increase in the nitration, but the best yield of nitropiperonal was obtained with nitric acid of sp. gr. 1.38 at 45°.

7. No trace of the isomeric nitropiperonal, m. p. 143°, present in Kahlbaum's commercial product, m. p. 80°, was obtained in any of the experiments.

8. That the isomeric nitropiperonal was probably formed as an intermediate product in the experiment using fuming nitric acid at 0° is indicated by the isolation of an isomeric mononitromethylenecatechol from the reaction mixture.

BOULDER, COLORADO

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

EQUILIBRIUM IN THE REACTION $C_2H_6 \rightleftarrows C_2H_4 + H_2$[1]

BY ROBERT N. PEASE[2] AND ELFORD S. DURGAN[3]

RECEIVED MAY 11, 1928 PUBLISHED OCTOBER 6, 1928

Bone and Coward[4] have shown that ethane is rather rapidly decomposed at 675°, and that the primary products of decomposition are ethylene and hydrogen; and it is well known that ethylene and hydrogen combine quantitatively to form ethane in the presence of catalysts from room temperature up to at least 350°.[5] The indications are, therefore, that the reaction $C_2H_6 \rightleftarrows C_2H_4 + H_2$ is reversible somewhere within the temperature region between 350 and 675°, and that equilibrium should be determinable. Indeed, Berthelot[6] has reported that dissociation and formation of ethane both occur at a low red heat. These results have encouraged us to attempt the measurement of equilibrium in this reaction.

Methods and Apparatus

The work of Bone and Coward having proved that prolonged heating of ethane or ethylene gives rise to by-products such as methane, it was necessary to show that the reaction under consideration was the main reaction under the conditions of our experiments. We therefore carried out forward and reverse reactions at each temperature, making a check-up of

---

[1] This paper contains the results of an investigation carried out as part of Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the American Petroleum Institute with the coöperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor of Princeton University is Director of Project No. 7.

[2] Research Associate, American Petroleum Institute.

[3] Research Assistant, American Petroleum Institute.

[4] Bone and Coward, *J. Chem. Soc.*, **93**, 1197 (1908).

[5] Sabatier and Senderens, *Ann. chim. phys.*, [8] **4**, 344 (1905).

[6] Berthelot, *Ann. chim.*, [4] **9**, 431 (1886).

reactants and products, and selecting times for heating such that side reactions constituted only a small fraction of the total. From these measurements the approximate position of equilibrium could be estimated. In order to obtain a more accurate value, mixtures of ethane, ethylene and hydrogen were made up to correspond to the calculated equilibrium, and were heated for the same lengths of time as the gases in the preliminary experiments. These measurements furnished the basis for our final values of the equilibrium constants.

Our method of experimentation was essentially as follows. The desired gas mixture was made up in a buret and delivered to an evacuated silica bulb which was heated electrically. After heating for the desired length of time, the pressure was determined, and a "snap" sample of the gas was transferred by means of a Töpler pump to a gas analysis apparatus. From the volume and composition of the gas admitted, the volume of the bulb together with the temperature and pressure, and the analysis of the gas sample, the amount of reaction could be determined.

The silica reaction bulb was connected to a gas buret, a mercury manometer and a Töpler pump through suitable stopcocks. The bulb occupied the middle third of a resistance furnace, the ends of which were packed with loose magnesia. The volume of the bulb was 207.5 cc. The temperature of the central portion of the furnace was determined by means of a calibrated two-junction chromel-alumel thermocouple. This central portion contained a sheath of sheet iron to insure uniformity of temperature.

The gas analysis apparatus was of the Bureau of Mines precision type. Ethylene was determined by absorption in dilute bromine water, the bromine subsequently being removed by absorption in a 30% solution of potassium hydroxide to which had been added sodium thiosulfate in order to minimize the evolution of oxygen. Fuming sulfuric acid proved very unsatisfactory because of the simultaneous absorption of ethane. No sharp end-point could be obtained. Oxygen was absorbed in alkaline pyrogallol. Hydrogen was determined by preferential combustion with copper oxide at 350°. The saturated hydrocarbons were determined by preferential combustion with copper oxide at 550° followed by absorption of carbon dioxide in 30% potassium hydroxide solution.

Hydrogen and ethylene were obtained from tanks of the pure gases. Ethane was prepared in 500cc. lots from ethylene and hydrogen by passage of a 50% mixture of these over a supported nickel catalyst at room temperature. The only purification consisted in freezing out moisture at −79°. The hydrogen contained 1.0% of nitrogen; the ethylene, 1.6% of nitrogen.

Results

Our equilibrium measurements were made at 600, 650 and 700°. Observations were also made at 500 and 550°, but the extreme slowness of the reactions and other factors rendered the measurements unsatisfactory. At 600° and above equilibrium could be approached more rapidly. Methane formation could not be avoided entirely, and at 700° would seem to have reached serious proportions. However, the consistency of our results inclines us to the belief that our final equilibrium values are not far from the truth.

Our final experimental results are presented in Table I. For each experiment we give the composition and pressure of the gas mixture as introduced into the reaction bulb, and the composition and pressure after heating.

Table I

Equilibrium Data

Heating time, min.	Mixture	Press., atm.	Composition of gas, %					$K_{atm.} = \frac{[C_2H_4][H_2]}{[C_2H_6]} \times \frac{P}{100}$
			C_2H_4	H_2	C_2H_6	CH_4	N_2	
			At 600°					
30	Initial	0.6730	...	5.80	92.00	...	2.20	
	Final	.7915	13.55	17.65	65.50	1.55	1.75	(0.0289)
30	Initial	.9770	48.40	50.20	...	...	1.40	
	Final	.6620	17.05	25.95	45.30	10.35	1.30	(0.0647)
30	Initial	.9115	14.35	16.05	67.95	...	1.65	
	Final	.9260	14.55	14.75	62.80	6.15	1.75	0.0316
			At 650°					
6	Initial	0.5555	...	5.80	92.00	...	2.20	
	Final	.7290	20.35	24.40	47.15	6.70	1.35	(0.0768)
8	Initial	1.0040	49.00	49.60	...	...	1.40	
	Final	0.7145	21.40	25.20	35.85	15.25	2.30	(0.1075)
6	Initial	1.0205	19.80	21.70	56.75	...	1.80	
	Final	1.0500	19.20	20.35	50.90	7.90	1.70	0.0806
6	Initial	0.9690	20.85	25.05	52.55	...	1.55	
	Final	.9785	17.30	23.60	47.60	10.65	0.85	0.0839
			At 700°					
5.75	Initial	0.5230	...	6.85	90.70	...	2.45	
	Final	.7345	19.00	26.55	21.15	31.45	1.90	(0.175)
4.5	Initial	1.0500	48.05	50.55	...	...	1.40	
	Final	0.7760	20.95	29.45	15.90	32.35	1.35	(0.301)
5	Initial	0.9975	24.75	30.95	42.40	...	1.90	
	Final	1.0925	15.60	26.10	22.55	34.10	1.65	0.197
5	Initial	0.9640	34.20	35.95	28.10	...	1.70	
	Final	.9735	17.45	26.15	22.65	31.78	1.95	0.196

Three other experiments carried out at 600° with mixtures initially close to equilibrium gave for the equilibrium constant the values 0.0309, 0.0307, 0.0315.

Our data indicate that the equilibrium constants at 600, 650 and 700° are 0.0310, 0.082 and 0.20, respectively. The plot of the corresponding values of log K against I/T gives a straight line. The data are satisfactorily reproduced by the Equation $\Delta F = -RT \ln K = 31{,}244 - 28.88T$.

According to the above equation, the heat of dissociation of one mole of ethane into ethylene and hydrogen at 600–700° is −31,244 cal. From the combustion data of Thomsen and of Berthelot[7] the heat of dissociation of ethane may be calculated to be −31,200 cal. (Thomsen) or −37,100 cal. (Berthelot), the average being −34,200 cal. Although adequate specific heat data are lacking, the indication is that our value at 600–700°

[7] Thomsen and Berthelot, Landolt-Börnstein, "Tabellen," **1923**, p. 1588.

might be reduced by 1000–3000 cal. at room temperature, making it approximately 28,000–30,000 cal. as compared to the above average of −34,200 cal., which also is for room temperature.

It is difficult to estimate the accuracy of our results. The most serious source of error is indicated by the presence of considerable amounts of methane among the products of some of the experiments. The corresponding side reaction undoubtedly has displaced equilibrium to some extent. However, in view of the facts that approximately the same end-point is reached from either side and that our calculated heat of reaction is not unreasonable, we are inclined to believe that our data are not greatly in error.

Summary

The position of equilibrium in the reaction $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ has been measured at 600, 650 and 700°. Equilibrium was approached from both sides. Some uncertainty exists owing to the simultaneous formation of methane, but the indications are that the equilibrium constants at the three temperatures are 0.0310, 0.082 and 0.20, respectively, partial pressures being expressed in atmospheres.

PRINCETON, NEW JERSEY

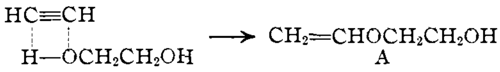
[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

THE MECHANISM OF THE ACETAL REACTION. THE EXPLOSIVE REARRANGEMENT OF HYDROXY-ETHYL VINYL ETHER INTO ETHYLIDENE GLYCOL[1]

HAROLD S. HILL[2] AND LLOYD M. PIDGEON

RECEIVED MAY 28, 1928 PUBLISHED OCTOBER 6, 1928

In a previous paper[3] dealing with the formation of cyclic acetals by the action of acetylene on polyhydroxy compounds in the presence of a catalyst, some speculations as to the mechanism of this interesting reaction were brought forward. Taking the reaction between ethylene glycol and acetylene as an example, it was assumed that the first change involves intermolecular addition of one glycol hydroxyl to the unsaturated acetylene carbons, giving hydroxy-ethyl vinyl ether, (A)



$$\begin{matrix} HC\equiv CH \\ \vdots \quad \vdots \\ H—OCH_2CH_2OH \end{matrix} \longrightarrow \underset{A}{CH_2{=}CHOCH_2CH_2OH}$$

---

[1] This paper represents one of a series of publications carried out under the joint auspices of the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their appreciation of the facilities placed at their disposal by the three coöperating agencies.

[2] Research Fellow, Canadian Pulp and Paper Association.

[3] Hill and Hibbert, THIS JOURNAL, **45**, 3128 (1923).