THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 35, NO. 1, 1965

STUDIES ON EXPLOSION LIMITS OF BUTADIENE-AIR MIXTURE

BY JIRO OSUGI, HIRONOBU KUBOTA AND KATSUKUNI UEBA

The explosion limits of butadiene-air mixtures were determined by means of the admission method and the reaction products, analyzed by gas-chromatography, were CO, CO_2, H_2O, C_2H_4, HCHO, etc.

The isochor curves show that the lowest butadiene composition of explosion is 20 vol % and the explosion peninsula are found at 2~3 vol % of butadiene, under at 25 cmHg of pressure. The isobar and isotherm curves show U type.

The reaction can be explained on the thermal explosion theory and the apparent activation energy is estimated to be about 32~34 kcal/mol at 2~30 vol % of butadiene. The reaction consists of oxidation, and polymerization.

Introduction

In our modern industry, butadiene has been one of the important materials, especially as the monomer of high-polymerized substances.

There have been some reports of the explosion accidents of plants or explosion phenomena under pressure, and about the explosion of butadiene[1], it seems no reports concerning the explosion limits.

The authors investigated the explosion limits of butadiene-air mixtures in the range of 2~80 vol % of butadiene, at temperature 440~700°C, and pressure 0~70 cmHg.

Experimentals

Materials

Butadiene: used after having been dried through sodium hydroxide, driarite and silica-gel and distillating by the trap-to-trap vacuum distillation method.

Air: used after having filtered and dried through sodium hydroxide, driarite and silica-gel.

Apparatus and operation

The apparatus and operation were the same which was used in the studies on the explosion reaction of monovinyl acetylene gas[2]. The pressure changes were recorded by using a membrane gauge, a strain meter, (Shinko Comm. Ind. Co. Ltd., model: OS6–R) an amplifier and a pen-oscillograph, and the explosion was decided by the sharp changes on the pen-oscillogram. The induction period of the explosion was too short to be measured by a stop-watch, and it was measured by pen-oscillogram.

The experiment was repeated at temperatures from 440°C to 700°C for every 5°C, at pressure below

---

(*Recieved December 6, 1965*)

[1] D. S. Alexander, *Ind. Eng. Chem.*, **51**, 733 (1959)

[2] T. Ikegami, *This Journal*, **32**, 13 (1962)

700 mmHg and compositions from 2 to 80 vol % of butadiene.

The quartz reaction vessel (ϕ: 30 mm, volume 85 ml) was used to determine the explosion limits. Other two hard glass vessels (ϕ: 10 mm and 20 mm, volume 10 ml, 40 ml, respectively) were used to study the effects of diameter on the explosion limits.

The products were determined by using the gaschromatograph (Yanagimoto inc. model G. C. G. 220).

Results

Pressure change-time curve

Typical curves on the charts of pen-oscillograph are shown in Fig. 1.

From the pressure change-time curves obtained in this experiment, these explosions belong to the normal explosion and the two stage explosion among three kinds of explosions[3)4)], namely mild explosion, normal explosion and two stage explosion.

The curve of Fig. 1 (a) found out at 3 vol % of butadiene mixture has only one peak and the pressure change is very violent.

In the cases of 10 vol % and 20 vol % of butadiene mixtures there sometimes appear two peaks, which seem to be two stage explosion. Above 30 vol % of butadiene mixture, these two peaks change into one, and pressure change becomes very small. According to the increase of butadiene vol %, the peak becomes plainer.

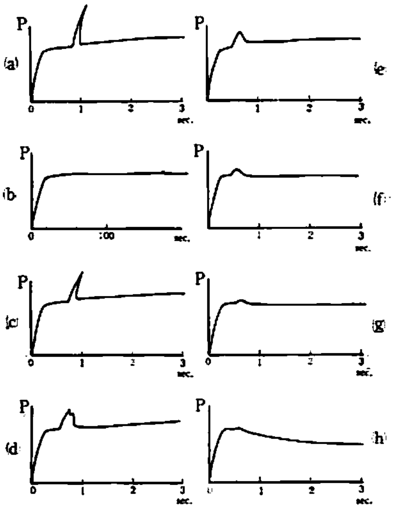

Fig. 1 Typical recordings of pressure change-time

(a) 3 vol %, C_4H_6 500°C I. A. P.* 460mmHg
(b) 3 vol %, C_4H_6 580°C I. A. P. 6.4cmHg
(c) 5 vol %, C_4H_6 460°C I. A. P. 61.9cmHg
(d) 10 vol %, C_4H_6 490°C I. A. P. 37.7cmHg
(e) 20 vol %, C_4H_6 540°C I. A. P. 15.4cmHg
(f) 40 vol %, C_4H_6 540°C I. A. P. 24.0cmHg
(g) 60 vol %, C_4H_6 500°C I. A. P. 52.0cmHg
(h) 80 vol %, C_4H_6 520°C I. A. P. 64.6cmHg
* I.A.P.: initial admission pressure

In the region of explosion peninsula obtained at 2~3 vol % of butadiene mixtures. the increase of pressure at explosion is not so large but sharp.

Below 40 vol % of butadiene mixtures, the pressure in the induction period increases, while in the 50~60 vol % of butadiene mixtures the pressure changes cannot be found and in the 70~80 vol % of

---

3) R. Kiyama, J. Osugi and S. Kusuhara, *This Journal*, **26**, 22 (1957)
4) M. Suga, *ibid.*, **29**, 73 (1960)

butadiene mixtures it decreases.

Explosion limits

Isochor curves

The limits in isochor are shown in Fig. 2 (A) (B).

The reaction vessel is made of quartz (ϕ: 30mm) as mentioned above. The pressure is denoted by the initial admission pressure. In this experiment, we find the explosion peninsula at 2~3vol % of butadiene.

Isotherms and isobars

The isotherm curves are shown in Fig. 3. The isobar curves are summarized in Fig. 4.

When the vol % of butadiene is high, it is difficult to recognize from the trace of pen-oscillogram whether the explosion occurred or not.

At 20vol % of butadiene, the explosion limits become the lowest. The isobar curves are not like

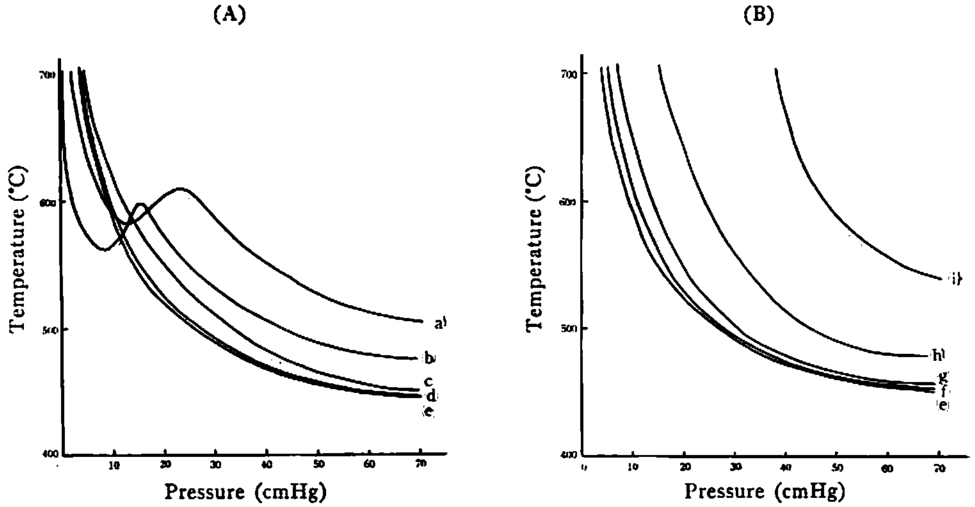

Fig 2 Isochors for explosion limits

(a) 2.0% C_4H_6
(b) 3.0% C_4H_6
(c) 5.0% C_4H_6
(d) 10.0% C_4H_6
(e) 20.0% C_4H_6
(f) 30.0% C_4H_6
(g) 40.0% C_4H_6
(h) 60.0% C_4H_6
(i) 80.0% C_4H_6

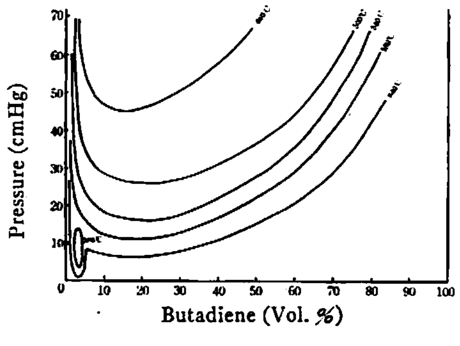

Fig 3 Isotherms for explosion limits of butadiene-air mixtures

those of monovinylacetylene2) which show ∽ type but show the same kind of U type as propylene does6). The isotherm curves also show U type.

Effect of tube diameter

We studied the effect of tube diameter on the explosion limits by using gaseous mixtures of 10 and 30 vol % of butadiene.

The reaction vessels used are made of hard glass (φ: 10 mm, V. 10 ml; φ: 20 mm, V. 40 ml).

The results are shown in Fig. 5. It shows that the explosion limit curves become low with increasing tube diameter.

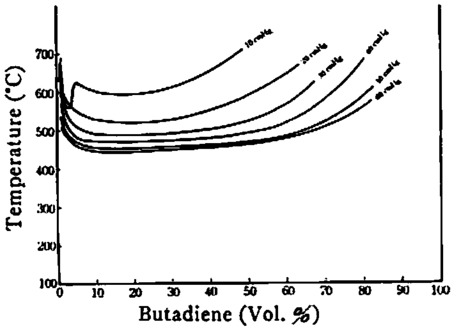

Fig 4 Isobars for explosion limits of butadiene–air mixtures

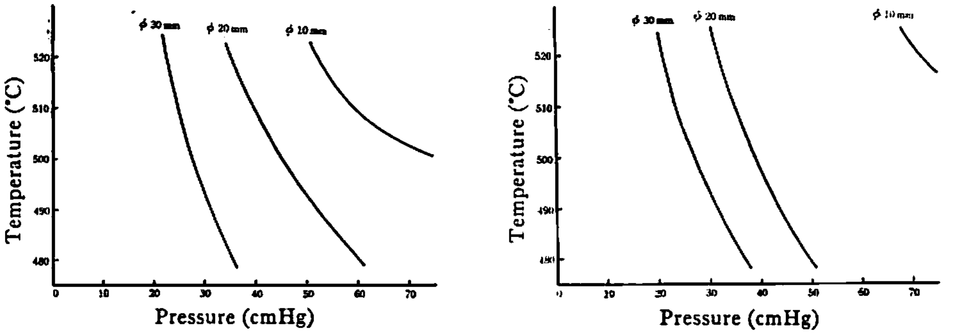

Fig 5 Effect of vessel diameter on the explosion limits of butadiene–air mixtures.

Induction period

In this experiment, the induction period was determined by the pressure curves on the pen-oscillograph as described above. From the experimental results, the following general tendencies are found for the induction period.

1. In the explosion peninsula, the induction period is very long and sometimes it takes about 200 seconds.
2. In the case of the same temperature and component, the higher the admission pressure, the shorter the induction period becomes.
3. In the case of the same pressure and component, the higher the temperature, the shorter the induction period becomes.

---

5) S. Kusuhara, *This Journal*, 28, 67 (1959)

6) S. Kusuhara, *ibid.*, 30, 34 (1960)

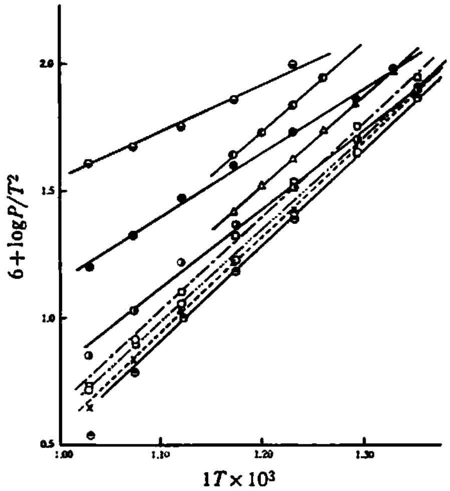

Fig 6 Relations between log P/T^2 and $1/T$.

◐ 2.0 vol%, C_4H_6
△ 3.0 vol%, C_4H_6
□ 5.0 vol%, C_4H_6
× 10.0 vol%, C_4H_6
◐ 20.0 vol%, C_4H_6
○ 30.0 vol%, C_4H_6
◑ 40.0 vol%, C_4H_6
● 60.0 vol%, C_4H_6
◒ 80.0 vol%, C_4H_6

4. In the case of the same temperature and pressure, the larger the butadiene vol %, the shorter the induction period becomes.

Products[7]

The reaction products were analyzed by using gas-chromotograph.

CO, CO_2, H_2O, C_2H_4, HCHO, CH_2=CHCHO, C_3H_6, C_3H_8 were detected as the reaction products. When the butadiene vol % was very high, we obtained the liquid product which seemed to be polymers of low molecular weight.

Flame color

In the region of the low butadiene composition, the flame color is blue, but as the composition of butadiene increases, it changes into orange.

Consideration

If the rate of temperature rising (W_1) in the exothermic reaction were faster than that of cooling (W_2), the temperature in that system would be increased and the rate would be also accelerated. From this point of view, if $W_1 > W_2$, even in a slow reaction, the reaction temperature would be raised and the reaction would also be accelerated faster and faster to what we found to be an explosion. The lowest initial temperature of explosion is called the explosion (or ignition) temperature (T_0). N. Semenoff[8][9][10] derived the following relation with assumption that 1) heat transmission was done only through the wall and 2) any surface reaction did not occur.

$$\log\left(\frac{P}{T^{1+\frac{2}{n}}}\right)=\frac{A}{T}+B \tag{1}$$

---

[7] G. J. Minkoff and C.F.H. Tipper, "Chemistry of Combustion Reactions" p. 174 London Butterworths (1962)

[8] N. Semenoff, *Z. Physik*, **48**, 57 (1928)

[9] N. Semenoff, "Chemical Kinetics and Chain Reactions" Oxford Univ. Press (1935)

[10] N. Semenoff, "Some Problems of Chemical Kinetics and Reactivity" Part 2. translated by J. E. S. Bradley, Pergamon Press Ltd. (1959)

where,
P: pressure at explosion limit
T: temperature of reaction vessel (°K)
n: order of reaction
B: constant
A: 0.217 E/n

Then

$$n=1 \qquad \log\frac{P}{T^3}=\frac{A}{T}+B$$

$$n=2 \qquad \log\frac{P}{T^2}=\frac{A}{T}+B$$

It has not been known, whether the explosion reaction of butadiene-air mixture is based on the thermal theory or the chain theory, what order of reaction it has, and what kind of reaction (polymerization, decomposition or oxidation) plays the main role.

The activation energy is estimated with the assumption that the thermal theory is better and the order of reaction is 2. The results obtained are given in Fig. 6. The apparent activation energy is obtained from the slope of the straight line. (Table 1) The apparent activation energy is about 17.3~34.5 kcal/mol, and in the range of 5~30 vol % of butadiene, it has almost a constant value, about 33 kcal/mol, and the larger the butadiene vol %. the smaller the activation energy becomes.

Table 1 Apparent activation energy ($n=2$)

Butadiene (vol %)	Apparent activation energy (kcal/mole)
2	31.8
3	31.8
5	33.6
10	33.6
20	34.5
30	32.7
40	29.1
60	23.6
80	17.3

Considering the results of the reaction products, pen-oscillogram and other experimental results, it seems that the oxidation reaction takes place in low butadiene vol %, while the polymerization reaction in high vol %.

In the explosion peninsula that appears in low butadiene composition, it seems that the chain explosion reactions may be caused by carbon monoxide[6].

Laborotory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan