

STUDIES ON THE REACTION OF ACETYLENE UNDER PRESSURE IN THE PRESENCE OF COPPER

BY RYO KIVAMA, JIRO OSUGI AND SIGERU KUSUHARA

Introduction

In 1898, Erdmann and Koethner¹⁾ reported that acetylene formed yellowish brown products, cuprene when heated at 230°C on a copper or copper oxide catalyst. Afterwards many studies have been reported on cuprene, but it is hard to find the kinetic investigations on its formation except those of Calhoun²⁾, and Lèger and Quellet³⁾, the former of which is the study of the reaction catalyzed by cupric oxide under constant acetylene pressure in a flow system, the latter of which was carried out under atmospheric or lower pressure on a copper wire catalyst. On the effect of copper alloys, Teranishi⁴⁾ studied, in our laboratory, the behavior of high pressure acetylene in the presence of brass and phosphor bronze. The authors will report, in this paper, the reaction of acetylene in contact with copper or variously annealed copper plates between 220 and 260°C under pressure (up to 13 kg/cm²) on the main standpoint of kinetics and to obtain some knowledge for handling acetylene under high pressure.

Experimentals

The reaction was followed at constant volume by measuring the pressure. The layout of the

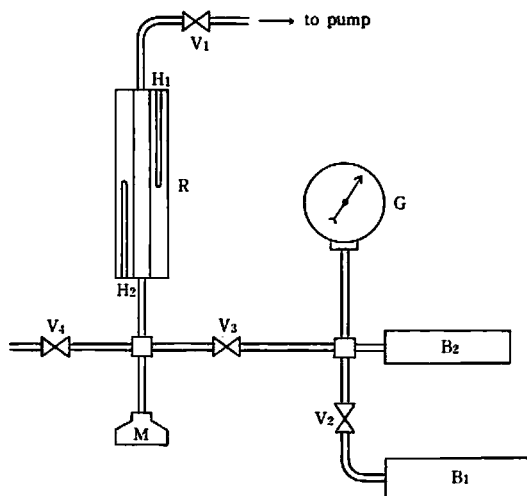


Fig. 1 Layout of the apparatus

B_1, B_2 : acetylene reservoir
 G: Bourdon-tube pressure gauge
 H_1, H_2 : small hole for the insertion of thermocouple
 M: steel membrane pressure gauge
 R: reaction vessel
 V_1, V_2, V_3, V_4 : valve

- 1) H. Erdmann and P. Koethner, *Z. anorg. Chem.*, **18**, 43 (1898)
- 2) J. M. Calhoun, *Canad. J. Res.*, **B 15**, 208 (1937)
- 3) A. E. Lèger and E. Quellet, *ibid.*, **B 28**, 358 (1950)
- 4) H. Teranishi, *This Journal*, **26**, 18 (1956)

apparatus is shown in Fig. 1. The reaction vessel R, a steel cylinder which is placed horizontally in an electric furnace, is 2 cm in inner diameter by 10 cm in length and 31.4 cc in capacity. The vessel in which a copper plate has been put is evacuated through valve V_1 by means of a rotary vacuum pump, and then heated to a given temperature which is measured by two alumel-chromel thermocouples inserted in the small holes, H_1 and H_2 in the wall of the vessel and kept constant within $\pm 0.5^\circ\text{C}$. The valve V_3 being closed, a definite quantity of acetylene gas is poured from the acetylene reservoir B_1 into the reservoir B_2 measuring the pressure by means of Bourdon-tube pressure gauge G. The acetylene is then introduced rapidly into the reaction vessel through the valve V_3 and the valve is closed as soon as the steady condition is attained. Thereafter the pressure change of acetylene in the vessel is measured at every definite time by means of a membrane gauge⁵⁾ which is constructed with a spring steel membrane* and a mirror rotating in proportion to the deflection of the membrane due to a pressure change. The displacement of a light spot on a scale is the measure of the pressure change**. The dead volume including the membrane gauge and connecting tube (1 mm in inner diameter) is 1.5 cc, and the error due to the volume of the pressure measurements is corrected by making use of the P - V - T relation of acetylene⁶⁾.

Acetylene gas prepared with calcium carbide and water is purified through refining reagents and stored in the reservoir, compressed up to 30 kg/cm² (purity: 99.4~99.6%). The coppers used are commercial plates of 0.5 mm in thickness, which are cut in size of 2 cm in width by 5 or 10 cm in length. They are polished with a corundum cloth***, followed by double washing with methanol and then dried in air. We also used copper plates (2×5 cm) annealed in vacuum, air or oxygen gas at 450 and 550°C, respectively for two hours, followed by the same treatment as before.

Results

As a preliminary test, in order to determine the temperature at which the reaction would occur, a definite quantity of acetylene reserved at room temperature in the reaction vessel containing a copper plate (about 60 cm² in surface area) was heated at a definite heating rate (about 1 deg./min.), and the relation of pressure and temperature, measured at every 10 minutes was obtained. The results are shown by curves a and b in Fig. 2. Curves c and d represent the pressure-time relation of acetylene gas in the steel vessel in absence of a copper plate and that of air in the same vessel respectively. The curves a and b exhibit pressure decrease above about 140°C notwithstanding the rise of temperature, whereas the other curves c and d do not, which suggest the occurrence of polymerization reaction. Comparing curve c with curve d, it is found that they are almost parallel at temperature below 250~260°C, and so acetylene contained in the steel vessel in absence of a copper plate seems to change scarcely. As a matter of fact, the results of blank tests without a copper plate reveal that at temperatures of 220, 240 and 260°C and

5) R. Kiyama, J. Osugi and H. Teranishi, *This Journal*, 24, 81 (1954)

* The membrane is 0.15 mm in thickness and 44 mm in effective diameter.

** The scale is 1.3 m away from the mirror, when the pressure sensitivity of the gauge is about 1 cm in the displacement of the light spot per 1 kg/cm² and calibrated for each run.

6) H. Teranishi, *This Journal*, 25, 25 (1955)

*** Made by Minnesota Mining & MFG. Co., PT 31

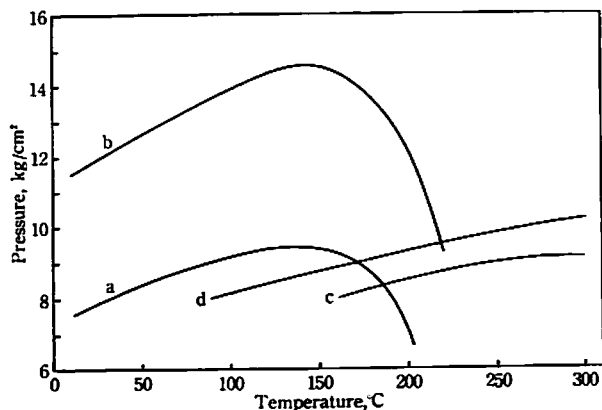


Fig. 2 Temperature dependence of acetylene or air pressure when heated at a definite heating rate

Curve a: acetylene at the initial pressure of 7.5 kg/cm² in the presence of copper

Curve b: acetylene at the initial pressure of 11.5 kg/cm² in the presence of copper

Curve c: acetylene at the initial pressure of 8.0 kg/cm² in absence of copper

Curve d: air at the initial pressure of 8.5 kg/cm² in absence of copper

initial pressures of from 4 to 13 kg/cm². acetylene has scarcely changed during 30 minutes except in the condition of 260°C and 13 kg/cm² where the gas shows only a slight pressure decrease which can be negligible compared with the great rate of reaction in the presence of a copper plate.

In order to examine the effect of the reaction product, cuprene, on the reaction rate, acetylene had been reacted for 30 minutes at the initial pressure of 7 kg/cm² and at 260°C, and the residual gas was pumped out and then the same experiment as before was repeated introducing fresh acetylene into the vessel. The result of such five successive reactions with the same copper plate leads to the conclusion that the pressure-time curves hardly show the difference of the rate of pressure change and are reproducible*. We used, therefore, the same copper plate in a few runs.

In the experiment using a new copper plate, the induction period within 5 minutes where the pressure hardly changes is observed, but in the presence of copper previously used there is a very short or no induction period.

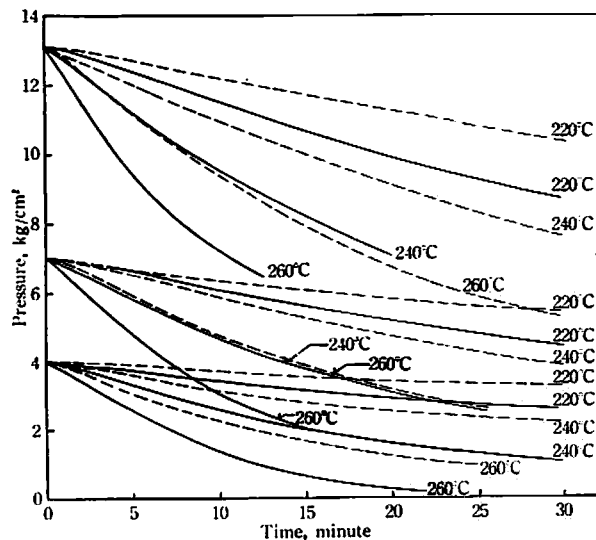


Fig. 3 Pressure as a function of time in the presence of copper plates at the temperatures of 220, 240 and 260°C

--- surface area of copper plate: 20 cm²
 — surface area of copper plate: 40 cm²

* This result is in agreement with that of H. Teranishi, *This Journal*, 26, 18 (1956).

Typical pressure-time curves using copper plates are shown in Fig. 3. The rate of pressure decrease becomes greater as the reaction temperature and the initial pressure increase and also as the apparent surface areas of the copper plates used do.

Experiments with annealed copper plates have the same tendencies as just mentioned above. A series of experiments in the presence of annealed copper plates having about 20cm² surface area were performed in order to elucidate the effect of conditions of annealing, and the experiment using cuprene itself as a catalyst stripped off from a copper plate was also practiced. Most of these were carried out at the initial acetylene pressure of 7.5kg/cm² and at 220, 240 and 260°C. The reaction curves having the same tendency at each reaction temperature, typical examples at 240°C are shown in Fig. 4. which indicates the following. (1) Copper plates annealed in vacuum,

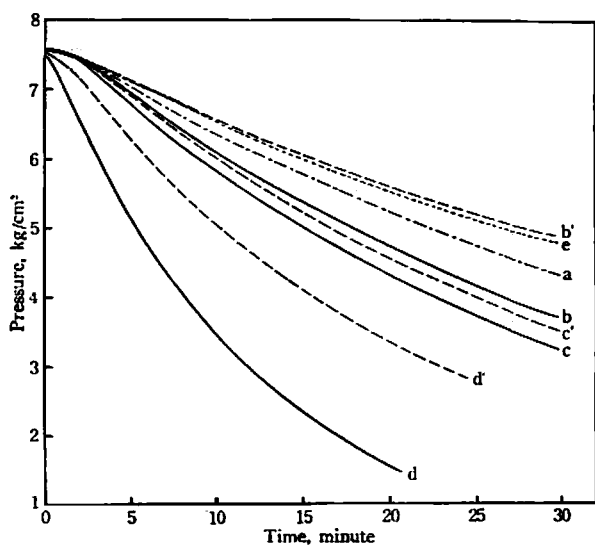


Fig. 4 Pressure as a function of time in the presence of variously annealed copper or cuprene at 240°C and the initial pressure of 7.5kg/cm²

- Curve a: copper
- Curve b: copper annealed at 450°C in vacuum
- Curve b': copper annealed at 550°C in vacuum
- Curve c: copper annealed at 450°C in air
- Curve c': copper annealed at 550°C in air
- Curve d: copper annealed at 450°C in oxygen
- Curve d': copper annealed at 550°C in oxygen
- Curve e: cuprene

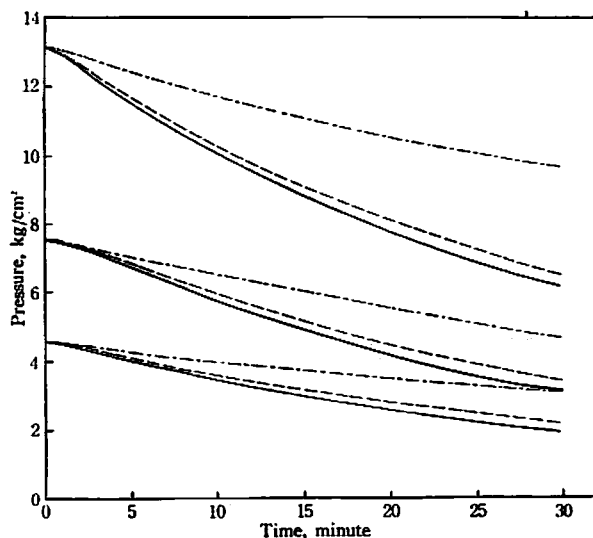


Fig. 5 Effect of initial pressure on the reaction at 240°C

- cuprene
- copper annealed in air at 450°C
- · - · copper annealed in air at 550°C

air or oxygen at 450°C have greater activity than those annealed at 550°C. (2) At each annealing temperature, 450 and 550°C the activity of copper diminishes in the order

those annealed in oxygen > those in air > those in vacuum

(3) those annealed in vacuum at 550°C are less active, and the other coppers annealed are more active than coppers without annealing. (4) Cuprene in absence of copper plate is still active though a little less than a copper plate.

Fig. 5 shows the effect of the initial pressure on the reaction rate in case of using cuprene plates, and copper plates annealed in air. The higher the initial pressure, the larger is the reaction rate.

Consideration

The color of cuprene changes generally from yellow to brownish yellow according to the rise of reaction temperature. The part directly contacted with copper surface is a dark brown thin layer on which yellow layer of cuprene lies. The thin dark brown layer does not exhibit activity as a catalyst, while the upper yellow layer has activity as mentioned above.

As to the direction of cuprene growth, it is found that in the presence of a copper plate it grows mainly in the direction perpendicular to the copper plate (i. e. increases the thickness), on the other hand when the cuprene is used as a catalyst without a copper plate, it grows in all

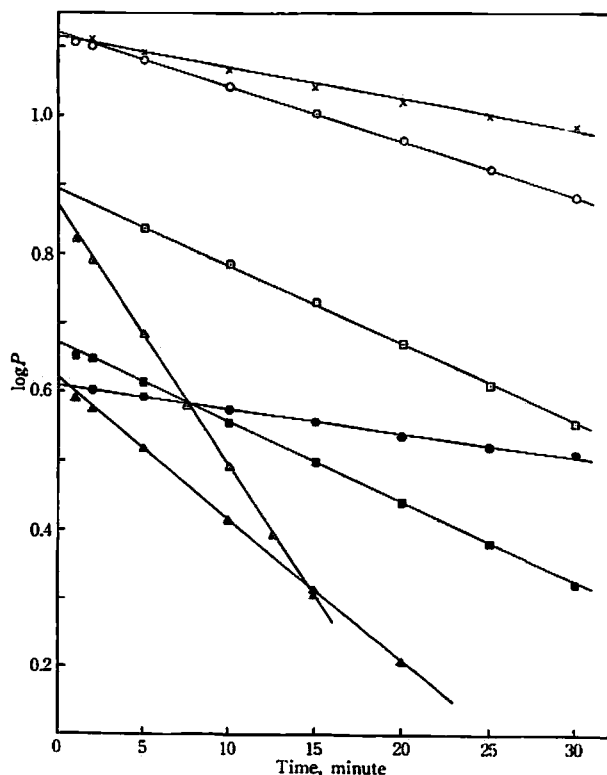


Fig. 6 Relations between $\log P$ and time t

- copper plate of 20 cm² surface area; at 240°C and 13 kg/cm²
- copper plate of 20 cm² surface area; at 220°C and 4 kg/cm²
- △ copper plate of 40 cm² surface area; at 260°C and 7 kg/cm²
- ▲ copper plate of 40 cm² surface area; at 240°C and 4 kg/cm²
- copper plate of 20 cm² surface area annealed at 450°C in vacuum; at 240°C and 7.5 kg/cm²
- copper plate of 20 cm² surface area annealed at 450°C in air; at 240°C and 4.5 kg/cm²
- × cuprene of 20 cm² surface area; at 240°C and 13 kg/cm²

Table 1 Rate constants and apparent activation energies for the reaction with copper plates catalyst

Initial pressure kg/cm ²	Temperature °C	Rate constant sec ⁻¹ × 10 ⁵	Activation energy kcal/mole
13.0	220	0.682	20
	240	1.62	
	260	3.13	
7.0	220	0.677	21
	240	1.56	
	260	3.48	
4.0	220	0.648	22
	240	1.62	
	260	3.42	

Table 2 Rate constants and apparent activation energies for the reaction with copper plates variously annealed or with cuprene itself

Material examined		Initial pressure of acetylene kg/cm ²	Temperature °C	Rate constant sec ⁻¹ × 10 ⁵	Activation energy kcal/mole
Condition of annealing					
Contact gas	Temperature of annealing °C				
vacuum	450	7.5	240	2.04	20
			260	4.02	
	550	7.5	240	1.35	21
			260	2.98	
oxygen	450	7.5	240	6.90	19
			260	13.6	
	550	7.5	240	3.86	19
			260	7.78	
air	450	13.0	240	2.12	18
		7.5	220	1.18	
			240	2.46	
			260	4.53	
	550	7.5	240	2.33	18
			260	2.00	
		4.5	240	1.13	
			240	2.26	
cuprene	13.0	7.5	240	1.35	23
			220	0.576	
			240	1.45	
			260	3.33	
cuprene	4.5	7.5	240	1.45	23
			240	1.45	

the directions and extends its apparent surface area, which seems to be due to the remaining of unsaturated double bonds.

In order to determine the order of the reaction the plots of logarithm of pressure p against time give straight lines except the part of induction period as shown in the examples in Fig. 6. and so the reaction is first order. The rate constants of the reaction calculated from the slopes of those straight lines are shown in Tables 1 and 2, but they are the values per unit area (cm^2) of copper plates*.

The plots of $\log k$ against the reciprocal of absolute temperature $1/T$ from these data are shown in Figs. 7 and 8, which are straight lines. Their slopes give the apparent activation energies and the values calculated are listed in the last columns of Tables 1 and 2. The value in case of using cuprene as a catalyst is 23 kcal/mole, which is the largest of all.

The pressure effect on a rate constant k is generally described in the following formula:

$$\frac{d \ln k}{dp} = -\frac{\Delta V^{\ddagger}}{RT^2}, \quad (1)$$

where ΔV^{\ddagger} is the increase of molal volume on activation. In the present experiments, however, the pressure effect on k is not certain. According to the theory of the absolute rate of reaction,

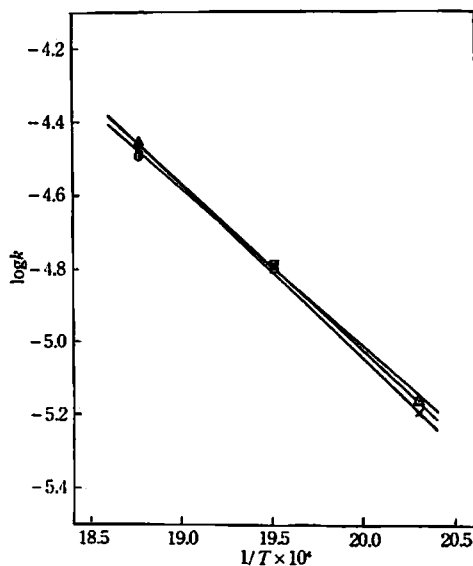


Fig. 7 Relations between $\log k$ and $1/T$ (in the presence of copper)
 ○ initial pressure; 13 kg/cm²
 △ initial pressure; 7 kg/cm²
 × initial pressure; 4 kg/cm²

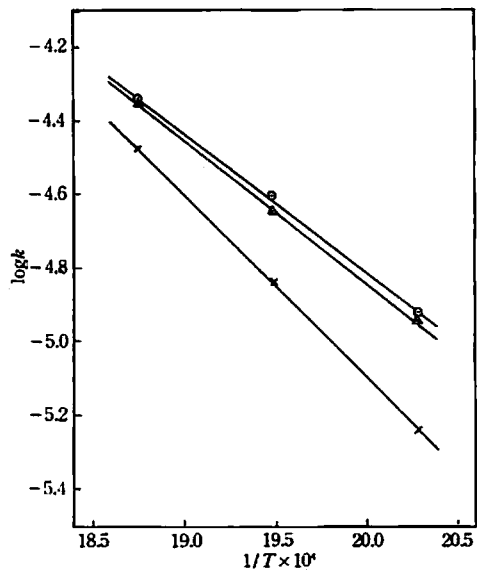


Fig. 8 Relations between $\log k$ and $1/T$ at the initial pressure of 7.5 kg/cm²
 ○ copper annealed at 450°C in air
 △ copper annealed at 550°C in air
 × cuprene

* According to the experimental results using copper plates of 20, 40 and 60 cm² surface area, the rate constants are nearly proportional to the apparent surface area of copper plates at each temperature and pressure, so all the rate constants are calculated and discussed per unit area of copper plates throughout this paper.

the relation between entropy of activation ΔS^\ddagger and rate constant k is expressed for a heterogeneous reaction involving one molecule of reactant as follows⁷⁾:

$$k = e^{\frac{k_B T}{h}} e^{\Delta S^\ddagger / R} e^{-E / RT}, \quad (2)$$

where h and k_B express the Plank constant and Boltzmann constant respectively.

Introducing the experimental values of k and E into the formula (2) ΔS^\ddagger can be calculated. The values of the reaction using copper plates without annealing are -43 to -48 E.U., and those for the reactions concerning annealed copper are -42 to -52 E.U. which differ hardly from the values of the former. The minus large value of ΔS^\ddagger means that the activated complex has small freedom and nearly in the state of solid. The variation of entropy of activation due to the initial pressure change is not certain within this experimental accuracy.

For the growth of cuprene the following reaction scheme may be suggested as a chain reaction.

In the polymerization reaction the rate of disappearance of monomer is generally given by

$$-\frac{d[M]}{dt} = k_p [M] \sum_{n=1}^{\infty} [M_n]. \quad (3)$$

Here M represents a molecule of monomer, acetylene gas, k_p the rate constant of propagation, and M_n an active polymeric substance containing n monomeric units. On the basis of the observation that under the same conditions the activity of a copper plate does not change in successive experiments, if assumed that the initial concentration of an initiating molecule M_1 is proportional to the apparent surface area of a copper plate $[S]^*$, and that $\sum_{n=1}^{\infty} M_n$ is constant and proportional to $[S]$ throughout the reaction possibly because once the reaction started, the process of initiation (i. e. the formation of M_1), chain branching and termination rarely occur, that is in general only the process of propagation occurs, the following relation is given from Eq. (3):

$$-\frac{d[M]}{dt} = k_p [M] \times k' [S] = k [M] [S]. \quad (4)$$

The rate of reaction is thus proportional to $[M]$ and $[S]$.

The increase of initial pressure causes the rate of the reaction increase, which owes to the increase of concentration of acetylene because the reaction is first order and the rate constants are hardly affected by the initial pressure of acetylene.

The less activity of copper annealed in vacuum at 550°C than that of copper without annealing may be due to the uniformity of its surface caused by the treatment of annealing and to the want of oxygen as mentioned below, but it cannot be reasonably explained that copper annealed at 450°C has the greater activity. On the other hand, the greater activity of copper annealed in air or oxygen would be due to the effect of oxygen contained in copper⁸⁾, because the surface of a copper plate was polished brightly. The fact that cuprene keeps its activity would be ascribed to

7) S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Process*, p. 397 (1941)

* If the surface of a copper plate is almost fully covered with acetylene molecule, the initial concentration of M_1 will not depend on $[M]$.

8) W. E. Garner, F. S. Stone and P. F. Tiley, *Proc. Roy. Soc., A* 221, 472 (1952)

what the cuprene produced on copper would either include copper in it⁹⁾ or leave free bonds, which would be active to the polymerization of acetylene.

Cuprene does not decompose explosively, nor has explosive combustibility though it burns well when flamed. Therefore it does not seem to cause explosion but is dangerous because of clogging pipes if much is formed.

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*The Laboratory of Physical Chemistry,
Kyoto University*

9) J. H. L. Watson, *J. Phys. & Colloid Chem.*, 54, 969 (1950)