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STUDIES ON EXPLOSIVE REACTIONS OF TETRAFLUOROETHYLENE AND ACETYLENE WITH OXYGEN OR AIR

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Introduction

A number of investigations have been made on the explosive reactions of lower unsaturated organic compounds, and have offered interesting results. The present authors studied an explosive reaction scarcely known and an explosive region undetermined by means of "admission" method in which gaseous samples were flowed into a hot vessel evacuated. The present experiment was performed in order to be compared with the data of the explosions under high pressure in this laboratory.

Tetrafluoroethylene in Part I is recently of industrial importance as a monomer of fluorocarbon compounds and the occurrence of explosion has been reported1), but any study has not been performed yet on the explosive reactions of tetrafluoroethylene-oxygen or air mixtures.

As to acetylene in Part II many studies have been reported by means of various experimental methods, but on the explosions of acetylene-oxygen mixtures by the admission method relatively little information is available2).

Experimentals

Materials Tetrafluoroethylene C_2F_4 used is reserved in a cylindrical glass vessel, after purified by fractionation by means of a Podbielniak-type distilation apparatus. The measurement of infrared absorption on the gas was carried out in this laboratory3). Acetylene gas is prepared with calcium carbide and water, purified through refining reagents and stored in a glass bulb at an atmospheric pressure (purity: 99.4~99.6%). Oxygen is used from a commercial bomb (purity: 99.4%). Air is used after being passed through two wash-bottles containing conc. aqueous solution of potassium hydroxide and conc. sulphuric acid respectively.

Apparatus and procedure The layout of the apparatus is shown in the figure below. Combustibles and oxygen or air are mixed in the glass reservoir B_1, the partial pressures of these gases being measured by the mercury manometer M_1, and reserved more than twelve hours to complete the mixing. Then making use of Toepler pump P, we transfer them into the glass reservoir B_2 until a definite pressure is attained. The glass reaction vessel having a fine tube H for the insertion of a thermocouple is evacuated to about 10^{-3} mmHg pressure and heated by the electric furnace F to a definite temperature which is measured by an alumel-chromel thermocouple T inserted

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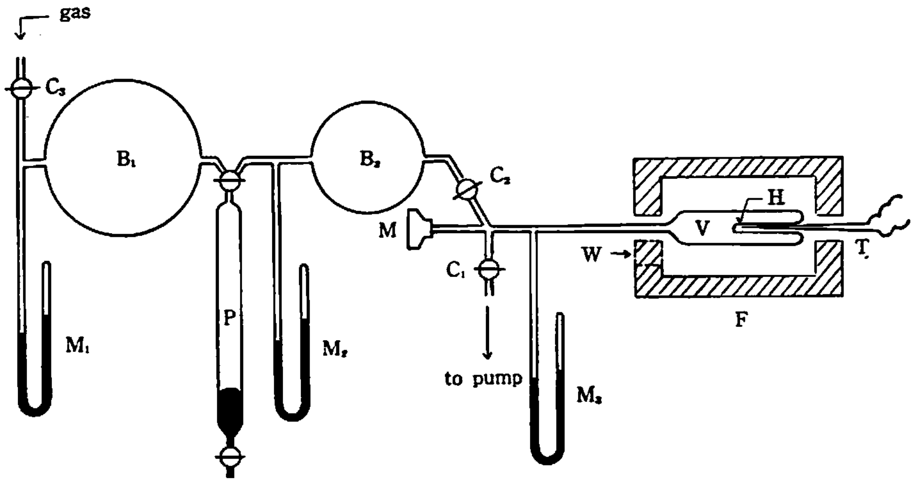
* *S. Kusuhara is in the postgraduate course, under the direction of Prof. R. Kiyama.*

1) H. C. Duss, *Ind. Eng. Chem.*, **17**, 1445 (1953)

2) P. Schäpper und M. Brunner, *Helv. Chim. Acta*, **13**, 1125 (1930)

3) R. Kiyama, M. Minomura and K. Ozawa, *This Journal*, **25**, 64 (1955)



Layout of the apparatus

B_1, B_2: gas reservoir
C_1, C_2, C_3: glass cock
F: furnace
H: narrow tube
M_1, M_2, M_3: mercury manometer
M: membrane pressure gauge
P: Toepler pump
T: thermocouple
V: reaction vessel
W: window

into the fine tube H. Immediately after the gaseous mixture in the reservoir B_2 is poured into the reaction vessel, an explosion phenomenon is observed.

The determination of the occurrence of explosion is made mainly from the observation of flame with eyes whose pupils are dilated in the dark through the window W equipped on the wall of the furnace. But in the case of the experiment of Part I we used in addition to the visual observations either an ink writing oscillograph recording the change of strain gauge pasted on the movable membrane manometer M, or an automatic mechanical pressure recorder.*

Induction period, the time between the admission of mixtures and the occurrence of explosion is measured by a stop-watch.

The reaction vessels used in Part I are those made of soft glass (at temperatures less than 350°C) and of quartz glass (at temperatures above 350°C) having the 10 cm length and 3 cm diameter. In order to examine the effect of diameter on the explosion limits, the vessels of equal length and of 1 cm and 2 cm diameters are used for mixtures of certain compositions.** The vessels used in Part II are those of the same length and of 1 cm, 2 cm and 3 cm diameters made of soft glass (at temperatures less than 400°C) and of hard glass (at temperatures above 400°C).

Experimental results and considerations of Part I and Part II are described separately.

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* The apparatus records on a rotating drum the deflection, being magnified by a lever, of the membrane due to a pressure change.

** Throughout this paper, composition will be expressed by percentage of combustibles.

Part I Explosive Phenomena of Gaseous Tetrafluoroethylene-Oxygen or Air Mixtures

Results

a) Explosive reactions of tetrafluoroethylene-oxygen mixtures

In order to determine the temperature at which the reaction between tetrafluoroethylene and oxygen would occur, a definite quantity of the gaseous mixture at fixed compositions being contained in the reaction vessel at room temperature, the temperature of the vessel was raised at a definite heating rate (about 1 deg./min.), and pressure and temperature were measured every 10 minutes by the manometer M_3 and thermocouple T. Fig. 1. 1 shows these pressure-temperature curves at specified compositions. The curve for pure tetrafluoroethylene does not exhibit any pressure decrease until about 250°C, whereas the other curves show slight pressure decreases deviated from the straight line shown in the case of pure tetrafluoroethylene at a temperature of, say, 200°C, which may suggest the occurrence of reactions between tetrafluoroethylene and oxygen. We performed our experiments in the anticipation that explosion temperature might be near 200°C. Thus the conditions of temperature and pressure that give rise to explosion at the compositions of 20, 40, 60 and 80% C_2F_4 can be obtained by the experimental method described above and are shown in Fig. 1. 2. At the temperature above 350°C, the curves become nearly parallel to the temperature axis and the asymptotic pressures are approximately 5 cm Hg.

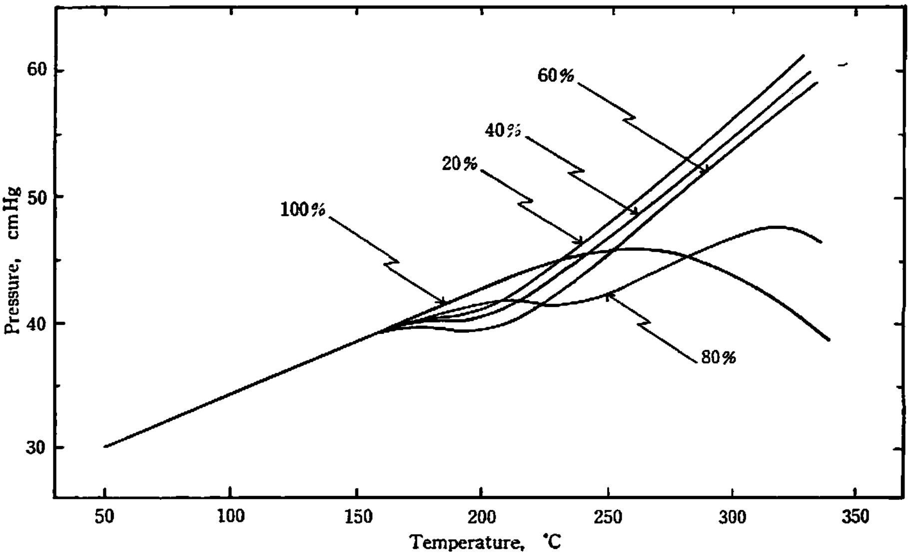

Fig. 1. 1 Temperature dependence of pressure of C_2F_4–O_2 mixtures when heated at a definite heating rate

The pressure-composition diagrams of explosion limits at various temperatures and the temperature composition diagrams of explosion limits at various pressures are shown in Figs. 1. 3 and 1. 4 respectively. The curves shown in these figures exhibit the minima at the composition of

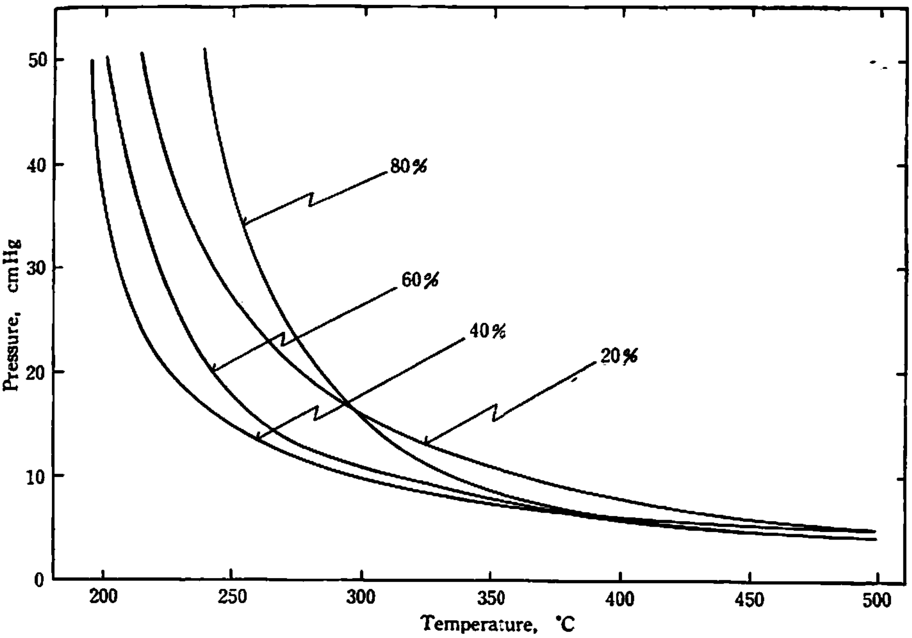

Fig. 1. 2 Relations between temperature and pressure of explosion limits at specified compositions in C_2F_4-O_2 mixtures

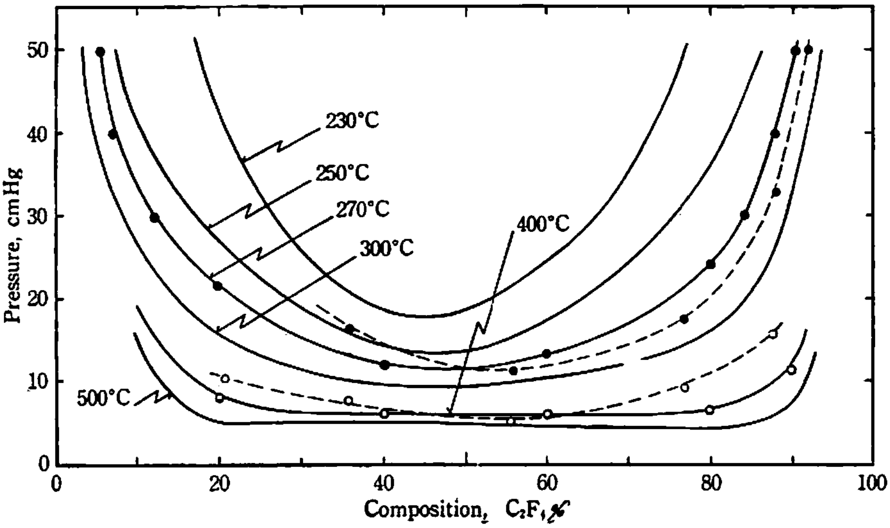

Fig. 1. 3 Relations between pressure and composition of explosion limits at specified temperatures in C_2F_4-O_2 mixtures (Broken lines represent the data calculated from the limits of C_2F_4-air mixtures, illustrated in Considerations. ● 270°C, ○ 400°C)

about 50%. The lowest explosion pressure and temperature are about 5 cm Hg and 196°C respectively.

To examine the wall effects, experiments were made for the mixture of C_2F_4 (50%)-O_2 in

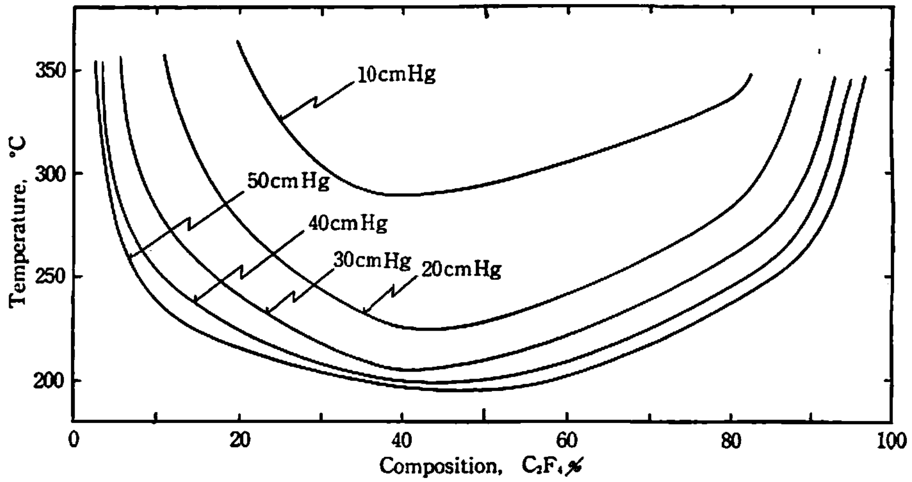

Fig. 1. 4 Relations between temperature and composition of explosion limits at specified pressures in C_2F_4-O_2 mixtures

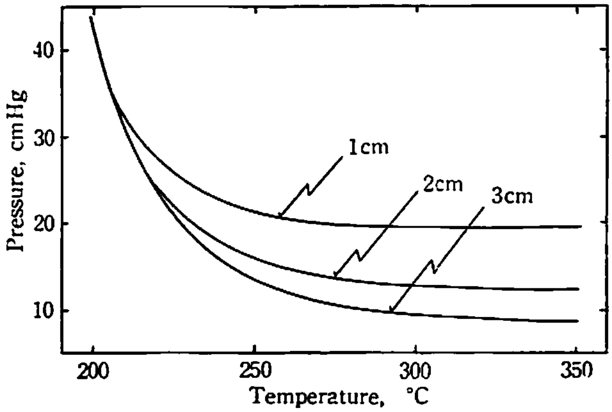

Fig. 1. 5 Effect of vessel diameter on explosion limits in C_2F_4 (50%)-O_2 mixture

the vessels having diameters of 1, 2 and 3 cm. The results are represented in Fig. 1. 5. At lower temperatures the curves of explosion limits are nearly coincident, but at higher temperatures the decrease in vessel diameter causes the explosion limits to be higher, and the tendency is more remarkable in the vessel of 1 cm diameter than in that of 2 cm diameter.

The colors of explosion flames, as shown in Fig. 1. 6, change in the order of orange, yellow and blue with the decreasing of the percentage of tetrafluoroethylene and have relation to reaction products, that is, orange flames usually deposit carbon on the vessel surface, while blue flames are accompanied with white products. Pale-blue flames observed near the explosion boundaries propagate at a slow speed along the long axis of the vessel. When we make use of quartz vessels at higher temperatures and lower pressures, feeble green flames are observable, which may be attributed to some oxidation reaction since in pure tetrafluoroethylene without oxygen these flames are not observed.

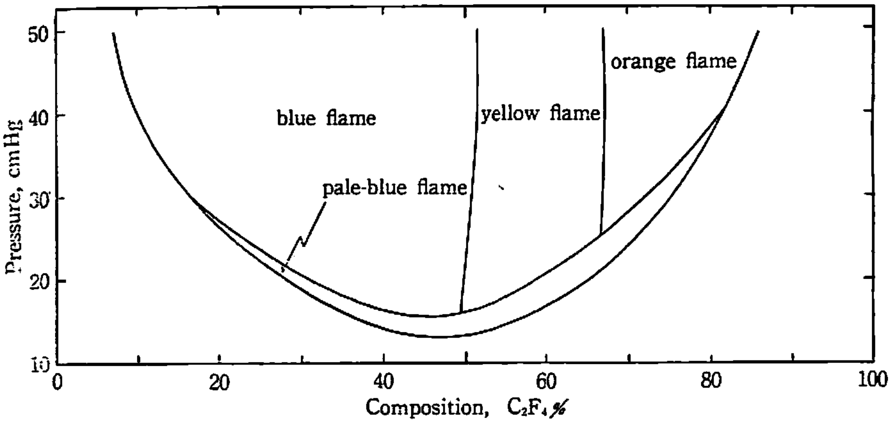

Fig. 1. 6 Colors of explosion flames at 250°C in the vessel of 3 cm diameter (C_2F_4–O_2 mixtures)

Typical pressure-time curves recorded by the strain gauge and the ink writing oscillograph are shown in Fig. 1. 7. Curve a indicates a very rapid increase of pressure with luminous orange or blue flash and this corresponds to a normal ignition. Curve b represents two-stage

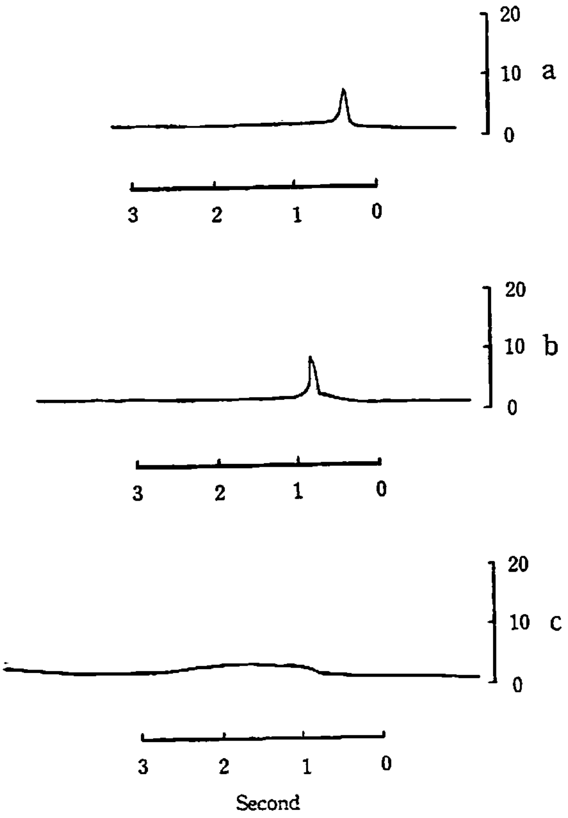

Fig. 1. 7 Typical pressure-time curves in C_2F_4–O_2 mixtures
Ordinate: $\triangle P$ in cm Hg

Curve a Normal explosion with luminous flame

Curve b Explosion with two-stage flame

Curve c Mild explosion with pale-blue flame in the regions in Fig. 1. 8

ignition in which pale-blue flame occurred near the wall of the vessel changes momentarily into luminous orange or blue flash. Curve c shows mild pressure increase due to slower reaction than the case of curve a or b and is accompanied with pale-blue flame found under the conditions near the explosion limits and has slow propagation of flame (several centimeters per second).

The regions of pale-blue flames determined by the automatic mechanical pressure recorder are given in Fig. 1. 8. Within the temperature range of 250–290°C, the higher the temperature, the wider becomes the pressure range of pale-blue flame at specified compositions.

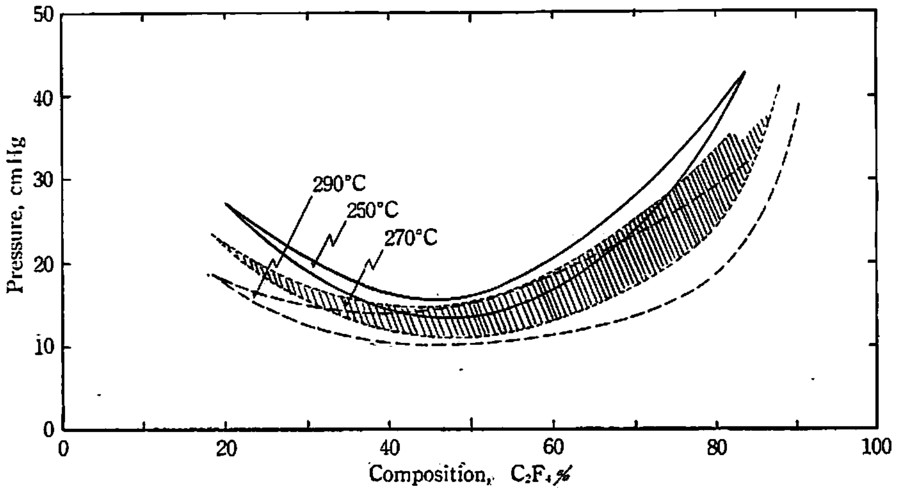

Fig. 1. 8 Regions of pale-blue flames in C_2F_4–O_2 mixtures at temperatures of 250°, 270° and 290°C

In addition to these experiments described above, several preliminary observations were performed as follows.

Observation of explosions has been done for 5 minutes immediately after the admission of the gaseous mixtures. This is based on the fact that in the explosive regions C_2F_4–O_2 mixtures explode within 2 minutes from the admission, and that outside the explosion regions they do not explode during the continuous measurement of 50 hours by the automatic pressure recorder.

Gases of tetrafluoroethylene and oxygen being mixed in a reservoir, they were kept generally more than 12 hours for the completion of mixing. The reservation is enough for mixing because mixtures kept in the reservoir at room temperature for a week, a month and half a year, give almost the same explosion limits as the mixture reserved for 12 hours.

It is sometimes found that the reaction products adhered to the inner surface of the vessel affect the explosion limits, that is, white products formed from rich oxygen mixtures will often widen the explosion area, while the carbon products from poor oxygen mixtures have a tendency to contract the area. So in order to remove these effects, the authors heated the reaction vessel at about 350°C evacuating about half an hour and made use of it several times. When the virgin surface of a reaction vessel is used, reproducible results are obtained after the first explosion.

These cares are taken to obtain satisfactory results.

Mercury manometer M_3 was sometimes used together for the measurement of pressure changes, and so for the purpose of testing the effect of mercury upon the explosion, experiments were carried out in hot vessels into which a few drops of mercury had been poured. It was recognized that mercury retarded the explosion to some extent. In the present experiments, however, the effect can be neglected owing to the low vapor pressure (1.2×10^{-3} mm Hg) at room temperature.

b) *Explosive reactions of tetrafluoroethylene-air mixtures*

The explosion limits were determined for tetrafluoroethylene-air mixtures by the same experimental method described above.

Figs. 1. 9 a and b show the explosion limits of temperature-pressure diagrams at specified compositions. At lower temperature, the curves become almost parallel to the pressure axis and are similar to hyperbolas. The pressure-composition diagrams of the explosion limits at definite temperatures, and the temperature-composition diagrams of the explosion limits at definite pressures are shown in Figs. 1. 10 and 1. 11 respectively. The limits exhibit the minima at a composition of some 20% C_2F_4. The lowest explosion pressure and temperature are about 15 cm Hg and 222°C respectively.

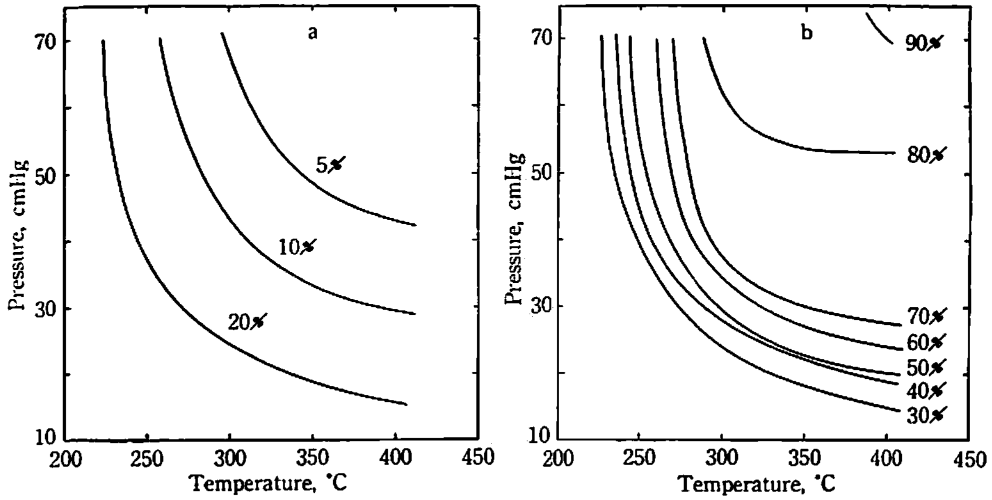

Fig. 1. 9 a, b Relations between temperature and pressure of explosion limits at specified compositions in C_2F_4-air mixtures

The explosion limits in the vessels of different diameters of 1, 2 and 3 cm at 20% C_2F_4 are given in Fig. 1. 12. The narrower the diameter of the vessel (i. e. the larger the ratio of surface to volume), the higher become the explosion limits, and this tendency is more remarkable in the vessel of 1 cm diameter than in that of 2 cm diameter.

The colors of explosion flames are almost the same as those of C_2F_4-O_2 mixtures, that is, they are generally found to be pale-blue, luminous blue, (orange) yellow, orange flames and two-stage flames the color of which changes from pale-blue into luminous blue or orange.

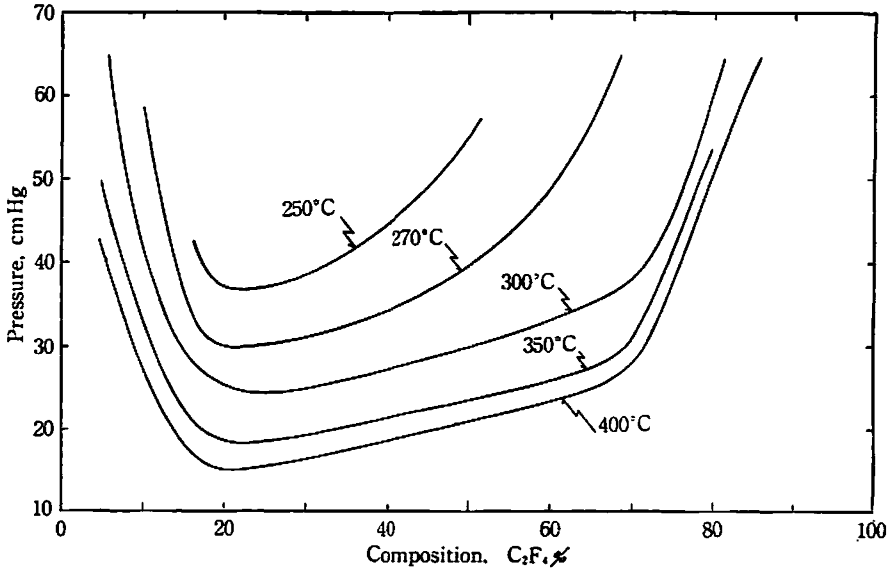

Fig. 1. 10 Relations between pressure and composition of explosion limits at specified temperatures in C_2F_4-air mixtures

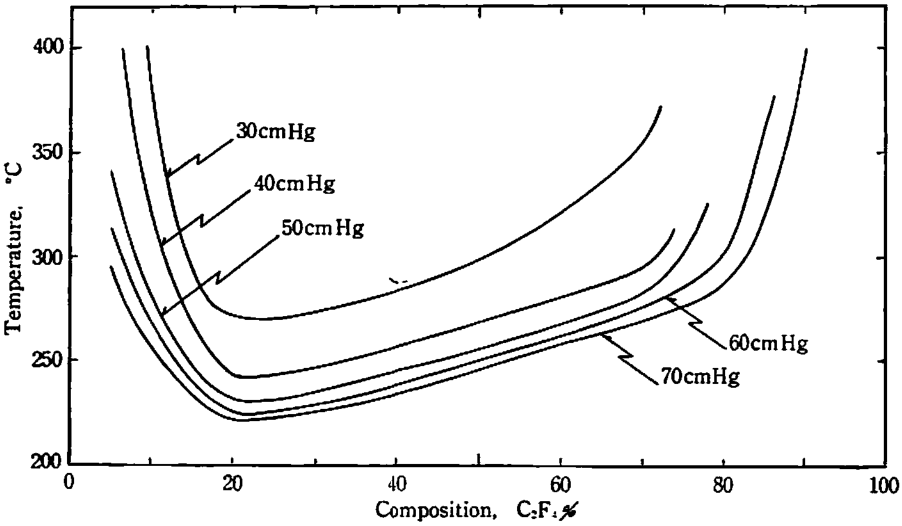

Fig. 1. 11 Relations between temperature and composition of explosion limits at specified pressures in C_2F_4-air mixtures

The reaction products after the explosion reaction consisted chiefly of white substances (probably polymerization products) and little of carbon contrary to the case of C_2F_4-O_2 mixtures.

The typical changes of pressure with time recorded by the ink writing oscillograph are depicted in Fig. 1. 13. Curve a shows an abrupt rise of pressure due to a normal explosion reaction with luminous blue or orange flame. Curve b corresponds to a two-stage ignition in which a pale blue flame occurring at the beginning is immediately changed to either a luminous

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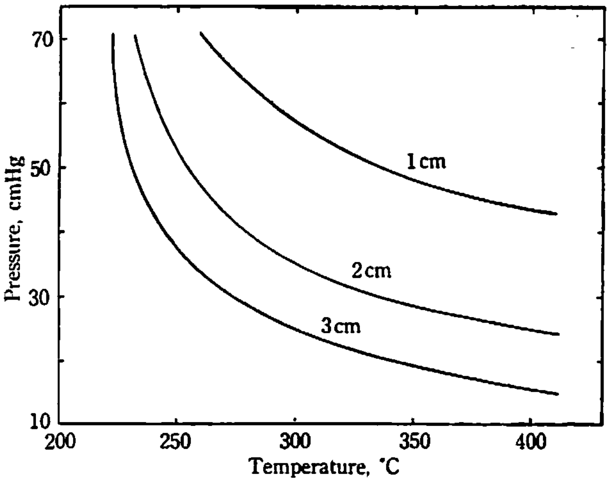

Fig. 1. 12 Effect of vessel diameter on explosion limits in C_2F_4(20%)-air mixture

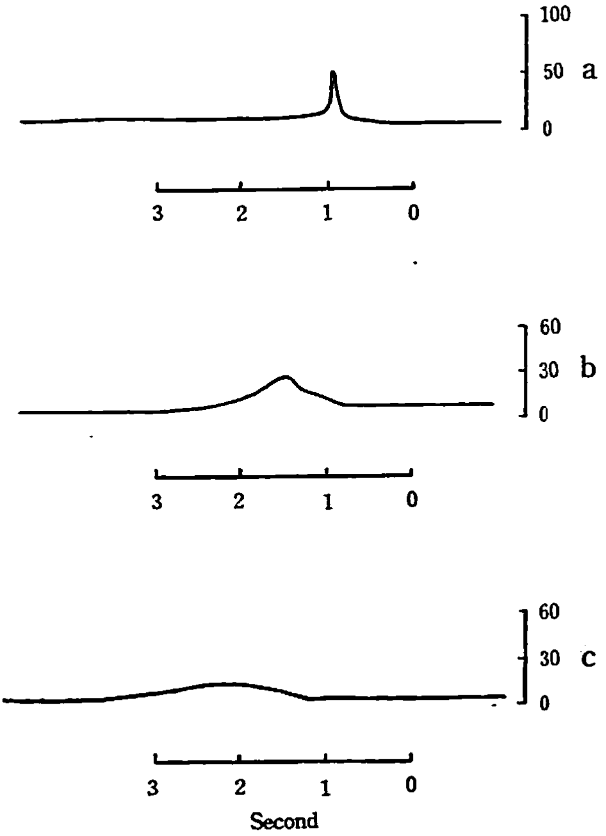

Fig. 1. 13 Typical pressure-time curves in C_2F_4-air mixtures Ordinate: $\triangle P$ in cm Hg

Curve a Normal explosion with luminous flame

Curve b Explosion with two-stage flame

Curve c Mild explosion with pale-blue flame in the region in Fig. 1. 14

blue or orange flame chiefly according to the composition of mixtures. Pressure increases of the second stages are often found to be more violent than that shown in this curve. Curve c represents a mild explosion with a feeble pale-blue flame.

The region where the pale-blue flame (the case of curve c) made its appearance at 290°C was determined by the automatic pressure recorder together from the observation of flame is shown in Fig. 1. 14. In comparison with Fig. 1. 8 it is found that with all compositions the

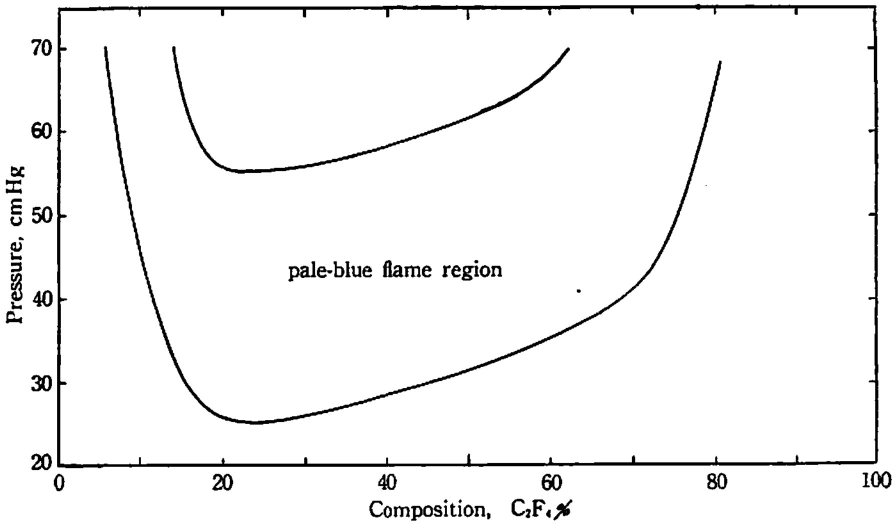

Fig. 1. 14 Pale-blue flame region in C_2F_4-air mixtures at 290°C

pressure ranges between the upper and the lower limits of the pale-blue flame region of the C_2F_4-air mixtures are much wider than those of C_2F_4-O_2 mixtures.

Considerations

In order to elucidate the effect of the foreign gas N_2, the limiting explosion pressures and compositions of C_2F_4-air mixtures at temperatures of 270°C and 400°C were converted into those of C_2F_4-O_2 mixtures by calculation subtracting the partial pressures of nitrogen. These calculations give the broken lines in Fig. 1. 3 which shift little from the corresponding full lines, and lead to the conclusion that the effect of nitrogen should be negligible.

Concerning the pale-blue flame region, however, the different result is obtained from the consideration that at the composition of equal mole ratio of C_2F_4 to O_2 with the mixtures of C_2F_4-O_2 and C_2F_4-air, that is, C_2F_4 (55%)-O_2 and C_2F_4 (20%)-air, the pressure ranges of pale-blue flames in Fig. 1. 8 and in Fig. 1. 14 are 6 cm Hg and 10.8 cm Hg respectively if the nitrogen pressure of the latter is removed. The pressure range becomes much wider than the increase in the pressure due to the addition of nitrogen.

Pale-blue flames in these regions have the properties that (1) the color is pale-blue, (2) the speed of flame propagation is slow (several centimeters per second), (3) pressure increase accompanied is slight and mild, and the variation with time is smooth and (4) the phenomena of two-stage ignitions being observed under slightly severer conditions than those of pale-blue flames, it seems that pale-blue flames occur in the early stages of normal flames. Though these properties may be those of cool flames, such closed areas as generally found on cool flames are not obtained in the present experiments because the upper limits of pale-blue flame regions cannot be determined by the oscillograph owing to very short induction period at higher temperatures.

Detailed observation of the curves of pressure change with time in Figs. 1. 7 and 1. 13 gives the fact that in the initial stages of explosions the pressure curves a are convex to the time axis and the curves c corresponding to the mild explosions with pale-blue flames are concave to the axis. These facts might be understood[4] if assumed that such reactions as curves a proceed by branching chains and such as c by non-branching straight chains, whereas as to the cool flame reaction, there is a view that it proceeds by straight chains[5].

If the induction period is assumed to be the time necessary for the production of a definite concentration of intermediates, the following relation can be obtained between absolute temperature T and induction period τ*.

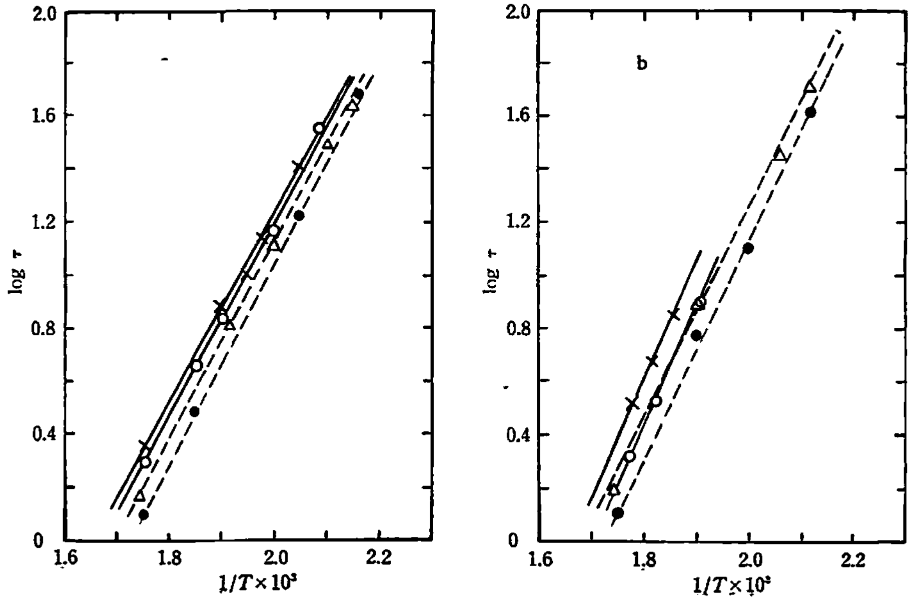

Fig. 1. 15 Relations between $\log\tau$ and $1/T$ in C_2F_4–O_2 mixtures

a
× 20% C_2F_4, 30 cm Hg
○ 20% C_2F_4, 40 cm Hg
△ 60% C_2F_4, 30 cm Hg
● 60% C_2F_4, 40 cm Hg

b
△ 40% C_2F_4, 30 cm Hg
● 40% C_2F_4, 40 cm Hg
× 80% C_2F_4, 30 cm Hg
○ 80% C_2F_4, 40 cm Hg

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4) J. Osugi, *This Journal*, Commemo. Vol. 76 (1946)
F. S. Dainton, *Chain reaction*, Methuen, p. 82 (1956)

5) B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases*, Academic Press Inc., p. 142 (1951)

* Assuming that the rate of the reaction producing intermediates is first order in the equation of Arrhenius $k=Ae^{-E/RT}$, τ is proportional to $\frac{1}{k}$. From these relations, the equation (1) is derived.

$$\ln\tau=\frac{E}{RT}+\text{constant}. \qquad (1)$$

This relation, as shown in Figs. 1. 15 and 1. 16, holds both with C_2F_4-O_2 and with C_2F_4-air

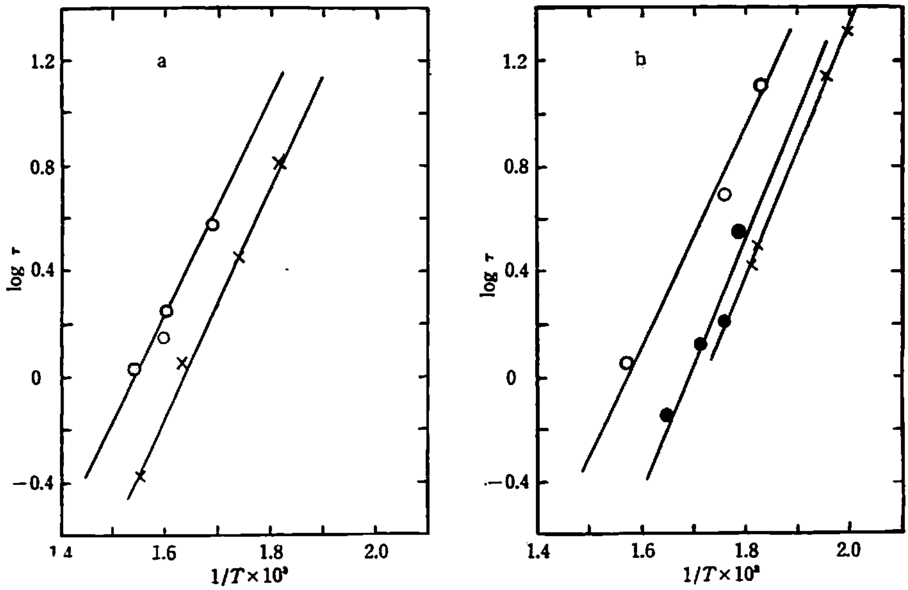

Fig. 1. 16 Relations between log τ and 1/T in C_2F_4-air mixtures

a ○ 5% C_2F_4, 50 cm Hg
× 10% C_2F_4, 50 cm Hg

b ○ 20% C_2F_4, 30 cm Hg
● 80% C_2F_4, 70 cm Hg
× 20% C_2F_4, 70 cm Hg

Table 1 Activation energies
(vessel diameter: 3 cm, C_2F_4-O_2 mixtures)

initial pressure cm Hg	composition C_2F_4 %	activation energy kcal/mole
30	20	17.8
30	40	18.1
30	60	17.6
30	80	22.6

Table 2 Activation energies
(vessel diameter: 3 cm, C_2F_4-air mixtures)

initial pressure cm Hg	composition C_2F_4 %	activation energy kcal/mole
30	20	18.5
50	5	18.6
50	10	19.8
70	20	21.7
70	80	21.4

mixtures. Calculation of apparent activation energies from the slopes of straight lines in these relations gives the values in Tables 1 and 2. With the mixtures of C_2F_4 (50%)–O_2 and C_2F_4 (20%)–air which have nearly the same mole ratios of C_2F_4 to O_2, the values of activation energies have little difference.

In a thermal explosion the condition of which is that the rate of temperature rise due to evolution of reaction heat exceeds the rate of cooling, the following relation can be derived[6].

$$\ln\frac{P}{T}=\frac{E}{2RT}+\text{constant}. \tag{2}^*$$

With the mixtures of C_2F_4–O_2 and C_2F_4–air the plots of $\log\frac{P}{T}$ against $\frac{1}{T}$ give nearly straight lines of slopes equal to $\frac{E}{2RT}$ only within the narrow temperature range. And the values of E calculated from the slopes of straight lines are nearly 10kcal/mole smaller than those shown in Tables 1 and 2. So the relation (2) does not hold satisfactorily.

As to the pressure limits of C_2F_4–air mixtures at definite temperatures if designated the partial pressures of tetrafluoroethylene, oxygen and nitrogen as $P_{C_2F_4}$, P_{O_2} and P_{N_2} respectively, the values of $P_{O_2}P_{C_2F_4}\left(1+\frac{P_{N_2}}{P_{O_2}+P_{C_2F_4}}\right)$ are almost constant for all compositions. Moreover, examining the effects of vessel diameters, the following empirical formula is obtained and the examples of the values are shown in Table 3.

$$P_{O_2}P_{C_2F_4}\left(1+\frac{P_{N_2}}{P_{O_2}+P_{C_2F_4}}\right)d^{\frac{3}{2}}=\text{constant}. \tag{3}$$

Table 3 Values of $P_{O_2}P_{C_2F_4}\left(1+\frac{P_{N_2}}{P_{O_2}+P_{C_2F_4}}\right)d^{\frac{3}{2}}$

temperature °C	vessel diameter cm	$P_{C_2F_4}$ cm Hg	P_{O_2} cm Hg	$P_{O_2}P_{C_2F_4}d^{\frac{3}{2}}\left(1+\frac{P_{N_2}}{P_{O_2}+P_{C_2F_4}}\right)^{**}$
270	1	13.7	11.0	4.2×10^2
	2	8.5	6.8	4.6 〃
	3	6.1	4.9	4.3 〃
300	1	11.4	9.1	2.9 〃
	2	7.0	5.6	3.1 〃
	3	4.9	3.9	2.8 〃
350	1	9.5	7.6	2.0 〃
	2	5.6	4.5	2.0 〃
	3	3.7	3.0	1.6 〃

Assuming $P_{N_2}=0$ in the equation (3), it becomes

$$P_{O_2}P_{C_2F_4}=\text{constant}. \tag{4}$$

This relation, however, is found not to be the case with C_2F_4–O_2 mixtures. In order to

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[6] N. Semenoff, *Z. Physik*, 48, 571 (1928)

* P and T express the limiting explosion pressure and temperature.

** Units of pressure and diameter are cm Hg and cm respectively.

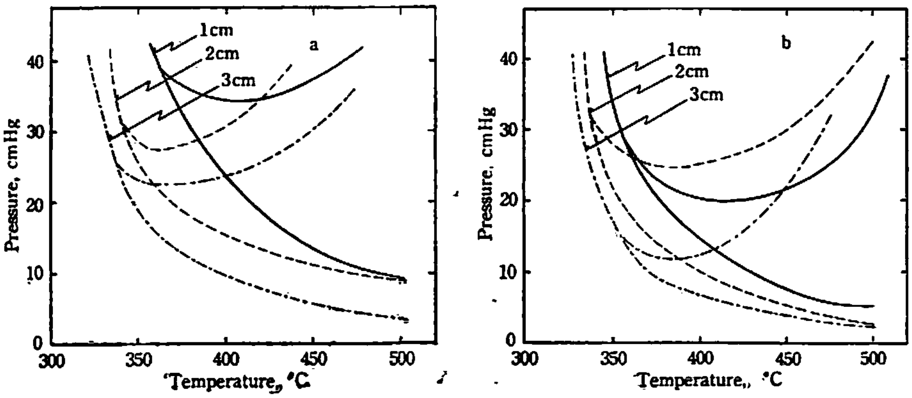
explain the relation (3) by the chain mechanism of hydrocarbon combustions, it should be necessary to modify the elementary reactions assumed in the derivation of equation (3)[7] considering that the triple collision process might be included. It may be considered that inapplicability of the relation (4) to C_2F_4–O_2 mixtures is due to the lower total pressures and to the different influence of the pressures upon the mechanism of chain branching, propagating and terminating processes.

Compared with equation (2), the relation (3) may be rather applicable to this explosion.

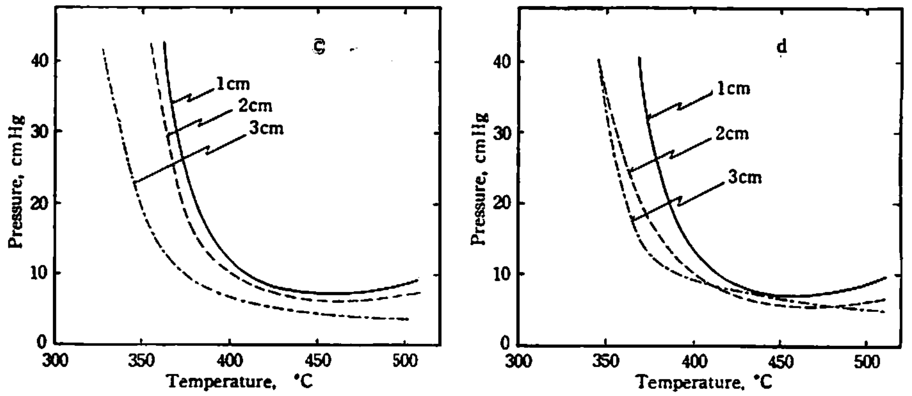
Part II Explosive Phenomena of Gaseous Acetylene-Oxygen Mixtures

Results

The explosion limits of gaseous C_2H_2–O_2 mixtures were determined at specified compositions, using glass reaction vessels of 1 cm, 2 cm and 3 cm diameters, and are shown in Figs. 2. 1 a (95% C_2H_2), 2. 1 b (90% C_2H_2), 2. 1 c (80% C_2H_2) and 2. 1 d (70% C_2H_2). The experiments on the



a C_2H_2 (95%)–O_2 b C_2H_2 (90%)–O_2



c C_2H_2 (80%)–O_2 d C_2H_2 (70%)–O_2

Fig. 2. 1 a, b, c, d Relations between temperature and pressure of explosion limits at specified compositions

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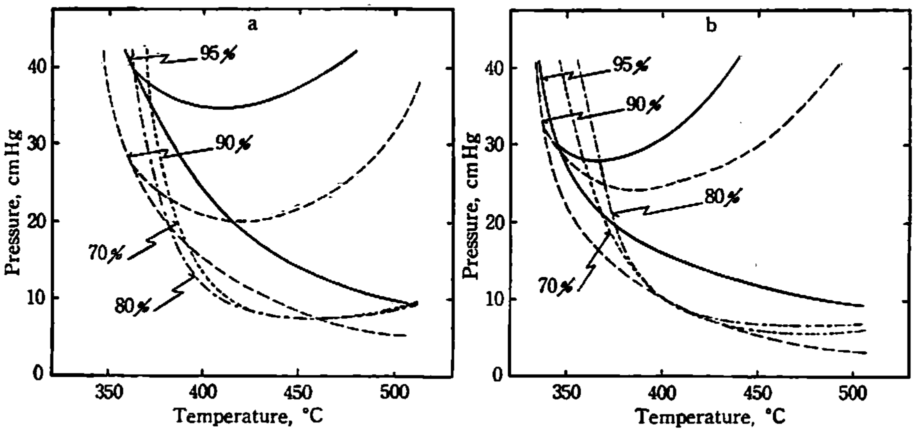
[7] K. J. Laidler, *Chemical Kinetics*, McGraw-Hill Book Co., p. 319 (1950)

mixtures containing more oxygen have short induction periods of less than 0.5 second, and are dangerous in the apparatus made of glass owing to catching fire to the reservoir.

It is remarkable as described below that the explosion regions of the mixtures containing 95% C_2H_2 and 90% C_2H_2 (Figs. 2. 1 a and b) are separated into two parts where red flames are observed in the higher part and pale-blue flames in the lower part. The minimum of the explosion limit curve shown in the higher (red flame) explosion limits has been reported in the result[2] obtained by the admission method as in the present experiment, but the regions of pale-blue flames have not yet been determined.

The color of the red flames becomes brighter with increasing oxygen content and the temperature of the flames becomes higher.

As to the effect of the diameter of the reaction vessel on the explosion limits, the limits become higher with decreasing diameter as shown in Figs. 2. 1 a, b, c and d. The effect is remar-



a vessel diameter, 1 cm

b vessel diameter, 2 cm

Fig. 2. 2 a, b Relations between temperature and pressure of explosion limits in the vessel of a definite diameter

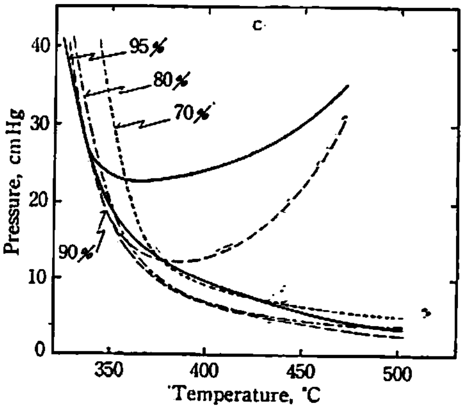


Fig. 2. 2 c Relations between temperature and pressure of explosion limits in the vessel of 3 cm diameter

kable in poor oxygen mixture in the order of 95%, 90%, 80% and 70% C_2H_2 mixtures. In other words, the effect is much remarkable in the condition where the explosion is gentle and less remarkable in the violent explosion.

The plots of the explosion limits at varying compositions in the vessel of the same diameter are shown in Figs. 2. 2 a (1 cm), 2. 2 b (2 cm) and 2. 2 c (3 cm). Considering these diagrams, the change of the limits with compositions is the most remarkable in the vessel of 1 cm diameter and the lower explosion limits are nearly coincident irrespective of the compositions in the vessel of 3 cm diameter.

The plots of the explosion limits (pressure) against compositions at a definite temperature (400°C) are shown in Fig. 2. 3. In the additional experiments on pure acetylene and 98% acetylene mixture, the red and pale-blue flames were not observed even in the severe condition (530°C, 40 cm Hg), so the curves in Fig. 2.3 may rise upwards on the left side. In addition, the regions

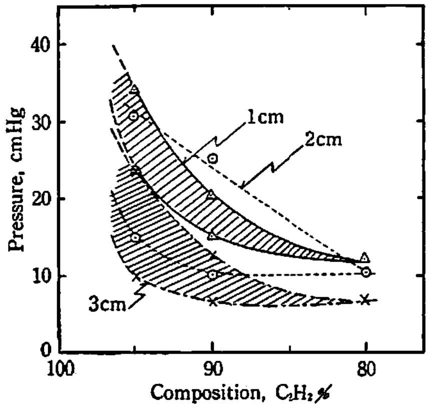


Fig. 2. 3 Relations between pressure and composition of explosion limits at 400°C

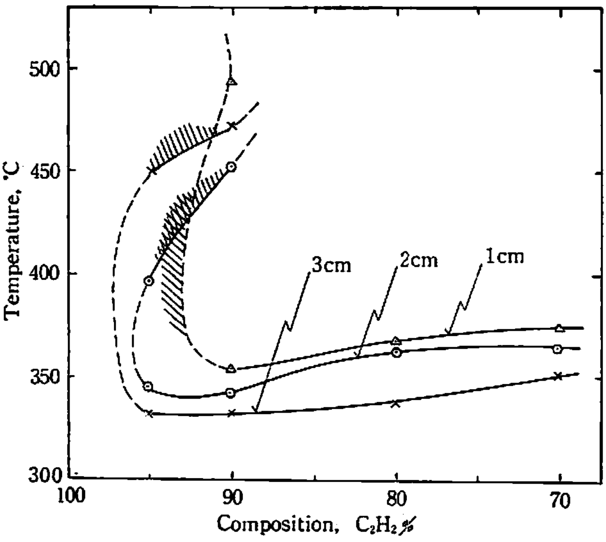


Fig. 2. 4 Relations between temperature and composition of explosion limits at 30 cm Hg

between two curves of each diameter (shaded parts in 1 cm and 3 cm diameters) are the regions of the pale-blue flames.

The plots of the explosion limits (temperature) against compositions at a definite pressure (30 cm Hg) are shown in Fig. 2. 4. The broken curves are also predicted from the additional experiments described above.

Considerations

On the pale-blue flames The pale-blue flames are observed in the gentle explosions of 95% and 90% acetylene mixtures. The lower limits of the pale-blue flames come near to the limits of oxygen rich mixtures as shown in Figs. 2. 2 a, b and c. In the regions of pale-blue flames, the violent explosion does not occur owing to the scanty of oxygen content, and the gentle explosive reaction gives rise to the pale-blue flame.

As the induction period becomes shorter with increasing temperature, the records of pressure-time curves can be obtained only in the range of relatively low temperature owing to the difficulty of experimental manipulation. Fig. 2. 5 shows the pressure-time curves at specified compositions.

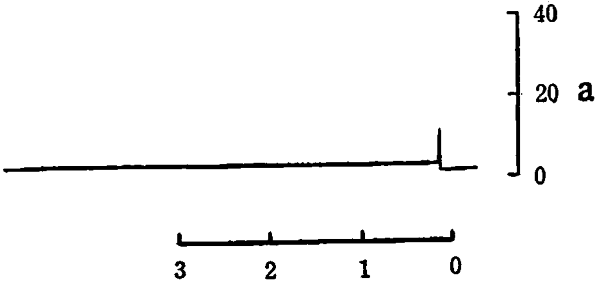
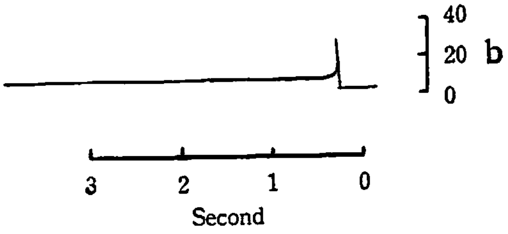


Fig. 2. 5 a, b Typical pressure-time curves at specified compositions of C_2H_2-O_2 mixtures
Ordinate: $\triangle P$ in cm Hg

Curve a Normal explosion with red flame in C_2H_2(70%)-O_2 mixture



Curve b Normal explosion with red flame in C_2H_2(80%)-O_2 mixture

The mixtures of 70% C_2H_2 (Curve a) and 80% C_2H_2 (Curve b) explode violently without pale-blue flames. The mixture of 95% C_2H_2 (Curves c, d and e), however, shows the different forms of pressure-time curves. As described in Part I on C_2F_4 mixtures, the curve of initial pressure increase is concave to the time axis in the region of pale-blue flames (Curve e), but convex to the time axis in the region of red flames (Curve c). And in the intermediate region, the two-stage ignition where the color of the flame changes from blue to red is confirmed by visual observation, but the pressure-time curve (Curve d) does not prove to be the two-stage ignition. The reason

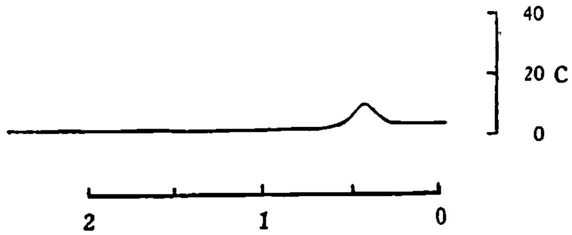
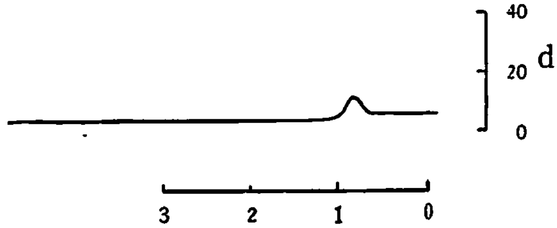
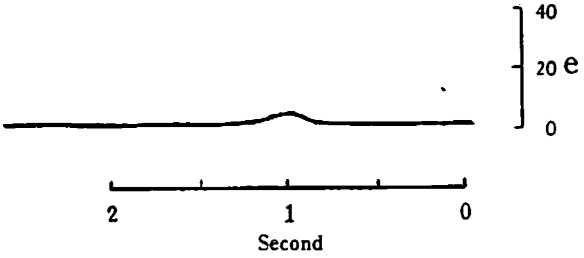


Fig. 2. 5 c, d, e Typical pressure-time curves at specified composition of C_2H_2-O_2 mixtures
Ordinate: ΔP in cm Hg

Curve c Normal explosion with red flame in C_2H_2(95%)-O_2 mixture



Curve d Explosion with two-stage flame in C_2H_2(95%)-O_2 mixture



Curve e Mild explosion with pale-blue flame in C_2H_2(95%)-O_2 mixture

for this may be considered that the heat of reaction is considerably large even in pale-blue flame and does not differ so much from that in red flame, which may be also due to the rapidity of the explosion.

The pale-blue flames are found, accordingly, in the gentle explosions and form the previous stages of the red flames. These natures of the pale-blue flames are the same as those in the case of C_2F_4 and may be considered to be so-called cool flames.* And the pale-blue flames are considered to be found in non-branching chain reaction[5], so the pressure-time curve may become concave to the time axis[4]. In addition, the pressure-time curve in the high temperature range of pale-blue flame region could not be recorded owing to the short induction period. And the experiment was not performed in the high temperature range over 500°C. So we can not predict how to be the region of pale-blue flames in high temperature range.

The explosive reaction may be assumed to be thermal in apparent character in the range shown in Figs. 2. 1 a~2. 1 d where the relations between pressure and temperature in the explosion limits are shown. The plots of $\log P/T$ against $1/T$ are shown in Fig. 2. 6 where the linear

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* During the time of printing, we found a report concerning cool flames of C_2H_2-O_2 mixtures (*Combustion and Flame*, **1**, 99 (1957)).

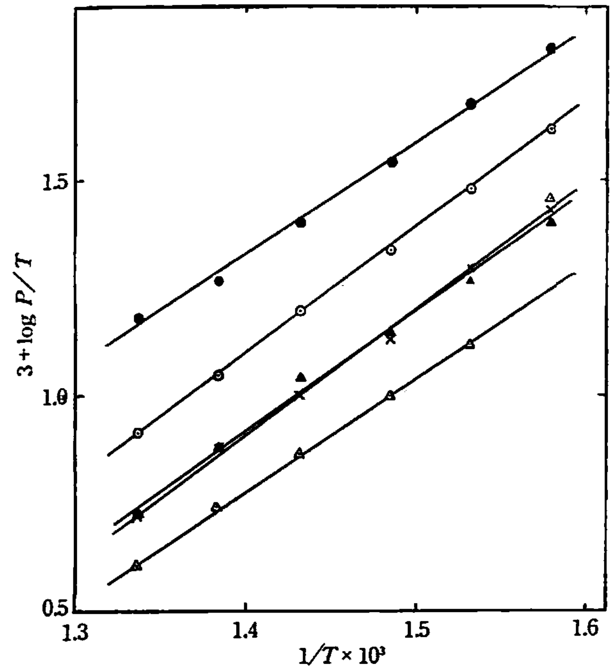

Fig. 2. 6 Relations between log P/T and $1/T$ of explosion limits

⊙ 90% C_2H_2, vessel dia. 1 cm
× 90% C_2H_2, vessel dia. 2 cm
△ 90% C_2H_2, vessel dia. 3 cm
● 95% C_2H_2, vessel dia. 1 cm
▲ 95% C_2H_2, vessel dia. 3 cm

relations are obtained in the lower limits of the mixtures of 95% and 90% C_2H_2. The linear relations also hold in the mixtures of 80% and 70% C_2H_2 in the case of 3 cm vessel diameter. From the slopes of these linear relations, the apparent activation energy may be estimated to be about 26 kcal.

The explosion limits of C_2H_2–air mixtures cited from literature[2)] were examined by plotting log P/T against $1/T$. The linear relations also hold in the low temperature range. The apparent activation energy calculated, being estimated to be about 28 kcal, agrees with the above value.

From the explosion limits of C_2H_2–air mixtures cited, the relation of

$$P_{C_2H_2}P_{O_2}\left(1+\frac{P_{N_2}}{P_{C_2H_2}+P_{O_2}}\right)=\text{constant}$$

was examined as in the case of C_2F_4 mixtures. The constancy of the relation is not good as compared with the case of C_2F_4 mixtures.

The explosive reactions of C_2H_2 with oxygen or air may be considered to be thermal in apparent character in the present experimental ranges.

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