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STUDIES ON EXPLOSION REACTION OF MONOVINYL ACETYLENE GAS

II. Explosion Limits of Monovinyl Acetylene-Oxygen, Nitrogen and Nitric Oxide Mixtures

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The explosion limits of MVA-N_2, MVA-NO and MVA-O_2 mixtures were determined by the admission method under the conditions of the temperatures below 700°C and the pressure below 600 mmHg. The curves of explosion limits in the MVA-N_2 and the MVA-NO systems were all above that of MVA-air. N_2 was found to be diluent and NO to behave as a retarder. The particular shape (ᔕ) of explosion limit similar to that of MVA-air was found in the isobars and isotherms of MVA-O_2 and the sharp peak was around 5% of MVA in volume.

The explosion reactions of MVA-N_2, MVA-NO and MVA-O_2 can be satisfactorily explained on the basis of the thermal explosion theory, and, assumed that the order of reaction is 2, the apparent activation energies are estimated to be 30.2–30.9 Kcal/mole(MVA-N_2), 27.2–27.3 Kcal/mole (MVA-NO) and 27.5–30.0 Kcal/mole (MVA-O_2) below 600°C.

In the previous paper[1], the explosion limits of monovinyl acetylene (MVA) and MVA-air mixtures were determined by the admission method. It was found that MVA was a self-explosive compound and that the curves of the isotherms and isobars of explosion limits in MVA-air system had a particular shape such as (ᔕ).

Various gases were added to the explosive gas for the purpose of examining the effect of anti-explosion. Nitrogen (N_2) and nitric oxide (NO) were mixed with MVA, and their explosion limits were determined in this experiment.

On the other hand, the limits of MVA-O_2 mixtures were determined to exclude the effect of N_2 on the limit and to see that of pure oxygen (O_2).

Experiments were done by the admission method as described in the previous paper[1].

Experimentals

Materials: MVA was the same as in the previous paper[1], (purity, over 99.7%). Oxygen (O_2) and nitrogen (N_2) were used directly from commercial cylinder. Nitric oxide (NO) was prepared from NaNO and $FeSO_4$ in acidic solution and purified by the ordinary method. The purity

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

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was over 99% and its impurities were NO_2 and air.

Apparatus and procedure: The apparatus and procedure were the same as in the previous paper[1]. The reaction vessels of 20 mm in diameter and 120 mm in length were mainly used. Measurements were done below 700°C and 600 mmHg in the present experiment. The MVA-N_2 and MVA-O_2 mixtures were tested in all the range of composition. However, with increasing O_2 composition and admission pressure, the explosion became violent and made it difficult to protect the apparatus. Then, the experimental conditions were limited as seen in the following sections. The MVA-NO mixture was tested up to 30% of NO in volume, because higher NO concentration was aside from the purpose of the present experiment.

Experimental results and Considerations

Pressure change-time curves

The pressure change-time curves obtained on the charts of the pen-oscillograph are almost similar to those of the previous experiments[1]. That is, in general, they have only one peak in $(O_2/MVA)>1$ and one peak and one plateau in the other region as cited in Fig. 1. Sometimes, two peaks are observed under any conditions in the MVA-O_2 system as seen in Fig. 1. The first peak seems to depend upon the oxidation reaction, and the second to be induced by the first.

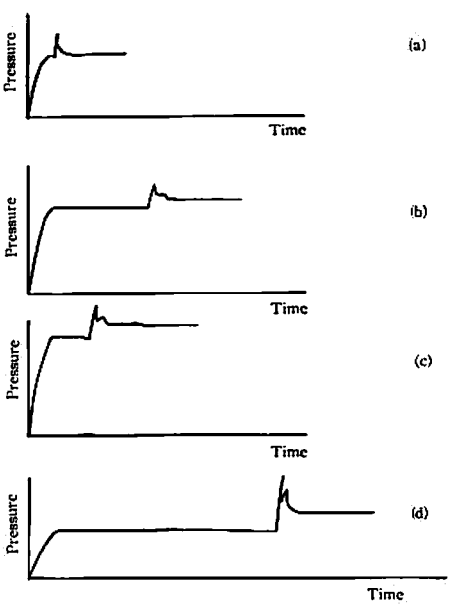


Fig 1. Typical recordings of pressure change-time
(a) MVA 40%, I. A. P. 46 mmHg, Temp. 510°C (b) MVA 92.5%, I.A.P. 550 mmHg Temp. 426°C (c) MVA 83%, I. A. P. 365 mmHg. Temp. 425°C (d) MVA 60%, I. A. P. 550 mmHg, Temp. 310°C. (I. A. P. Initial admission pressure)

The higher the O_2 composition, the higher the explosion pressure becomes in $(O_2/MVA)>1$. The maximum explosion pressure is often several times as much as the admission pressure.

Explosion limits

Isochor curves. The curves of explosion limits in isochor, using a vessel of 20mm in di

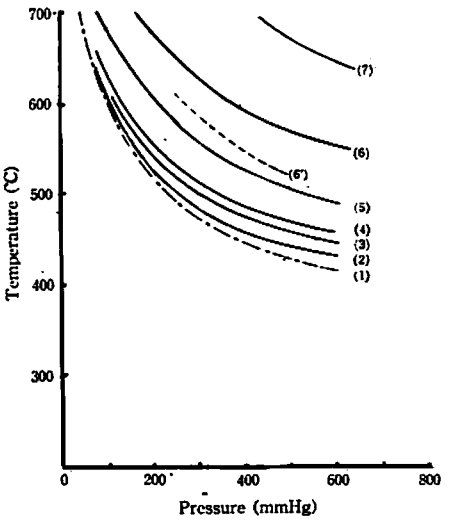


Fig. 2 Isochors for explosion limits of MVA-N_2 (ϕ 20mm vessel)
(1) T-100 (MVA>99.7%), (2) N-90 (MVA 85%), (3) N-80 (MVA 73%) (4) N-70 (MVA 67%) (5) N-50 (MVA 38%) (6) N-30 (MVA 25%) (6)′ N-30 (MVA 25%, ϕ 30mm vessel) (7) N-15 (MVA 15%)

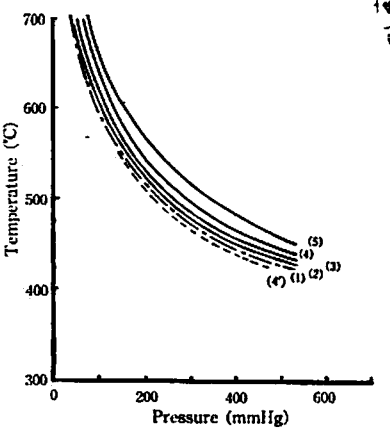


Fig. 3 Isochors for explosion limits of MVA-NO (ϕ 20mm vessel)
(1) T-100 (MVA>99.7%), (2) NO-3 (MVA 96.7%), (3) NO-5 (MVA 93.5%), (4) NO-15 (MVA 85.0%), (4)′ NO-15 (MVA 85%, ϕ 30mm vessel), (5) NO-25 (MVA 73%)

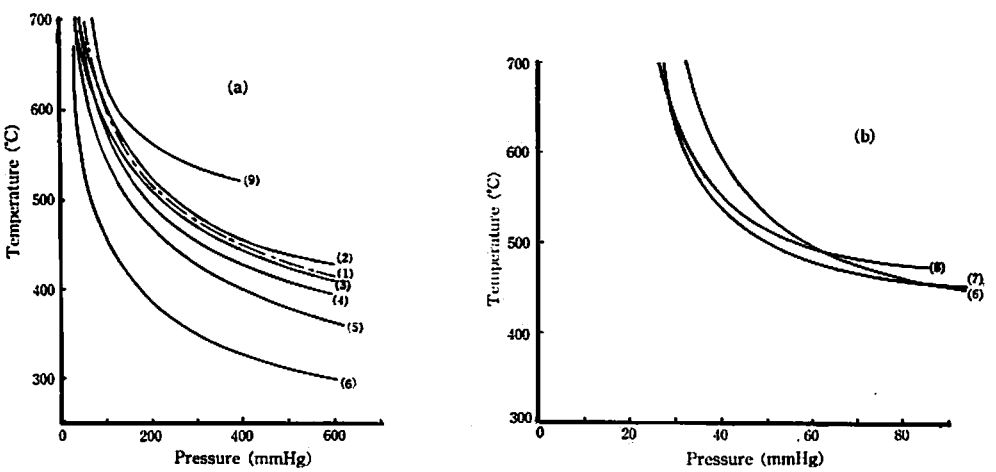


Fig. 4 (a) and (b) Isochors for explosion limits of MVA-O_2 (ϕ 20mm vessel)
(1) T-100 (MVA>99.7%), (2) O-1 (MVA 3%), (3) O-4 MVA 7.5%)
(4) O-6 (MVA 10%), (5) O-10 (MVA 83%), (6) O-35 (MVA 60%)
(7) O-50 (MVA 40%), (8) O-80 (MVA 22%), (9) O-97 (MVA 3%)

meter, are shown in Fig. 2 (MVA-N_2), Fig. 3 (MVA-NO) and Fig. 4 a), b) (MVA-O_2). Every curve are smooth, as described in the previous paper[1] and indicates no particular region. The effect of the vessel diameter is partly tested. The results obtained on a vessel of 30 mm in diameter are shown by the broken line in these figures. The limits are lowered as expected.

Isotherms aud isobars. The isotherm and isobar curves, using a vessel of 20 mm in diameter, are shown in Fig. 5 a), b) (MVA-N_2), Fig. 6 a), b) (MVA-NO) and Fig. 7 a), b) (MVA-O_2).

The curves of MVA-N_2 have a different shape from that of MVA-air. To see the effect of N_2, the limits of temperature at the admission pressure of pure MVA, corresponding to the dilution with N_2, are estimated from the isochor of MVA in the previous paper[1], and plotted in Fig. 5 b) as denoted with (○) and (◉). These points come goodly on the curve of isobars in high MVA composition and high admission pressure. It is suggested that N_2 behaves as diluent. However, deviation from curves is found in the case of the high N_2 composition and low admission pressure.

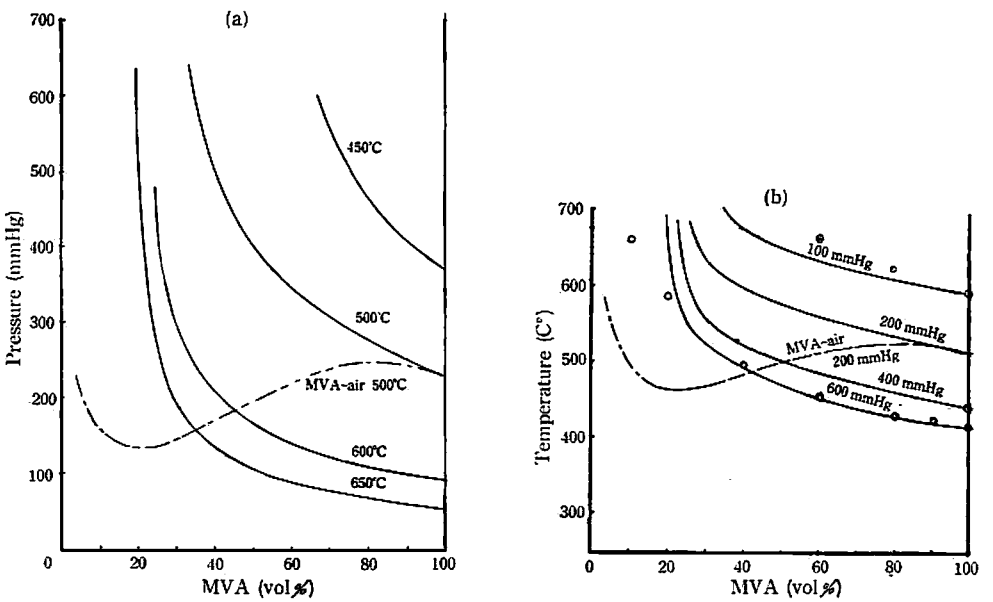


Fig. 5 (a) isotherms and (b) isobars for explosion limits of MVA-N_2 (ϕ 20 mm vessel)

The limit curves of MVA-NO indicate to be higher than those of MVA-N_2 as seen in Fig. 6 a), b). This means that NO acts as a chemical reactant rather than as a physical diluent. The curves have inverse curvature in comparison with MVA-N_2. This may be dependent upon the secondary reaction of NO and MVA.

The isotherms and isobars of MVA-O_2 are summerized in Fig. 7 a) and b). Although some of the curves are incomplete, the curves have the shape as seen in MVA-air, in which a peak is sharper than that of MVA-air. Assuming that N_2 is diluent, the values calculated from the previous paper (MVA-air)[1] are plotted in Fig. 7 with circle (○). They show good agreement

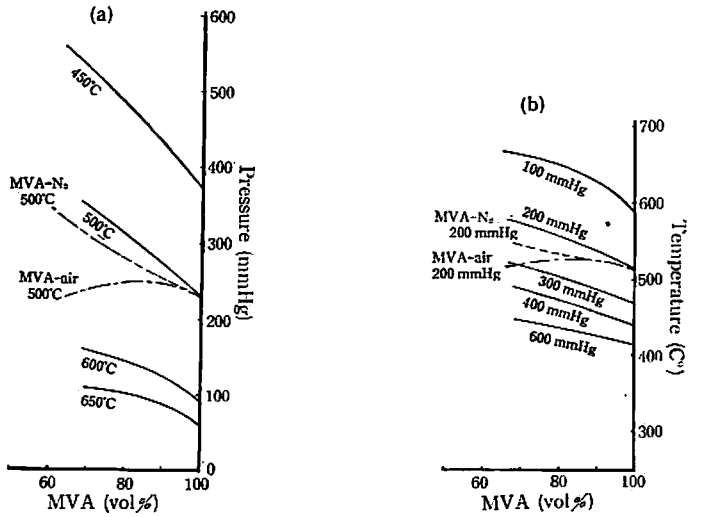


Fig. 6 (a) isotherms and (b) isobars for explosion limits of MVA-NO (ϕ 20mm vessel)

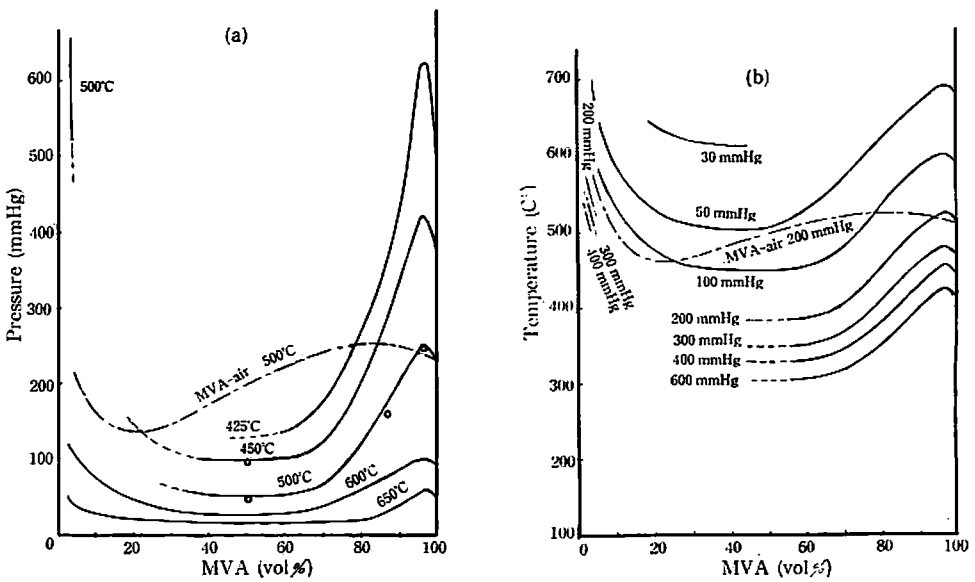


Fig. 7 (a) isotherms and (b) isobars for explosion limits of MVA–O_2 (ϕ 20mm vessel)

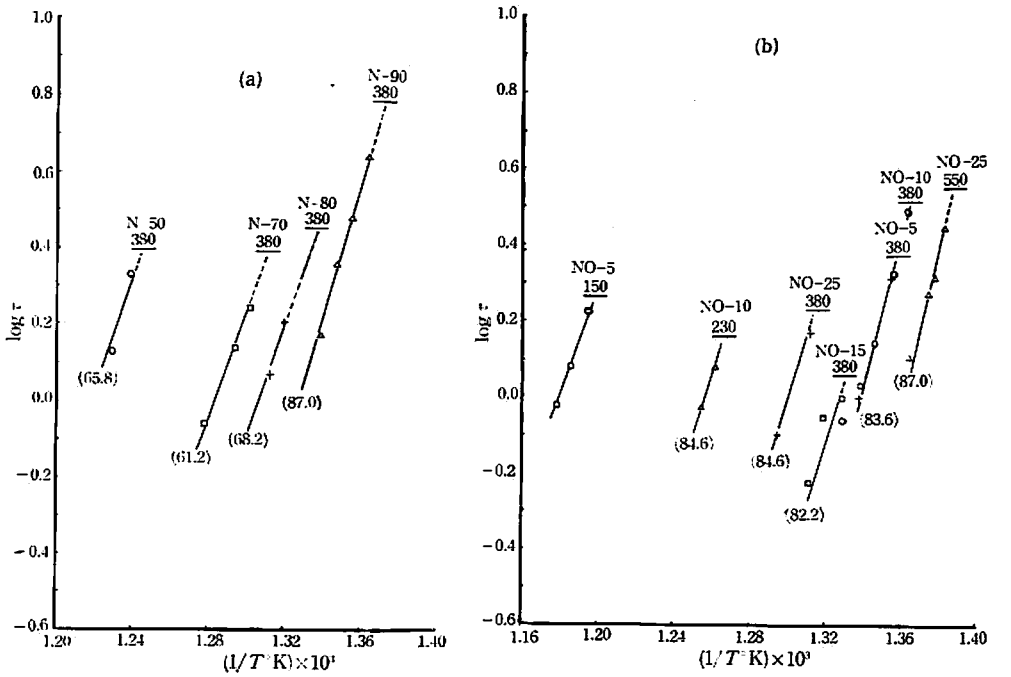
with the curve of MVA-O_2.

The peak, described above, appears to mean that small amounts of O_2 retard the explosive polymerization.

Induction period

The induction period was generally short and that of over 10sec. was not observed. The higher the MVA concentration, and the higher the admission pressure, the longer the period was. These phenomena are similar to those of MVA and MVA-air in the previous paper[1].

The linear relation between the induction period (τ) and the reaction temperature (T) is shown by the plotting of $\log\tau$ vs ($1/T$°K) in Fig. 8 a) (MVA-N_2), Fig. 8 b) (MVA-NO), and Fig.



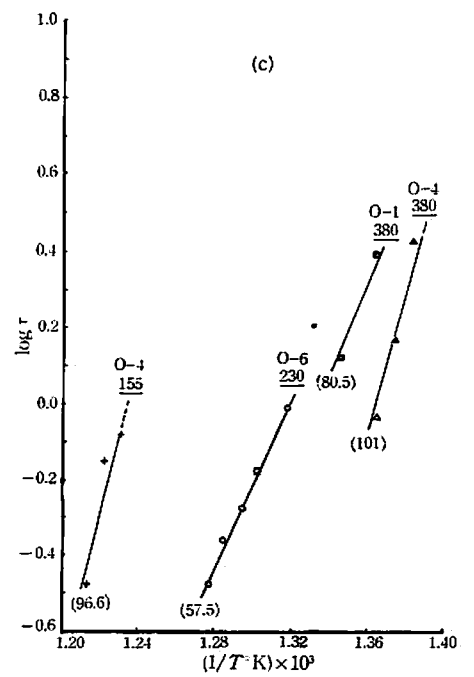


Fig. 8 Relation beween $\log\tau$ and ($1/T$°K) for (a) MVA-N_2, (b) MVA-NO and (c) MVA-O_2.
( ): activation energy (Kcal/mole)
——: initial admission pressure (mmHg)

8 c) (MVA-O_2).

On the other hand, the relation between the induction period (τ) and the admission pressure (P) is in Fig. 9. The definite linear relation can not be found. As this does not mean that the

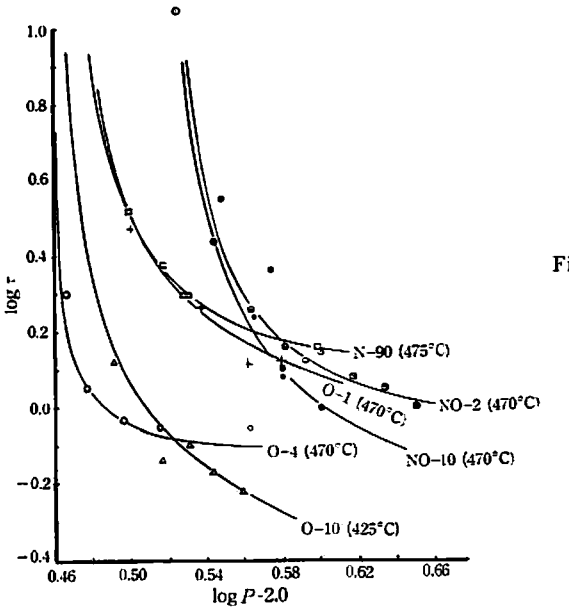


Fig. 9 Relation between log τ and log P. for MVA-N_2, MVA-NO and MVA-O_2.
( ): reaction temperature

following equation[2] obtained from the chain theory is held,

$$P^n \tau e^{-E/RT} = \text{constant.} \qquad (1)$$

the chain theory can not be considered to be principal in this explosion reaction.

Apparent activation energy

According to N. N. Somenov's thermal theory[3], the following relation with respect to the reaction pressure (P) and the reaction temperature (T) is reasonable with the assumption of bimolecular reaction. So, the apparent activation energy can be obtained from its slope of the following equation:

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

$$A = 0.11E$$

E: activation energy T: reaction temperature
P: reaction pressure B: constant

The results obtained with a vessel of 20 mm in diameter are shown in Fig. 10 a) (MVA-N_2),

2) N. N. Semenov, *Z. phys. chem.*, **B11**, 464 (1931)
3) N. N. Semenov, "*Some Problems of Chemical Kinetics and Reactivity*", Part 2, (translated by J. E. S. Bradley), Pargamon Press Ltd. (1959)

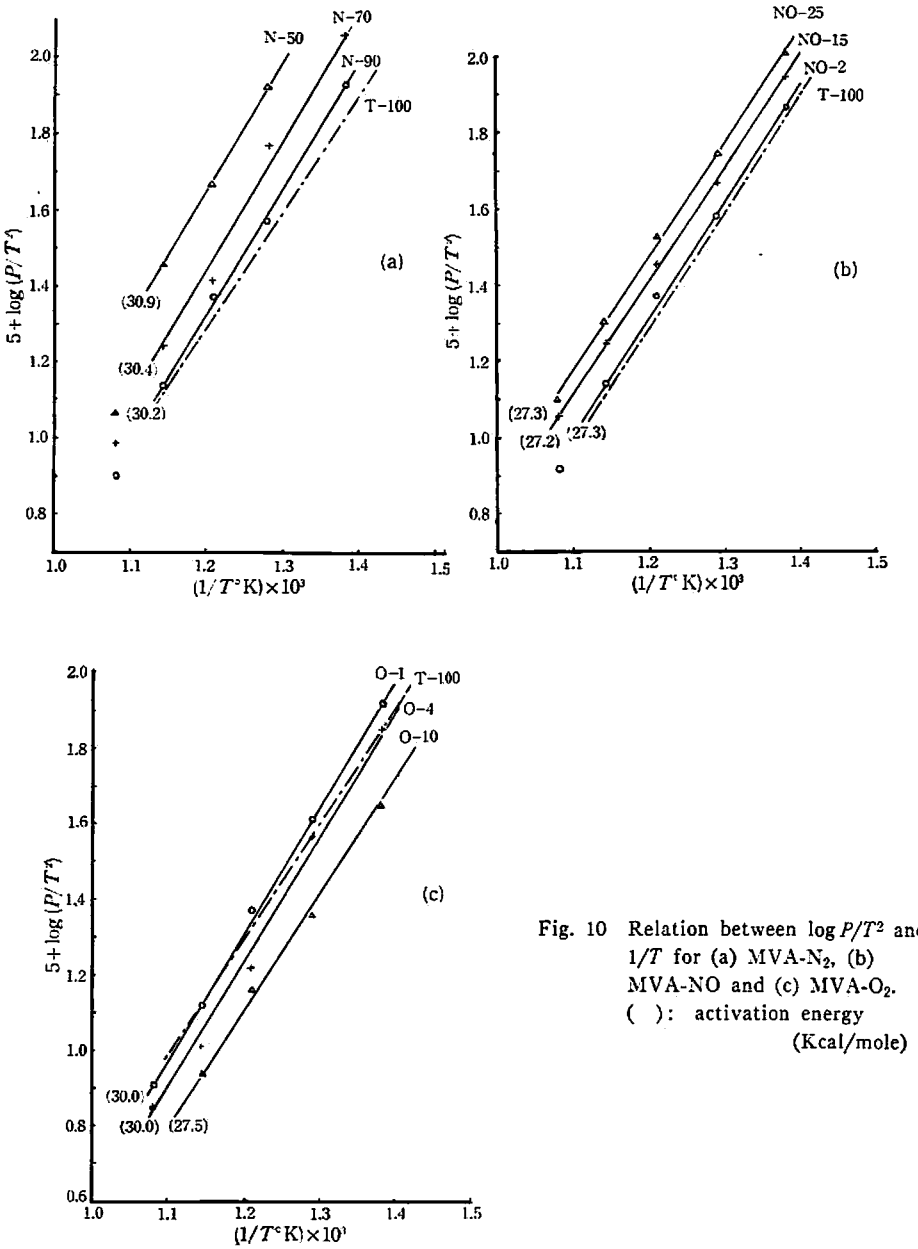


Fig. 10 Relation between $\log P/T^2$ and $1/T$ for (a) MVA-N_2, (b) MVA-NO and (c) MVA-O_2.
( ): activation energy (Kcal/mole)

Fig. 10 b) (MVA-NO), and Fig. 10 c) (MVA-O_2). The linear relation is found in the range of 450°C and 600°C, concerning $\log(P/T^2)$ vs $(1/T)$. Therefore, the explosion is suggested to be mainly based on the thermal theory. The apparent activation energies obtained are 30.2～30.9 Kcal/mole for MVA-N_2, 27.2～27.3 Kcal/mole and 27.5～30.0 Kcal/mole for MVA-O_2. These values are almost equal to those of MVA and MVA-air (about 29 Kcal/mole) in the previous

paper[1].

The following equation[4] is given from the relation between the production rate of intermediate products and the induction period (τ):

$$\log \tau = (E/RT) + \text{constant.} \qquad (3)$$

The approximate linear relation can be obtained in $\log \tau$ vs $(1/T)$ as seen in Fig. 11 a) (MVA-N_2), Fig. 11 b) (MVA-NO) and Fig. 11 c) (MVA-O_2). The apparent activation energies obtained from the slopes are 61.8～87 Kcal/mole for MVA-N_2, 82.2～87 Kcal/mole for MVA-NO and 57.5～101 Kcal/mole for MVA-O_2. The values are abnormally higher than those obtained from the thermal explosion theory and similar to those obtained by the reaction in the previous paper[1].

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