Hydrogenation and Polymerisation Reactions of Acetylene. III.(*)
Kinetics of Polymerisation by Use of Thermal Separation Column. I.

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Introduction. The literature on the polymerisation of acetylene is voluminous(1), but practically all of it deals with the yield and products of polymerisation by flow method.(2) The work dealing with the kinetics of the reaction is only due to Pease,(3) Schläffer and Brunner(4) and Taylor and Hook.(5) The results of these investigations clarify the reaction to some extent, but these results do not coincide with each other quantitatively. The followings are the brief historical survey of the kinetics of the concerned reaction.

Summary of the Previous Results. The thermal reaction of acetylene is chiefly consisted of polymerisation and decomposition reactions. At low temperatures, below 600°C, polymerisation predominates, the products being either yellow solid, probably cuprene, or liquid of aromatic character. From 600 to 1000°C, both polymerisation and decomposition occur, main decomposition products being free carbon, hydrogen and methane. Bone and Coward,(6) for instance, found that, at 800°C and higher temperatures, acetylene always flashed as soon as admitted to the reaction vessel unless largely diluted with nitrogen or hydrogen. According to them, the products of the reaction are as follows:

Temp. (°C.)		600	1000
Liquid products (% of C_2H_2 consumed)		19	7.5
Gaseous products (in mole %)......	C_2H_2	1.35	1.55
	C_2H_4	0.45	2.60
	C_2H_6	0.50	0.00
	CH_4	32.40	36.00
	H_2	63.50	59.85

The above figures show that the decomposition is remarkable at 600°C. The first data of any kinetic significance were obtained by Pease,(3)

(*) Second report, this Bulletin, **18** (1943), 13.

(1) Egloff, "Reactions of Pure Hydrocarbons," 395, New York (1937).

(2) G. Kita, T. Mazume, S. Wada, and R. Abe, *J. Soc. Chem. Ind., Japan*, **29** (1926), 738, 843. S. Iki and R. Ogura, *ibid.*, **30** (1927), 461. S. Hujio, *ibid.*, **31** (1928), 77. Y. Kato and H. Aikawa, *J. Electrochem. Assoc. Japan*, **3** (1935), 261. I. Orito, *ibid.*, **7** (1939), 51. T. Hujisaki, *J. Fuel Soc. Japan*, Sect. 1, **20** (1941), 782.

(3) Pease, *J. Am. Chem. Soc.*, **51** (1929), 3470.

(4) Schläffer and Brunner, *Helv. Chim. Acta*, **13** (1930), 1125.

(5) H. A. Taylor and van Hook, *J. Phys. Chem.*, **39** (1935), 811.

(6) Bone and Coward, *J. Chem. Soc.*, **93** (1908), 1197.

using a flow method. He found that at low temperatures the reaction was almost entirely polymerisation, very little gases, such as hydrogen, methane, and olefins, being formed at temperatures 550–600°C. Pease suggested that the primary product was $(C_2H_2)_4$. On the other hand, Zelinski(7) found diacetylene to be a product, and suggested that the primary step was

$$2\,C_2H_2 \rightarrow (C_2H_2)_2\,.$$

Pease found that the reaction was roughly bimolecular, although he did not investigate thoroughly on the order of the reaction. The reaction was also studied by Schläffer and Brunner.(4) They stated that the velocity constants fell when calculated for a first-order reaction, and rose when calculated for a second-order change. In their paper, however, no data of any kind are described except for one run at 420°C, so that the result is not so reliable.

A more thorough investigation was made by H. A. Taylor and van Hook,(5) who also employed the static method. They followed the reaction by pressure change and obtained considerably reproducible results, provided that the reaction vessel was aged for one or two runs. In their paper, however, no analysis of any kind was described, so that it was not certain that the pressure change was a reliable measure of the extent of the reaction. In the evaluation of velocity constant, it was necessary to assume that the reaction product was $(C_2H_2)_4$. The reaction was apparently bimolecular in the early stages, but deviated later. The velocity constants also depended on the initial pressure, and at 495°C, which was the lowest temperature, the velocity constant of the initial pressure 24 mm. is about one fourth or one fifth of that at the initial pressure 748 mm. At higher temperatures, the deviation is said to increase, although no data are given. These increasing deviations were attributed to the overlapping of decomposition, and the extrapolated value of velocity constant to infinite initial pressure was adopted, assuming that the predominating reaction is polymerisation at high pressure. The velocity constants obtained by them were greater than those of Pease by a factor of about two. Their results lead to an activation energy of 41.3 kcal. at 495°–535°C, but as there exist the above mentioned defects, both theoretical and experimental, this value may not be so accurate.

Such being the present situation of the kinetics of the polymerisation of acetylene, more accurate investigations are yet necessary, but a further development may be difficult by the usual method. To avoid these difficulties, such method as to suppress the decomposition, and also to remove the reaction products from the reaction system successively is desirable. To fulfil this demand, we have paid attention to the principle of thermal diffusion, and adopted the thermal separation column of Clusius and Dickel(8) as reaction vessel. The experiments according to this principle was first carried out by a flow method and the results were reported in the previous paper.(9)

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(7) Zelinski, *Ber.*, **57** (1924), 264.

(8) K. Clusius and G. Dickel, *Naturwissenschaften*, **26** (1938), 546.

(9) O. Kimura and K. Hirota, this Bulletin, **18** (1943), 13.

The Principle of the Present Method. Generally, when a mixture of two gases is enclosed in the thermal separation column of Clusius and Dickel, the enrichment of the heavier component may occur in the colder region by the combined action of thermal diffusion and the counter flow in the apparatus. Now, suppose that the acetylene is introduced into such an apparatus, the filament of which is heated sufficiently to cause polymerisation, then the reaction will be carried on under such favourable circumstances as follows: (1) the movement of the polymerised product from the reaction zone to the cold region, (2) the prevention of the decomposition of the produced substances, and (3) the removal of the reaction heat. Owing to these circumstances, the polymerisation may be the main reaction and the decomposition and other sub-reactions may be avoided. The experimental results have proved the validity of this theory. Here an example will be described to show the absence of decomposition from the data of gas analysis and also from carbon balance.

Experiment 6.

Reaction temperature 800°C, Flow velocity 4 l./hr.

Gas contraction	Gas Analysis (%)									c.c. of oil per l. of C_2H_2 consumed
	CO_2	C_2H_2	C_2H_4	C_nH_m	O_2	CO	H_2	CH_4	N_2	
22%	1.8	93.4	0.0	0.0	0.3	0.4	0.0	0.0	4.1	1.11

The above result that the reaction is nearly pure polymerisation at such high temperature as 800°C enables us to study the kinetics of polymerisation with high accuracy. It is true that the existance of temperature gradient in the reaction vessel makes the evaluation of the true velocity constant much complicated, but this point can be solved by mathematical calculations, which will be published in a later paper. The followings are the results of experiment using thermal separation column as reaction vessel.

Apparatus and Experimental Procedures. The apparatus is quite the same as that which is available for general kinetic investigation of gaseous reaction, except that the reaction vessel is substituted by a thermal separation column. The apparatus is shown schematically in Fig. 1. In the figure, A is a reservoir of acetylene, B a mercury manometer for observing the pressure of reaction vessel, and C a thermal separation column of heated wire type, the length and the diameter of which are 100 cm. and 1.5 cm., respectively. At the cener of the column a tungsten wire is situated

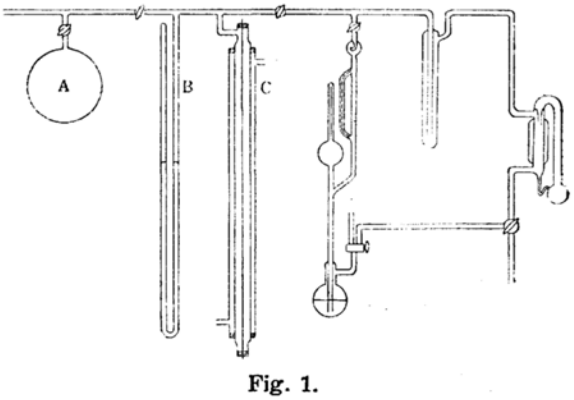

Fig. 1.

the upper and the lower ends being connected to copper wires, which serve as leading wires of electricity. The diameter and the length of the tungsten wire are 0.01 cm. and 51.0 cm., respectively. A direct current was used to heat the filament, the temperature of which was controlled by the current. The current and the voltage were read exactly in order to determine the temperatuer of the filament. The outer wall of the column was cooled by tap water. Of course, the temperature of the outer wall must be exactly constant, as its temperature fluctuation causes the errors in pressure measurement. This condition was fulfilled by flowing tap water in high velocity. The temperature fluctuation was less than ±1°C.

Acetylene was generated from calcium carbide and water. The gas was purified by passage through an acidic copper sulphate solution, a potassium chromate solution, and an alkaline pyrogallol solution. The gas was then dried by calcium chloride. The purity of acetylene was 99.0%.

The experimental procedures were as follows: The reaction vessel was first evacuated thoroughly, and then filled with acetylene to a certain pressure. The electric current was then switched on and the pressure decrease was followed by the manometer. After each run, the apparatus was thoroughly evacuated for two hours with a mercury vapour pump.

Experimental Results. As was described in the previous paper,(9) the material of the filament is an important condition to prevent the decomposition, and consequently to obtain a good yield of polymerised oil. Any metal which has catalytic power did not give a good result. Tungsten wire was found after many experiments to give a good result. Judging from this fact, we can suppose that the tungsten wire acts merely as heat source and has no catalytic activity. The reproducibility of the observed velocity constants in this experiment supports above supposition. The strict determination of the homogeneity of the reaction is, however, a remaining problem.

The experiments were carried out changing the initial pressure and the reaction temperature. The results are shown in Tables 1–11. As is stated above, the reaction in the thermal separation column is almost a pure polymerisation, and consequently the pressure decrease is a direct measure of the extent of the reaction. If we express the initial pressure by p_0 and the pressure at any instant by p, then $p_0-p\,(=x)$ is proportional to the amount of acetylene reacted, as the temperature of the polymerised substances is so low that the vapour pressure of them can be neglected. If the reaction is of second order as is stated by Taylor and Hook, $x/tp_0(p_0-x)\,(=k)$ must be constant. The above value was calculated in every run and the results are shown in the tables. From these tables, we see that the velocity constants are nearly constant especially in the early period of the reaction. Moreover the velocity constants are almost independent of the initial pressure at every reaction temperature. Above results lead us to conclude the bimolecularity of the reaction with safety standing on much more accurate basis than Taylor and Hook. In the later period of the reaction, when the temperature of the filament is high, the values of k deviate from the initial value, presumably by the effect of

Table 1.

$p_0=21.4$ $T=720°\text{C}$

t(min.)	p(cm.)	x(cm.)	k
10	21.0	0.4	0.000082
20	20.7	0.7	79
30	20.3	1.1	84
40	20.0	1.4	82
50	19.7	1.7	81
60	19.4	2.0	81
70	19.1	2.3	81
80	18.8	2.6	81
90	18.5	2.9	81
100	18.2	3.2	82
110	18.0	3.4	80
120	17.7	3.7	81
130	17.5	3.9	80
140	17.3	4.1	81
150	17.0	4.4	81
160	16.8	4.6	80
170	16.6	4.8	80
180	16.3	5.1	81
190	16.1	5.3	81
200	15.9	5.5	81
210	15.6	5.8	83
220	15.4	6.0	83
230	15.2	6.2	83
240	15.0	6.4	83
250	14.8	6.6	83

Table 2.

$p_0=43.4$ $T=720°\text{C}$

t(min.)	p(cm.)	x(cm.)	k
10	42.2	1.2	0.000066
20	41.1	2.3	65
30	40.0	3.4	65
40	39.0	4.4	65
50	38.1	5.3	64
60	37.1	6.3	65
70	36.1	7.3	66
80	35.0	8.4	69
90	34.0	9.4	70
100	33.1	10.3	72
110	32.1	11.3	74
120	31.1	12.3	75
130	30.4	13.0	76
140	29.5	13.9	79
150	28.7	14.7	79

Table 3.

$p_0=72.0$ $T=720°\text{C}$

t(min.)	p(cm.)	x(cm.)	k
5	70.2	1.8	0.000071
10	68.6	3.4	69
15	67.0	5.0	69
20	65.5	6.5	69
25	64.0	8.0	69
30	62.7	9.3	69
35	61.3	10.7	69
40	60.0	12.0	69
45	58.8	13.2	69
50	57.6	14.4	69
55	56.5	15.5	69
60	55.4	16.6	69
65	54.1	17.9	71
70	52.8	19.2	72
75	51.7	20.3	73
80	50.7	21.3	73
85	49.5	22.5	74
90	49.5	22.5	74
95	47.3	24.7	76
100	46.3	25.7	77

Table 4.

$p_0=21.0$ $T=805°\text{C}$

t(min.)	p(cm.)	x(cm.)	k
2	20.6	0.4	0.00046
4	20.3	0.7	41
6	19.9	1.1	44
8	19.5	1.5	46
10	19.2	1.8	45
12	18.8	2.2	46
14	18.4	2.6	48
16	18.2	2.8	48
18	18.0	3.0	44
20	17.7	3.3	44
22	17.3	3.7	46
24	17.0	4.0	47
26	16.8	4.2	46
28	16.5	4.5	46
30	16.2	4.8	47
32	16.0	5.0	46
34	15.7	5.3	47
36	15.5	5.5	46
38	15.3	5.7	47
40	15.1	5.9	46
42	15.0	6.0	45
44	14.7	6.3	46
46	14.5	6.5	46
48	14.3	6.7	47
50	14.1	6.9	47

Table 5.

$p_0=39.0$ cm. $T=805°C$

t(min.)	p(cm.)	x(cm.)	k
2	37.8	1.2	0.00041
4	36.8	2.2	38
6	35.6	3.4	41
8	34.5	4.5	42
10	33.5	5.5	42
12	32.8	6.2	40
14	31.8	7.2	42
16	31.0	8.0	41
18	30.0	9.0	43
20	29.2	9.8	43
22	28.4	10.6	43
24	27.8	11.2	43
26	27.2	11.8	43
28	26.5	12.5	43
30	26.2	12.8	42
32	25.7	13.3	41
34	25.3	13.7	41
36	25.0	14.0	40
38	24.6	14.4	39
40	24.3	14.7	39
42	24.1	14.9	38
44	23.9	15.1	37
46	23.6	15.4	36
48	23.4	15.6	36
50	23.2	15.8	35

Table 6.

$p_0=74.0$ cm. $T=805°C$

t(min.)	p(cm.)	x(cm.)	k
2	70.0	4.0	0.00039
4	66.4	7.6	39
6	62.6	11.4	41
8	59.4	14.6	42
10	56.3	17.7	43
12	54.0	20.0	40
14	51.8	22.2	42
16	49.8	24.2	42
18	47.8	26.2	41
20	46.0	28.0	41
22	44.6	29.4	39
24	43.2	30.8	40
26	42.0	32.0	40
28	41.0	33.0	39
30	40.0	34.0	38
32	39.0	35.0	38
34	38.2	35.8	37
36	37.3	36.7	37
38	36.6	37.4	36
40	36.0	38.0	36
42	35.2	38.8	35
44	34.6	39.4	35
46	34.0	40.0	35
48	33.3	40.7	34
50	32.8	41.2	34

Table 7.

$p_0=10.8$ $T=850°C$

t(min.)	p(cm.)	x(cm.)	k
2	10.5	0.3	0.0013
4	10.3	0.5	11
6	10.0	0.8	12
8	9.8	1.0	12
10	9.6	1.2	12
12	9.4	1.4	12
14	9.2	1.6	11
16	9.0	1.8	12
18	8.8	2.0	11
20	8.7	2.1	10
22	8.6	2.2	11
24	8.4	2.4	11
26	8.3	2.5	11
28	8.2	2.6	11
30	8.1	2.7	10
32	8.0	2.8	10
34	7.9	2.9	10
36	7.8	3.0	0.00099
38	7.7	3.1	98
40	7.6	3.2	97
42	7.5	3.3	97
44	7.4	3.4	97
46	7.3	3.5	96
48	7.2	3.6	96
50	7.1	3.7	95

Table 8.

$p_0=21.9$ cm. $T=850°C$

t(min.)	p(cm.)	x(cm.)	k
2	20.8	1.1	0.0012
4	19.8	2.1	12
6	18.9	3.0	12
8	18.0	3.9	12
10	17.2	4.7	13
12	16.7	5.2	12
14	16.2	5.7	12
16	15.5	6.4	12
18	15.1	6.8	11
20	14.8	7.1	11
22	14.6	7.3	10
24	14.2	7.7	10
26	13.9	8.0	10
28	13.5	8.4	10
30	13.2	8.7	10
32	13.0	8.9	0.00098
34	12.8	9.1	95
36	12.6	9.3	94
38	12.4	9.5	92
40	12.2	9.7	91
42	12.0	9.9	90
44	11.8	10.1	89
46	11.6	10.3	88
48	11.4	10.5	88
50	11.3	10.6	86

Table 9.

$p_0=42.0$ $T=850°C$

t(min.)	p(cm.)	x(cm.)	k
2	38.8	3.2	0.00098
4	36.0	6.0	98
6	33.7	8.3	98
8	32.7	10.0	93
10	30.4	11.6	91
12	29.1	12.9	88
14	28.1	13.9	85
16	26.9	15.1	84
18	26.0	16.0	82
20	25.2	16.8	80
22	24.4	17.6	78
24	23.8	18.2	76
26	23.0	19.0	76
28	22.2	19.8	76
30	21.6	20.4	75
32	21.2	20.8	73
34	20.6	21.4	72
36	20.3	21.7	71
38	20.0	22.0	69
40	19.5	22.5	69
42	19.2	22.8	67
44	18.8	23.2	67
46	18.5	23.5	66
48	18.2	23.8	65
50	17.8	24.2	65

Table 10.

$p_0=21.7$ cm. $T=895°C$

t(min.)	p(cm.)	x(cm.)	k
2	19.8	1.9	0.0022
4	18.2	3.5	21
6	17.1	4.6	20
8	16.3	5.4	19
10	15.4	6.3	19
12	14.9	6.8	18
14	14.2	7.5	17
16	13.9	7.8	16
18	13.5	8.2	15
20	13.0	8.7	15
22	12.7	9.0	15
24	12.4	9.3	0.0014
26	12.1	9.6	14
28	11.8	9.9	14
30	11.6	10.1	13
32	11.4	10.3	13
34	11.2	10.5	13
36	11.0	10.7	12
38	10.8	10.9	12
40	10.6	11.1	12
42	10.4	11.3	12
44	10.2	11.5	12
46	10.0	11.7	12
48	9.9	11.8	11
50	9.8	11.9	11

Table 11.

$p_0=43.0$ $T=895°C$

t(min.)	p(cm.)	x(cm.)	k
2	36.5	6.5	0.0021
4	32.3	10.7	19
6	29.3	13.7	18
8	27.2	15.8	17
10	25.4	17.6	16
12	24.0	19.0	15
14	22.8	22.2	15
16	21.8	21.2	14
18	22.0	22.0	14
20	20.2	22.8	13
22	19.6	23.4	13
24	19.0	24.0	12
26	18.3	24.7	12
28	18.0	25.0	12
30	17.5	25.5	11
32	17.1	25.9	11
34	16.8	26.2	11
36	16.4	26.6	10
38	16.2	26.8	10
40	15.8	27.2	10

sub-reactions, so that the extrapolated values of k at $t=0$, which are denoted by k_0, are calculated and tabulated in Table 12.

The determination of the temperature of the filament was carried out by measuring the electrical resistance, as the relation between the resistance and the temperature of tungstn is exactly known.⁽¹⁰⁾ The temperature was also checked by an optical pyrometer, and the coincidence of these two methods was fairly good, as seen in Table 12.

Table 12. Summarised Experimental Results.

Voltage (v.)	Current in Ampere	Resistance in Ohm	Temp. of filament (°C.)	Temp. measured by pyrometer	Initial pressure p_0 (cm.)	Velocity constant k_0 (min^{-1}. cm^{-1}.)	
35.0	1.85	18.9	720	740	21.4	0.000082	0.000072 (mean value)
					43.4	65	
					72.0	69	
40.0	1.95	20.5	805	800	21.0	0.00045	0.00042 (mean value)
					39.0	41	
					74.0	39	
45.0	2.07	21.7	850	860	10.8	0.0012	0.0011 (mean value)
					21.9	12	
					42.0	10	
50.0	2.20	22.7	895	900	21.7	0.0021	0.0021 (mean value)
					43.0	21	

The velocity constants were determined at four different temperatures. From these values, we can calculate the activation energy according to the formula of Arrhenius, but the value thus obtained is an apparent activation energy, as the temperature in the reaction vessel is not homogeneous. In this case, the linearity of the relation between log$k$ and $1/T$, the condition which Arrhenius' equation demands, need not be fulfilled necessarily, but this relation holds in the first approximation as is seen in Fig. 2. The inclination of the curves gives the apparent activation energy, which is found to be 44.8 kcal. This value is slightly higher than that found by Taylor and Hook at about 500°C., but the true activation energy is found to be 44 kcal., which is lower than the above value. The method of calculating the true activation energy will be published in a later paper.

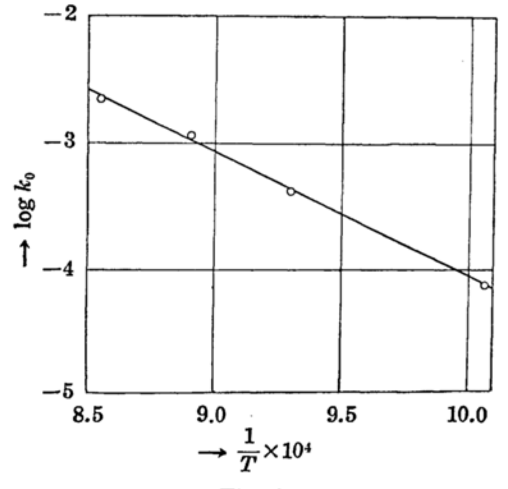

Fig. 2.

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(10) "Handbuch der Experimentalphysik," VIII, 2 Teil, 291.

Summary.

(1) In order to investigate the kinetics of the polymerisation reaction of acetylene, a thermal separation column has been used as reaction vessel, and the superiority of this device has been stressed, both theoretically and experimentally.

(2) The results of experiment have shown that the reaction is of second order, and that the apparent activation energy is 44.8 kcal.

In conclusion, the authors express their sincere thanks to Dr. M. Sato, the Director of the Laboratory, and also to Dr. R. Yoshimura, the Chief of the Department of Inorganic Chemistry, for their encouragement throughout this research.

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