The Thermal Polymerization of Acetylene. On the Formation of Cyclooctatetraene

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Introduction

It has been known for a long time that acetylene is readily but intricately polymerized on heating,[1-4] giving a complex of unsaturated hydrocarbons as well as benzene.[2,10] Nevertheless, in the flow method at the suitable velocity, the propagation stops up to the tetramer and all the products obtained are volatile.[5] On the mechanism of the polymerization Pease, Taylor, and others[5,6,9,10,11] have pointed out from the over-all reaction rate that acetylene reacts in the bimolecular way and so the dimerization of acetylene determines the over-all rate.

On the structure of dimer produced in the primary acts of the photopolymerization of acetylene, Kemula[7] supposed that it would be vinylacetylene. Mignonac[8] got the product consistent with C_4H_4 in the thermal polymerization, but said no word about what it was. Recently Bergman,[12] supposing vinylacetylene to be the dimer, explained the Reppe reaction forming cycloöctatetraene (C.O.T.) under the high pressure.

Some experiments were performed assuming the dimer to be vinylacetylene, and the results were as follows;[13] if one uses a mixture of vinylacetylene and acetylene in the reaction, benzene constituting the main product in the polymerization decreases and also, when making C.O.T. by the catalytic method with high pressure, one can not get any C.O.T. if one uses vinylacetylene as the starting material.

Here, supposing cyclobutadiene (C.B.D.) to be the dimer in the thermal polymerization as well as in the photopolymerization[14] we investigated the thermal polymerization anticipating the formation of C.O.T. by dimerization of C.B.D. and we have obtained C.O.T. as expected.

Experiments

I. Thermal Reactivities and Analysis of C.O.T.

a) Thermal Changes of C.O.T. C.O.T., being a cyclic conjugated double-bonded compound, has unlike benzene little resonance energy and much reactivity.[15,16] It is so labile thermally and photochemically that it causes decomposition, polymerization, and isomerization at high temperatures.[17,18]

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[1] W. Bone, *J. Chem. Soc.*, **93**, 1197 (1908).

[2] N. Zelinsky, *Ber.*, **57**, 264 (1924).

[3] H. W. Walker *J. Phys. Chem.*, **31**, 970 (1927).

[4] E. Hague, *J. Chem. Soc.*, 378 (1929).

[5] R. N. Pease, *J. Am. Chem. Soc.*, **51**, 3470 (1929).

[6] P. Schlaepfer and M. Brunner, *Helv. Chim. Acta*, **13**, 1125 (1930).

[7] W. Kemula and S. Mrazek, *Z. phys. Chem.*. B**23**, 358 (1933).

[8] G. Mignonac and E. Ditz, *C. r,*, **199**, 367 (1934).

[9] H. Austin Taylor and A. V. Hook, *J. Phys. Chem.*, **39**, 811 (1935).

[10] T. Fujisaki, *J. Jnst. Fuel Japan*, **20**, 782 (1941).

[11] H. D. Burnham and R. N. Pease, *J. Am. Chem. Soc.*, **64**, 1404 (1942).

[12] E. Bergman, "Chemistry of Acetylene Compounds", **91**, (1948).

[13] T. Fujisaki, *J. Inst. High Press. Gas Japan*, **15**, 244 (1951).

[14] Z. Kuri and S. Shida, This Bulletin, **25**, 116 (1952).

[15] I. Tanaka and S. Shida, ibid., **23**, 54 (1950).

[16] Y. Mori, I. Tanaka, and S. Shida, ibid., **23**, 168 (1950).

[17] I. Tanaka, S. Miyakawa, and S. Shida, ibid., **24**, 119 (1951).

[18] I. Tanaka, unpublished.

Thus we adopted the flow method in the thermal polymerization of acetylene and quickly introduced the reaction products to a trap to get C.O.T.

b) *Analysis of C.O.T.* C.O.T. was analysed by the polarography[19] as in the case of our previous work.[14] Its half wave potential was -1.49 volts vs. S.C.E. At the sensitivity of 2.4×10^{-3} μA/mm. of the galvanometer 1 mm. displacement of the diffusion current corresponded to 2.79×10^{15} molecules of C.O.T. at the experimental conditions.

II. Experimental Details

a) *Apparatus and Methods.* Acetylene gas was purified by the normal method. The whole arrangement of the experiment is shown in Fig. 1. Purified acetylene is led through A into a liquid air freezing trap B, where the non-condensable gas is removed from the solidified acetylene through a vacuum pump and is fractionated into a reservoir C. From the reservoir, pure acetylene goes through a quartz reaction tube D heated by an electric furnace E, passing a dry ice trap F into the liquid air trap B. Reaction products caught in the trap F are evaporated back into the reaction tube D, after the experiment and are analysed spectrographically in the gas phase.

For the analysis of C.O.T., products in the trap F were directly distilled into a tiny ampoule G using the dry ice bath, and then the ampoule was cut off at the neck. Its contents were dissolved into ethanol-tetramethylammoniumbromide solution, which was submitted to the polarographic analysis.

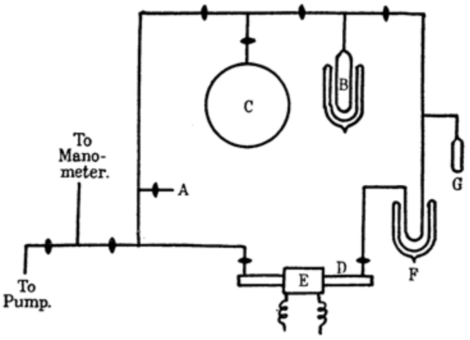
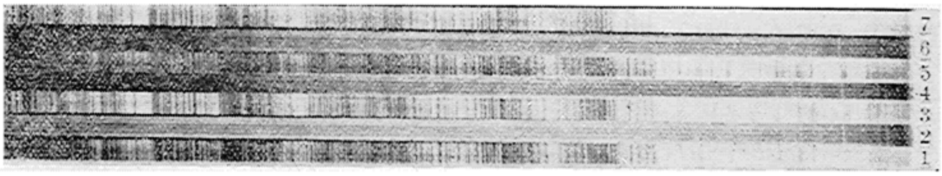


Fig. 1

b) *Products of the Reaction.* The absorption spectra of the reaction products are shown in Fig. 2. We see the products are benzene in the main and styrene in part. Besides them strong absorption lines characterized by 2808, 2720, 2687Å were always seen in the products of the photopolymerization, but in this case no trace of these lines belonging to the unknown substance appeared. This was a marked difference between the two cases. We suppose that the unknown substance is the intermediate of the polymerization and that it may be polymerized by heating in the thermal polymerization, for those lines disappear rapidly when irradiated with a mercury lamp. The absence of any thermal cracking can be inferred from the fact that there were not found any trace of the spectral lines of toluene and not any carbon or other sediments on the wall after the experiments.



(1), (3), (5) and (7) Iron spectrum (2) Blank (4) Spectrum of the products at 10 mmHg. (6) The same at 5 mmHg.

Fig. 2. Spectra of the products.

c) *The Rate of Formation of C.O.T. under the Varied Pressure of Acetylene.* If we put the volume passed at the pressure of p mmHg at the experimental temperature, V cc., the pass-time in the furnace, t sec., the height of diffusion current of the polarogram of C.O.T., h mm. (1 mm. corresponds to m mols of C.O.T.), the concentration of acetylene, A mol/cc., we can describe the rate of formation of C.O.T. in terms of the concentration of acetylene as follows.

$$dC/dt = hm/Vt = k_cA^n. \qquad (1)$$

Putting $h/Vt = H$, $\log H$ is seen linear to $n \log A$ and the constant n is determined as far as the reaction satisfies eq. (1). Using the pressure p instead of A, $\log H$ was, in Fig. 3, plotted against $\log p$ at each temperature.

Fig. 3 shows $n=2$ from the slope. It is because of the decomposition of C.O.T. that the line at 575°C lies beneath the one at 570°C. This fact is also seen by the deviation of $\log k_c$ at 575°C. from the straight line vs. $1/T$ as will be written below.

d) *The Rate of C.O.T. under the Varied Temperature.* At the constant pressure of 250 mmHg, the logarithm of the rate constant k_c of C.O.T. formation was plotted against the reciprocal of the reaction temperature T°K. Fig. 4 shows the result. Log k_c is linear against $1/T$ over the range of 525 and 570°C. The point at 575°C. deviates from the line, which means the decomposition of C.O.T. above at this temperature.

We get the activation energy $E_c = 46900$ cal. from the slope of the straight line in Fig. 4. So, the rate of C.O.T. formation is obtained as follows.

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[19] R. M. Elofson, *Anal. Chem.*, **21**, 917 (1949).

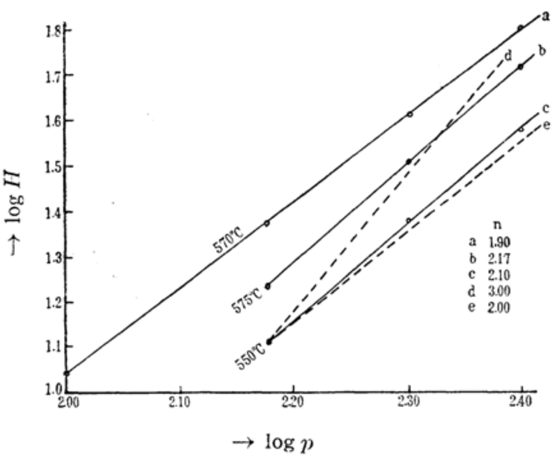


Fig. 3. Rate of formation of C.O.T. vs. acetylene pressure.

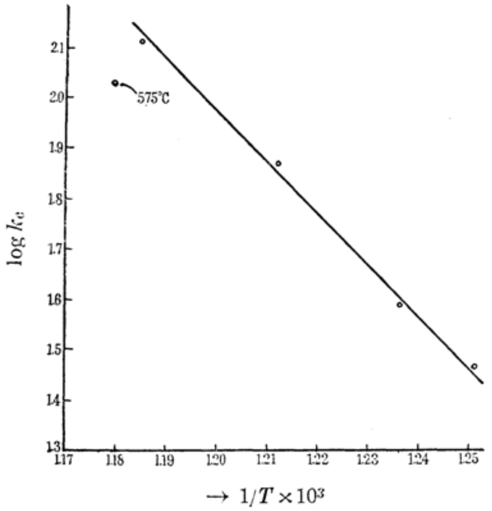
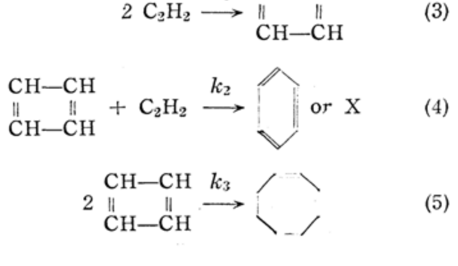


Fig. 4. Rate of formation of C.O.T. vs. reaction temperature.

$$dC/dt = 1.50 \times 10^{11} \exp(-46900/RT) \cdot A^2 \text{ mol. cc.}^{-1} \text{ sec.}^{-1} \quad (2)$$

Discussion of the Experimental Results

As we could determine the rate of formation from acetylene of C.O.T. as stated above, we assumed the following steps of the reaction mechanism.



$$2\ C_2H_2 \xrightarrow{k_1} \begin{array}{c} CH—CH \\ \| \quad\ \| \\ CH—CH \end{array} \quad (3)$$

For simplicity we will abbreviate the concentrations as follows; acetylene A, cyclobutadiene D, benzene B, cycloöctatetraene C, the unknown intermediate X. Under the condition of rapid flowing, we can ignore the steps forming higher polymers than C_8H_8. Then in the stationary state

$$dD/dt = 1/2k_1A^2 - k^2DA - k_3D^2 = 0 \quad (6)$$

$$dB/dt = k_2DA \quad (7)$$

$$dC/dt = 1/2k_3D^2 \quad (8)$$

From eq. (6) we obtain as the stationary dimer concentration

$$D = \frac{-k_2 + \sqrt{k_2^2 + 2k_1k_3}}{2k_3} \cdot A \quad (9)$$

Here the negative root was omitted. We get from eqs. (7), (8) and (9)

$$dB/dt = \alpha\{(1+k_1/\alpha)^{1/2} - 1\}A^2 \quad (10)$$

$$dC/dt = 1/2[\alpha\{1-(1+k_1/\alpha)^{1/2}\} + k_1/2]A^2, \quad (11)$$

where $\alpha = k_2^2/2k_3$. The value of k_1/α in eqs. (10) and (11) is of the smaller order than 10^{-3} as far as the values of $(2E_2 - E_3)$ are below 25 kcal. In fact the value of k_1/α is much smaller because the one of $(2E_2 - E_3)$ is smaller as will be stated below. Thus simplifying eqs. (10) and (11) by the binominal theorem

$$dB/dt = 1/2k_1A^2 \quad (12)$$

$$dC/dt = \frac{k_1^2k_3}{8k_2^2} A^2 \quad (13)$$

We compare eqs. (13) and (2) to find them to be of the same form. The details of the rate constants of eq. (13) may be written as follows,

$$\frac{k_1^2k_3}{8k_2^2} = \frac{(p_1Z_1)^2p_3Z_3}{8(p_2Z_2)^2} \exp -2(E_1 - E_2 + E_3/2)/RT \quad (14)$$

p_1Z_1 in eq. (14) is given as 4×10^{10} (525∼570°C) by Kamenetskii.[20] Z_2 and Z_3 are of the order of 10^{14}. Inserting these values we obtained $p_2^2/p_3 = 10^{-5}$ from the theoretical formula (14) and the experimental one (2). Substituting the various values of p_2 we find the corresponding ones of p_3 as follows.

p_2	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
p_3	10^{3}	10^{1}	10^{-1}	10^{-3}	10^{-5}	10^{-7}

In general the simpler the reacting molecules, the greater is the steric factor[21] and so $p_2 > p_3$ may be considered. From the values of p_2 and p_3 cited above, p_2 must be $<10^{-5}$, which follows $10^{-5} > p_2 > p_3$. If the dimer would be assumed to have the structure like butadiene biradical, its steric factor p_3 may be approximately of the same order with that

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[20] D. A. Frank-Kamenetskii, *Acta Phys. Chim. R.S.S.U.*, **18**, 148 (1943).

[21] H. Eyring, "The Theory of Rate Process", McGraw-Hill Book Co. (1941) p. 19.

of dimerization of butadiene which is of 10^{-4}.[22] This value of p_3 disagrees with $10^{-5} > p_2 > p_3$.

If C.B.D. is assumed to be the dimer, its steric factor of dimerization p_3 may be greater than that of chain structure 10^{-4}, because the steric factor of the reaction forming a non-linear complex tends to have the greater one than that of the reaction forming a linear complex.[21] Hence, when p_3 of dimerization of C.B.D. is assumed to be 10^{-3}, $p_2=10^{-4}$ is obtained; that is $p_2 < p_3$, which disagrees with the conditions $p_2 > p_3$ mentioned in the case of the chain structure. But that may be explained as follows; the activated state of dimerization of C.B.D. in eq. (5) has a looser structure than that of eq. (4); consequently, $\Delta S^{\neq}$ of eq. (5) is greater than that of eq. (4).

Comparing the exponential terms of eqs. (2) and (14) we obtain

$$2(E_1-E_2+E_3/2)=46900 \text{ cal.}$$

As $E_1=29900$ cal according to Kamenetskii[20]

$$E_2-E_3/2=6450 \text{ cal.}$$

Here, E_2 will be of the order of 7∼8 Kcal because it is the activation energy for the chain propagation.[11] Consequently E_3 becomes 1∼3 Kcal which is so small that this corresponds to the assumption that the reactive dimers react to give C.O.T. as shown in eq. (5).

By calculating the ratio of yields of benzene and C.O.T. from eqs. (12) and (13), we obtain

$$B/C=\frac{4k_2^2}{k_1k_3}$$

$$=\frac{4(p_2Z_2)^2}{(p_1Z_1)(p_3Z_3)}\exp(E_1-2E_2+E_3)/RT \quad (15)$$

That is, the ratio of benzene and C.O.T. is independent of the pressure of acetylene. In fact inserting the values

$$p_2^2/p_3=10^{-5},\ E_2-E_3/2=6450 \text{ cal}$$

etc., into eq. (15) we may compare the evaluated ones and the experimental ones as shown in Table I. The former will not be so accurate, since the experimental values were obtained by assuming the whole weight of the products to be that of benzene which is the main product. Nevertheless they coincide considerably well with each other and especially $(B/C)_{obs.}$ shows independence of pressure.

TABLE I

THE RATIO OF BENZENE AND C.O.T., OBSERVED AND CALCULATED

Temp. °C	Press. mmHg	B/C obs.	B/C calc.
535	250	1.59×10^3	3.72×10^3
550	250	1.28×10^3	3.02×10^3
	200	1.10×10^3	
570	250	4.59×10^2	2.37×10^3
	200	4.10×10^2	
	100	4.22×10^2	

Hence for increasing the yield of C.O.T. it is very efficient to diminish the exponential term of eq. (15) and so the yield as well as the rate of formation of C.O.T. will be increased very greatly if we can decrease, by the use of catalyser, for example, the value E_1, the largest among E_1, E_2, and E_3. On the other hand since the rate of formation of C.O.T. is proportional to the square of acetylene pressure, we may conclude from eqs. (13) and (15) that the use of high pressure and suitable catalyser diminishing E_1 will produce the large yield of C.O.T. This agrees qualitatively with the fact that Reppe[23] obtained C.O.T. in good yield using high pressure and nickel catalyser.

The existence of C.B.D. has not yet been proved, but Kamenetskii[24] considered from the chemical analysis of the polymerization products that the structure of dimer will be C.B.D. or methylenecyclopropene; and again C.B.D. was supposed to be the dimer by Reppe[23], too, who expected but did not succeed in finding C.O.T. in the thermal polymerization products and who said that C.O.T. is too labile thermally to be found in the products.

Concerning the stability of C.B.D., strain energy due to the bent C—C bonds is not so decisive according to Coulson[25], as Penney[26] denied its existence. C.B.D. is probably more stable in a rectangular form having the stretched single bonds than in a square form, after the calculation by Craig[27] and Coulson[28].

It is true that we can not determine these things only by the kinetic consideration we made, and we dare not insist upon our opinion. However from the view-point that the activation evergy E_2 and E_3 are very small, we may state the dimer will not be vinylacetylene but a more reactive and radical-like substance. This might be explained by the butadiene biradical, but we prefer C.B.D.

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[22] W. E. Vaughan, *J. Am. Chem. Soc.*, **54**, 3863 (1932).

[23] W. J. Reppe, "Acetylene Chemistry" (P. B. Report 18852-s) (1949).

[24] D. A. Frank-Kamenetskii, *C. R. Acad. Sci. U.S.S.R.*, **37**, 137 (1942).

[25] C. A. Coulson and E. M. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

[26] W. G. Penney, *Proc. Roy. Soc.*, A**144**, 166; A**146**, 223 (1934).

[27] D. P. Craiz, *J. Chem. Soc.*, 3175 (1951).

[28] C. A. Coulson, Private communication to S. Shida.

at present from the view-point concerning the values of the steric factors p_2 and p_3.

Summary

C.O.T. was found polarographically to exist in the thermal polymerization products of acetylene at the flow method. There did not occur any thermal cracking process below the temperature 570°C. on the experimental conditions. The polymerization of acetylene is fundamentally a bimolecular reaction and the dimer is supposed to be cyclobutadiene from the point of view of the steric factors of the reaction. Benzene is formed by the combination of cyclobutadiene and acetylene. C.O.T. is formed by the dimerization of cyclobutadiene; the rate of C.O.T. formation is of the second order in respect of acetylene. The activation energy and frequency factor of the rate is 46900 cal/mol and 1.50×10^{11} cc. $mol^{-1}. sec^{-1}$., respectively.

The ratio of yield of C.O.T. and benzene is independent of the pressure of acetylene and dependent of the temperature. In order to increase the ratio the activation energy E_1 must be lowered. The high yield of C.O.T. in the Reppe reaction was considered qualitatively.

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