On the Hydrogenation and Polymerisation Reaction of Acetylene. IV.(1), (2) Kinetics of Polymerisation by Use of Thermal Separation Column. II.

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It has been found by the authors(1) that the thermal separation column of Clusius and Dickel can be applied to the polymerisation of acetylene very effectively. As described in the previous paper, it was also shown(2) that the apparatus could be used for the study of kinetics of the concerned reaction, because the velocity of the reaction could be followed more distinctly than by the usual method, so that the order of the reaction was clearly determined to be of the second order. However, as there existed temperature gradient in the reaction vessel, the true reaction velocity constant or the velocity constant at any definite temperature could not be evaluated directly. Consequently the activation energy obtained according to the Arrhenius' equation contained some ambiguity, though it was not much different from the value determined by H. A. Taylor and van Hook(3) by the usual static method. The reason for this coincidence may be due to the fact that the reaction velocity increases rapidly as the temperature rises, and that the reaction takes place practically in the vicinity of the filament. In spite of the above coincidence the value thus obtained remains to be of preliminary nature, so the following method is devised to obtain the true velocity constant and the true activation energy.

Calculation of the Velocity Constant. It is considered that the amount of reaction in unit time at any elementary space in the reaction vessel is given by the kinetic mass action law. The total amount of the reaction in the same time is, therefore, obtained by the integrated amount in the whole reaction space. As determined in the previous paper, the concerned reaction is of the second order, the reaction velocity is given by the following equation:

$$\frac{dn}{dt}=\int_{r_1}^{r_2} k_c\cdot C^2\cdot l2\pi r\cdot dr \tag{1}$$

where k_c is the velocity constant at concentration C, l is the length of the filament, r_1 and r_2 are the radii of the filament and the reaction vessel, and r is the radial distance measured from the center axis of the reaction vessel. In the above equation, it is convenient to replace C by P which is constant at everywhere in the apparatus. Between these quantities there exists a relation,

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(1) The second report, this Bulletin, **18** (1943), 13.

(2) The third report, *ibid.*, **18** (1943), 45.

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

$$C = P/RT\,. \tag{2}$$

Then, according to the Arrhenius' equation, putting k_c as

$$k_c = A_c e^{-\frac{Q}{RT}}\,, \tag{3}$$

we obtain from equations (1), (2), and (3),

$$\frac{dn}{dt} = \frac{2\pi l P^2 A_c}{R^2}\int_{r_1}^{r_2}\frac{e^{-\frac{Q}{RT}}}{T^2}\cdot r dr\,. \tag{4}$$

If we designate the volume of the reaction vessel by V_o and the room temperature by T_o

$$\frac{dn}{dt} = V_0\frac{dc}{dt} = \frac{V_0}{RT_0}\frac{dp}{dt}\,. \tag{5}$$

Therefore,

$$\frac{dP}{dt} = P^2\frac{2\pi l A_c T_0}{RV_0}\int_{r_1}^{r_2}\frac{e^{-\frac{Q}{RT}}}{T^2}\cdot r dr\,. \tag{6}$$

By definition,

$$\frac{dP}{dt} = k_p P^2\,, \tag{7}$$

so

$$k_p = \frac{2\pi l A_c T_0}{RV_0}\int_{r_1}^{r_2}\frac{e^{-\frac{Q}{RT}}}{T^2}\cdot r dr\,. \tag{8}$$

To calculate the value of k_p, we must know the relation between T and r, i.e., the distribution function of the temperature in the reaction vessel. As the length of the column is much larger than its diameter, it may be allowed to neglect the longitudinal flow of heat, provided that the system is in stationary state. Moreover, the temperature rise due to the absorption of radiant energy from the filament can be neglected in our case. Then the temperature distribution can be given by the following differential equation:

$$\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr} = 0 \tag{9}$$

The general solution of this equation is

$$T = C_1 \log r + C_2\,, \tag{10}$$

where C_1 and C_2 are the integration constants. Taking into account of the boundary conditions that the temperatures of the filament and the outer wall are kept constant: T_1 and T_2, the temperature at the distance r will be given by

$$T = \frac{(T_2-T_1)\log r + T_1 \log r_2 - T_2 \log r_1}{\log r_2 - \log r_1} . \tag{10'}$$

From equation (8) and (10'), the value of k_p will be obtained at once provided that the integration is possible, but as it is not, the following approximate method is adopted.

Considering that $r_2 \gg r_1$, r_1 is taken as the unit of length, so $\log r_1 = 0$. Then equation (10') will be simplified as

$$T = \frac{(T_2-T_1)\log r + T_1 \log r_2}{\log r_2} \tag{11}$$

or

$$\frac{1}{T} \doteqdot \frac{1}{T_1}\left\{1 - \frac{T_2-T_1}{T_1}\frac{\log r}{\log r_2}\right\} . \tag{12}$$

Taking into consideration that $e^{-\frac{Q}{RT}} \gg 1$, when r is comparable with r_2, the integrand of equation (8) becomes(*)

$$\int_{r_1}^{r_2} \frac{e^{-\frac{Q}{RT}}}{T^2} r dr \doteqdot \frac{r_1^2}{T_1^2}\int_{r_1}^{r_2} r\, e^{-\frac{Q}{RT}\left(1+\frac{\Delta T}{T_1}\frac{\log r}{\log r_2}\right)}\left(1+\frac{2\Delta T}{T}\frac{\log r}{\log r_2}\right)dr ,$$

where $\Delta T = T_1 - T_2$. By partial integration it becomes

$$r_1^2 e^{-\frac{Q}{RT}}(I_1+I_2)/T_1^2 , \tag{14}$$

where

$$I_1 = 1\Big/\left(\frac{Q}{RT_1^2}\frac{\Delta T}{\log r_2}-2\right)+\frac{2\Delta T}{T_1 \log r_2}\Big/\left(\frac{Q}{RT_1^2}\frac{\Delta T}{\log r_2}-2\right)^2 ,$$

$$I_2 = \left\{\left(1+\frac{2\Delta T}{T_1}\right)\left(2-\frac{Q}{RT_1^2}\frac{\Delta T}{\log r_2}\right)-\frac{2\Delta T}{T_1 \log r_2}\Big/\left(\frac{Q}{RT_1^2}\frac{\Delta T}{\log r_2}-2\right)^2\right\} r_1^2 e^{-\frac{Q}{RT_1^2}\Delta T} ,$$

Then

$$k_p = r_1^2 \frac{2\pi l A_c T_0}{VR}\frac{e^{-\frac{Q}{RT}}}{T_1^2}(I_1+I_2) , \tag{15}$$

or taking the logarithm

$$\log_{10} k_p = \log_{10}\frac{2\pi l A_c T_0}{VR} r_1^2 - \frac{Q}{RT}\log_{10} e - 2\log_{10} T_1 + \log_{10}(I_1+I_2) .$$

The last formula has two unknown constants, A_c and Q. We can therefore determine them, if two or more measurements of k_p are done provided that the evaluation can be done numerically.

(*) Factor r_1^2 before the integrand occurred, because r_1 was taken as the unit of radial length.

Velocity Constant and Heat of Activation of the Polymerisation of Acetylene. According to the method described above, the velocity constant and the heat of activation of the concerned reaction is carried out. The experimental data used in the calculation are described in Table 1.

Table 1. Velocity of Polymerisation of Acetylene.(2)

Dimension of the reaction tube (thermal separation tube).

Outer radius of the filament ($2r_1$)	0.1 mm.
Length of the filament (l)	51 cm.
Inner diameter of the tube ($2r_2$)	1.5 cm.
Length of the tube	100 cm.
Volume of the tube	305 c.c.

Temp. of the filament (°C.)	Apparent velocity constant k_p (cm. Hg^{-1}, $min.^{-1}$)
720	0.000082
805	0.00042
850	0.0011
895	0.0021

The result of the calculation is as follows:

$$Q = 44\,\text{kcal.}, \qquad A_c = 3.0 \times 10^{15}\ \text{(c. g. s.)}$$

The activation energy is found to be slightly smaller than the preliminary value of the previous paper (44.8 kcal.), but larger than that given by Taylor and van Hook (40.5 kcal. and 42 kcal. at 495° and 595°C., respectively). On the other hand, the values of k_p at 720° and 500°C. are calculated by equation (3), and shown in Table 2 together with those of other authors. It is shown that our values are considerably larger than those given by Pease(4) and by Taylor and van Hook(3). However, considering that Taylor was obliged to assume the product as tetramer arbitrarily in order to obtain the above values, and that the temperature interval of the measurement is different, the agreement will be satisfactory.

Table 2. Velocity Constants of Polymerisation of Acetylene by Various Authors.

Temp. (°C.)	k_p ($Atm.^{-1}$, $sec.^{-1}$)	Authors
420	0.005–8	Schläpfer and Brunner
450	0.00016–22	Pease
495	0.0039	Taylor and van Hook
500	0.0011–15	Pease
”	0.020	Kimura and Hirota (extrapolated value)
515	0.0078	Taylor and van Hook
535	0.0145	” ” ”
550	0.0049–11	Pease
600	0.025–45	”
720	8.7	Kimura and Hirota.

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(4) R. N. Pease, *J. Am. Chem. Soc.*, **51** (1929), 3470.

Summary.

(1) A method for calculating both reaction velocity and activation energy in the case when the reaction has been carried out in the thermal separation column of Clusius and Dickel has been described.

(2) The method has been applied to the polymerisation reaction of acetylene previously investigated by the present authors.

(3) It has been found that the calculated heat of activation is slightly smaller than our preliminary value, but larger than the directly observed value by Taylor and van Hook, and that the calculated velocity constants are several times larger than those hitherto have been observed.

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