butanes. The dibromide from the synthetic 1-butene distilled almost entirely at 80.5–80.7° under 50.0 mm. and gave no indication that 2,3-dibromobutane was present. Its refractive index, n^{20}_{D}, was 1.5171. These constants were unaffected by subsequent distillation.

Summary

The hydrocarbon, 1-butene, is conveniently and rapidly prepared by adding allyl bromide to methylmagnesium bromide at 70° with stirring. The Grignard reagent should be previously heated in a bath at 130° in order to remove as much ether as possible. Dilute perchloric acid is effective in removing ether from the gas stream.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

EQUILIBRIUM IN THE REACTION $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$[1]

BY ROBERT N. PEASE[2] AND PAUL R. CHESEBRO[3]

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It has been shown by Sabatier[4] that the hydrogenation of carbon dioxide to produce methane and steam is effected in the presence of catalytic nickel at 200–350°. By employing the free energy equations of Lewis and Randall,[5] it may be calculated that the reverse reaction, $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$, should proceed to the extent of 28.6% at 500° and 1 atmosphere, using a stoichiometric ($1\ CH_4 : 2\ H_2O$) mixture. In view of the fact that little data are available on this reverse reaction, and that a determination of the position of equilibrium allows of an independent calculation of the free energy of methane, which is at present based solely on dissociation experiments conducted chiefly at high temperatures (1200–1600°), some further study of the reaction seemed desirable. We have, therefore, carried out both forward and reverse reactions at 500° and have determined the equilibrium position at this temperature. Since the result is in excellent agreement with the value calculated from the Lewis and Randall equations, we have considered that further work was unnecessary. This report deals with the above mentioned measurements.

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We wish to acknowledge also the assistance and advice of Professor Hugh S. Taylor of Princeton University, who is Director of Project No. 7. The title of this project is "Catalytic Methods Applied to Petroleum Hydrocarbons."

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[4] Sabatier and Senderens, *Compt. rend.*, **134,** 689 (1902).

[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923,** pp. 485, 571, 576.

Experimental Method

The flow method was employed. Methane and steam, or carbon dioxide and hydrogen, or mixtures of the four were passed at known rates of flow over a supported nickel-thoria catalyst at 505°, and the off-gas was measured and analyzed.

Calibrated flowmeters regulated the rates of flow of methane, carbon dioxide and hydrogen. These gases passed into a mixing chamber containing calcium chloride and the mixture then entered the heated catalyst tube. Steam was introduced as follows. Into the top of a 50 cc. buret was sealed a small dropping funnel, the stem of which was drawn out to a fine capillary. On the side of the buret near the top a capillary was sealed and bent downward. This capillary was joined at right angles to the tube conveying the gases to the catalyst and met the latter close to the furnace, at which point a plug of glass wool was introduced. Water was displaced from the buret at a constant rate by a fine stream of mercury flowing at constant head from the dropping funnel. The displaced water was taken up by the glass wool in the tube leading to the catalyst and was vaporized into the gas stream by the heat of the furnace. The furnace was tilted slightly to facilitate the passage of the liquid water.

The effluent gas was passed through weighed tubes of calcium chloride and of "askarite" (a form of soda lime) for absorption and determination of water vapor and carbon dioxide, respectively. To prevent condensation of water between the furnace and the calcium chloride tube, a small evaporating dish was placed directly under the connecting tube and gently heated. A thermometer in contact with the tube was kept at 100°. The unabsorbed gases were then collected over a 50% glycerine-water mixture in a 2-liter aspirator bottle. Hydrogen, carbon monoxide, methane and nitrogen were determined by fractional combustion with copper oxide. The total volume of this gas was measured in a gas buret.

The furnace consisted of a 30-inch length of steel tubing, 4 inches in diameter, set in a sheet-iron jacket about 1 foot in diameter. The latter was packed with loose magnesia. The steel tube was wound with heavy asbestos covered nichrome wire. The catalyst bulb occupied the middle fifth of this tube, the ends of which were packed with magnesia and blocked with asbestos disks.

Temperatures were measured with a chromel-alumel thermocouple set in a Pyrex tube in contact with the catalyst bulb. The couple was calibrated by taking the eutectic point (517.1°) of a mixture of 55% of sodium sulfate and 45% of potassium chloride.

In making a run the furnace was brought to temperature and the desired mixture passed through for at least one hour to ensure obtaining a steady state. The weighed absorption tubes were then connected to the aspirator bottle. Connection with the outlet tube of the catalyst bulb was then made and the time taken. The gas flow was then controlled by means of a stopcock through which the confining liquid in the aspirator bottle escaped to a receiver. The flowmeters were by this means kept at the proper mark. Considerable care was taken to maintain the flow and to hold the current through the furnace constant throughout the run.

The gases were of high purity. They were analyzed with the following results: methane—CH_4, 97.2%; N_2, 2.8%; hydrogen—H_2, 97.5%; N_2, 2.2%; O_2, 0.3%; carbon dioxide—CO_2, 99.4%; N_2, 0.6%.

In our earlier runs the catalyst was found to be slowly losing activity. We attributed this to traces of sulfur compounds in the methane and thereafter passed this gas over hot copper granules heated to 300–400°, with the result that no further poisoning was noted.

The rates of flow were of the order of 100–200 cc. per minute, and the apparent volume of the catalyst was about 100 cc. The space velocities were, therefore, of the order of 1 to 2 cc. of gas per cc. of catalyst per minute.

The catalyst was prepared by impregnating diatomite brick (10–20 mesh) with a solution of nickel nitrate and thorium nitrate. Twelve and five-tenths g. of $Ni(NO_3)_2.6H_2O$ and 0.5 g. of $Th(NO_3)_4$ were dissolved in water and the solution made up to 15 cc. This was allowed to fall drop by drop on 25 g. of the brick. The latter was then placed in the catalyst bulb, and dried and reduced in a current of hydrogen in the furnace. The temperature was slowly raised to 350° over several hours.

Results

The results of our measurements are given in Table I. We have calculated the volumes in liters of gases flowing into the system at 25° and 1 atm. from the flowmeter settings and the times (20 minutes) of the runs. (The volume of liquid water as read on the buret was converted to liters of vapor under these conditions.) These are given for comparison with the volumes of effluent gases. Under ideal conditions the volume, for example, of methane and carbon dioxide passed in should equal the volume of methane, carbon dioxide and carbon monoxide issuing from the system. Actually there is usually some discrepancy. This is doubtless in part due to temperature and pressure corrections to be applied to the flowmeters. It is also due to errors in the measurement and analysis of the off-gas.

TABLE I

EQUILIBRIUM MEASUREMENTS AT 505°

Temp., °C.	Press., mm. Hg.	Liters influent gas at 25°, 1 atm.					Liters effluent gas at 25°, 1 atm.						$K_{atm.} = \frac{[CO_2][H_2]^4P^2}{[CH_4][H_2O]^2}$
		CH_4	H_2O	CO_2	H_2	N_2	CH_4	H_2O	CO_2	H_2	CO	N_2	
Methane and Steam Only													
506	758.8	0.91	1.80	..	..	0.03	0.65	0.9	0.205	0.940	0.050	0.015	0.04
506	761.0	.97	1.95	..	..	.03	.73	.7	.180	.840	.040	.040	.04
506	765.2	.93	1.95	..	..	.03	.675	.6	.185	.820	.035	.040	.06
Carbon Dioxide and Hydrogen Only													
503	748.8	..	..	0.84	3.36	.07	.495	1.0	.290	1.030	.045	.020	.07
506	738.0	..	..	.82	3.27	.07	.505	1.0	.280	1.040	.045	.020	.07
Mixture Corresponding to 15% Conversion of Methane													
503	767.0	.72	1.40	.13	.50	.03	.505	1.45	.245	1.130	.040	.050	.033
508	744.5	.67	1.35	.12	.47	.03	.445	1.55	.260	1.160	.040	.025	.036
Mixture Corresponding to 45% Conversion of Methane													
502	761.8	.49	1.00	.40	1.59	.05	.535	1.40	.270	1.080	.035	.045	.030
505	766.0	.49	1.00	.40	1.59	.05	.515	1.45	.285	1.160	.040	.030	.046
Mixture Corresponding to 30% Conversion of Methane													
503	772.1	.62	1.25	.27	1.09	.04	.510	1.45	.300	1.130	.040	.050	.038
505	766.0	.59	1.20	.26	1.03	.04	.505	1.45	.280	1.140	.035	.040	.039
												Accepted value[a] of $K_{atm.}$ =	.037

[a] The equilibrium constants were calculated from the mole fractions of gases and their total pressure in atmospheres. Mole fractions were calculated from liters of the individual gases in the effluent and the total number of liters. The pressure represents the observed atmospheric pressure in millimeters divided by 760.

In the early runs there was some difficulty over the determination of the amount of water in the off-gas, due to condensation. Accordingly, only one significant figure is given for the first five runs. For the remainder of the runs, we believe that the composition of the off-gas is known to about 1%.

In the first three runs methane and steam only were introduced. Analysis of the off-gas revealed that 20–25% of the methane was converted to carbon dioxide. The next two runs were made with carbon dioxide and hydrogen only. These showed that 35–37% of the carbon dioxide was unchanged. These results indicated that equilibrium corresponded to the conversion of between 20 and 40% of the methane to carbon dioxide when stoichiometric mixtures were employed. Accordingly, three sets of two runs each were carried out, in the first of which a mixture corresponding to 15% conversion of methane was introduced, in the second a mixture corresponding to 45% conversion and in the third a mixture corresponding to 30% conversion. Equilibrium constants calculated from the results of these six runs all gave substantially the same result. We take the average—0.037—as our value at 505°, the average temperature of the runs.

The numerical value of the constant $K_{\text{atm.}} = [CO_2][H_2]^4P^2/[CH_4][H_2O]^2$ is highly sensitive to variations in the proportions of the gases. Thus a variation of 1% in the percentage of methane converted causes a 20% change in the value of K. Hence high precision in the latter is not to be expected. The extreme variations from our average value of 0.037 are 0.030 and 0.046, corresponding to a discrepancy of something like ± 2% in the determination of the equilibrium ratio. We take this to be our extreme experimental error.

We may compare our results with that calculated from the Lewis and Randall free energy equations already referred to. The latter give for the reaction, $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$, $\Delta F = 37010 - 7.88T \ln T - 0.00475T^2 + 0.000000105T^3 + 14.42T$. For $T = 778°$ K. (505°), $\Delta F_{778} = 5030$ cals., whence $\log K_{\text{atm.}} = -\dfrac{\Delta F}{4.579T} = 8.5880^{-10}$; and $K_{\text{atm.}} = 0.0387$. This value is in excellent agreement with our value of 0.037. We may therefore feel assured that the Lewis and Randall equations are adequate for the calculation of the equilibrium in this reaction at temperatures in the neighborhood of 500°. We may also conclude that the equation which these authors give for the free energy of methane expresses that quantity satisfactorily in the neighborhood of 500°. There was some question about this point since in this range the equation depended on data on the dissociation of methane into carbon and hydrogen in the presence of a nickel catalyst. Uncertainty arises as to the form of the deposited carbon.

It will be noted that we have reported in Table I quantities of carbon monoxide of the order of 1% in the effluent gas. This may be formed by the reaction, $CH_4 + H_2O \rightleftarrows CO + 3H_2$, or by the reaction, $CO_2 + H_2 \rightleftarrows CO + H_2O$. Calculations based on Lewis and Randall's free energy data show that the equilibrium constant for the first reaction is 0.00539 at 500°, and that the effluent gas from our experiments should contain 1.3% of carbon monoxide at 1 atm. total pressure. This is of the order of the amount obtained. The water-gas equilibrium has an equilibrium constant of 0.989 at 500°. This corresponds to a carbon monoxide concentration of 0.6% in the effluent gas from our experiments, which is somewhat less than was obtained.

In treating of experiments with methane and steam at 500° and above, it will in general be necessary to take account of the three reactions, $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$, $CH_4 + H_2O \rightleftarrows CO + 3H_2$ and $CO_2 + H_2 \rightleftarrows CO + H_2O$. There is no necessity that all these reactions shall take place under a given set of conditions, nor that the composition of off-gas shall be predictable from the equilibria in the above reactions. It is not unlikely, however, that with a catalyst such as we have used, and at temperatures of 500° and above, the off-gas will approximate to a composition which will satisfy all three reactions. For convenient reference we have tabulated below in Table II the equilibrium constants at 500, 600 and 700° for these reactions.

TABLE II

CALCULATED EQUILIBRIUM CONSTANTS

I—$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$; II—$CH_4 + H_2O \rightleftarrows CO + 3H_2$; III—$CO_2 + H_2 \rightleftarrows CO + H_2O$

Temp., °C.	Reaction I	II	III
500	0.0325	0.00539	0.0989
600	0.949	0.0696	.1983
700	15.06	11.03	.339

It is of interest to consider the reactions between methane and steam as a possible source of hydrogen. If carbon dioxide is formed, four volumes of hydrogen are obtained for every volume of methane reacting, while if carbon monoxide is formed, three volumes of hydrogen are obtained. Removal of water and carbon dioxide leaves a gas rich in hydrogen and containing as impurities methane and carbon monoxide. For example, a mixture of one volume of methane and two volumes of steam gives at 500° under equilibrium conditions a gas containing 40% of steam, 32% of hydrogen, 20% of methane, 8% of carbon dioxide and 1% of carbon monoxide. On removal of steam and carbon dioxide, the gas consists of 60% of hydrogen, 38% of the methane and 2% of carbon monoxide.

At higher temperatures the gas will be richer in hydrogen but also there will be somewhat more carbon monoxide. The actual composition will depend on the composition of gas admitted, and on the relative rates of the three reactions. At 700° the methane–steam reactions are both 70–80% complete. By using an excess of steam the reaction to form carbon dioxide is favored, and an excess of steam also tends to reverse the water-gas reaction (III), removing carbon monoxide. There is thus the possibility of obtaining a gas which is largely hydrogen. If carbon monoxide is desired as well, a decrease in the steam concentration will increase the concentration of this gas.

It is to be noted that patents have been granted for the operation of these reactions at still higher temperatures.[6] A comprehensive investigation of the field has recently been published by Neumann and Jacob.[7] The reactions were carried out in both directions between 300 and 1000°. Equilibrium was reached only above 800°.

Summary

1. The reaction, $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$, has been studied at 500° and atmospheric pressure. Equilibrium has been approached from both sides and the value of the constant found to be 0.037 (partial pressures being expressed in atmospheres) at 505°. This is in excellent agreement with the value calculated from Lewis and Randall's free energy equations, and thus supports in particular their equation for methane in the low temperature region.

2. It is pointed out that the reactions $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ and $CO_2 + H_2 \rightleftharpoons CO + H_2O$ are also to be taken into account at higher temperatures. Equilibrium constants at 500, 600 and 700° are given for reference.

3. Attention is called to the methane–steam reactions as a source of hydrogen and of hydrogen–carbon monoxide mixtures.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, THE ROOSEVELT HOSPITAL]

RED COMPOUNDS OF BARBITURIC ACID, PICRIC ACID AND SODIUM, OR LEAD, HYDROXIDE

BY ISIDOR GREENWALD

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Dox[1] has called attention to the red color obtained upon mixing solutions of barbituric acid, picric acid and sodium hydroxide. He stated that the color was due to the formation of picramic acid, although his only evidence therefor was the fact that the reaction mixture, treated with sulfanilic acid, sodium nitrite and acid, yielded yellow needles which appeared to be identical with those obtained from picramic acid under the same conditions.

It seemed to the writer that the matter was capable of more direct determination. His interest arose from the circumstance that Greenwald

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[6] Badische Anilin und Soda-Fabrik, British patent 12,978 (1913).

[7] Neumann and Jacob, *Z. Elektrochem.*, **30**, 557 (1924).

[1] Dox, *Z. physiol. Chem.*, **150**, 118 (1925).