8 of Table II. However, since in this case all the butane is formed via propane, we would expect very little butane at the lowest trapping temperatures. This objection might be overcome by assuming (22) followed by (5), (11), and (15). The main objection to (4) as the primary step, however, is the absence of ethylene as a product of the reaction. It seems very unlikely that (4) could be the primary step without any combination of methylidene radicals to form ethylene by (23), especially in view of the low quantum yield of the over-all reaction. The only way to avoid this difficulty would be to assume that at least one of (20), (21), and (22) was extremely fast. On dreierstoss grounds (20) and (21) should not be very rapid. To inhibit recombination to ethylene, therefore, it would be necessary for (22) to have an activation energy much below 7 kcal., which is very unlikely. There would also be the possibility of  $C_2H_4$  formation by the reaction  $CH_2 + C_2H_6 \rightarrow CH_4 + C_2H_4$ . As a matter of fact Storch and Kassel<sup>8</sup> assume this to be very rapid. It appears, therefore, that (4) is a much less plausible primary step than (1) or (2), and it will not be further considered.

(b) *The C—H bond split.*—It is also possible to account for the products of the reaction by assuming an initial C—H bond split (2). If this occurs the most likely fate of the hydrogen atoms produced would obviously be to react with ethane, since it is present in large quantity. We may therefore assume that (6) occurs producing methyl radicals, which react by (5). Recombination reactions (11), (12), and (15)

would then yield the experimentally found products. The low quantum yield can be explained partly on the basis of reactions (10) and (14) which regenerate ethane, and perhaps also in part by inefficiency in the primary step (2).

In order that this mechanism shall yield the products found experimentally, it is necessary to assume that reaction (7) is slow compared to (6), since the occurrence of (7) to any appreciable extent would yield far too much butane relative to methane, and would lead to the production of hydrogen, contrary to the experimental findings. Existing estimates of the relative rates of (6) and (7) are conflicting,<sup>9</sup> but it is possible that the necessary conditions are fulfilled.

The above question is, however, of minor importance compared with the main difficulty encountered by any mechanism which assumes a primary C—H split. If such a split occurs, it is necessary to explain the absence of hydrogen from the products, in spite of the possibility of its formation through reaction (13). In other words we must show that (6) can occur rapidly enough to prevent an appreciable fraction of the hydrogen atoms recombining by (13). (For a rough calculation we can neglect the other less important H atom consuming reactions (12) and (14).) We can test this condition by first calculating the average life of a hydrogen atom on the assumption that hydrogen atoms disappear by (6) only, and then ascertaining whether such a life is compatible with the rate of (13).

From the mechanism assumed the number of ethane molecules reacting by (2) to produce hydrogen atoms is approximately  $\frac{1}{3}$  of the experimentally found rate of disappearance of ethane. Taking run 7 as an example, we have

$$\begin{aligned} C_2H_6 \text{ pressure} &= 7 \text{ cm,} \\ \text{quantum yield} &= 0.15, \\ \text{energy input} &= 3.7 \times 10^{-6} \text{ einstein per sec.} \end{aligned}$$

volume of reaction vessel

$$= 320 \text{ cc.}$$

Hence the rate of production of hydrogen atoms according to this mechanism is

$$\begin{aligned} &(\frac{1}{3} \times 0.15 \times 3.7 \times 10^{-6}) / 320 \\ &= 5.8 \times 10^{-10} \text{ mole cm}^{-3} \text{ sec.}^{-1}, \end{aligned}$$

<sup>9</sup> Steacie and Phillips, J. Chem. Phys. 4, 461 (1936); Steacie, *ibid.*, 6, 37 (1938); Trenner, Morikawa and Taylor, *ibid.* 5, 203 (1937).

<sup>8</sup> J. Am. Chem. Soc. 59, 1240 (1937).



assuming that the reaction takes place throughout the entire cell. Now if hydrogen atoms disappear by (6) only, the mean life of a hydrogen atom is  $1/(k_6(C_2H_6))$ .  $k_6$  has been determined by Trenner, Morikawa and Taylor,<sup>9</sup> and by Steacie,<sup>9</sup> who obtained  $E=7.2$  kcal., with  $s=0.1$ , and 8.6 kcal., with  $s=0.1$ , respectively. Taking the lowest value of  $E$ , since it will be the most favorable for removing H atoms from the system, we obtain

$$k_6 = 3.6 \times 10^{-8} \text{ cm}^3 \text{ mole}^{-1} \text{ sec.}^{-1} \text{ at } 35^\circ\text{C.}$$

Hence, since  $(C_2H_6) = 3.6 \times 10^{-6} \text{ mole cm}^{-3}$ , we obtain

$$\text{mean life of a hydrogen atom} = 7.7 \times 10^{-4} \text{ sec.}$$

Now, if recombination occurs, it may be by diffusion of hydrogen atoms to the wall, or by three-body recombination in the gas. Considering only the wall effect, for the moment, we have for hydrogen atoms,

$$D = \frac{1}{3}\lambda c,$$

where  $D$  is the diffusion coefficient,  $c$  the average velocity of a hydrogen atom at  $35^\circ\text{C}$ , and  $\lambda$  is the mean free path. Assuming an average pressure in the gas of 7 cm of ethane plus 6.4 cm of methane, we obtain approximately

$$D = 9.1 \text{ cm}^2 \text{ sec.}^{-1}$$

Now the mean displacement  $\epsilon$  is given by

$$\begin{aligned} \epsilon^2 &= 2Dt, \\ \text{hence } \epsilon &= (2 \times 9.1 \times 7.7 \times 10^{-4})^{\frac{1}{2}} \\ &= 0.12 \text{ cm.} \end{aligned}$$

Now considering the geometry of the reaction vessel, about 60 cc out of the total volume of 320 cc is within 0.12 cm of the wall, so that on the average one-half of the atoms in this 60 cc will reach the wall during their lifetime. Approximately, therefore, 1/10 of the hydrogen atoms will form  $H_2$  at the wall instead of reacting by (6). The hydrogen formation will therefore be about

$$\begin{aligned} 1/10 \cdot \frac{1}{2} \cdot 5.8 \times 10^{-10} \text{ mole cm}^{-3} \text{ sec.}^{-1} \\ = 2.9 \times 10^{-11} \text{ mole cm}^{-3} \text{ sec.}^{-1} \end{aligned}$$

This is thirty times the minimum detectable amount with the analytical method used. Actually the discrepancy is even greater than

this for two reasons. (a) Practically all the incident radiation will be absorbed in the first mm or two of the cell. This will increase the wall recombination by a factor of about 5. (b) Also, we have neglected recombination in the gas, and this will make a considerable contribution. It follows that the amount of hydrogen is probably about 200 times smaller than the C—H bond split mechanism requires.

Processes such as (12) and (14) cannot be invoked to explain the discrepancy, since the slower diffusion coefficients of  $CH_3$  and  $C_2H_5$  will counteract any concentration factors in their favor. Further, the possibility of subsequent consumption of hydrogen by (3), or by the comparatively slow reactions (16) and (17), cannot explain the quantitative absence of hydrogen in the products of the reaction. It must therefore be concluded that if a C—H split occurred as the primary process hydrogen would be a product, and its absence rules out this mechanism.

(c) *The C—C bond split.*—It appears, therefore, that the primary process must be a C—C split. In this case the resulting methyl radicals can only react according to (5) yielding ethyl radicals. The various radical recombination reactions will then regenerate ethane (10), or yield butane (15), or propane (11). Such a mechanism gives a complete explanation of the products of the reaction, i.e. large formation of methane and no hydrogen production. The only additional reactions which merit consideration are (18), (9), (8), and (19). (8), (9), and (18) can be eliminated since they produce hydrogen atoms, and in any case the consensus of opinion is that such reactions are slow, thus Morikawa, Benedict and Taylor assign an activation energy of about 16 kcal. to (18). It is also unlikely that (19) should be fast, and in any case its presence would produce little change in the mechanism.

We are thus left with the relatively simple series of reactions (1), (5), (10), (11), and (15). If (10) did not occur, the maximum value of the quantum yield would be 3. The occurrence of (11) will lower the quantum yield, but cannot reduce it below 2. The occurrence of (10), i.e., the recombination of methyl radicals to ethane, will, of course, lower the quantum yield without otherwise affecting the situation. It seems un-

likely, however, that the low yield of 0.2 is to be ascribed entirely to this cause, since diminishing the pressure, and thus increasing the wall-effect, does not lower the quantum yield. It is probable, therefore, that the low quantum yield is to be at least partly ascribed to inefficiency in the primary process (1), perhaps owing to ethane quenching the excited mercury atoms to some extent only to the metastable  $2^3P_0$  level.

### The reaction in the presence of added hydrogen

The quenching cross section of hydrogen for excited mercury atoms is much greater than that of ethane. Thus for hydrogen  $\sigma_E^2$  is  $6.01 \times 10^{-16} \text{ cm}^2$ , and for ethane it is  $0.42 \times 10^{-16} \text{ cm}^2$ , a ratio of about 15 to 1.<sup>10</sup> Furthermore the velocity of hydrogen molecules is about 4 times that of ethane. Hence in 2 : 1 mixtures of hydrogen and ethane, as used in the experiments given in Table IV, hydrogen will absorb about 120 times as much energy as does ethane. Reaction (3) thus becomes the only important primary step.

Since much methane is formed and hydrogen is consumed, we presumably have (6) followed by (5), (10), (11), and (15). Actually, however, about twice as much methane is formed as would be expected on this basis. There are two possible explanations of this. (a) Methyl radicals do not react exclusively by (5), but also disappear by (12) or (17). Of these (12) might occur at the wall sufficiently rapidly to account for the facts. Available estimates of the rate of reaction (17)<sup>11</sup> make it appear to be too slow to be effective. (b) The other possible explanation of the large methane production is that (6) is followed by (5), but that some other reaction of ethyl radicals prevents the exclusive formation of propane and butane. If such a reaction occurs, it must involve hydrogen to explain the difference between the runs in the presence and in the

absence of hydrogen. We might thus assume that (16) occurs reforming ethane and regenerating a hydrogen atom. On such a basis we can account for the products formed. Of course this involves the assumption that (16) occurs rapidly enough. What evidence there is seems to be against this, and indicates an activation energy of about 15 kcal.<sup>12</sup> It is worth noting that if (16) is postulated in this way there is no need to rule out (7) as an alternative reaction step to (6), since if (7) were largely followed by (16) the net stoichiometric result would be zero. The same result might also be arrived at by assuming reformation of ethane by (14).

It is hoped that further work now in progress on the reaction at high temperatures, and in the presence of deuterium, may enable a decision to be made between some of the various alternative mechanisms discussed above.

### The reaction at high trapping temperatures

Under these circumstances the reaction is complicated by secondary processes, and the results are thus only of minor importance. Since the addition of hydrogen to ethane at low trapping temperatures leads to hydrogen consumption rather than production, it is apparent that the production of hydrogen from ethane alone at high trapping temperatures is not "auto-catalytic," and must be due to secondary decomposition of butane. Also, the low methane production relative to the butane and higher products formed must be due to the presence of butane. It thus appears that the butane decomposition leads to the formation of higher products from ethane in some manner not involving the production of methane.

### The decomposition of butane

Since these experiments were made merely to confirm the production of hydrogen, no discussion is necessary. In any case an investigation of the butane decomposition in the near future is contemplated. The propane decomposition is at present under investigation.

<sup>10</sup> Bates, J. Am. Chem. Soc. **52**, 3825 (1930).

<sup>11</sup> Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937); v. Hartel and Polanyi, Zeits. f. physik. Chemie **B11**, 97 (1930); Sickman and O. K. Rice, J. Chem. Phys. **4**, 608 (1936); Patat, Zeits. f. physik. Chemie **B32**, 274 (1936); Paneth Hofeditz and Wunsch, J. Chem. Soc. 372 (1935).

<sup>12</sup> Leermakers, J. Am. Chem. Soc. **55**, 4508 (1933).