

STUDIES ON EXPLOSION REACTION OF MONOVINYL ACETYLENE GAS

III. Thermal Reaction of Monovinyl Acetylene Gas

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The thermal reaction of monovinyl acetylene (MVA) was investigated by the admission method at 130 mmHg to 460 mmHg, and at 300°C to 400°C. The rapid polymerization reaction was separated from the slow decomposition. The reaction order (2), reaction rate and activation energy (25.3 Kcal/mole) were determined. The structure of cyclobutane or cyclobutene is elucidated for polymer products from the heat of reaction, estimated from the explosion limits and the above rate constant.

On the other hand, the main reaction products of decomposition of MVA were found to be hydrogen, ethylene, ethane, methane and small amounts of C_2H_2 with the approximate constant ratio in gaseous phase. Considering these products, the decomposition mechanism is assumed to contain the complete decomposition and the partial decomposition.

The explosive reaction at 416°C was also investigated. The different ratio of the products was found.

That the heat evolving reaction induced by the initial polymerization accelerates the decomposition and results in the explosion is presumed.

A lot of references^{1a),1b)} on the thermal reaction of hydrocarbons are available, but there are very few on acetylenic compounds with exception of C_2H_2 ^{2)3)4a)4b)}. Among them, Hurd⁵⁾⁶⁾ etc. studied on the thermal reaction of methyl- and ethyl-acetylene and U. V. Henderson⁷⁾ did on higher acetylenic compounds such as 1-hexyne etc. However, no paper has been published on the thermal reaction of monovinyl acetylene (MVA) at high temperature.

In the previous paper⁸⁾, the self-explosion of MVA was mentioned and the explosion limits were determined. It was proposed that the thermal theory was held for the explosion reaction

(Received August 20, 1963)

1a) E. W. R. Steacie, "Atomic and Free Radical Reactions", 2nd Ed., Reinhold Pub. Corp., New York, (1954) 1b) G. J. Minkoff and C. F. H. Tipper, "Chemistry of Combustion Reactions", Butterworths Sci. Pub. London, (1962)

2) Von P. Schlöpfer and M. Brunner, *Helv. Chim. Acta*, **13**, 1125 (1930)

3) C. G. Silcocks, *Proc. Roy. Soc., A* **242**, 412 (1957)

4a) E. A. Blyumber and D. A. Frank-Kamenetzsky, *J. Phys. Chem. (U. S. S. R.)*, **20**, 1301 (1946), *C. A.*, **41**, 2969 (1947) 4b) D. A. Frank-Kamenetzsky, *J. Phys. Chem. (U. S. S. R.)*, **18**, 329 (1944), *C. A.*, **39**, 31956 (1945)

5) C. D. Hurd and R. N. Meinert, *J. Am. Chem. Soc.*, **52**, 4540 (1930)

6) C. D. Hurd and R. N. Meinert, *J. Am. Chem. Soc.*, **53**, 289 (1931)

7) U. V. Henderson Jr., *J. Phys. Chem.*, **65**, 309 (1961)

8) T. Ikegami, *This Journal*, **32**, 13 (1963)

of MVA and that both polymerization and decomposition reaction occurred together. However, further investigations were needed in order to refer to the mechanism of the reaction.

Studies on the thermal reaction of MVA are mentioned in this paper to obtain suggestion of the reaction mechanism. The reaction rate, reaction order, products and so on are also determined.

Experimentals

Materials

Monovinyl acetylene (MVA) was the same as used in the previous paper⁶⁾. The purity was tested by the gas chromatograph at every run and was confirmed to be more than 99.7%.

Apparatus and Manipulation

The apparatus used to study is shown schematically in Fig. 1 and was almost the same apparatus as described in the previous paper⁶⁾ and a gas collector (B) was added.

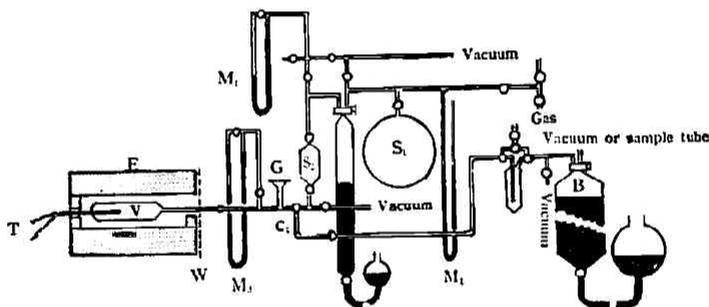


Fig. 1 The Apparatus for thermal reaction of MVA

The product was sucked into the gas collector (B), immediately after the reaction went on at a definite time interval. The pressure was increased to a desired pressure by aid of the Toepler pump and then transferred to the gas sampler for gaschromatographic analysis.

Analysis

The gas chromatographs were used for analysis of the reaction gas. The instruments used were Yanagimoto Co.'s GCG-220 type and GCG-2 type and were used under conditions as shown in Table 1. Three columns and two kinds of carrier gases were used for identification. Double underlines (==) in Table 1 were applied for standard quantitative analysis and single ones (—) were used for subsidiary analysis. As the amounts of solid and liquid products were too little to analyse, the analysis was not done. Typical examples in the gas chromatographic analysis are shown in Fig. 2 a)-c).

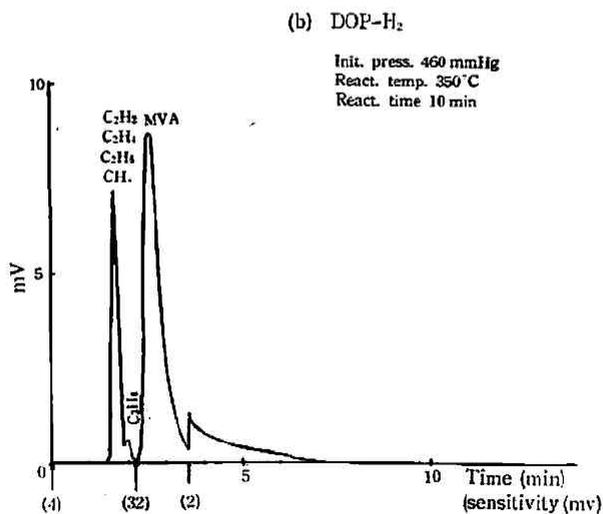
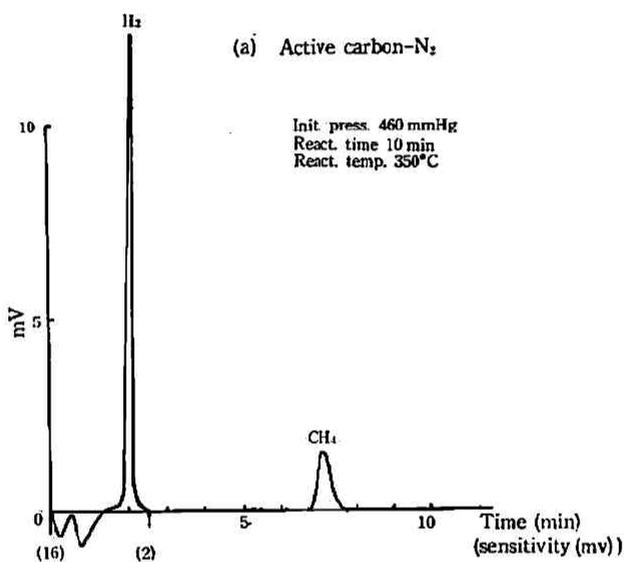
Experimental Results

Studies on Explosion Reaction of Monovinyl Acetylene Gas

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Table 1 Analytical conditions of gas chromatograph

Column bed	Carrier Gas	Flow rate	Temp.	Main peaks (separated)
DOP on Celite	H ₂	40 ml/min	80°C	<u>C₃H₆</u> , <u>MVA</u>
Active carbon	H ₂	40 ml/min	80°C	<u>CH₄</u> , <u>C₂H₂</u> , <u>C₂H₄</u>
Active carbon	N ₂	40 ml/min	80°C	<u>H₂</u> , <u>CH₄</u> , <u>C₂H₂</u> , <u>C₂H₄</u>
Silica gel	H ₂	40 ml/min	140°C	<u>CH₄</u> , <u>C₂H₆</u> , <u>C₂H₄</u> , <u>C₂H₂</u> , <u>C₃H₆</u> , <u>MVA</u> etc.



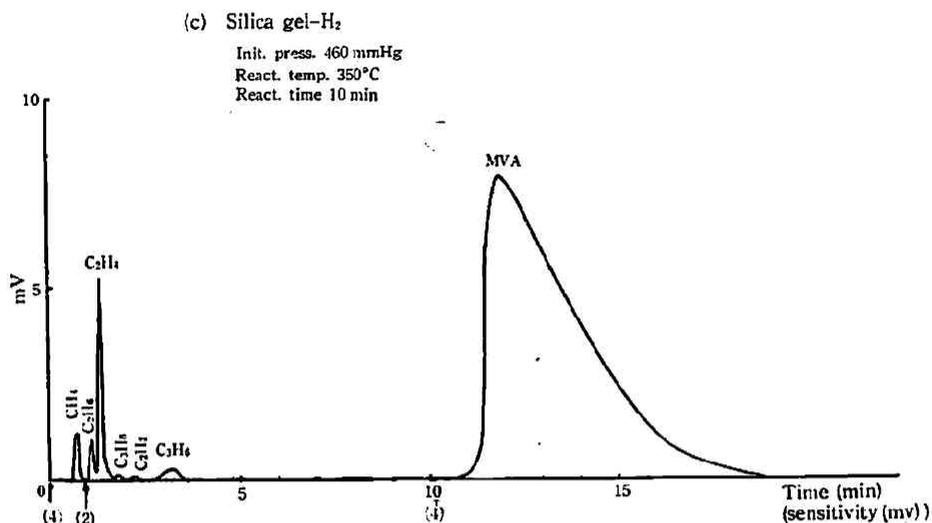


Fig. 2 Gas chromatographs of reaction products

Preliminary experiments

In order to get an introductory information of the thermal reaction of MVA, the following preliminary investigation was carried out. MVA of a constant pressure was led into the vessel (V), its temperature was raised at the constant rate (ca. 3°C/min.) and the gas pressure was read by the mercury manometer (M₃). To correct the error due to the dead space, a blank test was performed using air. After the temperature had been raised up to 400°C, the gas was kept on

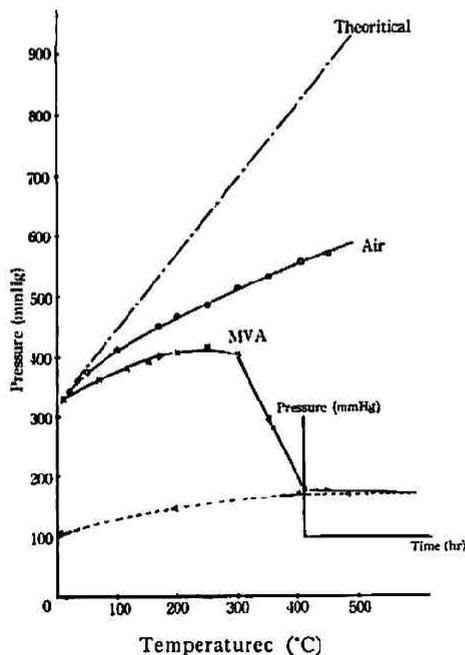


Fig. 3 Pressure change-time curve at constant rate of temperature rising

for a few hour at the same temperature and then cooled. The results are shown in Fig. 3.

The rate of pressure increase becomes lower and lower than the rate in air. At about 300°C, the pressure begins to decrease rapidly. At 400°C, it remains constant. These facts indicate that 1) MVA is very easy to polymerize and the polymerization reaction starts at about 100°C and is very rapid over 300°C. 2) MVA is unstable and is pyrolysed at high temperature and changed to lower compounds (such as H_2 , CH_4). This is supported by keeping pressure constant at 400°C.

Pressure change-time relation

Effects of initial admission pressure and reaction temperature.

Using hard glass reaction vessels of 30 mm in diameter, MVA was studied at 350°C in 10 min., in order to see the effects of pressure. The initial admission pressure was varied from 130 mmHg to 460 mmHg. The results are summarized in Fig. 4. The relative decrease of the total pressure becomes larger with increasing initial pressure.

The thermal reaction of MVA at the constant initial pressure (460 mmHg) was performed at various temperatures for 10 min. The pressure change-time curves are shown in Fig. 5. The higher the reaction temperature, the more rapid the reaction proceeds. No pressure decrease is observed after about 10 min. at the temperature of higher than 350°C.

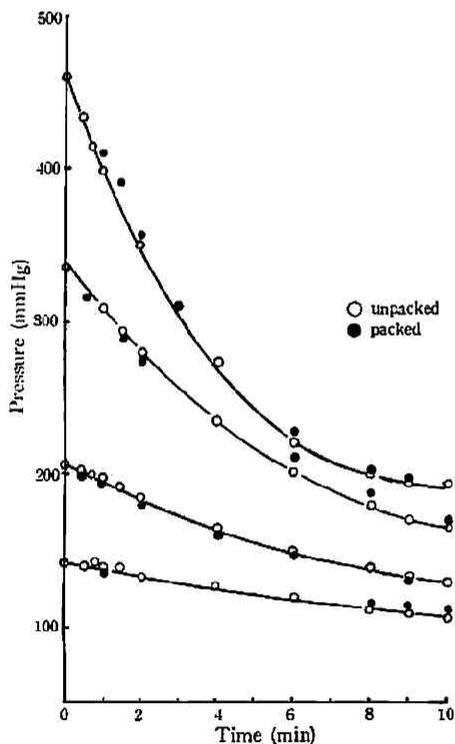


Fig. 4 Pressure change-time curve at different initial pressure (350°C)

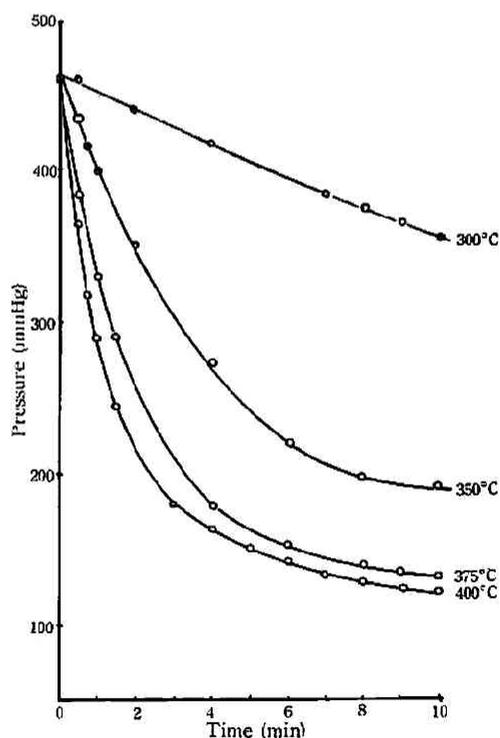


Fig. 5 Pressure change-time curve at various temperature

Effect of surface

To find whether the thermal reaction of MVA is affected by the surface of the reaction vessel or not, the vessel of 30mm in diameter, packed with small glass tubes (4 mm in outside diameter and 100mm in length) was used. The surface area was thus increased about 2.5 times as much as that of the unpacked.

At 350°C, the initial pressure was varied from 130mmHg to 460mmHg. The duration of the reaction was 10min. The results obtained are shown in Fig. 4. The curves of pressure decrease have no difference between the packed and the unpacked vessel as seen in Fig. 4. That is, the thermal reaction of MVA is not affected by the surface as much as that of C_2H_2 ³⁾, which consists of first order heterogeneous reaction and second order homogeneous reaction. The thermal reaction of MVA is considered to be a homogeneous reaction.

Thermal reaction products

The residual products, left in the vessel after the gaseous products being taken out, were mainly carbon, resinous products and liquids of high boiling point. The resinous products had various features (dark brown sticky solid, yellow brown powder and so on), depending upon the reaction conditions. The liquid products were yellowish and seemed to be low polymers. Unfortunately, the liquid and solid products at every run were too little to collect for analysis. So, further investigation has not been done.

The gaseous reaction products stored in the gas collecting bulb (B) were analyzed after pressurizing to a definite pressure. The principal products were H_2 , C_2H_4 , CH_4 , C_2H_6 , C_3H_8 , trace of C_2H_2 and some unidentified compounds. The amount of each product was determined.

A lot of the gas samples under various conditions were analyzed in order to investigate the mechanism.

Pressure-time relations of gaseous products

The pressure-time relations of the main gaseous products are shown in Fig. 6 on the reaction at a reaction temperature of 400°C and the initial admission pressure of 460mmHg. In Fig. 6,

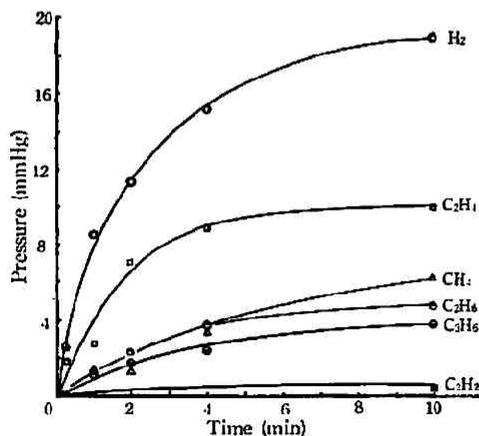


Fig. 6 Products change-time curve (460 mmHg, 400°C)

the amounts of products are indicated by their pressure (mmHg) at the end of the reaction. Every curves show simple increase and the ratio among the main products is almost constant at each time with exception of C_2H_2 .

Effect of reaction temperature and initial admission pressure

The analytical data at the initial pressure of 460 mmHg and 10 min. on various reaction temperatures are shown in Fig. 7. The ordinate unit is indicated by the mole ratio to the initial MVA. The products ratio remains also constant.

To investigate the effect of pressure on the products, the products at 400°C and 10 min. were examined at various initial pressures and their results are shown in Fig. 8. The reaction products are denoted by the mole ratios as described above. The increase of the products is not recognized until 300 mmHg, but it occurs above this pressure. The ratio of various products is independent of the initial admission pressure and is approximately constant.

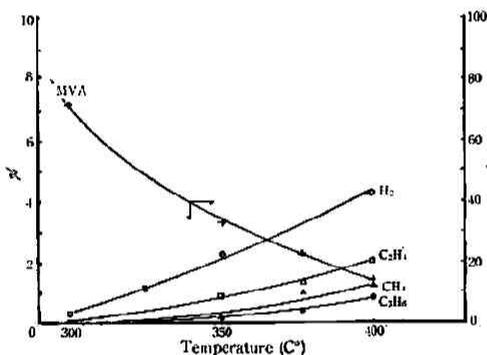


Fig. 7 Yields-reaction temperature
(460 mmHg, 10 min.)

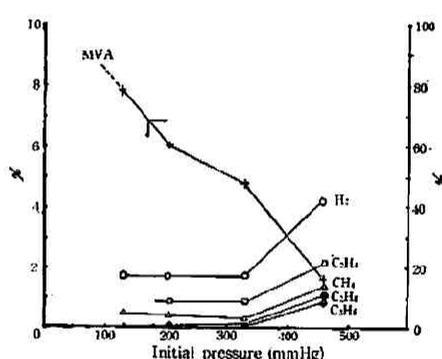


Fig. 8 Yields-initial pressure
(400°C, 10 min.)

Ratio of gaseous reaction products

The ratio of products at 460 mmHg, 400°C and 10 min. in Fig. 7 is shown in Table 2.

Table 2 Ratio among main reaction products
(Initial pressure 460 mmHg, 400°C, 10 min.)

Products	Final pressure	Relative ratio
H_2	19 mmHg	4.0
C_2H_4	10 mmHg	2.0
CH_4	6 mmHg	$(1.2) \approx 1.0$
C_2H_6	5 mmHg	1.0
C_3H_6	4 mmHg	$(0.8) \approx 1.0$
C_2H_2	0.5 mmHg	0.1

The constancy of the ratio is always held within the range of this experiment.

The mole ratio of H_2 in the products is generally low in the thermal reaction of hydrocarbons⁵⁾. But it is characteristic of the thermal reaction of MVA to find large amounts of H_2 in the reaction products as observed in the pyrolysis of C_2H_2 ³⁾.

Gaseous products before and after the explosion

In order to study the changes of products before and after the explosion, an experiment was performed, that is, MVA of 460 mmHg was exploded at the lowest explosion temperature of 415°C, the induction period being 5.89 sec. So, the explosion products at 416°C were compared with the non-explosion products at 413°C. The gaseous products were taken out in 20 sec. after the admission. The analytical data are found in Table 3.

Table 3 Analysis of the gaseous products after the explosion
(Initial pressure 460 mmHg, 20 sec. after the admission)

Reaction temp. (°C)	Induction period (sec.)	Final pressure (mmHg)	Reaction products (mole% to initial MVA)						
			MVA	H ₂	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₃ H ₆	C ₂ H ₆
420	4.46	530	25.0	68.0	?	13.6	5.3	?	
416	5.87	520	31.5	50.3	14.3	16.5	7.82	3.14	
413	∞	360	77.0	1.23	0.313	trace	trace	trace	trace

Next, the explosion products were compared with the gaseous products obtained just before the explosion at 416°C and 460 mmHg. Unfortunately, the induction period was too short to obtain many data. The results are given in Table 4.

Table 4 Analysis of the gaseous products after and before the explosion
(Initial pressure 460 mmHg, temperature 416°C)

Time (sec.)	Final pressure (mmHg)	Reaction products (mole% to initial MVA)						
		MVA	H ₂	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₃ H ₆	C ₂ H ₆
20 (5.87)*	520	31.5	50.3	14.3	16.5	7.82	3.14	
2.67	450	≈ 98%	0.3	0	0	0	0	0

It is found in Tables 3 and 4 that the constant ratio among the products, described in the thermal reaction, are lost. That is, H₂ and C₂H₂ are increased very much and the ratio of C₂H₄ to C₂H₂ is reversed. Higher temperature due to explosion seems to change the ratio of the products.

In the reaction products at the explosion temperature and in 2.67 sec. after the admission, only a small amount of H₂ appears. This indicates that MVA decomposes during the induction period, but no information of intermediate is given, because 2.67 sec. is far from the explosion time (5.89 sec.).

Considerations

In general, the thermal reaction of MVA proceeds with decrease of the total pressure, which is due to the polymerization reaction. On the other hand, the analysis of gaseous products shows

* Exploded at 5.87 sec.

that the thermal decomposition proceeds competitively. So the polymerization and the decomposition are discussed separately. The explosion reaction will be also dealt with later.

Polymerization reaction

J. A. Nieuwland⁹⁾ reported simply that the polymer of MVA in thermal polymerization under high pressure (probably, few atmospheres) would have a linear structure. F. J. Dykstra¹⁰⁾ investigated further, and concluded that polymer product, obtained after 6 hr. at 105°C. had cyclobutane or cyclobutene structure.

As the above reactions were, however, assumed to occur in the liquid phase, the results cannot be directly applied to the thermal reaction in the gas phase. So the comparison between the results in this experiment and those mentioned above is interesting.

The stoichiometrical balance among total pressure, MVA pressure and cracked gas pressure (being equal to the difference between the total gas pressure and the remaining MVA pressure, and nearly equal to the sum of partial pressure of the main products) is shown in Fig. 9. The polymerization reaction causes, in general, pressure depression. Comparing the rate of pressure decrease of MVA with the rate of formation of the cracking gas, the former is more than 10 times as fast as the latter as estimated in Fig. 9. This fact means that the consumption of

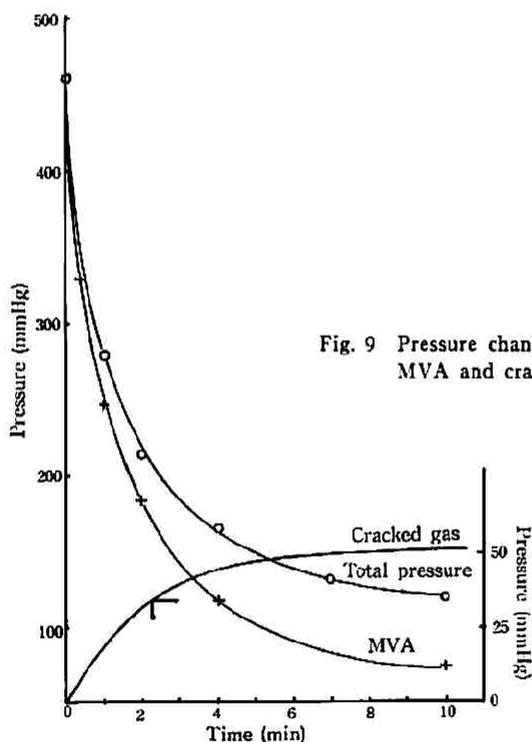


Fig. 9 Pressure change-time curve of MVA and cracked gas (400°C)

9) J. A. Nieuwland, W. S. Calcott, F. B. Dowing and A. S. Carter, *J. Am. Chem. Soc.*, 53, 4197 (1931)

10) F. J. Dykstra, *J. Am. Chem. Soc.*, 56, 1625 (1934)

MVA is caused mainly by the polymerization reaction and the consumption by the cracking reaction is negligible. So, the consumption rate of MVA appears to be approximately equal to that of polymerization.

Order of reaction and activation energy

On the basis of the above considerations, the order of polymerization reaction is obtained by applying the graphical method (differential method) to curves in Figs. 4 and 9. The rate (dP/dt) against MVA pressure (P_M) is not on a straight line. (This may depend upon the effect of the cracked gas.) Then, the initial rate ($(dP/dt)_0$) obtained by extrapolating the plot of $(dP/dt)_M$ (or (dP/dt)) against P_M (or total pressure (P)), to the initial pressure (P_0) is required in order to get the true rate. The plots of $\log(dP/dt)_0$ against $\log P_0$ at various initial pressures at 350°C in Fig. 4, as shown in Fig. 10, are of a straight line. From the slope the order of reaction is 1.94. This indicates the polymerization reaction is second order.

$$w_p \text{ (polymerization rate)} = -\frac{d[\text{MVA}]}{dt} = k[\text{MVA}]^2$$

The initial rates obtained at various temperatures in Fig. 5 by the same method as mentioned above, against $(1/T)$ are plotted in Fig. 11. A straight line is obtained in the range of 300°C to 400°C and the apparent activation energy is calculated from the slope as

$$E = 25.3 \text{ Kcal/mole.}$$

This value is slightly different from that in the previous paper⁸⁾.

The rate constant (k_0) is also obtained as

$$k_0 = 1.85 \times 10^8 \times \exp(-25300/RT) \text{ l. mole}^{-1} \text{ sec}^{-1}.$$

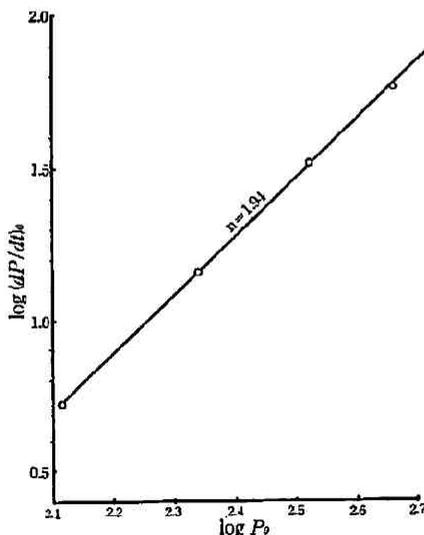


Fig. 10 Relation between $\log(dP/dt)_0$ and $\log P_0$

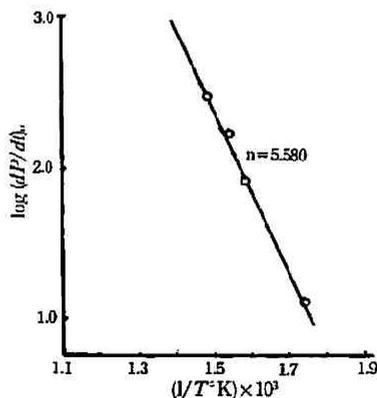


Fig. 11 Relation between $\log(dP/dt)_0$ and $(1/T)$

Structure of polymer

A study on polymer structure was not done from the structural and organic chemical point of view, because the amounts were so small, but the cyclobutane or cyclobutene structure, assumed by Dykstra¹⁰⁾ on polymer formed in the liquid phase polymerization reaction under pressure seems to be reasonable, considering the reaction heat calculated from the explosion limits, activation energy and reaction order etc. in the proceeding section. That is, the heat of polymerization reaction will be

$$H = 80 \text{ Kcal/mole (for polymer)}$$

as described later. If the polymer had linear structure, the heat of reaction would, in general, not exceed 50 Kcal/mole as in the case of linear polymer described below (Table 5).

Table 5 Heat of polymerization

Monomer	$-\Delta H$, Heat of polymerization
$\text{CH}\equiv\text{CH}^{11)}$	35.6 Kcal/mole (for MVA) 71~73 Kcal/mol (for cyclobutadien)
$\text{CH}_2=\text{CH}_2^{12)}$	22.3 Kcal/mole* (for linear high polymer)
$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2^{12)}$	20.5 Kcal/mole* (for linear high polymer)
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2^{12)}$	17.4~18.2 Kcal/mole* (for linear high polymer)

Then, large heat of reaction such as 80 Kcal/mole indicates that the polymer of MVA has cyclic structure.

Decomposition reaction

No publication has been done on the decomposition of MVA up to date. The pyrolyzed products were mainly carbon, H_2 , C_2H_4 , CH_4 , C_2H_6 , C_3H_6 , C_2H_2 etc. and the relative ratio was independent of temperature, pressure, and time. It is remarkable that H_2 is so much in amount in comparison with that in the thermal reaction of hydrocarbons in general, considering less hydrogen (H_2) content in MVA molecule. This fact and the presence of carbon deposited indicate that the major part of H_2 is formed by the complete decomposition of MVA. On the other hand, the constant ratio of the products (including H_2) means that both complete and partial decompositions have the same initiation step.

Reaction order

It is difficult to analyze the decomposition reaction because of the coexistence of both polymerization and decomposition reaction. Combined Fig. 6 with Fig. 9, (dP/dt) of each main product against the pressure of MAV (P) is plotted in Fig. 12. The points of each product are on a straight line**. The reaction orders, calculated from the slopes, are 1.485 for H_2 , 1.40 for

* per consumed monomer

** This relation is held for the first 4 min.

11) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity", Part II, (translated by J. E. S. Bradley) Pergamon Press Ltd. (1959)

12) P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press (1953)

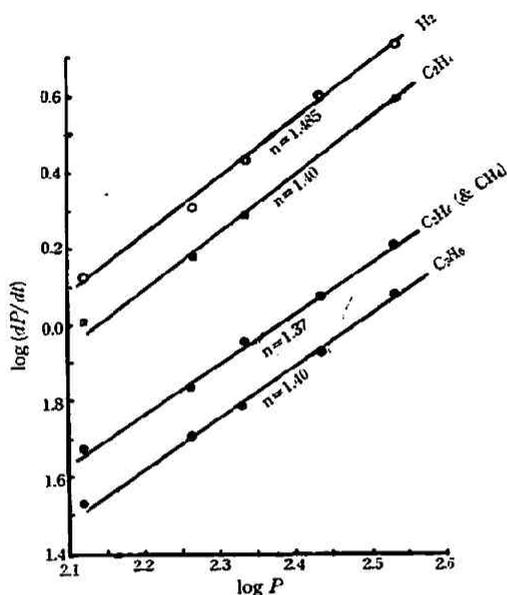


Fig. 12 Relation between $\log(dP/dt)$ and $\log P$

C_2H_2 , 1.37 for C_2H_6 (and CH_4) and 1.40 for C_3H_6 , and, considering the experimental error, are concluded to be 1.50 for each. The order of reaction for C_2H_2 is difficult to estimate, but it does not seem to be 1.5.

Reaction mechanism of decomposition reaction

It is necessary to discuss the bond dissociation energy for elucidating the reaction mechanism. Using the values of C-H (104 Kcal) and C-C (59 Kcal), described in the ordinary text book, the decomposition reaction would be taken to start at the homolytic cleavage of the C-C bond. However, considering the reaction products, it does not seem to be so simple. Then, further estimation of the C-C bond was tried, using the heat of formation of vinyl radical* ($CH_2=CH-$) and ethynyl radical** ($CH\equiv C-$) and MVA***. As the result, the bond energy for C-C in MVA was about 115 Kcal****. Then, it does not seem to be reasonable to break the central C-C bond alone at first. This is supported by the fact of smaller amount of the C_2H_2 found in the thermal reaction, too. So, the initial reaction is thought to be the formation of C_3H_4 radical.

* Cited from the table¹³⁾

** Cited from the table¹³⁾

*** Calculated by Franklin's¹⁴⁾ group contribution method.

**** This value may be slightly incorrect, because of lack of correction of resonance, but seems to be fairly good, comparing with values obtained by F. H. Coats¹⁵⁾ from the electron impact method for C_2H_2 , $CH_3-C\equiv CH$ and $CH_3-CH_2-C\equiv CH$ and presumed by U. V. Henderson Jr⁷⁾, for 1-hexyne.

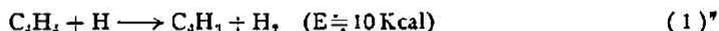
13) Chem. Soc. Japan, "Kogaku Binran", Maruzen Co. (1958)

14) J.L. Franklin, *Ind. Eng. Chem.*, 40, 1070 (1949)

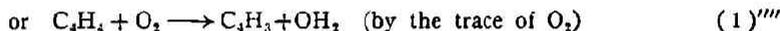
15) F. H. Coats and R. C. Anderson, *J. Am. Chem. Soc.*, 79, 1340 (1957)



or by hydrogen abstraction,



(R: radical produced in other process)



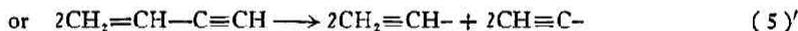
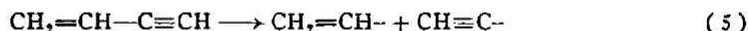
The mechanism of Westbrooks¹⁶⁾ etc. on C_2H_2 decomposition seems to be reasonable for the complete decomposition of MVA from the view of energy. That is,



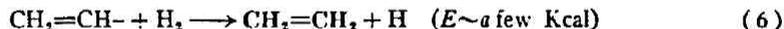
even down to



All of those reactions (2)–(4) should have low activation energies (ca. 10Kcal) and favorable enthalpy values* and be highly reactive intermediate products. Considerable amounts of hydrocarbons such as CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_4H_6 etc. were obtained besides hydrogen formation and carbon deposition. The bond energies of MVA suggest another possibility of cleavage, in addition to the complete decomposition described above. It may be C–C splitting, C–C having slightly higher energy than C–H bond.



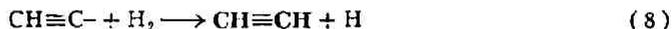
In the atmosphere of excessive hydrogen formed by the complete decomposition, the reaction of vinyl radical is



Some radicals react each other,



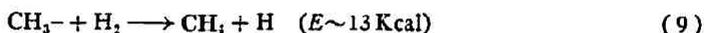
On the other hand, ethynyl radical reacts with hydrogen,



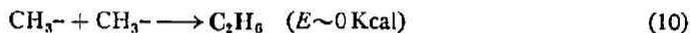
* For example, $\text{C}_4\text{H}_3 + \text{H} \rightarrow \text{C}_4\text{H}_2 + \text{H}_2$; $\Delta H^{298} = -54 \text{ Kcal}$.

16) E. A. Westbrook, K. Hellwig and R. C. Anderson, "The fifth Symposium (International) on Combustion", Reinhold Pub. Corp. (1955).

The trace formation of C_2H_2 suggests that most of the ethynyl radicals decompose to carbon, H_2 , CH_4 etc. It is possible for vinyl and ethynyl radicals to produce methyl radical (CH_3) by a reaction with H_2 (or H), because CH_4 was formed in cracked products of C_2H_4 and C_2H_2 . CH_3 would react as follows.



Also,



Each reaction can proceed readily because of its low activation energy.

Considering that the ratio of C_2H_2 to the total of other products formed by $CH_3\cdot$ is about 3:4, and that $C_2H\cdot$ would be less stable than $C_2H_3\cdot$, the above mechanism seems to be probable.

Another step may be suggested from the intermediate products of the complete decomposition, though the mechanism is not certain now. That is, the intermediate products, C_nH_m , react with H_2 to yield $CH_3\cdot$, $CH_2\cdot$, etc.

These radicals would react to give hydrocarbons such as C_2H_4 , CH_4 , etc.

Explosion reaction

To elucidate the reaction mechanism of explosion, it is necessary to know how high the heat of reaction is. However, it was elucidated that 1) thermal theory was reasonable for this reaction in the previous paper⁸⁾ and that 2) this thermal reaction mainly depended upon the polymerization reaction. So, assuming that only polymerization would be a main reaction for explosion, the reaction heat of MVA polymerization would be approximately calculated from the Frank-Kammentsky relation¹¹⁾ derived from the temperature distribution for thermal explosion.

$$\delta_{cr} = \frac{HEr^2ka^n}{\lambda NRT_0^2} \exp(-E/RT_0) \quad (12)$$

δ_{cr} : critical limit (a dimensionless parameter)	λ : thermal conductivity
H : heat of reaction	N : Avogadro's number
E : activation energy	R : gas constant
r : radius of vessel	T_0 : explosion limit temperature
a : concentration	k : rate constant
n : order of reaction	δ_{cr} is 2 for cylindrical tube.

The limit (at 430°C and 460 mmHg, using a vessel of 20 mm in diameter) and the values obtained for the polymerization reaction in this paper ($k_0 = 1.853 \times 10^8 \text{ l. mole}^{-1} \text{ sec}^{-1}$, $n=2$, $E=25300 \text{ cal/mole}$) are put into the above equation. It is assumed to be $1.7 \times 10^{-4} \text{ cal/cm sec } ^\circ\text{C}$

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for λ^* of MVA at 430°C, as there is no data for λ . The result obtained is

$$H \cong 40 \text{ Kcal/mole (for MVA consumed)}$$

Supposed that the polymer would be dimer at the initial step

$$H \cong 80 \text{ Kcal/mole}$$

As the reaction heat of polymerization is so large and the rate of polymerization is more rapid than that of decomposition as described in the previous section, the heat supply on this thermal explosion may be concluded to be mainly due to the reaction of polymerization. The contribution from the decomposition reaction, however, should not be negligible, too.

The rate of pressure decrease just before the explosion, as shown in Fig. 13, supports the above fact, considering volume increase, caused by the decomposition reaction. The temperature-rise may bring the pressure increase, in the system, as the pre-explosion temperature rise. $\Delta T = RT^2/E$ is about 40°C, but the polymerization reaction is also accelerated with rising temperature and, then, the pressure would be decreased. In spite of the above discussion, the reduction of pressure decrease are found just before the explosion as seen in Fig. 13. So the contribution of the decomposition reaction should be considered. It is concluded that the polymerization supplies

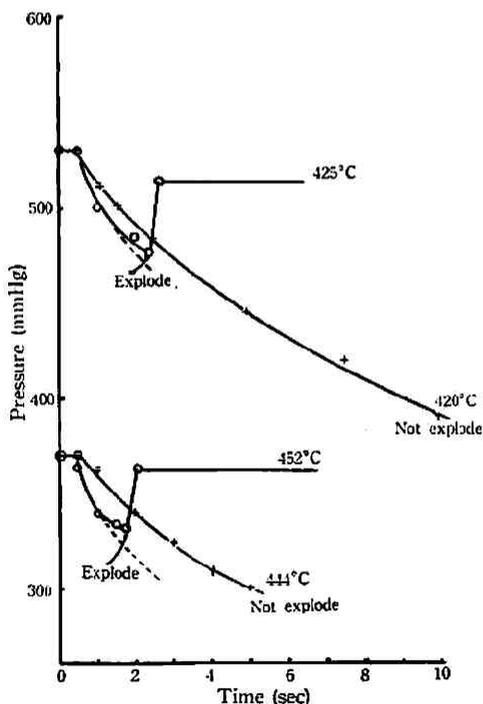


Fig. 13 Pressure change-time and curves before and after explosion

* This value is estimated by extrapolating λ of C_2H_2 to 430°C. Considering the temperature dependence of thermal conductivity and the similarity of structure, this value is not believed to be far from the true one.

heat at first and the heat accelerates the decomposition reaction and the heat of both reactions results in the explosion at last.

The relative ratios of gaseous products formed at the explosion are different from that of thermal reaction as seen in Table 2. One of the remarkable phenomena is the increase of C_2H_2 and CH_4 formation in the former.

The explosive reaction proceeds at higher temperature ($>1000^\circ C$) and in short time (less than 0.2 sec.) At high temperature, the formation of C_2H_2 is favorable from the energetic point of view. Besides, the C_2H_2 formed brings itself to low temperature in very short time without change. So, a lot of C_2H_2 should be presumed to produce.

Acknowledgement

The author has great pleasure in expressing his sincere thanks to Prof. W. Jono, Prof. J. Osugi and Dr. H. Teranishi for their valuable guidance and encouragement throughout this work. He is also grateful to the Kanegafuchi Chem. Ind. Co. for the permission of publication and cooperative assistance.

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