

The Kinetics of the Reaction $\text{H} + \text{C}_2\text{H}_6 = \text{CH}_4 + \text{CH}_3$

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The Kinetics of the Reaction $\text{H} + \text{C}_2\text{H}_6 = \text{CH}_4 + \text{CH}_3$

E. W. R. STEACIE

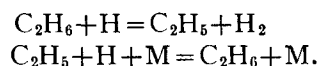
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(Received November 3, 1937)

The production of methane in the reaction between hydrogen atoms and ethane has been investigated by the discharge-tube method. It is found that the reaction $\text{H} + \text{C}_2\text{H}_6 = \text{CH}_4 + \text{CH}_3$ proceeds with an activation energy of 8.6 Kcal. (assuming a steric factor of 0.1) in satisfactory agreement with the value of 7.2 Kcal. found by Trenner, Morikawa, and Taylor. The error introduced by methane formation into Steacie and Phillips' determination of the activation energy of the reaction $\text{D} + \text{C}_2\text{H}_6 = \text{HD} + \text{C}_2\text{H}_5$ appears to be negligible on the basis of the present results. At present no explanation can be offered of the discrepancy between the results of Trenner, Morikawa, and Taylor, and of Steacie and Phillips for the latter reaction.

INTRODUCTION

IN their classical investigation of the reactions of hydrogen atoms, Bonhoeffer and Harteck¹ found that luminescence occurs on mixing hydrogen atoms and ethane, but that the major part of the ethane is recovered unchanged at the end of the reaction. A further investigation was made by v. Wartenberg and Schultze² who found that there was a considerable loss of gas in their experiments (up to 25 percent), which might have been due to methane formed in the reaction, since with their technique methane would have passed through the liquid-air trap and been lost. They suggested that the main process was



Chadwell and Titani,³ in the course of another investigation, also made two experiments with ethane and hydrogen atoms. They found less than 5 percent of methane in the ethane after an experiment, i.e., less than 2.5 percent decomposition of ethane to form methane. They suggest that the gas lost in the investigation of v. Wartenberg and Schultze was ethane which passed the liquid-air trap, rather than methane. It is certainly to be expected that some ethane would be lost under the experimental conditions of v. Wartenberg and Schultze.

Steacie and Phillips⁴ investigated the reaction

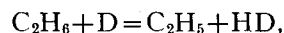
¹ Bonhoeffer and Harteck, *Zeits. f. physik. Chemie* **139**, 64 (1928).

² v. Wartenberg and Schultze, *Zeits. f. physik. Chemie* **B2**, 1 (1929).

³ Chadwell and Titani, *J. Am. Chem. Soc.* **55**, 1363 (1933).

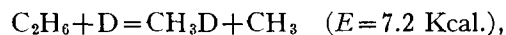
⁴ Steacie and Phillips, *J. Chem. Phys.* **4**, 461 (1936).

of deuterium atoms with ethane. They assumed the primary step in the process to be

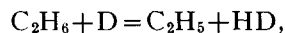


and found an activation energy of 6.3 Kcal. for the reaction. In their investigation they accepted the conclusion of Chadwell and Titani that methane formation was negligible, and determined the extent of the "exchange" by merely separating the hydrogen, burning the remaining products, and analyzing the resulting water for deuterium.

The reaction of deuterium atoms with ethane has recently been re-investigated by Trenner, Morikawa, and Taylor.⁵ Their results differ sharply from those of Steacie and Phillips. At room temperature they conclude that the main reaction is



and that the exchange reaction is only appreciable at temperatures above 100°C, with an activation energy of 11.4 Kcal. In their experiments from 10 to 20 percent of the ethane was found to be decomposed to methane. They made very thorough analyses of the products of the reaction, and determined the deuterium content of each product separately. The methane formed was found to be about 50 percent deuterized, but the ethane was entirely light at temperatures below 100°C. They conclude that above 100°C the reaction also goes as suggested by Steacie and Phillips,



⁵ Trenner, Morikawa, and Taylor, *J. Chem. Phys.* **5**, 203 (1937).

but there is a very large discrepancy between the activation energies found in the two investigations (6.3 and 11.4 Kcal.).

Since Steacie and Phillips did not isolate the separate products, it follows that any deuteromethane formed in their investigation would be reported as deuterioethane. Their rates for the exchange reaction should therefore be too high on account of methane formation. The present investigation has been undertaken to determine the extent to which methane is formed under experimental conditions similar to those employed by Steacie and Phillips, and thus to determine the error, if any, introduced by this cause into their value of the activation energy of the exchange reaction.

EXPERIMENTAL

The general experimental arrangement was exactly the same as that employed in the previous investigation. Hydrogen was admitted to the system from cylinders at a constant rate and was pumped rapidly through the discharge and mixed with ethane. The ethane, methane, etc. were removed from the flowing stream and later analyzed.

The discharge was run on alternating current at about 3000 volts, the current through the tube being maintained constant at 350 milliamperes. Hydrogen passed through the discharge at a

TABLE I. *Efficiency of separation and recovery of gases.*

ENTERING GAS, CC			DESORBED GAS, CC			HYDROCARBON LOST, PERCENT
H ₂	C ₂ H ₆	CH ₄	H ₂	C ₂ H ₆	CH ₄	
1024	470	0	7	465	0	1.1
763	350	0	5	342	0	2.3
828	0	380	6	0	362	4.7
796	0	365	6	0	349	4.4

TABLE II. *Operating conditions.*

Discharge current = 350 ma
Volume of reaction vessel = 1370 cc

RUN NOS.	FLOW RATES cc/sec. at N. T. P.		PRESSURE, MM
	H ₂	C ₂ H ₆	
3, 4, 5	0.284	0.130	0.39
6, 7, 9, 10, 11	0.284	0.047	0.32
8	0.414	0.047	0.38

TABLE III. *The products of the reaction.*

RUN No.	GAS RECOVERED, PERCENT				DECOM- POSITION, PERCENT	REMARKS
	C ₂ H ₆	CH ₄	H ₂	Higher products		
1	97.9	0.6	1.5	—	(0.2)	Blank experiment, no discharge
2	97.9	0.5	1.6	—	(0.2)	Blank experiment, no discharge
3	86.4	10.1	3.5	0.0	5.5	
4	83.7	12.8	3.5	0.0	7.1	
5	82.6	13.3	4.1	0.0	7.4	
6	75.0	18.0	7.0	0.0	10.7	
7	76.3	17.6	6.1	—	10.3	
8	70.2	22.8	7.0	—	13.8	
9	70.5	21.0	8.5	—	12.9	Walls of system very wet
10	54.2	38.2	7.6	0.0	26.0	200°C
11	59.2	35.5	5.3	0.0	23.1	200°C

streaming velocity of about 1 liter per second and a pressure of about 0.3 mm, and entered a 1-liter reaction vessel. In this vessel it was mixed with ethane, and after a contact time of about 1 second, the mixture passed out of the reaction vessel. The walls of the system were poisoned in the usual way with phosphoric acid to cut down the rate of recombination of the hydrogen atoms.

The pumping system consisted of a three-stage diffusion pump backed by an oil pump. The speed at the entrance to the pump was about 20 liters per second.

The atom concentration in the reaction vessel was measured with a Wrede diffusion gauge of the usual type. At 20°C the mean value of the atom concentration was 24.1 percent, and at 200°C 18.6 percent.

As in the previous investigation, hydrocarbons were separated from hydrogen by adsorption on silica gel at -180°C in a trap situated between the diffusion pump and the backing pump. Check runs showed that hydrogen could be almost entirely separated from methane and ethane in this way, with very little loss of the hydrocarbons. The efficiency of the separation is illustrated by the data of Table I. In experiments in which higher hydrogen/ethane ratios were used correspondingly more hydrogen was recovered with the hydrocarbons, but the loss of hydrocarbons was not increased. The gases separated in this way were then analyzed by low temperature fractional distillation in a still of the Podbielniak type. In the distillation methane

TABLE IV. *The rate of reaction.*

RUN No.	TEMP., °C	COLLISION YIELD	E, KCAL., ASSUMING A STERIC FACTOR OF 0.1
3	20	2.5×10^{-8}	8.9
4	20	3.3×10^{-8}	8.8
5	20	3.4×10^{-8}	8.8
6	20	4.9×10^{-8}	8.5
7	20	4.7×10^{-8}	8.5
8	20	5.9×10^{-8}	8.4
9	20	5.9×10^{-8}	8.4
10	200	3.1×10^{-7}	12.0
11	200	2.8×10^{-7}	12.1

and hydrogen were taken off together, and this fraction was analyzed by combustion.

The ethane used was taken directly from cylinders supplied by the Ohio Chemical and Manufacturing Co. It was stated by them to contain better than 97.0 percent ethane. Analyses by low temperature distillation, and for olefins by the usual absorption method, showed the following impurities:

$\text{CH}_4 + \text{H}_2$ less than 0.3 percent
 C_2H_4 1.3 percent
 higher hydrocarbons less than 0.3 percent.

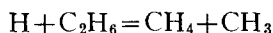
No olefins were present in the products of an experiment, showing that the initial 1.3 percent of ethylene must have largely disappeared, presumably by hydrogenation, during the process.

The operating conditions are summarized in Table II. In general an experiment lasted for from 90 to 180 minutes, and was continued until some 600–700 cc of ethane had been put through the system. This gave a sample large enough to analyze accurately by the distillation method.

RESULTS

The analyses of the products of the reaction are given in Table III. It is evident that a considerable amount of ethane is decomposed to methane, in agreement with the findings of Trenner, Morikawa, and Taylor.

Calculation from the above data gives the values of the collision yield and of the activation energy given in Table IV. It will be seen that the mean value of the activation energy of the reaction

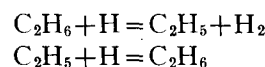


is 8.6 Kcal. when the calculations are made from

TABLE V.

	VALUES GIVEN BY STEACIE AND PHILLIPS	CORRECTED VALUES
Mean D content of ethane, percent	15.8	11.3
Mean "percent exchange"	25.4	18.7
Mean collision yield	1.86×10^{-6}	1.37×10^{-6}
E, Kcal., assuming a steric factor of 0.1	6.3	6.4

collision yields at room temperature. This is in good agreement with the value calculated in the same way by Trenner, Morikawa, and Taylor. A considerably higher activation energy is obtained from the collision yield at 200°C. In other words, the temperature coefficient of the reaction is much lower than would be anticipated from the collision yield at room temperature. This is also in agreement with the results of Trenner, Morikawa, and Taylor, who found practically no change in the methane yield with increasing temperature. It seems probable that this effect is to be associated with a diminution in the hydrogen atom concentration in the presence of ethane at higher temperatures, where the reactions



are becoming more prominent.

DISCUSSION

It is evident from the above results that the conclusions of Trenner, Morikawa and Taylor regarding the formation of methane in the reaction of hydrogen atoms with ethane have been completely confirmed. It remains to discuss the effect of this production of methane on the calculated value of the activation energy of the exchange reaction previously given by Steacie and Phillips.

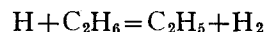
In Steacie and Phillips investigation of the exchange reaction the mean D content of "ethane" from runs at room temperature was 15.8 percent. The present work shows, however, that this "ethane" was really $\text{C}_2\text{H}_6 + \text{CH}_4$. The mean value of the amount of decomposition of ethane from the present work is 8.2 percent. Trenner, Morikawa and Taylor's investigation indicates that this methane is about 53.5 percent

exchanged. It follows that in Steacie and Phillips' work the apparent D content of ethane due to the presence of deuteromethane was 5.7 percent. Allowing for this we obtain the corrections to Steacie and Phillips' data shown in Table V.

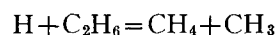
It follows that the formation of methane found here introduces only a negligible correction into Steacie and Phillips' value of the activation energy of the exchange reaction.

The formation of methane is not, therefore, a sufficient explanation of the discrepancy between the results of Steacie and Phillips and of Trenner, Morikawa, and Taylor for the exchange reaction. In order to explain this discrepancy on the basis of methane formation in Steacie and Phillips' investigation, it would be necessary to assume that 60 percent of their ethane decomposed, as compared with a mean value of 8.2 percent found here. It does not appear to be possible at the moment to offer any explanation of the lack of agreement between the two investigations.

It was pointed out in the previous paper that the activation energy of the reaction



is of considerable importance in connection with the Rice-Herzfeld free radical chain theory.⁶ It was shown that an activation energy of 6.3 Kcal. for this reaction introduces insurmountable difficulties into the application of the scheme to the ethane decomposition. It is worth pointing out that even the much higher value of Trenner, Morikawa, and Taylor would introduce serious difficulties into the application of the scheme. Also, the presence of the reaction



with an activation energy of about 8 Kcal. would fundamentally alter the nature of the chain carrying steps in the Rice-Herzfeld scheme, and would destroy its agreement with experiment.

⁶ Rice and Herzfeld, *J. Am. Chem. Soc.* **56**, 284 (1934).

The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The Heat Capacity from 15°K to the Boiling Point. The Heat of Vaporization and Vapor Pressure. The Equilibria $\text{N}_2\text{O}_4 = 2\text{NO}_2 = 2\text{NO} + \text{O}_2$

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The heat capacity of nitrogen tetroxide has been measured from 15°K to the boiling point, 294.25°K. The melting point is 261.90°K. The heats of fusion and vaporization were found to be 3502 and 9110 cal./mole, respectively. The vapor pressures of solid and liquid nitrogen tetroxide were measured with a mercury manometer by means of an arrangement in which carbon dioxide protected the mercury surface from reaction with the nitrogen tetroxide. The data have been represented by the equations: Liquid nitrogen tetroxide 261.90 to 294.9°K $\log_{10} P(\text{int. cm Hg}) = -1753.000/T + 8.00436 - 11.8078 \times 10^{-4}T + 2.0954 \times 10^{-6}T^2$. Solid nitrogen tetroxide 240.3 to 261.90°K, $\log_{10} P(\text{int. cm Hg}) = -2460.000/T + 9.58149 + 7.6170 \times 10^{-3}T - 1.51335 \times 10^{-6}T^2$. By applying the third law of thermodynamics to the calorimetric measurements, the entropy of the gas, which is dissociated to the extent of 16.1 percent into nitrogen dioxide at the boiling point, was found to be 80.62 cal./deg. per mole of gas as N_2O_4 . From a consideration of the available data on the equilibria

$\text{N}_2\text{O}_4 = 2\text{NO}_2 = 2\text{NO} + \text{O}_2$ in combination with spectroscopic data for the several substances, and the experimental entropy value given above, a number of quantities of thermodynamic interest have been evaluated. For $\text{N}_2\text{O}_4(\text{g})$, $S_{298.1}^0 = 72.73$ and for $\text{NO}_2(\text{g})$, $S_{298.1}^0 = 57.47$ cal./deg. per mole. These values, which are the ones which should be used in ordinary thermodynamic calculations, do not include the nuclear spin entropy, $R \ln 3 = 2.183$, for each nitrogen atom. The absolute entropies are $\text{N}_2\text{O}_4(\text{g})$, $S_{298.1}^0 = 77.10$; $\text{NO}_2(\text{g})$, $S_{298.1}^0 = 59.65$ cal./deg. per mole. For the reactions: $2\text{NO}_2 = \text{N}_2\text{O}_4$, $\Delta F_{298.1}^0 = -1,110$ cal., $\Delta H_{298.1}^0 = -13,693$ cal.; $\text{N}_2 + 2\text{O}_2 = \text{N}_2\text{O}_4$, $\Delta F_{298.1}^0 = 23,440$ cal., $\Delta H_{298.1}^0 = 2,239$ cal.; $\text{NO} + \frac{1}{2}\text{O}_2 = \text{NO}_2$, $\Delta F_{298.1}^0 = -8,375$ cal., $\Delta H_{298.1}^0 = -13,562$ cal.; $\frac{1}{2}\text{N}_2 + \text{O}_2 = \text{NO}_2$, $\Delta F_{298.1}^0 = 12,275$ cal., $\Delta H_{298.1}^0 = 7,964$ cal. The experimental entropy value obtained in this investigation, together with band spectrum data, has made possible a much better correlation of the various measurements on the above equilibria than has hitherto been possible. The good agree-