3. A direct method for the determination of solubilities in highly volatile solvents has been utilized.

4. The solubility of zirconium tetrachloride in liquid-sulfur dioxide from 0 to 20° has been determined and the solvate $ZrCl_4 \cdot SO_2$ has been established.

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[Contribution from the Laboratory of Physical Chemistry, Princeton University]

# THE REACTIONS OF ETHYLENE, HYDROGEN AND THE SATURATED HYDROCARBONS UNDER THE INFLUENCE OF EXCITED MERCURY[1]

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Received May 4, 1929 Published October 5, 1929

The photosensitized combination of hydrogen and ethylene has been the subject of a number of investigations.[3] The results have been in such disagreement that it seemed worth while to reopen the subject in the hope of discovering the mechanism of what would *a priori* be considered one of the simplest of hydrocarbon reactions. This hoped-for simplicity has not been found, and no final statement as to mechanism may be ventured, but it is believed that the facts to be presented afford an empirical explanation of the variations previously found. It may also be possible, we believe, to correlate them with experiments in which the same gases, although activated by other means, react to give very similar products. We may cite, for example, the reactions of ethylene[4] in the presence of hydrogen under the influence of alpha particles. Correlation should also be possible with other reactions due to hydrogen atoms, which Franck and Cario[5] have shown are produced under the experimental conditions employed.

## Experimental Details

**Apparatus.**—The apparatus used in these studies consisted of a quartz reaction vessel which surrounded the arc concentrically, thus securing as great an intensity of illumination as possible, together with a constant-volume manometer to follow the pressure changes. A gas buret and a storage reservoir were also attached through

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[1] This paper is based upon a thesis submitted by Douglas G. Hill to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Albert Plaut Fellow in Chemistry.

[3] (a) Berthelot and Gaudechon, *Compt. rend.*, **150,** 1169 (1910); (b) Taylor and Marshall, *J. Phys. Chem.*, **29,** 1140 (1925); (c) Olson and Meyers, This Journal, **48,** 389 (1926); (d) **49,** 3131 (1927); (e) Taylor and Bates, *ibid.*, **49,** 2483 (1927).

[4] Lind, Bardwell and Perry, *ibid.*, **48,** 1556 (1926).

[5] Franck and Cario, *Z. Physik,* 11, 162 (1922).

a three-way stopcock, and connection to the pump and to the gas analysis apparatus was made through a stopcock at the other end of the reaction vessel. Temperature control was provided by a copper water-bath in which the reaction vessel was immersed and which could be cooled by a stream of water previously brought to the desired temperature, or heated by a burner placed beneath it. A few drops of mercury were always present in the vessel, as well as in the storage reservoir, so that the gas might be saturated with mercury vapor at the temperature of the experiment.

The source of illumination was a mercury arc of the type described by Taylor,[6] constructed of pyrex glass, with a quartz section where it passed through the vessel to permit emission of the desired ultraviolet light. The base of the arc was cooled in a water-bath to 30°. This cooling is essential in order to keep the excess mercury vapor in the arc itself from absorbing the 2536.7 Å. light before it reaches the reaction vessel. An arc of this type also emits light of wave length 1860 Å., but the transmission of the quartz for this wave length is quite poor and but little could have reached the reaction system. This is indicated too by the fact that the rates were only slightly different at the end of many hundred hours of running the arc, when the quartz was quite brown. It is known that to secure transmission of 1860 Å. the quartz must be new and unusually clear. The arc was connected through a large-bore stopcock at the top to a mercury vapor pump which was kept in operation during almost all runs. It was not practicable to exhaust and seal off the arc, though this would have provided more constant conditions of intensity.

The current for the arc was supplied by a D. C. generator giving 125 volts, and resistances so adjusted that it burned at 8 amperes. The potential drop across the arc itself was about 50 volts, but due to large fluctuations in the local line voltage supplying the motor-generator, the watt load of the lamp could not be kept constant. On this account, only indirect comparison of the rates found in different experiments is possible.

The reaction vessel was exhausted by a Cenco Hyvac Oil pump capable of maintaining a vacuum of 0.001 mm. of mercury. This pressure was not attained in practice, for liquid polymers accumulated in the vessel which must have had a vapor pressure much higher than the lower limit of the pump. These would be without effect on the reaction. Air, however, was not present in the system, for unpublished experiments of Taylor and Marshall, and of Mr. A. A. Vernon in this Laboratory have shown that small quantities of oxygen added to such a reacting system cause a very large increase in rate until the oxygen is used up, when the rate drops to normal. Such an irregularity was not observed at any time in these experiments.

**Preparation of Gases.**—Hydrogen was taken from a cylinder, purified from oxygen by passage over hot platinized asbestos and dried by condensing the water in a trap cooled with carbon dioxide snow.

Ethylene was taken from a cylinder and dried in the same way. Analysis of the gas showed it to be better than 99% pure, with the impurity apparently higher unsaturates, which would be largely removed by the freezing mixture.

Ethane was made by catalytic combination of hydrogen and ethylene, purified as above, over nickel at room temperature. This was always accomplished in the presence of excess hydrogen, the amount being subsequently determined by analysis of the resulting mixture. For pure ethane, the hydrogen was pumped off from solid ethane at liquid air temperature, the ethane then being distilled *in vacuo* until no further gas was evolved. In most cases more hydrogen was added to the ethane as prepared to make the desired mixture for experiment.

Propane and butane were taken from cylinders and found to be upward of 98% pure. Since the impurities were other saturated hydrocarbons, they were used as they

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[6] Taylor, THIS JOURNAL, **48,** 2840 (1926).

came from the cylinders, and the whole was considered as a hydrocarbon of the average composition found by analysis.

**Gas Analysis.**—The gases were analyzed in a Williams gas analysis apparatus over water. Acetylene was absorbed in ammoniacal silver nitrate, saturated with ammonium nitrate to diminish the ammonia vapor pressure. Ethylene was estimated with bromine water, after which the excess bromine vapor was removed by passing the gas through a pipet which contained a strong solution of sodium thiosulfate dissolved in 33% potassium hydroxide solution. Hydrogen was determined by combustion over copper oxide at 300°, and the saturated hydrocarbons were identified by repeating the combustion on the residual gas at 500°, absorbing the carbon dioxide in potassium hydroxide solution. All the possible constituents likely to be present could be identified, though the hydrocarbons could only be given an average composition.

## Experimental Results

**General Considerations.**—It has been observed by all the investigators who have studied the photosensitized reaction of hydrogen and ethylene that the pressure drops on illumination of mixtures containing excess hydrogen until that pressure is reached, which would be calculated, assuming that ethane was the sole product of reaction. Bates and Taylor seem to have been the first to observe that mixtures in which ethylene was the constituent present in excess must react in some other way, for the pressure drop did not stop at the theoretical point but continued at approximately the same rate. They did not follow the reaction to completion, or they would have found that the pressure change finally ceased at the pressure of the original hydrogen in this case also. This has proved to be a quite general phenomenon. In all of the mixtures of the two gases which we have used the pressure has always fallen on illumination until it reached approximately that of the hydrogen originally present, and has then remained practically constant. This change in rate is extremely sharp, dropping from 5 or 10 mm. per minute to one or two mm. per hour.

The pressure measurements alone, however, really afford no certain indication as to what the hydrocarbon may be. In a mixture of equal parts of the two gases at the start, combination to form any saturated gaseous hydrocarbon would, after the ethylene had all reacted, leave the final pressure just one-half of the initial.

Other considerations also showed that there must be other reactions taking place than the formation of ethane. For one thing, ethylene alone reacts with excited mercury, giving first an increase and subsequently a decrease in pressure, which continues at a constant rate, but so slowly that it has never been followed to the end-point. Even with the very high light intensities used in these experiments, it would have required a number of days of illumination to bring the reaction to an end. There must therefore be at least two distinct reactions.

That there were still other possibilities was shown by the appearance of a liquid oily substance in the reaction vessel. This had been noted by previous investigators in the case in which the initial ethylene concentration was high, but our investigations show that it is formed in all cases, though most rapidly under the conditions mentioned.

## Experimental Procedure I

**A. The Temperature Coefficient.**—In order to control the reaction as regards temperature, it was arranged to use a very rapid stream of water of the desired temperature, which should flow into the water-bath between the reaction vessel and the arc and be removed at the outside edge of the jacket. Even with as fast a stream as possible, the heat from the arc raised the temperature several degrees shortly after starting. It was necessary then to allow the arc to run with the reaction vessel evacuated until temperature equilibrium was reached, and then admit the gas as rapidly as possible from the gas buret. The pressure could be read one-half minute after the admission, and extrapolated back to the true initial pressure with sufficient accuracy. The water stream was unnecessary with runs at a temperature of 100°, where a burner beneath the vessel kept the water boiling or nearly so.

As an indication of the presence of a temperature coefficient, two experiments are given in which the temperature was varied during the course of the run, so that no other variables were introduced.

Table I

Results of Experiments

| | I | | II | | | |
|---|---|---|---|---|---|---|
| | $C_2H_4$, 203 mm.; $H_2$, 203 mm. | | $C_2H_4$, 395 mm.; $H_2$, 0 mm. | | | |
| Temp., °C. | 18 | 40 | 55 | 23.5 | 100 | 23.5 |
| $-\Delta p/\Delta T$, mm./min. | 1.5 | 10.8 | 0.12 | 0.15 | 0.40 | 0.15 |

**Discussion.**—The absolute magnitudes of these temperature coefficients are not of sufficient accuracy to be of use in theoretical calculations, which will be based on later measurements, but the actuality of the temperature sensitivity is evident, and also the fact that the reaction of ethylene alone has but a very small dependence on temperature. We may therefore say that some reaction involving hydrogen is largely dependent on temperature, or is a thermal reaction, while the rate-determining process with ethylene alone is a purely photochemical one and depends on the quantity of light absorbed. This fact must be deducible from whatever mechanism is proposed.

**B. Experiments with Partial Gas Analysis.**—The analysis system used for the following experiments permitted the determination of the composition of the saturated hydrocarbons by combustion over copper oxide. The temperature of burning was slightly under 500°, at which point all hydrocarbons except methane burn readily. By determining the carbon dioxide formed by the combustion, the complexity of the hydrocarbons was measured and the unburned residue was considered to be methane. The results are given in Table II. The figures give pressure of the gas in mm. of mercury. Time is in minutes.

Table II

Experimental Results

| *T*, °C. | Time, min. | Total, *P* | $H_2$ | $C_2H_4$ | End *P* | $C_2H$ | $C_2H_4$ | $H_2$ | Hydrocarbon | $C_2H_4$ | $-\Delta C_2$ | $-\Delta H_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 98 | 30 | 215.5 | 107.7 | 107.7 | 111.5 | 0 | 0 | 42 | 46 $C_2H_6$ | 23.5 | 51 | 100 |
| 98 | 24 | 235 | 117.5 | 117.5 | 122.5 | 0 | 0.5 | 53 | 27 $C_{2.6}H_{7.2}$ | 42 | 60 | 118 |
| 100 | 42 | 482 | 241 | 241 | 250.5 | 0 | 2 | 149 | 66.5 $C_{3.3}H_{8.6}$ | 33 | 113 | 220 |
| 97 | 25 | 650 | 325 | 325 | 332 | 0 | 2.5 | 199 | 104.5 $C_4H_{10}$ | 26 | 100 | 199 |
| 53.5 | 45 | 254.5 | 127.3 | 127.3 | 135.5 | 0 | 1 | 42 | 42.5 $C_{2.1}H_{6.2}$ | 50 | 56 | 107 |
| 44 | 73 | 295 | 147.5 | 147.5 | 148 | 0 | 0 | 103 | 37.5 $C_{3.8}H_{9.6}$ | 8 | 70 | 138 |
| 53 | 76 | 409 | 204.5 | 204.5 | 208 | 0 | 0 | 119 | 56 $C_{3.5}H_9$ | 33 | 89 | 178 |
| 28 | 30 | 420 | 210 | 210 | 222.5 | 0 | 0 | 116.5 | 69 $C_4H_{10}$ | 37 | 53 | 95 |
| 51 | 70 | 483 | 241.5 | 241.5 | 245.5 | 0 | 1.5 | 125.5 | 45 $C_{5.1}H_{12.2}$ | 73.5 | 88.5 | 177 |
| 52.5 | 75 | 302.5 | 151.3 | 151.3 | 149.5 | 0 | 0 | 86 | 23 $C_{4.6}H_{11.2}$ | 40.5 | 78 | 157 |
| 50 | 91 | 620 | 310 | 310 | 317.5 | 0 | 2 | 144 | 121 $C_{3.8}H_{9.6}$ | 50 | 53 | 102 |
| 52 | 90 | 700 | 350 | 350 | 351 | 0 | 7.5 | 80.5 | 188 $C_{2.3}H_{6.8}$ | 75 | 98 | 192 |
| 20–100 | 604 | 395 | 0 | 395 | 294.5 | 20.5 | 221 | 2 | 50.5 $C_{1.5}H_5$ | 0 | 116 | 199 |

**Discussion.**—It will be observed that when ethylene alone is allowed to react with excited mercury, acetylene is formed. Bates and Taylor showed that both acetylene and hydrogen could be identified among the products of decomposition in the absence of initial hydrogen. Von Wartenburg and Schulze have also found acetylene but under quite different conditions, and their results will be considered later. In these experiments definite indication of acetylene was not found except in the case of ethylene alone, and the subsequent experiments show that it should only appear in mixtures initially richer in ethylene than those of Table II.

The last two columns give the amounts of carbon and hydrogen, calculated as $C_2$ and $H_2$ which have disappeared from the gas phase. This loss should be the liquid which is formed, and it will be noted that in all cases twice as much hydrogen as carbon has gone to this product.

**C. The Liquid Polymer.**—The liquid which is deposited in the reaction vessel during the runs is a thick, viscous oil, and difficult to remove from the vessel in quantities large enough to work with. Since the quantity formed from one hundred cubic centimeters of ethylene, which was about the average amount present during an experiment, would be very small, the oil was allowed to accumulate in a small trap over a large number of runs, and drained off by breaking a capillary *tip* when desired. By this means, of course, only the least volatile fraction was removed, for the components of low boiling point were pumped off in the course of evacuation.

Lind[7] has obtained liquid and in some cases solid substances from the

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[7] Lind, Bardwell and Perry, This Journal, **48**, 1556 (1926); Lind and Bardwell, *ibid.*, **48**, 2335 (1926); Lind and Glockler, *Trans. Am. Electrochem. Soc.*, **52**, (preprint), No. 6, September, 1927.

bombardment of ethylene and of various saturated hydrocarbons by alpha particles and has examined in detail the properties of such a liquid when produced by subjecting ethane to the silent electrical discharge. It is of interest that the polymer we have obtained by yet a third method from ethylene, and as will be shown presently from saturated hydrocarbons, agrees so closely in its properties with the substance described by Lind and Glockler. They have shown that the oil is of constant composition, close to $(CH_2)_x$ but of variable molecular weight. We have reason to believe that the oil from the photosensitized reaction is similarly constituted, since its physical properties are quite variable, but its composition as calculated from a carbon–hydrogen balance sheet is the same.

The substance, then, is a viscous, colorless, or slightly yellow oil, with an odor very reminiscent of a terpene. The mean molecular weight of a sample determined by the freezing-point depression in benzene solution was 230.

Finally, as a confirmation of the calculated composition, a sample was analyzed by combustion; 0.0308 g. of oil gave on burning 0.0393 g. of water and 0.0929 g. of carbon dioxide. A few droplets of mercury unavoidably present in the oil are responsible for the failure of the weights to correspond exactly with that of the oil. However, the calculated composition from these figures is $(C_1H_{2.07})$, which is considered satisfactory confirmation of the supposed formula.

**D. The Reaction Rate.**—The rate of the pressure drop seemed so great, as compared with all previous photochemical reactions, that experiments were conducted to compare it with a better known reaction. Taylor and Marshall[3b] showed that the pressure decrease was more rapid than that in the hydrogen–oxygen combination. Marshall[8] has subsequently investigated the latter reaction in more detail, and finds it a chain reaction, in which at least six molecules must react for each quantum of 2536.7 Å. light absorbed. Table III gives a comparison of several experiments in the first three of which the hydrogen pressure was the same, and the other gas was respectively excess ethylene, an equivalent amount of oxygen, namely, half as much as the hydrogen, and, third, one with this same amount of ethylene. The fourth experiment contains different amounts of the gases, but in the same proportions as the first, and serves to show that the rate is fairly reproducible. All of these experiments were performed on the same day and with as nearly identical conditions as possible.

The discussion of these results will be reserved until later, for they will have more bearing on the mechanism ultimately to be proposed than in the present place.

**E. Secondary Reactions.**—With the same procedure as before, the possibility of secondary reactions until now unrecognized was investigated.

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[8] Marshall, *J. Phys. Chem.*, **30**, 34 (1926); **30**, 1078 (1926).

TABLE III

RESULTS OF EXPERIMENTS (ALL AT 100°)

| $P$ | Time | $-\Delta P/\Delta t$ | $P$ | Time | $-\Delta P/\Delta t$ | $P$ | Time | $-\Delta P/\Delta t$ |
|---|---|---|---|---|---|---|---|---|
| $H_2$, 150 mm.; $C_2H_4$, 450 mm. | | | $H_2$, 154 mm.; $O_2$, 75 mm. | | | $H_2$, 100 mm.; $C_2H_4$, 300 mm. | | |
| 599 | 0 | (9.5) | 229 | 0 | 14 | 400 | 0 | 15.5 |
| 589.5 | 1 | 12.7 | 214 | 1 | 13.5 | 384.5 | 1 | 17.5 |
| 564 | 3 | 12 | 201.5 | 2 | 11.5 | 367 | 2 | 16.5 |
| 552 | 4 | 13.3 | 191 | 3 | 10 | 334 | 4 | 18.5 |
| 525.5 | 6 | 14.5 | 181 | 4 | 4.5 | 315.5 | 5 | 16.5 |
| 496.5 | 8 | 13.5 | 176.5 | 5 | 2 | 282.5 | 7 | 16.5 |
| 442 | 12 | 14.5 | 174.5 | 6 | 1.7 | 266 | 8 | 16 |
| 427.5 | 13 | 13.3 | 171 | 8 | 2 | 250 | 9 | 16.3 |
| 387.5 | 16 | | 168.5 | 9 | 2.1 | 217.5 | 11 | 15.5 |
| Av. $-\Delta P/\Delta t$ = 13.4 mm./min. | | | 160 | 13 | | 186.5 | 12 | 16.1 |
| | | | | | | 138 | 16 | |
| $H_2$, 152 mm.; $C_2H_4$, 83 mm. | | | Cooled to 22.5°, 61.5 = 78.5 at 100°. Therefore residue is water. Av. = (Total gas lost, calcd.)/(Total time). Av. $-\Delta P/\Delta t$ = 11.5 mm./min. | | | Av. $-\Delta P/\Delta t$ = 16.5 mm./min. | | |
| 235.5 | 0 | 30.5 | | | | | | |
| 205 | 1 | 43 | | | | | | |
| 162 | 2 | (4.5) | | | | | | |
| 157.5 | 3 | | | | | | | |
| Av. $-\Delta P/\Delta t$ = 36.7 mm./min. | | | | | | | | |

Several experiments were made in which a sample of the gases after illumination was removed and analyzed, and the remainder, of known composition, was re-illuminated for a further period. Analysis at the end of this time would show the later course of the reaction after the main pressure drop. The results of three typical experiments are presented in Table IV.

TABLE IV

RESULTS OF EXPERIMENTS

| | $T$, °C. | $H_2$ | $C_2H_4$ | Hydrocarbon | $CH_4$ | $-\Delta C_2$ | $-\Delta H_2$ |
|---|---|---|---|---|---|---|---|
| Composition at start | .. | 350 | 350 | .......... | .. | ... | ... |
| After 90 min. run | 52 | 80.5 | 7.5 | $188C_{2.3}H_{6.6}$ | 75 | 89 | 184 |
| After withdrawing sample | .. | 59.2 | 5.1 | $136.2C_{2.3}H_{6.6}$ | 54.3 | ... | ... |
| After 60 min. more run | 51 | 138.5 | 0 | $48C_{3.8}H_{9.6}$ | 59.5 | 68 | 136 |
| Composition at start | .. | 310 | 310 | .......... | .. | ... | ... |
| After 90 min. run | 50 | 144 | 2 | $121C_{3.8}H_{9.6}$ | 50 | 53 | 102 |
| After withdrawing sample | .. | 87.1 | 1.2 | $73.1C_{3.8}H_{9.6}$ | 30.2 | ... | ... |
| After 30 min. more run | 49 | 111.5 | 0 | $38.1C_{4.3}H_{10.6}$ | 41.5 | 52 | 104 |
| Composition at start | .. | 307.5 | 307.5 | .......... | .. | ... | ... |
| After overnight run | 42 | 235 | 0 | $3.7C_{5.5}H_{13}$ | 31.3 | 277 | 599 |

**Discussion.**—It is evident that very considerable reaction has occurred during the second period, for the hydrocarbons have changed both in amount and composition, while more polymer has been deposited. The remarkable fact is that the total pressure in the system has remained unchanged, or practically so, during the second stage.

## Experimental Procedure II

It was necessary, therefore, to investigate these secondary reactions in a more complete manner. A number of experiments were performed on various hydrocarbons with and without hydrogen, under the same conditions of temperature and illumination as with ethylene and hydrogen.

In these experiments, the method of analysis was modified to avoid the error which was likely to result from an assumption that methane could be quantitatively separated from the other saturated gases by preferential combustion. There was no assurance that the separation was complete, and the wide variations in the relative proportions of methane and other hydrocarbons shown in Table III were an indication that methane was being burned to an undetermined extent along with the other gases.

Therefore, from this point onward in the research, the copper oxide tube was kept at a dull red heat when burning hydrocarbons, and their composition was found as an average of the entire gas. This procedure also eliminated the errors which may so readily appear in an analysis when a substance is determined solely by difference. The results of a number of runs on the hydrocarbons are given in Table V.

TABLE V

RESULTS OF RUNS ON HYDROCARBONS

| *T*, °C. | Time, min. | Total *P* | $H_2$ | H. C. | End *P* | $C_2H_2$ | $C_2H_4$ | $H_2$ | Hydrocarbon | $-\Delta C_2$ | $-\Delta H_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $C_2H_6$ | | | | | | | |
| 98 | 60 | 589.0 | 56.5 | 532.5 | 596.0 | 0 | 0 | 62.5 | 534 $C_{1.7}H_{5.4}$ | 73 | 147 |
| 100 | 60 | 248.0 | 23.8 | 224.0 | 251.0 | 0 | 0 | 28.5 | 222 $C_{1.4}H_{4.8}$ | 67 | 135 |
| 97 | 60 | 414.0 | 56.5 | 358.0 | 417.5 | 0 | 0 | 33.5 | 384 $C_{1.6}H_5$ | 71 | 139 |
| 100 | 60 | 399.5 | 70.5 | 329.0 | 395.5 | 0 | 0 | 82.5 | 313 $C_{1.96}H_{5.9}$ | 22 | 49 |
| 97 | 60 | 691.0 | 332.6 | 338.4 | 693.0 | 0 | 0 | 318.0 | 375 $C_{1.85}H_{5.7}$ | 11.5 | 24 |
| 97 | 60 | 686.0 | 341.0 | 345.0 | 691.0 | 0 | 0 | 324.0 | 367 $C_{1.7}H_{5.4}$ | 30 | 54 |
| 46 | 105 | 536.5 | 90.2 | 446.3 | 527.5 | 0 | 0 | 61.5 | 466 $C_{1.4}H_{4.8}$ | 117 | 242 |
| 46 | 120 | 389.5 | 225.0 | 164.5 | 388.5 | 0 | 0 | 211.0 | 177 $C_{1.85}H_{5.7}$ | 3.5 | 6.5 |
| | | | | $C_2H_6$ alone | | | | | | | |
| 94 | 60 | 289 | 0 | 289 | 291.5 | 3 | 0 | 29.0 | 258 $C_{1.9}H_{5.8}$ | 41 | 79 |
| | | | | $C_3H_8$ alone | | | | | | | |
| 90 | 30 | 502.5 | 0 | 477.4 $C_3$<br>25.1 $C_2$ | 509 | 12.5 | 0 | 81 | 415 $C_3H_8$ | 106 | 228 |
| 94 | 93 | 430.5 | 0 | 411.5 $C_3$<br>19.0 $C_2$ | 420 | 0 | 0 | 169 | 251 $C_{2.85}H_{7.7}$ | 277.5 | 566 |
| | | | | $C_4H_{10}$ alone | | | | | | | |
| 94 | 30 | 426.5 | 0 | 426.5 $C_{4.02}$ | 432 | 13 | 0 | 84.5 | 334.5 $C_{3.9}H_{9.8}$ | 219 | 405 |
| 95 | 180 | 282.0 | 0 | 282 $C_{4.02}$ | 280 | 0 | 0 | 159.0 | 121 $C_{3.85}H_{9.7}$ | 330 | 663 |
| | | | | $CH_4$ | | | | | | | |
| 97 | 930 | 575.5 | 386.5 | 189 $CH_4$ | 574.5 | 0 | 0 | 384 | 190.5 $CH_4$ | ... | ... |
| | | | | $CH_4$ alone | | | | | | | |
| 95 | 64 | 314 | 0 | 314 $CH_4$ | 318.5 | 0 | 0 | 7 (?) | 311 ($C_{1.6}H_{4.8}$) ? | ... | ... |

**Discussion.**—The general trend is clear, though the constancy of the results is not very satisfactory. All the saturated hydrocarbons with the exception of methane are decomposed either by excited mercury or by hydrogen atoms, giving as final products methane, polymer and hydrogen. The small amount of reaction which the last experiment on methane and hydrogen would seem to show is ascribed to reaction of the polymer in the vessel with the hydrogen atoms. It seems quite likely that such hydrogen atoms as strike this liquid cause reaction and vaporization of small quantities of hydrocarbon. Work by Tolloczko[9] and by Bonhoeffer[10] confirms the hypothesis that methane is stable to excited mercury and to hydrogen atoms, respectively. The reason for this is not known, for from the linkage energies as commonly given, methane should react as readily as the others.

In general, then, the higher hydrocarbons react more readily than the lower. Hydrogen seems to have an inhibiting action when it is present in large quantities. Any mechanism proposed will have to take account of this fact.

**Experimental Procedure** III.—In order to find which of the various reactions have ethylene as a basic material, and which depend on saturated hydrocarbons, analyses were made at different times during the reaction of hydrogen and ethylene. Mixtures of the same composition were illuminated until a predetermined pressure was reached, and then analyzed. A sufficient number of repetitions of this process gave the course of reaction until all ethylene had disappeared. A few experiments in which longer illumination was used gave the course of reaction after pressure changes had ceased. Due to the variations in intensity already mentioned, the stage of reaction could not be estimated from the time. Therefore, arbitrarily, the percentage of ethylene used was taken as a standard of reference, and the percentage figures in the table apply to that. In this way comparisons between various gas mixtures were possible. These experiments are summarized in Table VI.

TABLE VI

RESULTS WITH EXPERIMENTAL PROCEDURE III

| % | T | Time, min. | Total P | $H_2$ | $C_2H_4$ | End P | $C_2H_2$ | $C_2H_4$ | $H_2$ | Hydrocarbon | $-\Delta C_2$ | $-\Delta H_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 75% $C_2H_4$ | 25% $H_2$ | | | | | | |
| 36 | 100 | 17 | 410.5 | 102.6 | 307.9 | 333.5 | 13.5 | 195 | 60 | 65 $C_{2.9}H_{7.8}$ | 0 | 0 |
| 47 | 99 | 39 | 410.5 | 102.6 | 307.9 | 308.5 | 14 | 162 | 50 | 82.5 $C_{2.5}H_{7.0}$ | 28.5 | 41 |
| 57 | 100 | 38 | 412.0 | 103.5 | 309.0 | 273.5 | 16 | 134.5 | 35.5 | 87.5 $C_{2.9}H_{7.8}$ | 32 | 59 |
| 78 | 99 | 99 | 407.5 | 101.9 | 305.6 | 200.0 | 9.5 | 66.5 | 22.0 | 102 $C_{2.7}H_{7.4}$ | 94.5 | 179 |
| 84 | 98 | 76 | 410.5 | 102.6 | 307.9 | 179.0 | 10 | 51 | 18.0 | 100 $C_{3.1}H_{8.2}$ | 92 | 179 |
| 92 | 96 | 129 | 410.5 | 102.6 | 307.9 | 143.0 | 2.5 | 24.5 | 15.5 | 101 $C_{2.7}H_{7.4}$ | 147 | 283 |
| 95 | 98 | 113 | 411.0 | 102.8 | 308.2 | 103 | 0 | 19 | 21.5 | 62.5 $C_{2.7}H_{7.6}$ | 201 | 429.5 |
| 99 | 98 | 95 | 409.5 | 102.4 | 307.1 | 100 | 0 | 4 | 17 | 79 $C_{3.8}H_{9.6}$ | 153.5 | 313.0 |
| 100 | 98 | 347 | 411.0 | 102.8 | 308.2 | 88.5 | 0 | 2.5 | 45.5 | 40.5 $C_{1.5}H_5$ | 275 | 566 |
| 100 | 95 | 763+ | 410.0 | 102.5 | 307.5 | 94 | 0 | 0 | 60.5 | 33.5 $CH_4$ | 291 | 590 |
| 38 | 16 | 49 | 410.0 | 102.5 | 307.5 | 288 | 6.5 | 191 | 59 | 29.5 $C_{2.6}H_{7.2}$ | 71.5 | 164 |
| 60 | 15 | 79 | 410.5 | 102.6 | 307.9 | 190.5 | 2.5 | 121 | 42.5 | 24.5 $C_{2.4}H_{6.8}$ | 155 | 339 |
| 97 | 16 | 765 | 410.0 | 102.5 | 307.5 | 81.5 | 0 | 2.5 | 13.5 | 65.5 $C_{2.5}H_7$ | 223 | 470 |

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[9] Tolloczko, *Przemysl Chem.*, **2,** 245 (1927).

[10] Bonhoeffer and Harteck, *Z. physik. Chem.*, **139A,** 64 (1928).

TABLE VI (*Concluded*)

| % | $T$ | Time, min. | Total $P$ | $H_2$ | $C_2H_4$ | End $P$ | $C_2H_4$ | $C_2H_4$ | $H_2$ | Hydrocarbon | | $-\Delta C_2$ | $-\Delta H_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 62% $C_2H_4$ 38% $H_2$ | | | | | | | | | | | | | |
| 41 | 98 | 5 | 400.5 | 152.2 | 248.3 | 318 | 14.5 | 146 | 105.5 | 52 | $C_3H_8$ | 10 | 28 |
| 72 | 99 | 14 | 400.5 | 152.2 | 248.3 | 229.5 | 6 | 69 | 76.5 | 78 | $C_{3.2}H_{8.4}$ | 48 | 100 |
| 98 | 98 | 13 | 399.5 | 152.0 | 247.5 | 156 | 0 | 4.5 | 48.5 | 103.5 | $C_{3.2}H_{8.4}$ | 77.5 | 155 |
| 40 | 15 | 168 | 400 | 152.0 | 248.0 | 316.5 | 8.5 | 147.5 | 104 | 56.5 | $C_3H_8$ | 7 | 15 |
| 64 | 16 | 269 | 400 | 152.0 | 248.0 | 224.5 | 5.5 | 65.5 | 69 | 84.5 | $C_{3.5}H_7$ | 29 | 62 |
| 98 | 17 | 398 | 400.5 | 152.2 | 248.3 | 146.0 | 0 | 4.5 | 48 | 95.5 | $C_{3.3}H_{8.8}$ | 89.5 | 190 |
| 50% $C_2H_4$ 50% $H_2$ | | | | | | | | | | | | | |
| 25 | 96 | 3.5 | 411.5 | 205.7 | 205.7 | 367.5 | 0 | 153.5 | 189.5 | 24 | $C_{3.7}H_{9.4}$ | 0 | 0 |
| 41 | 99 | 5.25 | 391.0 | 195.5 | 195.5 | 326 | 0 | 115.0 | 163.0 | 48 | $C_{3.8}H_{8.8}$ | 0 | 0 |
| 56 | 100 | 11.5 | 392.0 | 196.0 | 196.0 | 294 | 0 | 87 | 145 | 62 | $C_{3.4}H_{8.8}$ | 0 | 0 |
| 75 | 100 | 9.5 | 393.0 | 196.5 | 196.5 | 262 | 0 | 50.5 | 135.5 | 70.5 | $C_{3.8}H_{9.6}$ | 0 | 0 |
| 75 | 100 | 20 | 392.0 | 196.0 | 196.0 | 245 | 0 | 43.0 | 123.5 | 78.5 | $C_{3.4}H_{8.8}$ | 19.5 | 32.5 |
| 93 | 100 | 20.5 | 393.5 | 196.7 | 196.7 | 216.5 | 0 | 14 | 118 | 84.5 | $C_4H_{10}$ | 13.7 | 21.2 |
| 98 | 100 | 20 | 392.0 | 196.0 | 196.0 | 204.5 | 0 | 4.5 | 110 | 89.5 | $C_{3.3}H_{9.6}$ | 21.5 | 40.0 |
| 99 | 100 | 23 | 393.5 | 196.7 | 196.7 | 202 | 0 | 3.5 | 111 | 81.5 | $C_{3.7}H_{9.4}$ | 32 | 61.5 |
| 100 | 53 | 76 | 409.5 | 204.7 | 204.7 | 208 | 0 | 0 | 119 | 89 | $C_{2.5}H_7$ | 89 | 178 |
| 100 | 28 | 30 | 420.0 | 210.0 | 210.0 | 222.5 | 0 | 0 | 116.5 | 106 | $C_{2.9}H_{7.8}$ | 53 | 95 |
| 37 | 99 | 9 | 600 | 300 | 300 | 500 | 0 | 188 | 235 | 77 | $C_{3.1}H_{8.2}$ | 0 | 0 |
| 69 | 100 | 23 | 602.5 | 301.3 | 301.3 | 402 | 0 | 93.5 | 201 | 107 | $C_{3.5}H_8$ | 0 | 0 |
| 96 | 100 | 26 | 599 | 299.5 | 299.5 | 307.5 | 0 | 11.5 | 158 | 138 | $C_{3.7}H_{9.4}$ | 32.7 | 69 |
| 42 | 99 | 5.5 | 198 | 99 | 99 | 165.5 | 0 | 57.5 | 84 | 24 | $C_{3.9}H_{9.8}$ | 0 | 0 |
| 72 | 99 | 11.5 | 199.5 | 99.7 | 99.7 | 134 | 0 | 27.5 | 69.5 | 39 | $C_{3.8}H_{9.6}$ | 0 | 0 |
| 96 | 100 | 17 | 198.5 | 99.3 | 99.3 | 104.5 | 0 | 4.0 | 59.5 | 41 | $C_{3.9}H_{9.8}$ | 15.3 | 29.3 |
| 50% $C_2H_4$ 50% $H_2$ | | | | | | | | | | | | | |
| 36 | 15 | 108 | 401.5 | 200.7 | 200.7 | 334.5 | 0 | 128 | 162 | 44.5 | $C_{3.7}H_{9.4}$ | 0 | 0 |
| 69 | 15 | 261 | 399.5 | 199.5 | 199.5 | 226 | 0 | 61 | 133.5 | 71 | $C_{6.8}H_8$ | 13.5 | 21.7 |
| 98 | 15 | 391 | 402.0 | 201 | 201 | 202.5 | 0 | 5.5 | 115.5 | 81.5 | $C_{3.7}H_{9.4}$ | 45 | 94 |
| 25% $C_2H_4$ 75% $H_2$ | | | | | | | | | | | | | |
| 19 | 99 | 0.75 | 410 | 307.5 | 102.5 | 394.5 | 0 | 83.5 | 293 | 18 | $C_{2.6}H_{7.2}$ | 0 | 0 |
| 27 | 99 | 1.33 | 410 | 307.5 | 102.5 | 383.5 | 0 | 74.0 | 287 | 22.5 | $C_{2.7}H_{7.4}$ | 0 | 0 |
| 48 | 100 | 3 | 410 | 307.5 | 102.5 | 359.0 | 0 | 53 | 268 | 38 | $C_{2.7}H_{7.4}$ | 0 | 0 |
| 73 | 100 | 6.25 | 411 | 308.3 | 102.7 | 336 | 0 | 27 | 252.5 | 56 | $C_{2.7}H_{7.4}$ | 0 | 0 |
| 73 | 94 | 7 | 410.5 | 307.9 | 102.6 | 334.5 | 0 | 26.5 | 259 | 49 | $C_{2.9}H_{7.8}$ | 5 | 10 |
| 98 | 96 | 7 | 409.5 | 307.1 | 102.4 | 309.5 | 0 | 2 | 248 | 60 | $C_{2.8}H_{7.6}$ | 16.5 | 33 |
| 98 | 98 | 11 | 409.5 | 307.1 | 102.4 | 310.5 | 0 | 2 | 261.5 | 47 | $C_{2.9}H_{7.8}$ | 32 | 64 |
| 100 | 98 | 180 | 409.5 | 307.1 | 102.4 | 310.5 | 0 | 0 | 280.0 | 28 | $C_{1.8}H_{5.6}$ | 77 | 154 |
| 100 | 87 | 750 | 413 | 309.8 | 103.2 | 319 | 0 | 0 | 299.5 | 19.5 | $CH_4$ | 93.5 | 177 |
| 37 | 16 | 49 | 409.5 | 307.1 | 102.4 | 376.5 | 0 | 65.0 | 287.5 | 24 | $C_{2.8}H_{7.2}$ | 0 | 0 |
| 68 | 15 | 65 | 410 | 307.5 | 102.5 | 339.5 | 0 | 32.5 | 261 | 46 | $C_{2.4}H_{6.8}$ | 15 | 30 |
| 99 | 16 | 206 | 410.5 | 307.9 | 102.6 | 310.5 | 0 | 1.5 | 257 | 52 | $C_{2.7}H_{7.4}$ | 31 | 60 |
| 10% $C_2H_4$ 90% $H_2$ | | | | | | | | | | | | | |
| 33 | 96 | 1.5 | 600.5 | 540.4 | 60.1 | 580.5 | 0 | 40 | 515.5 | 25 | $C_{1.95}H_{5.9}$ | 0 | 0 |
| 77 | 97 | 2 | 600 | 540 | 60 | 556 | 0 | 13.5 | 499 | 42 | $C_{2.05}H_{6.1}$ | 0 | 0 |
| 97 | 97 | 4.5 | 599.5 | 539.5 | 60 | 542 | 0 | 2 | 489 | 50.5 | $C_2H_6$ | 7.5 | 15 |
| 100 | 98 | 164 | 599.5 | 539.5 | 60 | 541 | 0 | 0 | 517 | 24 | $CH_4$ | 48 | 96 |
| 31 | 16 | 107 | 599 | 539 | 60 | 574 | 0 | 41.5 | 511 | 21.5 | $C_{1.8}H_{5.6}$ | 0 | 0 |
| 74 | 16 | 167 | 600 | 540 | 60 | 553 | 0 | 15.5 | 491 | 47 | $C_{1.9}H_{5.8}$ | 0 | 0 |
| 100 | 16 | 411 | 600 | 540 | 60 | 532.5 | 0 | 0 | 499 | 33.5 | $C_{1.4}H_{4.8}$ | 36.5 | 81 |

**Discussion.**—It appears at once that the primary reaction of ethylene and hydrogen is the formation of saturated hydrocarbons, but not, in most circumstances, ethane. The composition of this saturated product depends on the concentration of the original mixture and is independent of the pressures used in our experiments. It is also practically independent of temperature. It may be that there is a temperature dependence which requires greater accuracy of analysis than was possible. Such a relation might be expected on the basis of the dependence of the reaction rate on temperature, which is very clearly shown.

The polymerization is a secondary reaction, and all, or at least practically all, polymer must go through the intermediate stage of saturated hydrocarbon. This is subsequently decomposed and deposits polymer, changing in composition at the same time, until nothing but methane and hydrogen is left in the gas phase.

The rate of reaction depends both on temperature and on composition of the gas. The temperature coefficient is very much greater for an initial mixture richer in hydrogen, so that this temperature dependence involves some reaction with hydrogen. All these restrictions must be satisfied by the proposed mechanism.

## Mechanism of the Reactions

Taylor and Bates[3e] have proposed a mechanism for the reaction between ethylene and excited mercury which seems to be in accord with the results presented here. Their scheme of reaction between ethylene and hydrogen atoms, which reaction seems to be the more important in many cases, requires revision. The actual processes must be quite complex, so that a qualitative explanation is all that may be given. The following, then, is offered as one, possibly of many conceivable mechanisms, which will explain the observations. The reactions will be tabulated here and discussed in detail subsequently.

$$\begin{array}{lr}
C_2H_4 + Hg' \longrightarrow C_2H_2 + H_2 + Hg & (1) \\
C_2H_2 + Hg' \longrightarrow \text{Cuprene} & \\
C_2H_2 + H \longrightarrow \text{Liquid polymer} & \\
H_2 + Hg' \longrightarrow 2H + Hg + 12{,}000 \text{ cal.} & (2) \\
H + C_2H_4 + H_2 \longrightarrow C_2H_6 + H + 5000 \text{ cal.} & (3a) \\
H + C_2H_4 + C_2H_4 \longrightarrow C_2H_5 + C_2H_4 + 15{,}000 \text{ cal.} & (3b) \\
C_2H_5 + C_2H_4 + H_2 \longrightarrow C_4H_{10} + H + 5000 \text{ cal.} & (4a) \\
C_2H_5 + C_2H_4 + C_2H_4 \longrightarrow C_4H_9 + C_2H_4 + 15{,}000 \text{ cal.} & (4b) \\
C_2H_5 + C_4H_9 \longrightarrow C_4H_8 + C_2H_6 + 55{,}000 \text{ cal.} & (5) \\
C_2H_6 + H \longrightarrow CH_3 + CH_4 + 20{,}000 \text{ cal.} & (6) \\
C_4H_{10} + H \longrightarrow C_3H_7 + CH_4 + 20{,}000 \text{ cal.} & \\
C_4H_{10} + Hg' \longrightarrow C_3H_7 + CH_3 + Hg + 52{,}000 \text{ cal.} & (7) \\
C_2H_5 + C_2H_6 \longrightarrow C_4H_9 + H_2 - 10{,}000 \text{ cal.} & (8) \\
C_2H_5 + H_2 \longrightarrow C_2H_6 + H - 10{,}000 \text{ cal.} & (9)
\end{array}$$

The reactions under (1) have been discussed by Taylor and Bates[3e] and Reaction 2 has been well established by the work of Franck and Cario,[5] so that neither need be treated here.

It is to reactions of the types indicated in (3) that we ascribe the principal course of reaction. Modern ideas, arising originally from quantum considerations, have shown that direct addition of two molecules to form one in the gas phase is an extremely improbable occurrence. For that reason we cannot assume that a hydrogen atom can add directly to an ethylene molecule to form a free ethyl radical. Such an addition can take place, however, if a third body is present at the collision, or, which amounts to the same thing, if a third molecule collides with the reactants during the short time during which an unstable pseudo-molecule might exist. If the third body is an ethylene molecule, as in (3b), it seems unlikely that anything other than the stabilization of a free ethyl radical would result. If the third body is hydrogen, however, a reaction to form ethane with liberation of a hydrogen atom is possible. This may, of course, take place in two steps, an ethyl radical being formed first, which subsequently reacts with another hydrogen as in Reaction 9, but the great rapidity of the reaction in the case where ethane is the sole product makes a mechanism of as few steps as possible the more preferable. It will be noted that (3a) has the character of a chain reaction, in that the hydrogen atom is capable of forming a large number of ethane molecules. The comparative rate measurements in Table III indicate that a chain is formed, since the rate is much faster than that of an established chain reaction.

Presumably the temperature coefficient is also to be ascribed to Reaction 3a, since the ethane is formed by this process. The results show that the temperature coefficient is greatest in the gas mixture which is transformed almost quantitatively to ethane. By inserting the temperature coefficient in this case in the Arrhenius equation, we can calculate that it corresponds to an activation energy of about 10,000 calories. In spite of this agreement, it is probably unjustifiable at the present time to connect this with the endothermic Reaction 9 and attempt to maintain the multi-stage reaction so indicated.

The reactions included in (4) are assumed to be typical of the early stages of the reaction, where ethylene is present in considerable quantities. It is possible to invent reactions which are possible energetically, almost at will. All that is necessary is that higher saturated hydrocarbons and higher radicals should result, as in (4a and 4b).

Reaction 5 is of a different type, and is the method by which the unsaturated polymer must be formed. Just what hydrocarbons are the products is unknown, and it is not improbable that Reaction 5 should form amylene and methane instead of butylene and ethane. Work of Mr. W. H. Jones in this Laboratory (to be published shortly) confirms the mechanism advanced here in so far that free radicals react to form unsaturated and saturated hydrocarbons, and that in the presence of hydrogen and ethylene, products similar to those of Reaction 4 occur.

The saturated hydrocarbons which are formed by a process such as (4a) or (5) have been shown in Table V to be decomposed both by hydrogen atoms and by excited mercury atoms. Since radicals must be formed by such reactions, we have postulated in Reactions 6 and 7 that methane or methyl and a residue are formed at once. The fact that methane is not attacked under the conditions of the reaction, but, on the contrary, is formed as a stable product in increasing quantities as exposure is continued, speaks for this hypothesis. These radicals will, as a rule, no longer react as in (4), owing to the low concentration of ethylene at the stage in the reaction where the saturated hydrocarbons are largely attacked. They will be limited primarily to Reaction 5, forming low concentrations of unsaturates which will be rapidly built up to high molecular weights as in (4b), and finally condense as liquid polymer by a repetition of (5). One would predict from this scheme that polymer, which implies high unsaturates, would be formed more rapidly after the primary ethylene was used up, for in this case the sole reaction of the hydrogen or the excited mercury is the production of the necessary radicals. This hypothesis is wholly confirmed, for Table VI shows that polymer appears late in the reaction in those cases in which reactions of the type of (3a) would predominate.

Reactions 8 and 9 are endothermic, but of small enough heat value so that their occurrence is of moderate frequency. In fact it is not unreasonable to expect that reactions of this type which can be calculated to occur on about one collision in a million will be quite appreciable, since the other possibility involves two radicals, which must be of very small concentration. Granted these reactions, then, we can explain the retarding effect on the decomposition of saturated hydrocarbons which large amounts of hydrogen appear to have.

## Discussion of Other Results

The mechanism which is proposed can be shown to accord with the experimental results of other investigators.

Olson and Meyers[3] analyzed the gases resulting from the photosensitized reaction of hydrogen and ethylene by positive ray methods and found methane, propane and butane in the gas phase as well as the ethane that was expected. No mention is made of polymer formation in connection with these analyses, though they observed its formation in their earlier work.

We are not able to understand, however, the statement of these authors that ethane does not react when bombarded by excited mercury atoms. That there is no material pressure change is in accord with our findings, but the positive ray analysis should have shown a number of other hydrocarbons present and also hydrogen. This latter might have escaped notice on account of its small mass. The work of Tolloczko[9] confirms that reported here in that ethane is and methane is not attacked by excited mercury.

Bonhoeffer and Harteck[10] have recently published a paper in which they present spectroscopic evidence to show that ethylene, ethane and other hydrocarbons, except methane, are attacked by hydrogen atoms and stripped of their own hydrogen until very simple residues remain. They pulled atomic hydrogen from a discharge tube into the gas, and observed in the resulting luminescence the bands which are assigned to the C–C and the C–H radicals. We may suggest that the fact of spectral emission does not require the presence of more than a very minute quantity of the excited substance. In their experiments only slight quantities could be present, for it requires a number of collisions with hydrogen atoms to produce the radicals under any mechanism, and the nature of the method requires low pressures, where such multiple collisions will be rare.

Their results are explicable under our mechanism. It should be impossible to split an ethylene molecule into two $CH_2$ radicals on collision with a hydrogen atom. Fracturing a double bond demands about 125,000 calories, which the hydrogen atom cannot supply. If the primary process is that postulated here, the reaction would involve primary formation of ethane, and decomposition of that, which according to our mechanism would give both methyl and ethyl radicals. These may then lose hydrogen further, and will do so the more readily under their conditions, since the concentration of hydrogen atoms is so much greater.

Von Wartenburg and Schulze[11] have analyzed the products of reaction conducted by Bonhoeffer and Harteck's method, and find results quite compatible with our own. The saturated hydrocarbon is practically pure ethane, as it should be with the large excess of hydrogen present. In the decomposition of ethane they find but slight change in the gas. It would be but slight under their conditions and would probably have escaped notice, for the analysis depended on freezing the effluent gases. Methane and hydrogen would have passed through the liquid-air trap even if formed.

## Conclusion

1. The reaction between hydrogen and ethylene under the influence of excited mercury atoms has been investigated with varying conditions of pressure, concentration and temperature. The concentration is the only factor which has any effect on the course of the reaction.

2. The reaction proceeds the more quantitatively to form saturated hydrocarbon the greater is the concentration of hydrogen. The particular hydrocarbon formed is also dependent on the composition of the original mixture illuminated. High hydrogen concentration favors mainly ethane formation.

3. These saturated hydrocarbons are subsequently decomposed both by excited mercury atoms and by atomic hydrogen, and yield methane as the stable product in the gas phase. At the same time a liquid polymer of composition $C_xH_{2x}$ is deposited on the walls. Methane is unattacked by either excited mercury or by atomic hydrogen.

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[11] Von Wartenburg and Schulze, *Z. physik. Chem.*, [B] **2,** 1 (1929).

4. A mechanism is proposed to explain these results. It can be shown to be in accord also with the results of other experimenters.

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# REDUCTION REACTIONS WITH CALCIUM HYDRIDE. I. RAPID DETERMINATION OF SULFUR IN INSOLUBLE SULFATES[1]

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RECEIVED MAY 6, 1929 PUBLISHED OCTOBER 5, 1929

Almost all quantitative methods of determining sulfur in either organic or inorganic matter have as their method of procedure the oxidation of the sulfur to sulfate and subsequent precipitation with barium chloride. With reductive reactions of calcium carbide and calcium hydride in mind it was thought of interest to see whether the sulfur in various compounds, both organic and inorganic, could be quantitatively converted to calcium sulfide by ignition with these substances. If the sulfur were quantitatively changed to calcium sulfide, it could be estimated by acidifying the soluble sulfide solution, followed by iodimetric titration.

The hardest test to which this reasoning could be put was to attempt quantitative reduction of sulfates to sulfides. The amount of soluble sulfide formed was then to be determined with standard iodine solution. The present paper will report results of such experiments.

Sulfur in a steel has long been determined by heating a sample of steel filings with hydrochloric acid in a closed system, dissolving the evolved hydrogen sulfide from the sulfide in the steel in either ammoniacal cadmium chloride or caustic soda solution. The absorbing solution is then diluted with water, acidified with hydrochloric acid and titrated with iodine, using starch as indicator. Soluble sulfides such as calcium sulfide and sodium sulfide may also be determined by iodine titration.

A few investigators have studied reductions of sulfur compounds to sulfides in a quantitative way. Luigi Losana[2] has attempted to reduce sulfur to sulfide by ignition with a mixture of sodium bicarbonate and iron powder. The ignited mass was placed in an evolution flask and treated with acid much as in the determination of sulfur in steel. The method is said to be of general application for inorganic sulfur compounds.

Other metals and mixtures of metals and salts have been tried in effecting conversion of oxy-compounds of sulfur to sulfides. H. Bahr and W. van

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[1] This paper is prepared from the first part of a dissertation on reduction reactions with calcium hydride, to be presented by William E. Caldwell in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Losana, *Giorn. chim. ind. applicata,* 4, 204–206 (1922).