The Review of Physical Chemistry of Japan Vol. 32 No. 1 & 2 (1962)

STUDIES ON EXPLOSION REACTION OF MONOVINYL ACETYENE GAS

I. Explosion Limits of Monovinyl Acetylene and Monovinyl Acetylene-Air Mixture

By Tatsuya Ikegami

(*Received February 20, 1963*)

The explosion limits of MVA and MVA-air mixtures were determined by use of the heated filament method and the admission method.

In the former, the limit is 2.2∼9.2 MVA vol. % at 760 mmHg and room temperature, and the lowest limit pressure is 365 mmHg at 4.8 MVA vol. %. The after glow is found near the normal explosion region. In the latter, isochors, isotherms and isobars were obtained under the conditions of below 700°C and below 700 mmHg. Isotherms and isobars in the explosion limits have a specific shape (∽). That is, there is a peak in 80∼90 MVA vol. % as shown in Figs. 10, 11 and 14. MVA is self-explosive.

The reaction can be satisfactorily explained on the thermal explosion theory, and, assuming that the order of reaction is 2, the apparent activation energy is estimated to be 26∼39 Kcal/mol below 550°C. The reaction consists of polymerization, decomposition and oxidation.

Since 1930s, monovinyl acetylene (MVA) has been one of important industrials chemicals manufactured by polymerization of acetylene by use of the Nieuwland type catalyst, as an intermediate material in the field of synthetic rubber.

Explosions have been often occured in the process of the production. No study on the explosion, however, has been reported. Only two or three patents were reported on its unstability under pressure.

The explosion of MVA is supposed to be similar to that of acetylene from the consideration of its structure and endothermic nature, but no report of self-ignition or limits of explosion of its mixtures is available.

To investigate the explosion limits of MVA and MVA-air mixtures and to elucidate its mechanism in industrial interest as well as in academic research is the object of this paper.

It is very important to study the explosions of acetylenic compounds, because of their endothermic compounds. A lot of papers on acetylene and mixtures of acetylene–O_2 or air have been published. Among them, the determination of the limits by the admission method was done on the region of below a few atm by von P. Schläpfer1) and R. Kiyama2), and on higher pressure by R. Kiyama *et al.*3,4) in details.

The limits of explosion by the fused metal ignition under high pressure were determined in

---

1) von P. Schläpfer and K. Brunner, *Helv. Chim. Acta*, **13**, 1125 (1930)

2) R. Kiyama, J. Osugi and S. Kusuhara, *This Journal* **27**, 22 (1957)

3) R. Kiyama, J. Osugi and H. Teranishi, *ibid.*, **23**, 43 (1953), *ibid.*, **24**, 41 (1955)

4) H. Teranishi, *ibid.*, **25**, 58 (1956)

The Review of Physical Chemistry of Japan Vol. 32 No. 1 & 2 (1962)

details by W. Reppe⁵⁾. The self-explosion of methyl acetylene under pressure was briefly reported by F. Fitzgerald⁶⁾. No information concerning to the explosion of MVA has been reported.

Various methods⁷⁾ have been used for the determination of explosion limits. Generally, the explosion limits are measured by the U. S. Bureau of Mines (U. S. B. M.) method⁸⁾ at room temperature, but it is not suitable for the purpose of elucidating the reaction mechanism. Furthermore, experimental conditions such as pressure, temperature and so on are restricted. The admission method is better for making mechanism clear.

In "Part 1" of this paper, the explosion limits at room temperature were determined by use of the modified U. S. B. M. method in order to be compared with other data. On the other hand, the admission method was applied to get more informations (that is, induction period, explosion temperature, products analysis and so on, which are mentioned in "Part 2".)

Part 1. The Explosion Limits by the Heated Filament Method

Experimentals

Materials

Monovinyl acetylene (MVA) ($CH\equiv C-CH=CH_2$)

MVA, prepared by polymerization of acetylene with the Nieuwland catalyst, was used. Its purity was checked by gas chromatographic analysis at every run. Analytical results are given in Table 1.

Table 1. Analysis* of MVA (vol. %)

Monovinyl acetylene	99.70–99.94%
Acetylene	trace
Acetone	0.04–0.08%
Nitrogen or air	0.01–0.20%
Divinyl acetylene	0.00–0.04%
Others (Vinyl chloride, acetaldehyde, methyl vinyl ketone)	none

* by gas chromatograph, using DOP (bed) and H_2 (carrier gas)

It was confirmed that the amount of impurities did not affect the experimental results.

Apparatus and operation The explosion limits in the available tables have been generally determined by the U. S. B. M. method⁸⁾. This method has a disadvantage.

It is the Kitagawa's Laboratory (K. L.) method⁹⁾ that the above method was simplified and

---

5) W. Reppe, "*Chemie und Technik der Acetylen-Druck-Reaktion*", Velag Chemie, G. m. b. H. (1952) *et al.*

6) F. Fitzgerald, *Nature*, **186**, 386 (1960)

7) For example, F. S. Dainton, "*Chain Reaction*", Methuen Co., London (1956)

8) H. F. Coward and G. W. Jones, "*Limits of Flamability of Gases and Vapors*", Bur. Min. Bull., No. 503 (1952)

9) T. Kitagawa and Y. Numano, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo-Kagaku Zasshi*), **60**, 132 (1957)

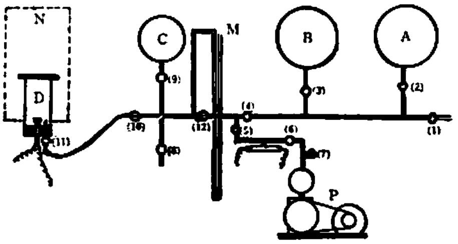


Fig. 1 Apparatus of heated filament method.

A: Reservoir
B: Reservoir
C: Mixing bulb
D: Reaction chamber
M: Manometer
N: Safety net
P: Pump

modified. In this experiment, the K. L. method, slightly modified on ignition source, was used. The schematic diagram is shown in Fig. 1.

The combustion chamber (D) was a hard glass tube of about 150 mm in length and 50 mm in diameter. The upper part was covered with a polished glass plate (G) and the lower was closed by a rubber stopper (R), fitted with a gas lighter on sale (Matsushita Elec. Co.) and a glass cock (E), as shown in Fig. 2. After evacuating the whole system, the combustible gas-air mixture of desired conditions (fixed composition and pressure) was led into the combustion chamber (D). Ignition was done by closing electric circuit of the gas lighter for constant time (usually, 1 sec.) to elevate filament temperature.

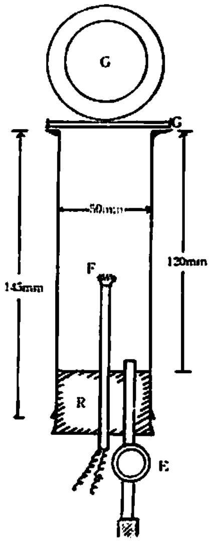


Fig. 2 Reaction chamber.

F: Filament
G: Glass plate
R: Rubber stopper
E: Glass cock

In the case of non-ignition, ignition operation was repeated for longer periond (2 sec. and 3 sec.). If the gas mixtures were within the explosion limits, explosion would blaste the glass plate (G).

In this experiment, another region, in which the after-glow was found around the filament for a few to some hundreds seconds after the start of ignition and not propagated, was found in addition to the usual explosion phenomena. So, the period of the after-glow was measured with a stop watch.

The reproducibility in this method was very good and the error was within ±0.1 vol. % in composition. The smaple gas and unexploded gas were examined by gas chromatographic analysis.

Results and Considerations

The explosion limits at room temperature (10°C) are shown in Figs. 3 and 4. P mmHg. denotes the initial pressure of gas mixture, $\boxed{A}$ the usual explosion area, and $\boxed{B}$ the after-glow area. In the $\boxed{A}$, the induction period was too short to be measured. In the $\boxed{B}$ area, a small after-glow was observed in a few to some hundreds seconds with reducing its intensity, after opening the electric circuit. The periods are indicated with numbers in second in Fig. 4. Though the definite relations between the period of the after-glow and other factors are not found, the following tendencies are recognized, that is, 1) the nearer to the $\boxed{A}$ region, the longer the after-glow period is, and 2) the farther from the boundary, the longer the period is in the $\boxed{B}$ area.

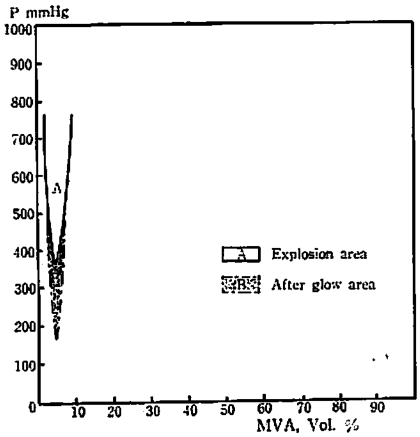


Fig. 3 Isotherm for explosion limit of MVA-air mixtures at room temperatur.

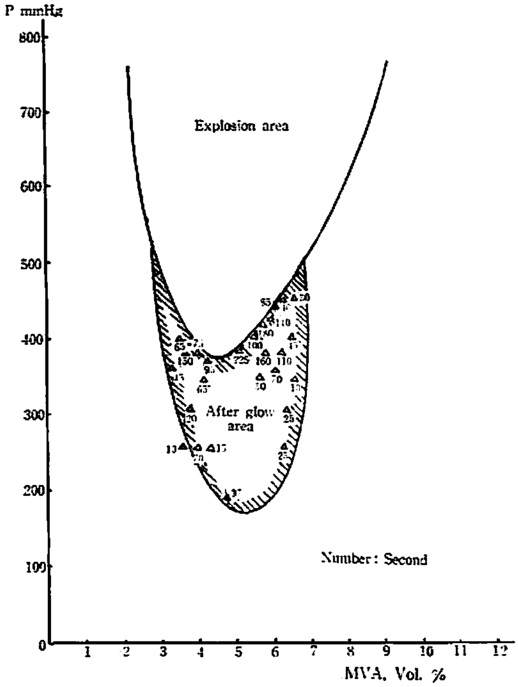


Fig. 4 After-glow area at room temperature.

The phenomena of the after-glow as described above has not been found in literature. It seems that there was relation between it and the explosion. There was no pressure change before and after the after-glow. This means that the reaction is localized around the filament and is not propagated.

As the results of this experiment, the following explosion limits at 760 mmHg of the MVA-air system were obtained;

2.2~9.2 MVA vol. %.

The lowest pressure at the limit was

365 mmHg at 4.8 MVA vol. %.

The comparison of MVA with other gases or vapors is tried. Though exact comparison is difficult, because of the lack of the data on the same apparatus, since the results obtained in this experiment seem to be almost the same as those in the U. S. B. M. and K. L. method, they are cited in Table 2.

In the table, it is known that MVA is less dangerous at normal pressure and room temperature in spite of its acetylenic structure.

Table 2 Explosion limits* of some combustible gas-air mixtures

Gas	Mol. formula	Mol. wt.	Explosion limits (vol. %) Lower (x_1)	Upper (x_2)	Degree of danger (H)**
Acetylene	C_2H_2	26.0	2.5	80	31.4
Ethylene	C_2H_4	28.0	3.1	32	9.3
Propylene	C_3H_6	42.1	2.4	10.3	3.3
Ethane	C_2H_6	30.1	3.0	12.5	3.2
Propane	C_3H_8	44.1	2.2	9.5	3.3
Butane	C_4H_{10}	58.1	1.9	8.5	3.5
Hydrogen	H_2	2.0	4.0	75	17.7
MVA	C_4H_4	52.0	2.2	9.2	2.7

* Cited from the below book[10] with exclusion of MVA

* * $H=(x_2-x_1)/x_1$

Part 2. The Explosion Limits by the Admission Method

The results in the previous experiment were obtained by local heating in the sample gas at room temperature. The apparatus is restricted in changing experimental conditions such as temperature and pressure, and in analysing reaction products. As it is not suitable to get basic data, the admission method, which has not a local heating zone, is performed for the fundamental research in this part.

On various compositions of MVA and MVA-air mixtures, using reaction tubes of 10~30 mm. in diameter and 120 mm. in length below 700°C and below 600 mmHg, the explosions (flames, pressure-rising etc.) observed during were a few minutes after admission. The explosion limits were determined.

Experimentals

Materials

Monovinyl acetylene (MVA): the same as in the part 1.

Air: used after filtering and drying as usual

---

[10] B. Lewis and G. von Elve, "*Combustion, Flames and Explosions of Gases*", 3rd. Ed., Academic Press(1961)

Apparatus and operation

The apparatus used to study is shown schematically in Fig. 5. The gas sample of desired composion was prepared by the partial pressure method, using a mercury manometer (M_1), and stored in the reservoir (ca. 2000 ml.) (S_1) over 15 hr for completemixing. Just before the experiment, the composition was tested and determined by gas chromatographic analysis.

Part of sample gas in the gas reservoir (S_1) was led to the glass bulb (ca. 200 ml.) (S_2) at the fixed pressure by the aid of a Toepler pump (P).

The reaction vessel (V) (ϕ: 10～20 mm., l: 120 mm., silica* or hard glass) was horizontally set at the center of the electric furnace (F) and, after preheated at about 500°C for 30 min. under vacuum of ca. 10^{-3} mmHg, was kept at the desired temperature for more than 30 min. Immediately after the sample gas in the reservoir (S_2) was rapidly admitted to the heated and evacuated reaction vessel (V), the cock (C_3), was closed. The explosion was observed for a few minutes (over 2 min.). The relation between the pressures admitted in (V) and those of the sample gas in (S_2) was previously obtained by a strainmeter, calibrated by blank test.

Pressure changes (pressure change against time) after admission were recorded by using a membrane gauge (G), a strainmeter, an amplifier and a pen-oscillograph. (Fig. 6) The explosion or the non-explosion was decided by the observation of flame through mica window (w) in dark room, and the rapid pressure-rising on the chart of pen-oscillograph.

The induction period was determined by the pressure change on the chart (Fig. 6) because it was too short to be measured with a stop watch.

The above experiment was repeated to determine the explosion limits at various temperatures

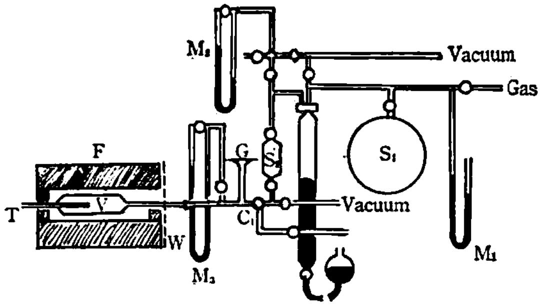


Fig. 5 Apparatus for admission method.

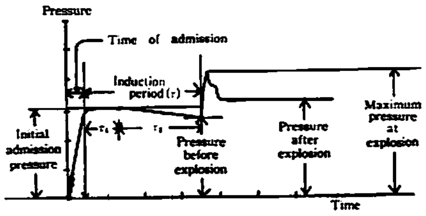


Fig. 6 Pressure change-time diagram.

---

* Silica tube was used over 600°C

(every 5°C in the temperature range of below 700°C), initial pressures (below 700 mmHg) and compositons (0~100 MVA vol. %).

Three kinds of tubes of different diameter (10 mm, 20 mm, and 30 mm.) were used to investigate the effects of diameter.

The results obtained were reproducible in this experiment.

Experimental Results

1) Pressure change-time curve Typical curves on the charts of pen-oscillograph are as follows (Fig. 7 (a)~(f)).

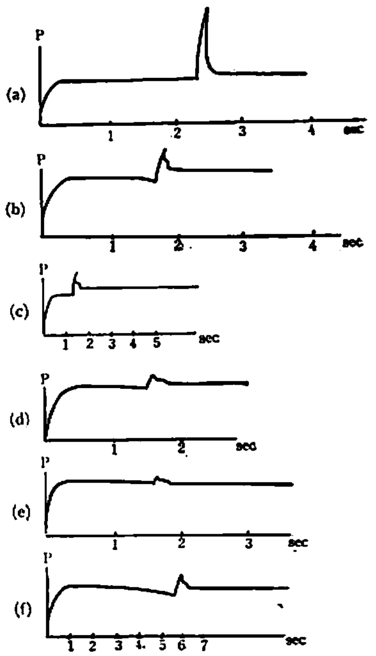


Fig. 7 Typical recordings of pressure change-time.

6 vol. %, MVA
I. A. P.*: 460 mmHg

16 vol. %, MVA
I. A. P.: 330 mmHg

33 vol. %, MVA
I. R. P.: 460 mmHg

85 vol. %, MVA
I. A. P.: 200 mmHg

99.7 vol. %, MVA
I. R. P.: 600 mmHg

99.7 vol. %, MVA
I. A. P.: 330 mmHg

* I. A. P.: Initial admission pressure

Though the pressure change-time curves obtained in this experiment are substantially belonged to the "*normal explosion*" among three kinds of curves (normal explosion, mild explosion and explosion with two stage flame) found by R. Kiyama[12], H. Suga[11] and S. Kusuhara[13], they have slightly different feature according to the composion of gas mixtures.

The curve of Fig. 7-(a) which is found below 15 vol. % of MVA has only one peak and both pressure increase and decrease are large. Above 15 vol. % of MVA, two stage pressure drop is observed after rapid pressure rising. That is, the curves have a peak and a plateau during the explosion, and the higher concentration of MVA, the more gentle the first pressure drop is. Though this phenomenon seems to be similar to the two stage ignition, the arrangement of peaks

---

[11] M. Suga, *This Journal*, **29**, 73 (1960)

[12] R. Kiyama, J. Osugi and S. Kusuhara, *ibid.*, **27**, 22 (1957)

[13] S. Kusuhara, *ibid.*, **28**, 67 (1959)

is reverse. That is, the highest peak is at the initial part and the pressure decreases in two steps. Specific flames were not found in this period.

The pressure rising during the induction period was not generally found here, but, inversely, considerable rapid pressure decreasing was recognized at higher concentration of MVA.

2) Explosion limits *i) Isochor curves* The limits in isochors with the use of ϕ 20 mm. tube are shown in Fig. 9 (a)~(c). (Pressure is denoted by the initial admission pressure as in Fig. 6).

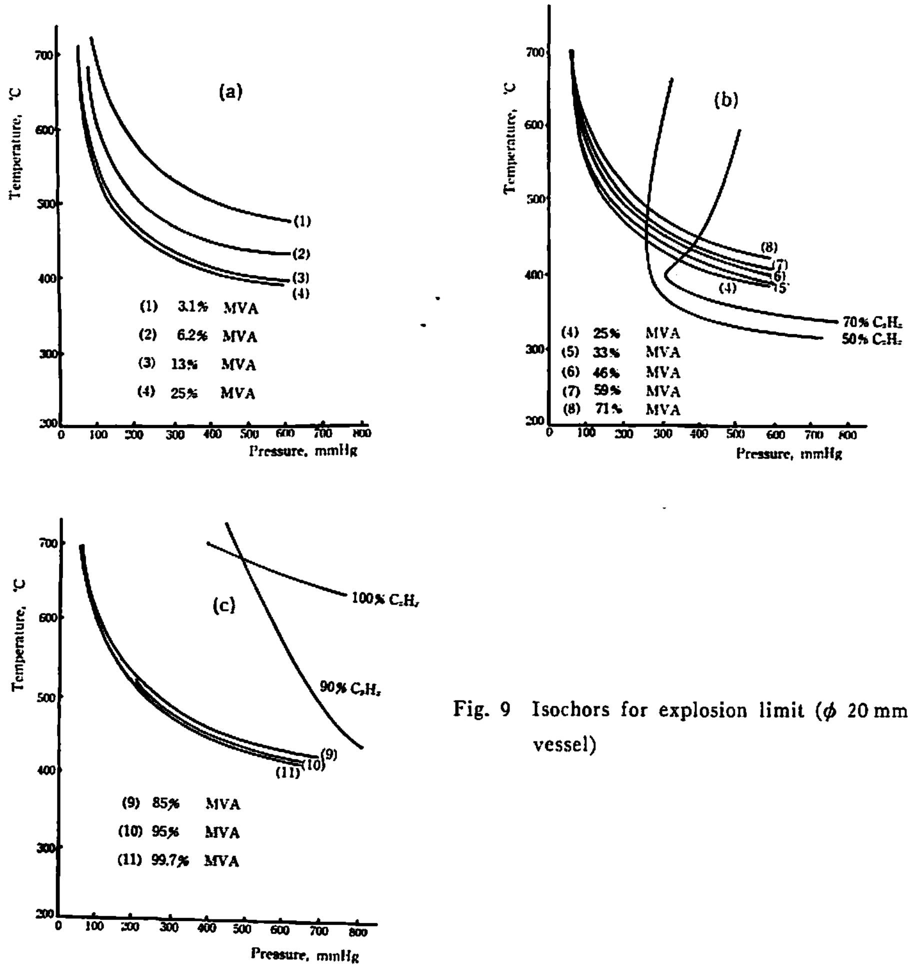


Fig. 9 Isochors for explosion limit (ϕ 20 mm vessel)

Every curve is smooth, and the explosion peninsula and the cool flame region are not observed.

No difference was recognized between silica and hard glass tube as seen in Fig. 8.

P. Schläpfer's results¹⁾ on C_2H_2, which was obtained with a vessel of 15 mm. in diameter and 70 mm. in length, are added in the Figs. 9 (b) and (c). Even though experimental conditions are not completely the same, the following conclusions are reasonable:

1) In higher composition, MVA is more stable than C_2H_2, 2) but it becomes more unstable

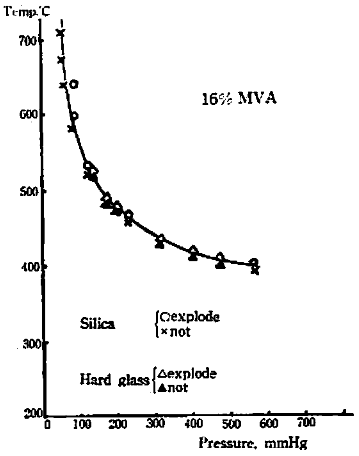


Fig. 8 Isochor for silica and hard glass (ϕ 20 mm vessel)

with reducing composition.

ii) *Isotherms and isobars* Isotherm curves are shown in Fig. 10 with that of C_2H_4[14]. Isobar curves are summarized in Fig. 11.

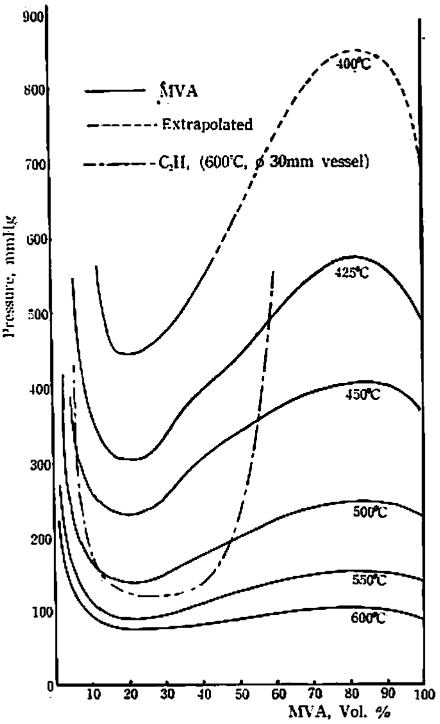


Fig. 10 Isotherms for explosion limit of MVA-air (ϕ 20 mm vessel)

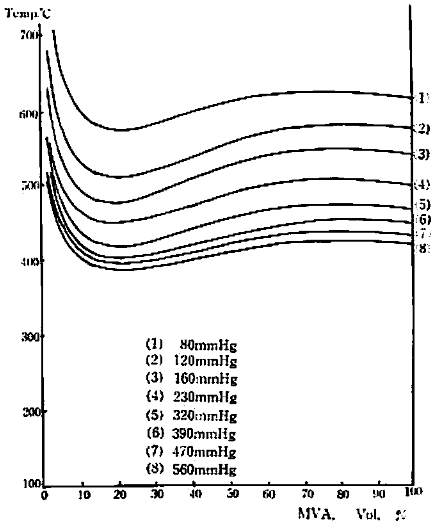


Fig. 11 Isobars for explosion limit of MVA-air (ϕ 20 mm vessel)

---

[14] M. Suga, *Memories Ehime Univ. Sec.* II, 3, 145 (1959)

It is known that 1) MVA explodes all over the range of composition, and 2) explosion limits curve is lowest at about 16% (that is, $(MVA/O_2)\fallingdotseq 1$) and 3) has a peak in 80~90 MVA vol. %.

It should be noted that curves show ∽ shape and it changes to L shape with rising temperature as seen in Fig. 11 and that MVA is self-explosive and has a lower limit value (420°C at 560 mmHg) than that of C_2H_2 (575~620°C at 760 mmHg).

3) Flame color The flame color, which changed from blue, green, yellow and orange to red with increasing MVA composition, was observed, though definite boundaries between each color were not obtained (Fig. 12).

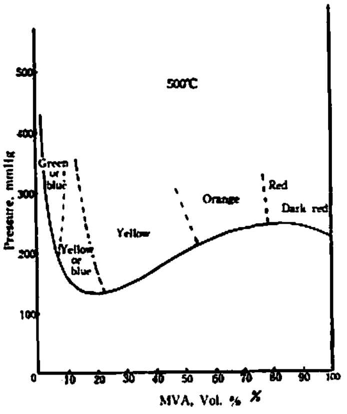


Fig. 12 Flame color region

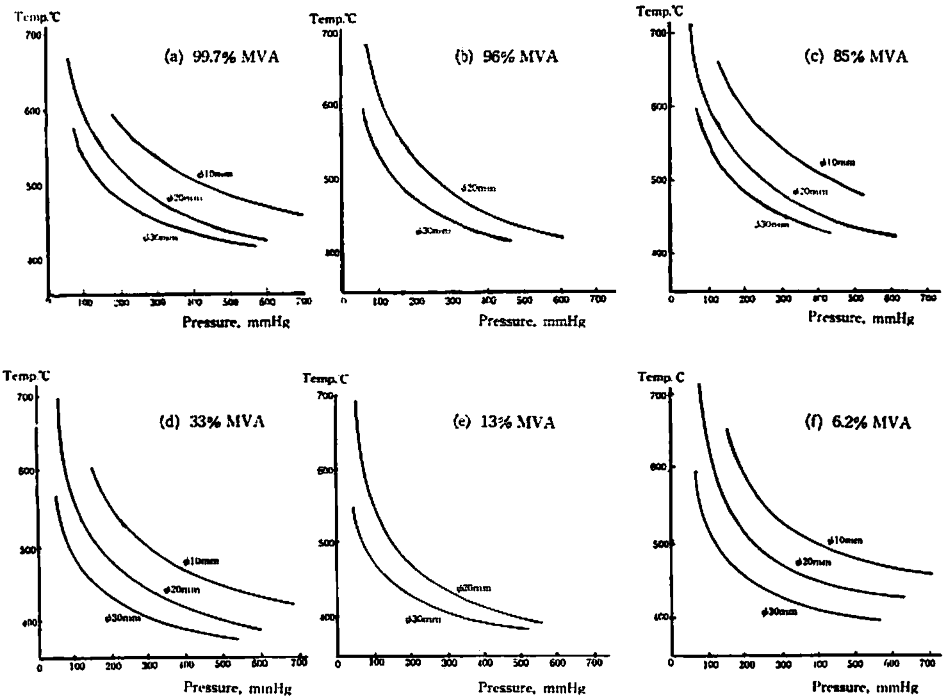


Fig. 13 Effect of vessel diameter on explosion limits of MVA-air mixtures

4) Effect of tube diameter The silica or hard glass tubes of 20 mm in diameter and 120 mm in length were used as the standard reaction vessels to determine the limits of explosion, but tubes of 30 mm or 10 mm in diameter and of the same length were also employed in order to examine the effect of diameter. The results are shown in figures. (Fig. 13 (a)~(f) for isobars, and Fig. 14 for isotherms.)

The larger the diameter, the lower limits the explosion had. The peaks at 80~90 MVA vol. % did not disappear.

5) Induction period The induction periods in this experiment were determined on the

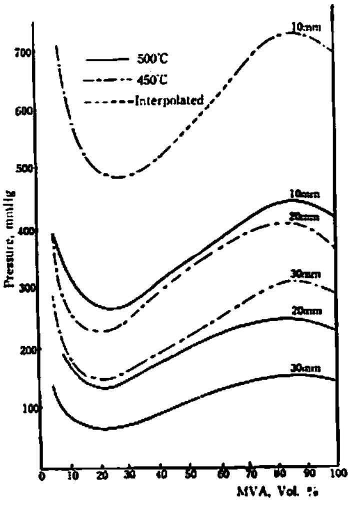
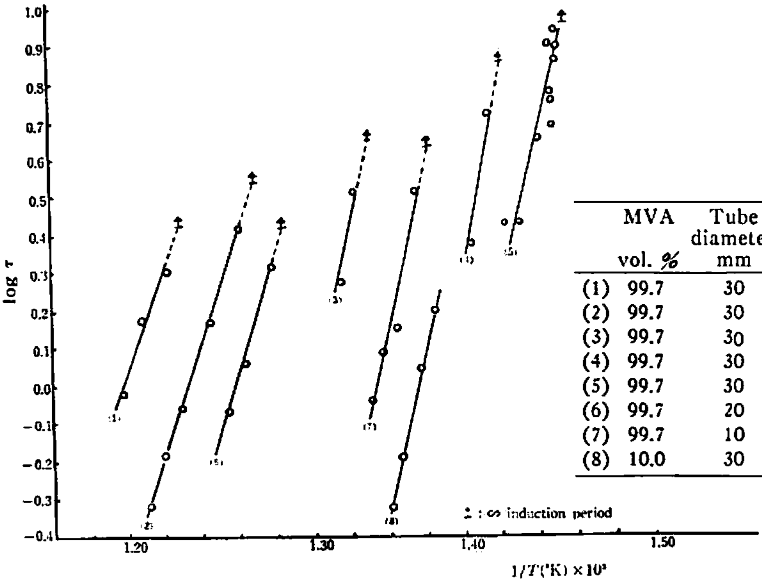


Fig. 14 Effect of vessel diameter on explosion limits (isotherms) of MVA-air mixture



	MVA vol. %	Tube diameter mm	Initial pressure mmHg	Activation energy kcal/mol
(1)	99.7	30	100	62.5
(2)	99.7	30	130	69.2
(3)	99.7	30	195	76.3
(4)	99.7	30	330	77.5
(5)	99.7	30	460	74.3
(6)	99.7	20	195	72.6
(7)	99.7	10	620	76.3
(8)	10.0	30	190	73.2

Fig. 15 Relations between log. τ and $1/T$

Table 3 Induction period

MVA composition	3.1%		13.0%		30%		46%		59%		71%		>99.7%	
Init. press.	460 mmHg		460 mmHg		460 mmHg		460 mmHg		460 mmHg		460 mmHg		460 mmHg	
Vessel diameter	20 mm		20 mm		20 mm		20 mm		20 mm		20 mm		20 mm	
	Temp.	I. P.*	Temp.	I. P.	Temp.	I. P.	Temp.	I. P.	Temp.	I. P.	Temp.	I. P.	Temp.	I. P.
	492°C	∞	405°C	∞	400°C	∞	415°C	∞	425°C	∞	425°C	∞	450°C	∞
	495°C	0.80	410°C	2.25	405°C	0.88	420°C	1.25	428°C	1.92	440°C	1.80	460°C	2.90

>99.7%		>99.7%		>99.7%		>99.7%		>99.7%		>99.7%		>99.7%	
460 mmHg		460 mmHg		460 mmHg		330 mmHg		195 mmHg		130 mmHg		100 mmHg	
20 mm		30 mm		10 mm		30 mm		30 mm		30 mm		30 mm	
Temp.	I. P.	Temp.	I. P.	Temp.	I. P.	Temp.	I. P.	Temp.	I. P.	Temp.	I. P.	Temp.	I. P.
455°C	∞	413°C	∞	495°C	∞	440°C	∞	480°C	∞	515°C	∞	540°C	∞
460°C	2.07	415°C	8.01	500°C	1.04	445°C	5.25	485°C	3.28	520°C	2.59	545°C	2.00
		420°C	4.46										

* I. P.: Induction period (sec.)

chart of the recorder as described above. The results obtained are given in Table 3 and Fig. 15.

The definite rules or regularities are not found, but the following general tendencies are found.

At the lowest explosion temperature:

1) The higher the admission pressure, the longer the induction period is.

2) The wider the tube diameter, the longer the induction period is.

3) The induction period is longer with increasing MVA composition (over 20%) in air.

4) The induction periods are, in general, short. The longest induction period is 10 sec.

The pressure depression during the induction period was seen at the higher MVA composition. Two kinds of the induction periods (τ_1 and τ_2) were found by Suga[14], but, in this experiment, too, the induction period (τ_1), during which pressure did not change, and (τ_2), during which pressure decreased, was observed at higher composition of MVA (Fig. 6). Further investigation of it, however, was not done.

Consideration

Apparent activation energy of the reaction 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 observed as explosion. The lowest initial temperature is called the explosion (or ignition) temperature (T_0). N. Semenoff[14,15a,15b] derived the following relation with assumption that 1) heat transmission was done only through the wall and 2) any surface reaction did not occur.

$$\log (P/T)=(E/2RT)+\text{const.} \qquad (1)$$

More exactly,

$$\log(P/T^{1+(2/n)})=(A/T)+B \qquad (2)$$

Here, $A=0.217\,E/n$, $B=\log C/n$, $C=(NR\kappa S)/(QVkE\times 10^{19})$

P: Pressure at explosion limit.
T: Temperature of reaction vessel (°K)
n : Molecurarity or order of reaction
E: Activation energy (Kcal/mol)
S : Surface area of vessel
k: Rate constant
N: Avogadro's number
R: Gas constant
κ : Heat transfer factor
V: Volume of vessel
Q: Heat of reaction

Then, $n=1$, $\log(P/T^3)=(A/T)+B \qquad (3)$

$n=2$, $\log(P/T^2)=(A/T)+B \qquad (4)$

$A=0.11\,E$

Whether the explosion reaction of MVA and MVA-air mixture is based on thermal theory or the chain theory, what order of reaction it has, and what kind of reaction (polymerization, decomposition or oxidation) takes the main role, have not been known. The above equations, however, are tested, assuming that the thermal theory is better and the order of reaction is 2 or 1. So, the results

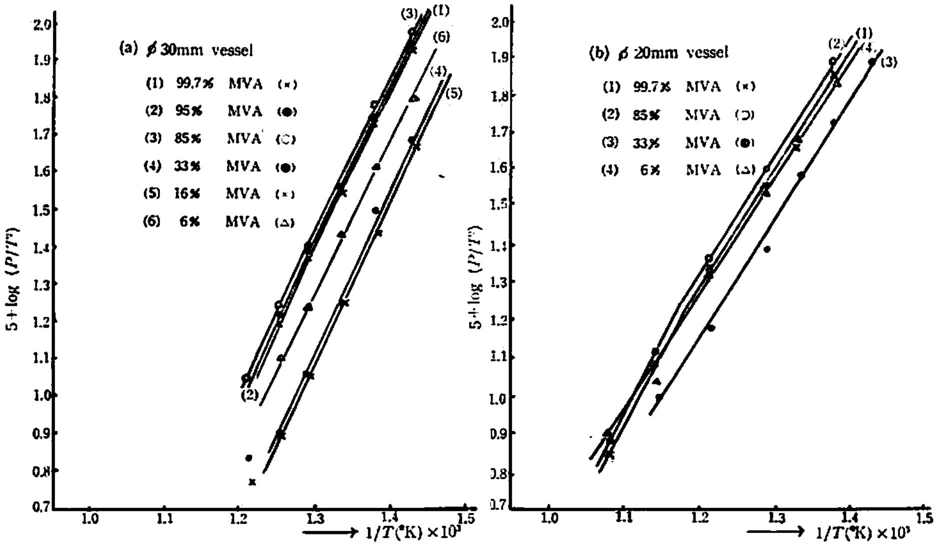


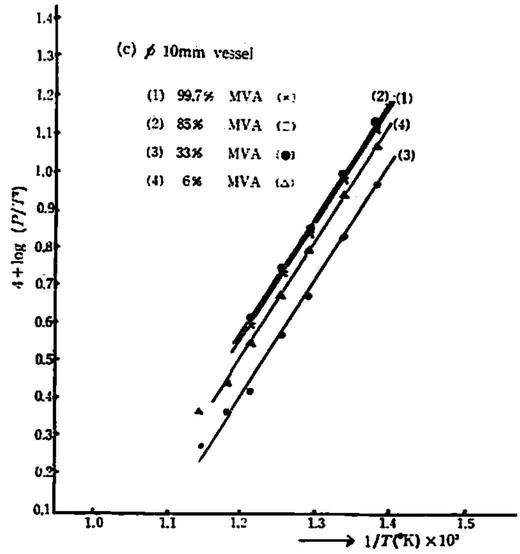
Fig. 16 Relations between log. P/T^2 and $1/T$

---

15) N. Semenoff, *Z. Physik*, 48, 57 (1928)

16a) N. Semenoff, "*Chemical Kinetics and Chain Reaction*" Oxford Univ. Press (1935)

16b) N. Semenoff, "*Some Problems of Chemical Kinetics and Reactivity*" Part 2, translated by J. E. S. Bradley, Pergamon Press Ltd (1959)



obtained are given in Fig. 16 (a)~(c).

The relation (4) of $\log(P/T^2)=(A/T)+B$ is held between 400°C and 500°C, independent of tube diameter and composition. Above 550°C, inflection points are appeared in the case of higher MVA composition. The slope of the straight line of $\log(P/T^2)$ *vs.* $(1/T)$ diagram changes at

Table 4 Apparent activation energy

MVA (vol. %)	Tube diameter (mm)	Slope	Apparent activation Energy (Kcal/mol)
99.7	30	A	36.4
96	30	A	39.4
85	30	A	38.2
33	30	A	40.3
16	30	A	38.2
6.2	30	A	33.2
99.7	20	A	28.2
85	20	A	29.1
33	20	A	28.8
6.2	20	A	28.9
99.7	10	A	29.1
85	10	A	27.3
33	10	A	31.8
6.2	10	A	28.0
99.7	30	B	54.6
99.7	20	B	36.4
85	30	B	40.5
85	20	B	36.4

A : below the inflection temperature
B : over the inflection temperature

the point and it moves to the higher temperature side with the reduction of the MVA composition and tube diameter.

The apparent activation energy is estimated from the slope of the stright line. (Table 4) The apparent activation energy (E) is round 29 Kcal/mol below the inflection temperature in the case of 10 mm and 20 mm in diameter. In a tube of 30 mm in diameter, E increases to about 39.0 Kcal/mol.

Next, assuming n=1, (that is, if the reaction was a monomolecular decomposition) equation (3) was tested and the apparent activation energy was calculated. The examples of MVA are shown in Fig. 17, concerning the $\log(P/T^3)$ *vs.* $(1/T)$.

The similar results to the above are obtained. Their activation energies are as follows: (Table 5)

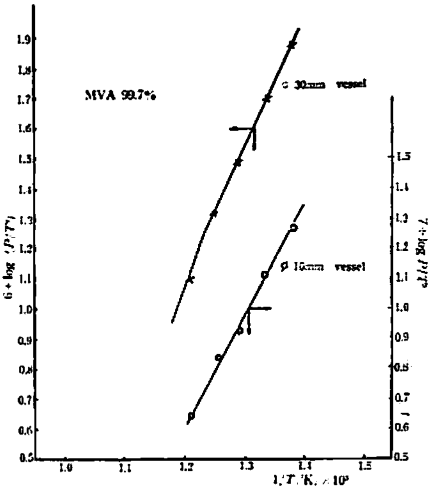


Fig. 17 Relation between log. P/T^3 and $1/T$

Table 5 Apparent activation energy

Tube diameter (mm)	Slope	Apparent activation energy (Kcal/mol)
30	A	20.3
10	A	16.8

Now, if the induction period is assumed to be the time necessary to produce a definite amount of the intermediate, the following relation[17,16b] is given.

$$\log \tau = (E'/RT) + \text{const.} \qquad (5)$$

τ : Induction period. E' : Activation energy

R : Gas constant T : Reaction temperature

Although some flactuations are found, because of slight inaccuracy of manipulation and apparatus, almost a linear relation is obtained in the experiment of over 99.7% MVA, concerning $\log \tau$ *vs.* $(1/T)$. So, the activation energy estimated is shown in the table of Fig. 15. The values are

---

17) B. P. Mullins, "*Spontaneous Ignition of Liquid Fuels*" Butterworths Sci. Pub., London, (1955)

62~78 Kcal/mol and they are higher than the above mentioned.

Reaction mechanism No academic and systematic reports on the reaction mechanism of MVA and MVA-air mixture have been published. Then, any definite conclusion for the mechanism could not be done, but some consideration for the reaction mechanism will be given from phenomena in this experiment.

The explosion reactions of MVA and MVA-air mixture are concluded to be thermal-explosive in all range of composition, because the N. N. Semenoff relation as described above can be applied for this experiment. The inflection of slope, however, at higher MVA composition and temperature does not indicate that the reaction is simple. The fact that the activation energy depends upon the tube diameter suggests that other factors such as the diffusion and complex reaction mechanism have to be considered.

The nearly equal gradients at the same diameter and different compositions in Fig. 16 indicate that the reaction previous to the explosion is also bimolecular, because the oxidation reaction is generally bimolecular at dilute concentration of MVA and the above gradients are derived from the same basis of the thermal theory.

The pressure change-time curve at higher concentration of MVA shows pressure depression. This is considered to be the polimerization reaction.

MVA, an acetylenic compound, is unstable endothermic one as shown in the following table (Table 6). Its decomposition is accompanied with large heat evolution.

Table 6 Heat of Formation

Ethane	CH_3-CH_3	−20.2 Kcal/mol
Ethylene	$CH_2=CH_2$	12.5 Kcal/mol
Acetylene	$CH\equiv CH$	54.9 Kcal/mol
Methyl acetylene	$CH\equiv C-CH_3$	44 Kcal/mol
Ethyl acetylene	$CH_3-CH_2-C\equiv CH$	ca 40 Kcal/mol*
Monovinyl acetylene	$CH\equiv C-CH=CH_2$	ca 69 Kcal/mol*
n-Butane	$CH_3-CH_2-CH_2CH_2$	−30.1 Kcal/mol
n-Butylene	$CH_2=CH-CH_2-CH_3$	0 Kcal/mol
Butadiene	$CH_2=CH-CH=CH_2$	ca 30 Kcal/mol*

* Calculated by Franklin's group contribution method18) and not corrected for conjugation.

The decomposition is verified by deposition of carbon on the surface of the reaction vessel. On the other hand, the pressure increase in the induction period at lower MVA concentration is due to the oxidation reaction.

In $(MVA/O_2)>1$, two step pressure depression after the explosion in Fig. 7 indicates that the reaction has more than two different steps. It is supposed that the first rapid pressure rising is caused by violent oxidation reaction, because there is only one peak in the excess of O_2 $(MVA/O_2<1)$ as seen in Fig. 7 (a), and that, the following plateau is due to the decomposition reaction of MVA because it is self-explosive.

---

18) J. L. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1949)

The Review of Physical Chemistry of Japan Vol. 32 No. 1 & 2 (1962)

It is concluded that the explosion reaction of MVA consists of complex reactions such as polymerization, decomposition and oxidation.

Acknowledgement

The author wishes to thank Professor W. Jōno (Kobe Univ.), Professor J. Ōsugi (Kyoto Univ.) and Dr. H. Teranishi for their kind guidance and advice throughout this work. He is also grateful to the Kanegafuchi Chem. Ind. Co., Ltd. for admittance of this publication and supply of the sample.

The Kanegafuchi Chem. Ind. Co., Ltd.
Osaka, Japan