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STUDIES ON EXPLOSIVE REACTION OF VINYL CHLORIDE
MIXED WITH OXYGEN

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The explosion limits of vinyl chloride mixed with oxygen are determined at reduced pressures by the admission method. Isochors and isotherms of the explosion limit and also the colors of ignition flames are shown. There is no essential difference between the behavior of vinyl chloride mixed with oxygen and that of ethylene mixed with oxygen except the generation of hydrogen chloride under the slow reaction. Patterns of these explosion limits are similar to each other. The induction periods in the explosion peninsula of vinyl chloride mixed with oxygen have also been measured and it is found that these periods are shorter than those of ethylene mixed with oxygen. The apparent activation energy of the reaction is estimated from the explosion limits of vinyl chloride mixed with oxygen according to Semenoff's theory and its value, E , is about 34 kcal.

In recent years vinyl chloride has come to assume commercial importance as a monomer of its polymer. There are a few data¹⁾ in the literature in regard to "limit of inflammability", but observations experienced under certain conditions can hardly be accepted as indicative of the monomer's safety range in other set of conditions. And with the increasing use in industry of monomer vapor at elevated temperatures and pressures, it is important for information relevant to these conditions to be available over sufficiently wide ranges.

In the previous papers^{2,3,4)}, the explosion limit of ethylene mixed with oxygen and that with the air were determined by the "admission method". The present author has continually studied the explosion limit of vinyl chloride mixed with oxygen by the same method, for the purpose of gaining the knowledge of the explosive reaction. These results are compared with the results of ethylene mixed with oxygen and briefly discussed. In this case, the results obtained are unsatisfactory from the practical point of view. However, it is interesting to mention that the explosion peninsula is found also in the explosion limit of vinyl chloride mixed with oxygen, and it is made sure that the explosion peninsula involved in the explosion limit of ethylene mixed with oxygen is not the sole nature of ethylene itself as reported in the previous work³⁾.

Experimentals

1) Division Coating Technical Service Bulletin, *Vinyl Chloride Monomer*, The Dow Chemical Co. plastics

2) M. Suga, *Bull. Chem. Soc. Japan*, **31**, 515 (1958)

3) M. Suga, *ibid.*, **32**, 425 (1959)

4) M. Suga, *This Journal*, **28**, 67 (1959)

Materials The vinyl chloride employed in this experiment was prepared by dehydrochlorinating 1,2-dichloroethane (b. p. 83.5°C) through the action of alkali in methanol solution and then stored in a small cylinder. When necessary, it was fractionated, purified by the action of concentrated aqueous solution of sodium hydroxide, ammoniacal cuprous chloride solution and dilute sulfuric acid, and then dried with soda lime and phosphorous pentoxide. The oxygen employed was obtained from a commercial cylinder (purity: 99.4%), after being passed through a train of bottles containing a concentrated aqueous solution of sodium hydroxide, concentrated sulfuric acid and phosphorous pentoxide.

Apparatus and procedure The apparatus used and the procedure adopted were of the types described in the previous paper²⁾ except the removal of the mercury manometer previously connected with the reaction vessel, taking into consideration the mercury vapor effects on the explosion limit. Next, since the results were particularly influenced by the previous history of the reaction vessel and these effects not being reproducible, the following standard procedure was adopted for the purpose of eliminating these effects.

After a previous run, the reaction vessel was heated to 600°C and evacuated to 10^{-3} mmHg for an hour.

Pressure change was measured with a movable membrane manometer containing a thin mica or aluminium membrane, with the object of recording the pressure-time curve. Thereupon, the displacement of membrane was recorded by an ink oscillograph and strain meter* connected with a strain gauge pasted on the membrane. But on the general experimental runs of the determination of the occurrence of explosion, all manometers were removed in order to simplify the operations.

Results and Considerations

Observation The determination of the occurrence of explosion was made directly by naked eyes. The results of observation are classified thus:

- 1) After the lapse of various induction periods (usually less than 10sec) luminous flames (blue, green or yellow flames) were normally preceded by a glow which rapidly built up into a bright flash filling the vessel and accompanied by a sound.
- 2) After the lapse of relatively longer induction periods, pale blue flames were observed in the dark room.
- 3) After the lapse of shorter induction periods, consecutive glows were observed for several seconds in the dark room. This is not found in the experiments of ethylene mixed with oxygen.
- 4) No change was observed.

It was noticed that the white products, presumably polymer, adhered sometimes on the inner wall of the vessel after the reaction in case (3). Besides, after the explosion of case (1) black products containing carbon were found on the inner wall of the tube connected with the reaction

* DS6-P type wire resistance strain meter, Shinkoh Communication Industry Co., Ltd., Tokyo

vessel. It is pointed out that this phenomenon differs from the case of ethylene mixed with oxygen. Fine points aside, cases (1), (2) and (3) are conveniently defined to be the explosions.

Recording of pressure variation with time The typical pressure-time curves which were measured by means of the movable membrane manometer are schematically indicated in Fig. 1. Curve (A) indicates a very rapid increase of pressure with luminous yellow, green or blue

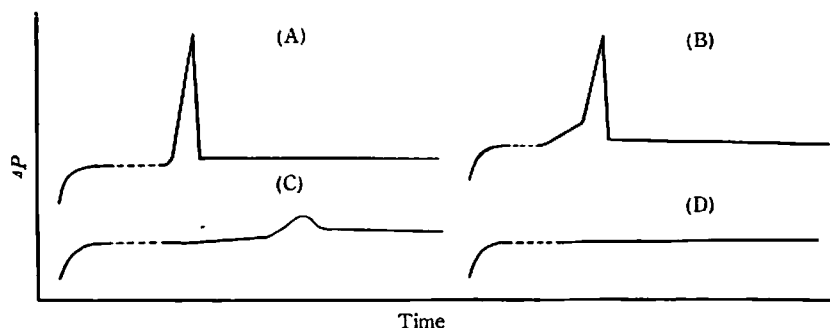


Fig. 1 Schematic pressure-time curves

flames and this corresponds to a normal ignition. Curve (B) shows the pressure change which appears to be a two-stage ignition and occurs under conditions near the thermal explosion limit. Dark blue flames which occurred on the vessel wall grew immediately into luminous flames. It is considered that curve (A) is essentially the same as curve (B). Curve (C) indicates a feeble and milder increase of pressure due to slower reaction than in the case of curve (B) and is ac-

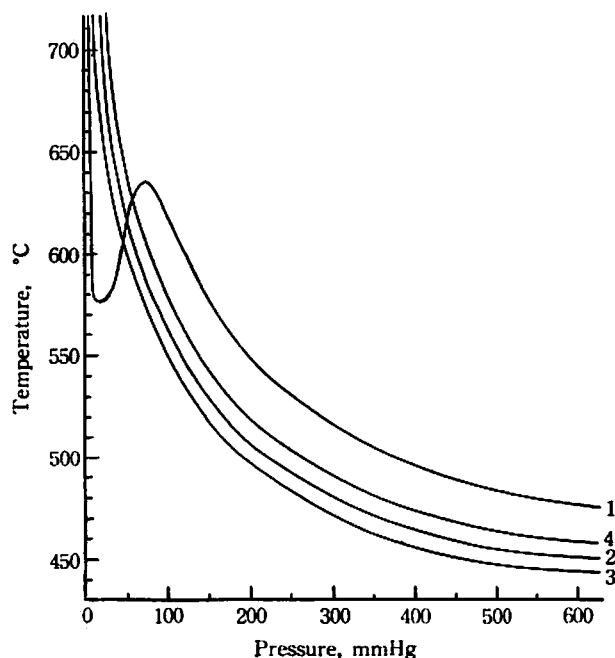


Fig. 2 Isochors for explosion limit of vinyl chloride-oxygen mixtures

Curve 1 = 20%, 2 = 40%, 3 = 60%,
4 = 80% vinyl chloride

accompanied with pale-blue flames found under the explosion peninsula. Curve (D) indicates no increase of pressure with no flame. This corresponds to the so-called "slow reaction".

The explosion limit of vinyl chloride mixed with oxygen Isochors were determined for the mixtures of the various compositions. Some of the isochors are shown in Fig. 2. Only the isotherm at 600°C is shown in Fig. 3. The curves shown in these figures exhibit the minima

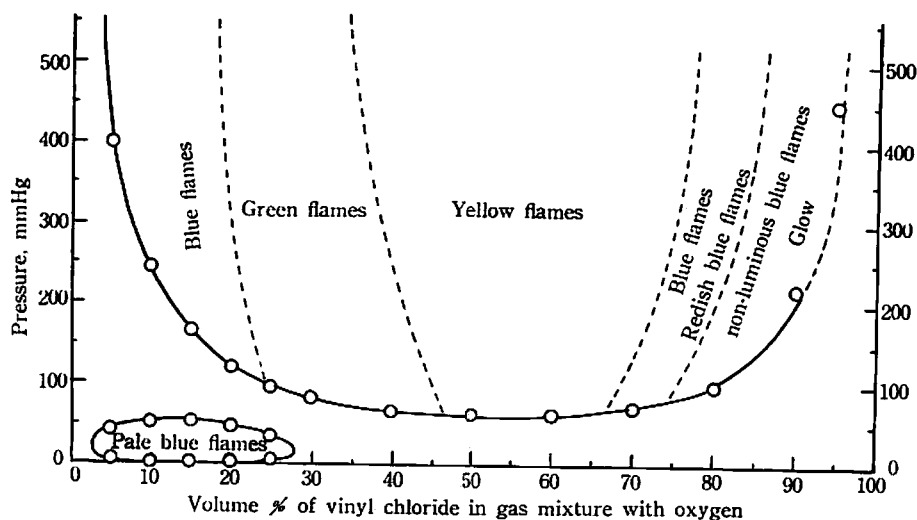


Fig. 3 Isotherm for explosion limit of vinyl chloride-oxygen mixtures at 600°C

at the composition of about 50% vinyl chloride and the explosion limit situated about 3~95% vinyl chloride (containing glow range). The explosion peninsula is found at the definite temperature and in pressure condition in the mixture range 3~27% vinyl chloride as indicated in the lower closed curve in Fig. 2. The glow which was observed in the region of the mixture of more than 90% vinyl chloride could not be recognized in the case of ethylene, and its presumed limit is indicated with the broken line.

The explosion peninsula The explosion peninsula lies on the range bounded by the first and second pressure limits of the explosions with which pale blue flames occur. Fig. 4 shows isochor for the explosion limit of 20% vinyl chloride mixed with oxygen. ⊙, ○ and × indicate respectively the cases (1), (2) and (4) of the observations. Also, ⊙ indicates the case of the luminous flame propagating into the storage bulb through the induced capillary tube owing to very short induction period. The broken line in Fig. 4 represents the explosion of 20% ethylene mixed with oxygen.

At this point, the present author first considers that the explosion peninsula of ethylene mixed with oxygen was not always related to the nature of ethylene but was caused by carbon monoxide accumulated in the slow reaction^{3,4}. Then, the following mechanism is supposed⁵:

5) C. N. Hinshelwood, *The Kinetics of Chemical Change*, Oxford (1940), p. 168

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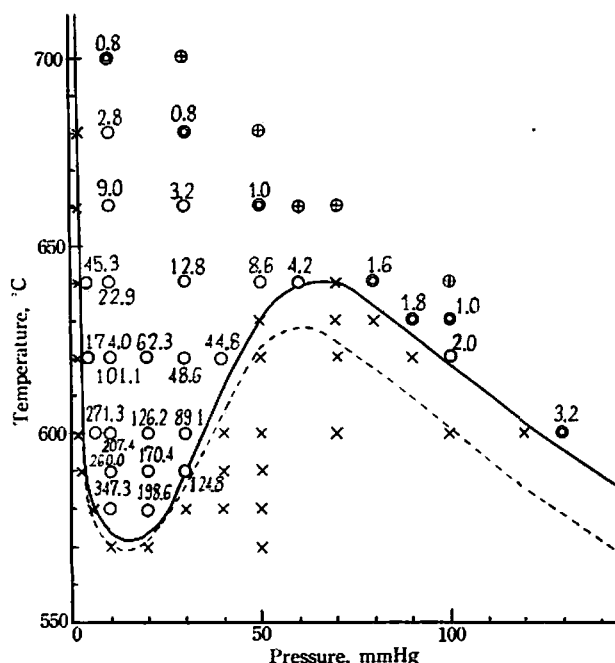
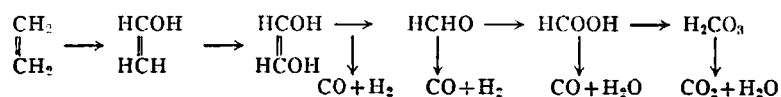
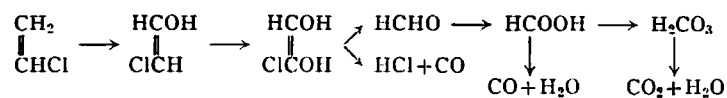


Fig. 4 Explosion limit of 20% vinyl chloride mixed with oxygen (Induction periods in seconds are indicated by numbers beside observation points.)



In analogy to this mechanism it is considered that in the case of vinyl chloride, carbon monoxide is accumulated and is followed by the generation of hydrogen chloride in the process of slow reaction.



If the essential difference between the respective behaviors of ethylene and vinyl chloride mixed

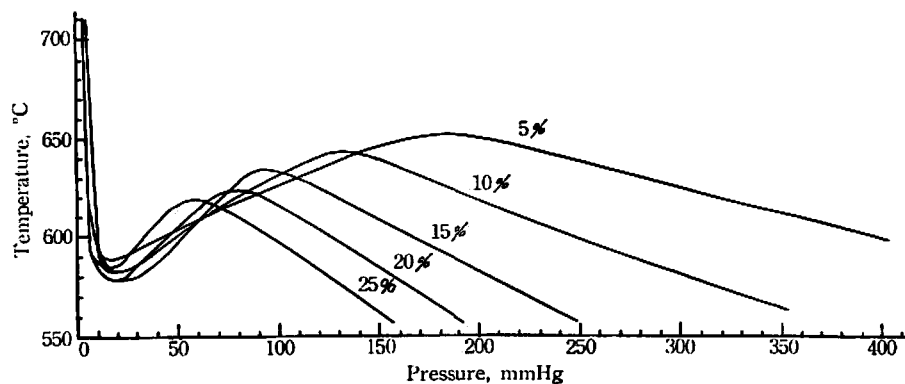


Fig. 5 Isochors for explosion limits of vinyl chloride-oxygen mixtures

with oxygen is the generation of hydrogen chloride, the discrepancy between the explosion limits is well understood in conformity with the fact⁶⁾ that hydrogen chloride is an inhibitor of carbon monoxide oxidation. Fig. 5 shows the various isochors for the explosion limit of vinyl chloride mixed with oxygen, which indicate the various shapes of the explosion peninsula according to the composition of gas mixtures. That is to say, the composition of gas mixtures considerably affects the explosion limit, and particularly it is noticed that the explosion peninsula disappears at over 25% vinyl chloride. It is similar to the case of ethylene.

The explosion limit and induction period The results of the experiment with regard to the induction period are shown by numbers beside the observation points in Fig. 4. The induction period was measured by a stopwatch. Fortunately, the induction periods are fairly long in the region of the explosion peninsula and are reproducible so far as precautions are taken in accord with the standard procedure. Fig. 6 shows the relationship between the explosion limit pressure

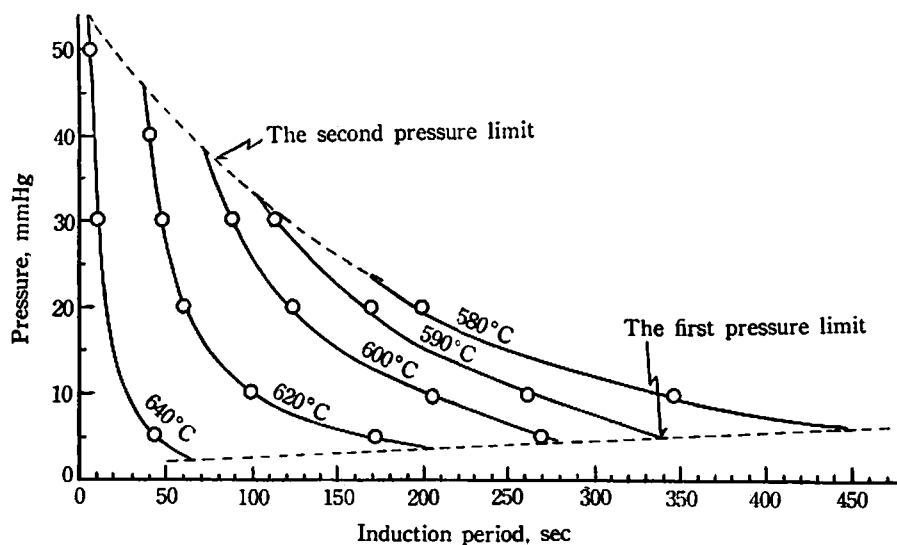


Fig. 6 Relationship between the explosion limit pressure and induction periods at the definite temperature for 20% vinyl chloride mixed with oxygen

Table 1 The induction periods (in sec) at the definite pressures and temperatures for 20% ethylene or vinyl chloride mixed with oxygen

| Temp. °C | 10 | | 30 | | 50 | |
|----------|----------|----------------|----------|----------------|----------|----------------|
| | ethylene | vinyl chloride | ethylene | vinyl chloride | ethylene | vinyl chloride |
| 590 | 617.7 | 260.0 | 251.0 | 124.8 | × | × |
| 600 | 368.7 | 207.4 | 169.4 | 89.1 | × | × |
| 620 | 128.9 | 101.1 | 72.4 | 48.6 | 38.1 | × |
| 640 | 33.1 | 22.9 | 20.6 | 12.8 | 13.1 | 8.6 |

× : non-explosion

6) D. E. Houre and A. D. Walsh, *Trans. Faraday Soc.*, **50**, 37 (1954)

and the induction period at various constant temperatures for 20% vinyl chloride mixed with oxygen. In Table 1, the induction periods in the explosion peninsula of vinyl chloride mixed with oxygen are compared with 20% ethylene mixed with oxygen.

It is interesting to say that the explosion peninsula is more restricted but the induction periods of the explosion are shorter in the case of vinyl chloride than in those of ethylene. In other words, it is considered that hydrogen chloride is an inhibitor of carbon monoxide combustion but will eventually be a promoter of the slow reaction of vinyl chloride.

The apparent activation energy of the reaction In Fig. 7 is shown the relationship

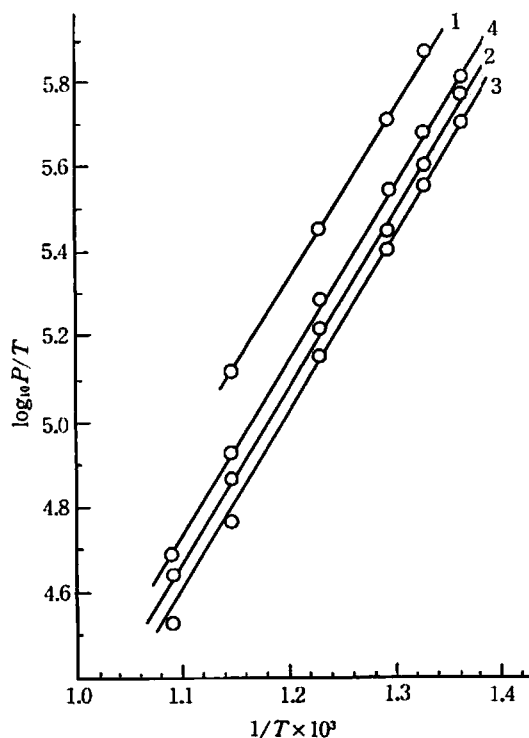


Fig. 7 $\log_{10} P/T$ against $1/T$ curves for the explosion limit of vinyl chloride-oxygen mixtures

Curve 1 = 20%, 2 = 40%, 3 = 60%, 4 = 80% vinyl chloride

between $\log_{10} P/T$ and $1/T$ for the third pressure limit of Fig. 2. These graphs are essentially linear at a lower temperature than 600°C. This corresponds to the relationship $\log_{10} P/T = A/T + B$. The case is similar to that of ethylene mixed with oxygen. If the third pressure limit is thermal in

Table 2 Activation energies estimated from the explosion limits of vinyl chloride-oxygen mixtures

| C_2H_3Cl % | A | $E = 2.303 \times 2 \times 1.987 \times A$ (kcal/mole) |
|--------------|------|---|
| 80 | 3.70 | 33.8 |
| 60 | 3.74 | 34.2 |
| 40 | 3.71 | 33.9 |
| 20 | 3.73 | 34.1 |

character, the gradient of these lines, A , will be equal to $E/2.303 \times 2 \times R$. Thus, values for E , the apparent activation energy, may be calculated as in Table 2.

By comparison with the values of ethylene mixed with oxygen²⁾, it is found that the " E " values of vinyl chloride mixed with oxygen almost analogous to those of ethylene. Of course, there will be no direct meaning in the kinetic interpretation, but the explosion reaction of vinyl chloride mixed with oxygen may apparently be considered as thermal in nature in this experimental ranges as in the case of ethylene.

Summary

The explosion limit of vinyl chloride mixed with oxygen was determined at reduced pressure by the "admission method". Isochors and isotherms of the explosion limit and also the colors of ignition flames are shown. It is considered that there is no essential difference between the behaviours of vinyl chloride mixed with oxygen and ethylene mixed with oxygen except the generation of hydrogen chloride under the slow reaction. The induction periods in the explosion peninsula of vinyl chloride mixed with oxygen have also been measured and it is found that these values are shorter than those of ethylene mixed with oxygen. The apparent energy of the reaction is estimated from the explosion limit of vinyl chloride mixed with oxygen according to Semenoff's theory and its mean value " E " is about 34kcal.

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