STUDIES ON THE EXPLOSIONS UNDER HIGH PRESSURES, IV

The Explosions of Tetrafluoroethylene
mixed with Oxygen or Air

By Hiroshi Teranishi

Introduction

Tetrafluoroethylene is recently of industrial importance as a monomer of tetrafluoroethylene resin (Teflon). It is normally a gas, which boils at $-76.3°C$ and has a critical temperature of $33.3°C$ and a critical pressure of 38.9 atm. Although the gas can be stored at the temperature of solid carbon dioxide for substantial lengths of time without any polymerization, it would polymerize slowly at room temperature, except when the gas is extremely pure or proper antioxidant-type inhibitors are mixed to prevent the polymerization[1]. The presence of oxygen, even very small amount of it, is responsible for the polymerization reaction. Under controlled conditions of high temperature and high pressure, tetrafluoroethylene may be converted into a high molecular weight polymer *via* the exothermic polymerization reaction. Pure, uninhibited tetrafluoroethylene, however, would spontaneously polymerize with violence, especially under super-atmospheric pressure. The high temperatures generated by the uncontrolled polymerization can lead to an explosive polymerization and can break the container.

When tetrafluoroethylene contains a small amount of oxygen in it, spontaneous polymerization would be considerably promoted and it would become much more difficult to control the reaction. Furthermore, it would be expected that the explosive combustion of tetrafluoroethylene would take place under the conditions of such high temperature and high pressure as would be generated by the uncontrolled violent polymerization.

On the explosive combustion of tetrafluoroethylene, however, nothing has been reported in literature, and no basic data is found for handling this material safely in its industrial polymerization processes. Therefore, the explosion of tetrafluoroethylene mixed with oxygen or air was investigated in our laboratory and the results of the experiment under sub-atmospheric pressure were reported previously by Kiyama, Osugi and Kusuhara[2].

In the present paper the author will report on the results of the experiments performed in order to explain the thermal explosion of the gas mixtures under the conditions of pressure up to $100 \, kg/cm^2$.

Experimentals

Apparatus and procedure   In the present experiment explosion limits were studied by

1) E. I. du Pont de Nemours and Co., *Brit. Pat.* 620, 296
2) R. Kiyama, J. Osugi and S. Kusuhara, *This Journal*, 27, 22 (1957)

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means of the "admission" method, in which gaseous samples were made to flow into a hot vessel evacuated. The layout of the apparatus is shown in Fig. 1 and Photos. 1 and 2.

A steel reservoir A is 78 mm and 54 mm in outer and inner diameters, 3 m in length and about 7 liters in capacity, and into it pure uninhibited tetrafluoroethylene C_2F_4 is compressed up to about 10 kg/cm². In order to prevent the dangerous spontaneous polymerization, the two safety-valves S_1 and S_2 are employed. The former is of the spring-loaded cone type, being set so as to relieve the gas whose pressure would attain to over 20 kg/cm². The latter is an automatic relief valve which is opened by means of a motor when the gas temperature elevates over 40°C. The gas reservoir is connected by a steel pipe to the laboratory of the second floor. B and C are oxygen and air bombs respectively. D is a steel vessel for gas mixing, having 4 cm or 6 cm inner diameter and 125 cc or 900 cc capacity respectively. A steel ball whose diameter is about two thirds of the vessel diameter is put in each vessel in order to promote the gas mixing. An intensifier E is 250 cc or 500 cc in capacity, in which the gas mixture is compressed to a desired pressure by means of an air driven piston. The reaction vessels F used are those made of mild steel having 1 cm, 2 cm and 4 cm diameters and 4.0 cc, 6.3 cc and 50 cc capacities respectively. The reaction vessel is heated by an electric furnace H_1 and the temperature is measured and controlled by means of two thermocouples which are inserted in the holes bored in the wall of the reaction vessel. The membrane pressure gauge I is constructed by a spring steel membrane (1.2 ~ 5.0 mm in thickness and 44 mm in effective diameter *cf.* Table 1) and a mirror which rotates propor-tionally to the deflection of the membrane due to pressure. The pressure is (i) measured from the displacement of a light spot N reflected from the mirror, (ii) recorded on a smoked paper of rotating drum J like a seismograph whose pen is connected by a lever with the membrane, and (iii) recorded with time by an electromagnetic oscillograph which records the change of electric resistance of a strain gauge cemented on the membrane[3]. K is a glass vessel of gas mixture, L a Toepler pump, M a mercury manometer, and $G_1 \sim G_3$ are Bourdon type pressure gauges. In order to prevent the liquefaction of C_2F_4, the intensifier E and steel pipes which contain the compressed gas mixture are heated above 33.3°C, the critical temperature of C_2F_4, by means of an electric heater H_2.

C_2F_4–O_2 or C_2F_4–air mixtures of desired compositions* are prepared in the vessel D under super-atmospheric pressure or in the glass vessel K under sub-atmospheric pressure. After complete mixing, the gas mixtures are made to flow, or compressed by means of the Toepler pump L into the intensifier E. Then the gas mixtures, being compressed to certain pressures by the compressed air of the bomb C, are made to flow into the reaction vessel which is previously evacuated and heated to the experimental temperature. When explosions take place, their occurrences are per-ceived by their sounds, observed by very rapid and discontinuous displacements of the light spot and confirmed by the pressure curves recorded.

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3) R. Kiyama, J. Osugi and H. Teranishi, *This Journal*, 24, 81 (1954)
*   Throughout this paper, composition will be expressed by volume percentage of tetrafluoroethylene.

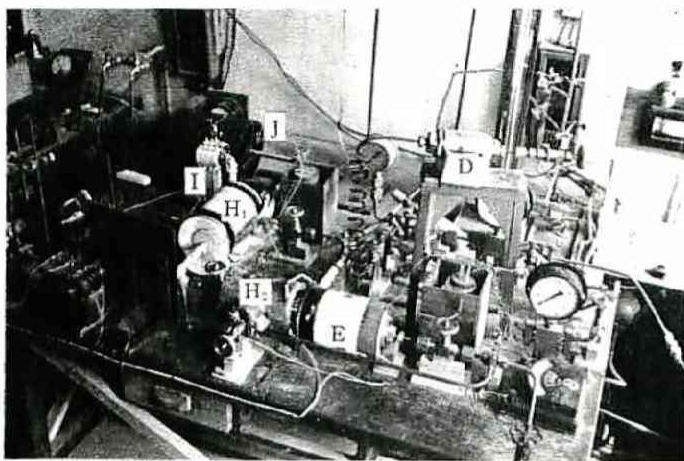Studies on the Explosions under High Pressures, IV

Photo. 1 Apparatus for high
pressure explosion

Photo. 2 Reservoir and safety device of
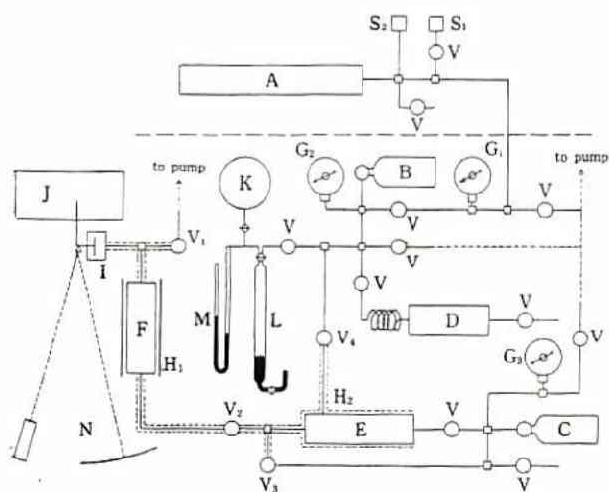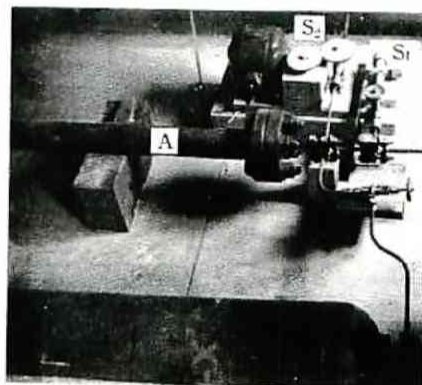tetrafluoroethylene gas under
high pressure

Fig. 1 Layout of the apparatus

A : C_2F_4 gas reservoir
B : O_2 bomb
C : air bomb
D : steel vessel for gas mixing
E : intensifier
F : reaction vessel
G_1, G_2, G_3 : Bourdon type pressure gauges
H_1, H_2 : electric furnaces
I : membrane pressure gauge
J : pressure recorder
K : glass vessel for gas mixing
L : Toepler pump
M : mercury manometer
N : light source and scale
S_1, S_2 : safety-valves
V : high pressure valves

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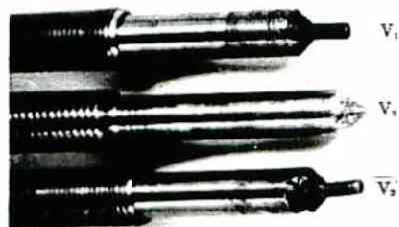Photo. 3 Spindles of valves V_1, V_2 and V_3 abraded by the detonations

Photo. 4 Steel pipe bursted by the detonation (6.0 and 1.6 mm in outer and inner diameters respectively.)
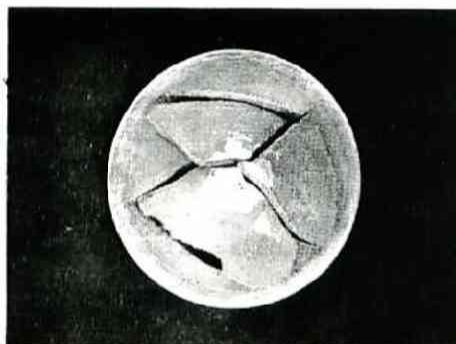

Photo. 5 Spring steel membrane (3.0 mm in thickness) ruptured by the detonation

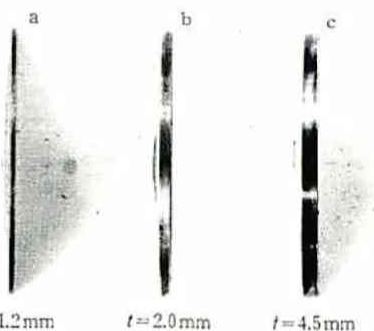$t = 1.2$ mm $t = 2.0$ mm $t = 4.5$ mm

Photo. 6 Spring steel membranes deformed (a is 1.2 mm, b 2.0 mm and c 4.5 mm in thickness t respectively.)
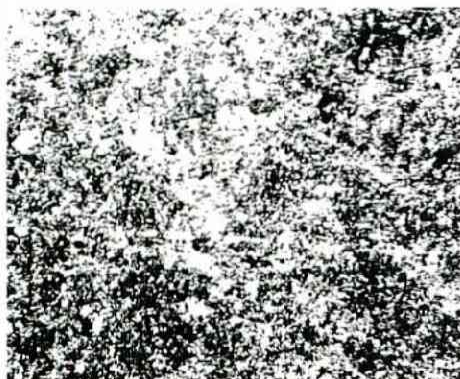

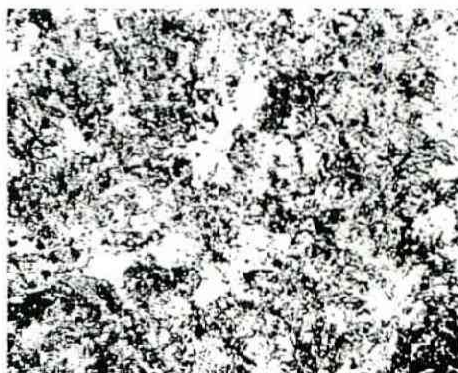Photo. 7 Photomicrograph of the membrane before plastic deformation

Photo. 8 Photomicrograph of the membrane after the plastic deformation (The test piece was taken from the ruptured membrane shown in Photo. 5.)

Table 1   Properties of the spring steel used for the membrane

	Composition %		Hardness Number		Mechanical Strength kg/cm²			
			Vickers	Brinell	σ_e	σ_y	σ_u	
Before plastic deformation	C ··· 0.77 Cu···0.04	Mn···0.36 Ni···0.04	310	295	8293	8790	9980	Troostite (Photo. 7)
After plastic deformation*	Si ··· 0.16 Cr···0.11	P ··· 0.007 S···0.004	325	307		9140	10400	" (Photo. 8)

∗   The test piece was taken from the ruptured membrane shown in Photo. 5.

Materials   Tetrafluoroethylene C_2F_4 used is prepared by pyrolysis of chlorodifluoromethane (Freon–22, $CHClF_2$), and purified by fractionation by means of a Podbielniak-type distiller. The distillation curve is shown in Fig. 2.   The distillate at $-76 \sim -75°C$ is liquefied again by liquid air, and after evacuation the liquid C_2F_4 is evaporated and reserved in a cylindrical glass vessel or compressed into a steel bomb up to about 10 kg/cm². The pure C_2F_4 thus obtained showed no polymerization under atmospheric pressure and at 10 kg/cm² pressure a few per cent decrease of the pressure was observed for several weeks in winter and that of about 50 per cent in summer.

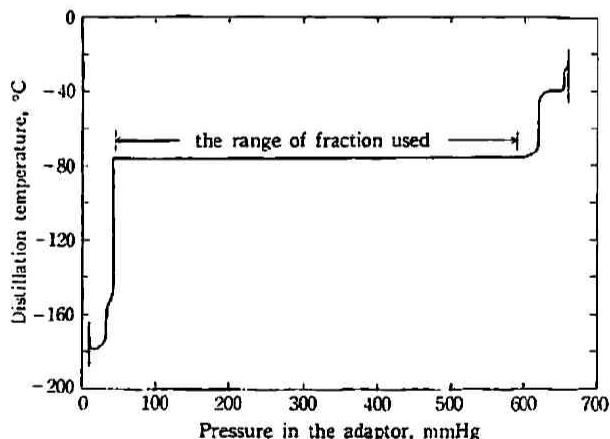Oxygen used is that from commercial bomb having about 99.4 per cent purity.

Fig. 2   Distillation curve of tetrafluoroethylene

Results

a)   **Explosion of tetrafluoroethylene-oxygen mixtures**

As described in the previous report on the explosion under sub-atmospheric pressure[2], when C_2F_4–O_2 mixtures are heated slowly at a definite rate (about 1 deg/min), the curves representing the pressure-temperature relations change their inclinations first at about 150°C and secondly at about 200°C. It is suggested from these facts that some reaction between C_2F_4 and O_2 should take place at these temperatures.   And actually the minimum explosion temperature of the C_2F_4–O_2 mixture was found at about 200°C.   As shown in the case of acetylene explosion, the

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temperatures of explosion limits of hydrocarbons-oxygen mixtures are generally decreased as increasing their total pressures[4.5]. If the same behavior would also be shown in the C_2F_4–O_2 mixture, it is supposed that the explosion temperature under higher pressure would decrease at least to about 150°C. Therefore the temperatures of explosion limits of C_2F_4–O_2 mixtures were measured at the total pressures of 2, 7, 10, 50 and 100 kg/cm². The results of the experiment using the reaction vessels of 1 cm and 2 cm diameters are shown in Figs. 3a and 3b respectively.

In the present experiment, the observation of explosion has been done for 5 minutes immediately after the admission of the gas mixture. This was based on the results of the preliminary test, that is, the gas mixture which showed no explosion for 5 minutes did not explode during the continuous measurement of 50 hours. In the experiment under 7 kg/cm² or less pressures, the gas mixtures were prepared in the glass vessel (K) and were kept for more than 12 hours for complete mixing. On the other hand, in the experiment under 10 kg/cm² or higher pressures, the steel vessel (D) was employed and the gases were completely mixed by the removal of the balls. Under the same conditions, however, the two mixtures prepared by both methods showed good coincidence in their explosion limits.

When virgin surface of the reaction vessel is used, reproducible results are obtained after the first explosion. The products of the preceding explosion may affect the explosion limits and, however, by the evacuation of the vessel for about half an hour after a run, no effect was observed (on the limits) even if the reaction vessel contained some amount of carbon produced in the preceding run.

Fig. 3a Relations between temperature and composition of explosion
limits at specified pressures in C_2F_4–O_2 mixtures (vessel diameter: 1 cm)

4) R. Kiyama, J. Osugi and H. Teranishi, *This Journal*, 24, 41 (1954)
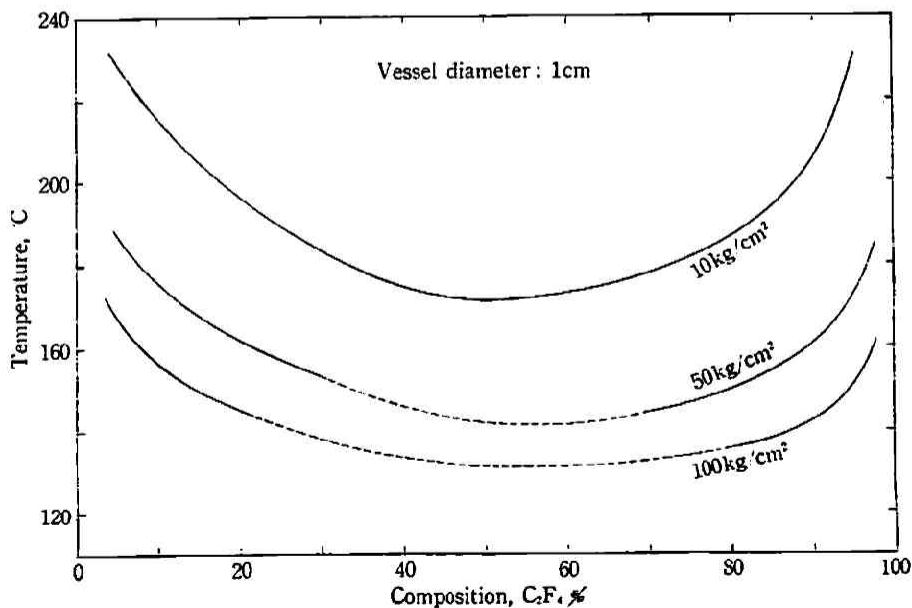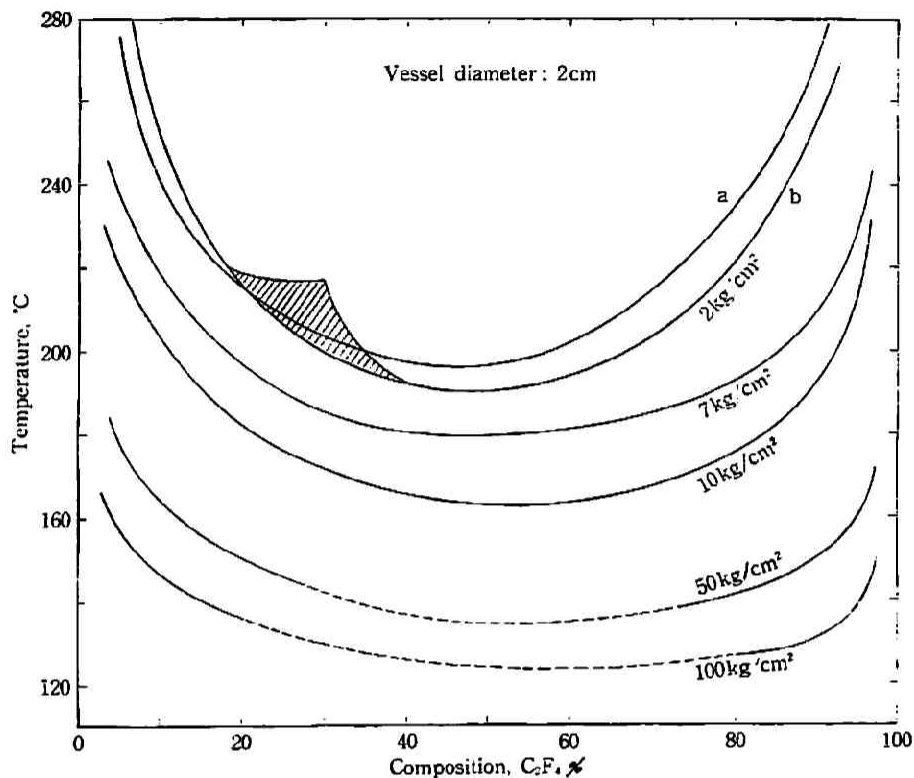5) H. Teranishi, *ibid.*, 25, 58 (1955)

Fig. 3b   Relations between temperature and composition of explosion
limits at specified pressures in C_2F_4–O_2 mixtures (vessel diameter: 2 cm)

*Curve a shows the explosion limits under 50mmHg pressure in the glass
vessel of 3cm diameter reported in the previous paper*[2].

In order to compare the results with those under lower pressure, the curve a in Fig. 3b is cited from the previous report[2] and it shows the explosion limits under 50mmHg pressure in the glass vessel of 3 cm diameter. Owing to the differences on the material, inner diameter and capacity of the reaction vessel, it is, of course, impossible to discuss quantitatively but qualitative resemblance of the temperature-composition relations is shown between curve a and curve b, that is, the limits under $2 kg/cm^2$. The explosions at the shaded region in Fig. 3b are very weak and the occurrence of the explosion could scarcely be perceived either by the sound or by the displacement of the light spot, but only it could be determined from the pressure curve recorded.

As shown in Figs. 3a and 3b, the higher the total pressure of C_2F_4–O_2 mixture, the lower the temperature of its explosion limits and the wider the range of its explosive composition, and the minimum temperature of the limits under $100 kg/cm^2$ pressure is presumed to be at about $120°C$. In Fig. 4, the explosion limits are shown by isothermal curves on the pressure vs. composition diagram. At $200°C$, the minimum temperature of explosion under atmospheric pressure, the C_2F_4–O_2 mixtures of almost every composition (about 1~99% of C_2F_4) would explode under $100 kg/cm^2$.
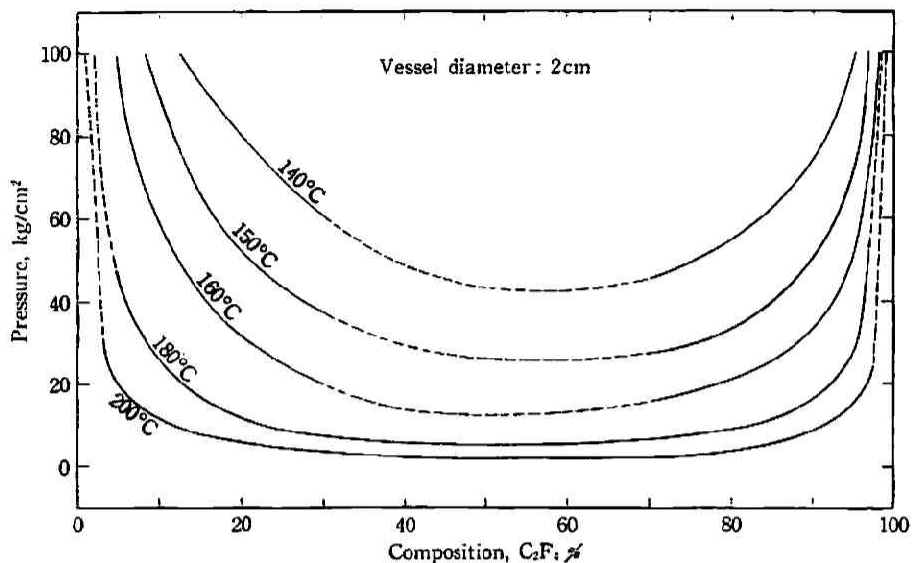
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Fig. 4 Relations between pressure and composition of explosion limits at
specified temperatures in $C_2F_4-O_2$ mixtures (vessel diameter: 2 cm)

To examine the effect of the vessel diameter, the explosion limits are measured using the
respective vessels of 1 cm, 2 cm and 4 cm diameteres, and the results under the pressure of 10 kg/cm^2
are shown in Fig. 5. The increase in vessel diameter causes the explosion temperature to be lower,
and the tendency is more remarkable in the cases of 1 cm and 2 cm diameter vessels than in those
of 2 cm and 4 cm diameters. It is supposed from the fact that even if the vessel having 5 cm or
more diameter would be used, the explosion temperature would scarcely be affected, conforming
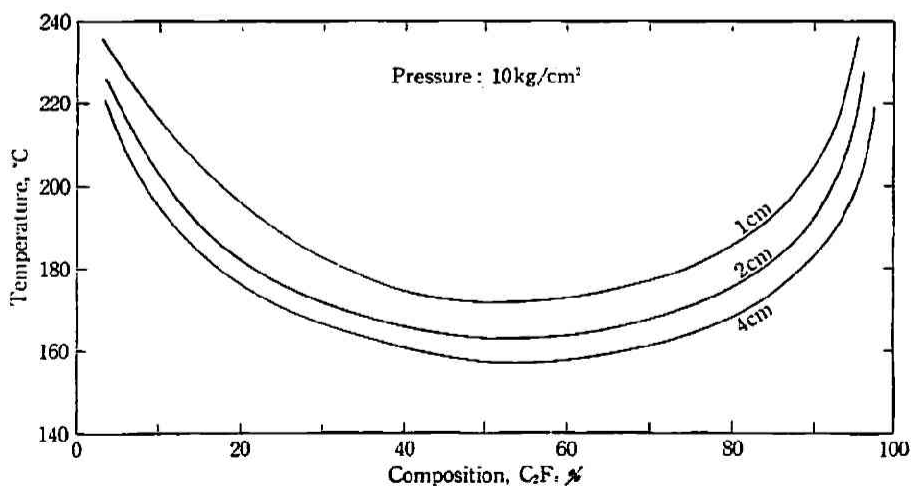to the general tendency of explosion phenomena[6]. As shown in Fig. 6, the pressure *vs.* temperature

Fig. 5 Effect of vessel diameter on explosion limits at the pressure of
10 kg/cm^2 in $C_2F_4-O_2$ mixtures

6) A. G. White, *J. Chem. Soc.*, **121**, 1244 (1922); **125**, 2387 (1924)

curve	composition C₂F₄ ％	vessel dia.
a	5	
b	10	1 cm
c	20	
a'	5	
b'	10	
c'	20	2 cm
d'	30	
e'	50	

curve	composition C₂F₄ ％	vessel dia.
g	80	
h	90	1 cm
i	95	
e'	50	
f'	70	
g'	80	2 cm
h'	90	
i'	95	

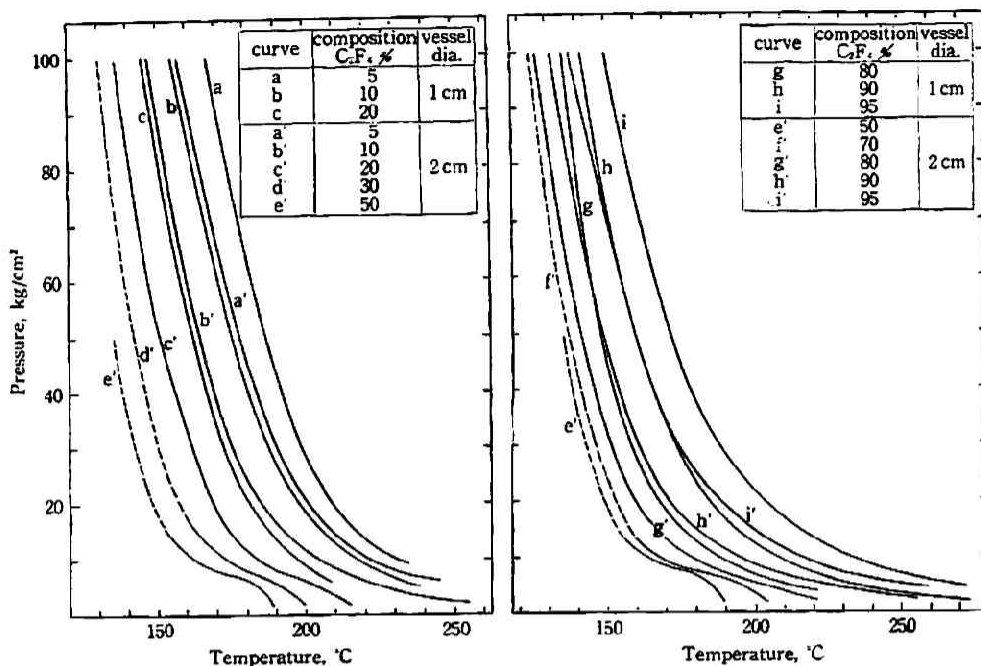Fig. 6 Relations between temperature and pressure of explosion limits at specified compositions in C₂F₄-O₂ mixtures

diagrams of the explosion limits, for the same composition, the difference of explosion limits due to the diameter is kept nearly constant for the wide range of the pressure.

The explosion limits for constant compositions are shown by the smooth exponential curves in Fig. 6, and however, the curves show some deviations from the exponential nature in the range of pressure of lower than $7 \, kg/cm^2$, especially when the composition of the mixture approaches to the equimolecular one.

Some typical pressure vs. time curves recorded for C_2F_4-O_2 mixtures are shown in Fig. 7. Curve a indicates a weak explosion, which starts and ceases within $1/10$ sec, and the maximum explosion pressure attains to only 20％ higher than the initial pressure. Such explosion would take place under the conditions that the pressure is lower than $7 \, kg/cm^2$ and the composition of C_2F_4 is lower than 10％ or more than 90％, or that the experimental pressure and temperature are near to those of the limiting conditions. In the case of the explosion under these conditions, the pressure curves happen to show two or more peaks (of pressure) in the explosion period (curves b and c in Fig. 7). and in the case of curve d, two explosions occurring separately at intervals of 0.8 sec are observed. It is considered from these facts that under such conditions as described above, the explosion would be initiated locally in the reaction vessel and it would cease without propagating to the whole gases. Curve e indicates a very rapid increase of pressure and corresponds to the normal explosion. The maximum pressure (at the instance) of the explosion would attain to about twofold or more of the initial pressure.
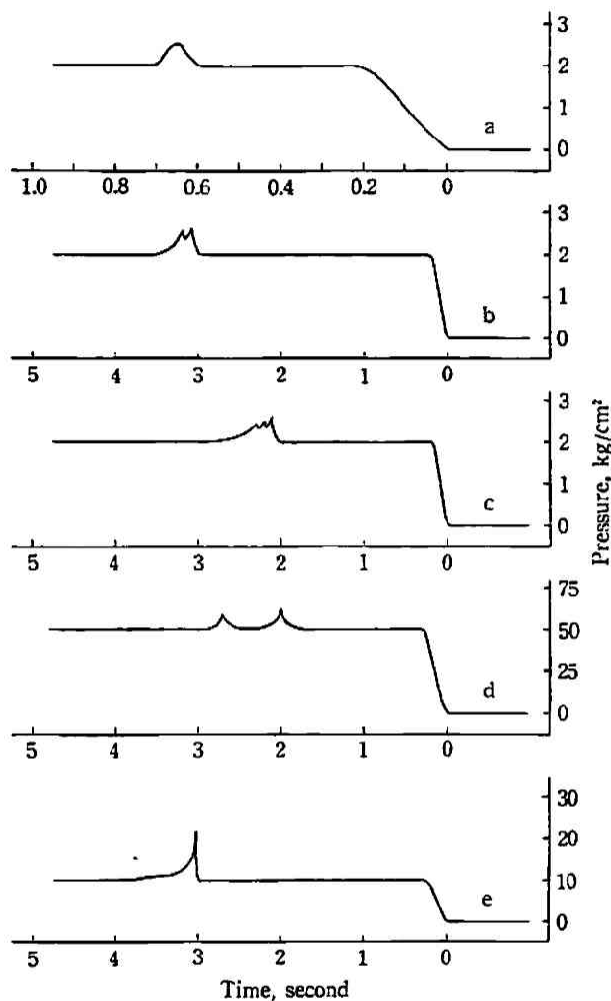
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Fig. 7 Typical pressure–time
        curves of explosions in
        C_2F_4–O_2 mixtures

Curves a, b, c and d :
              mild explosions
Curve e :
              normal explosion

b) Detonation of tetrafluoroethylene-oxygen mixtures

When the conditions become severer, that is, the pressure becomes higher, the composition approaches to be equimolecular, or the experimental temperature becomes over 10 degrees higher than

Table 2   The observed detonations of C_2F_4–O_2 mixtures

Vessel diameter cm	Experimental Conditions			Induction period sec	T_o* °C	Destruction caused
	Pressure kg/cm²	Composition C_2F_4 %	Temperature °C			
1	10	66	220	10.6	178	1.2 mm membrane was deformed (Photo. 6-a).
1	50	10	206	5.0	176	3.0 mm membrane was ruptured (Photo. 5). Pipe and valve were destructed (Photos. 3, 4).
2	50	80	151	30.6	142	Valves were destructed. (Photo. 3)
2	100	94	145	57.7	136	Pipe was destructed.

*   The temperature of explosion limit under the respective condition

those of respective explosion limits, the propagation velocity of the explosion would be considerably accelerated and would cause a detonation which could destruct the experimental apparatus. Some examples of the detonations which were of extraordinary violence and destructed the membranes of the pressure gauge, pipes and valves (Photos. 3~6) are listed in Table 2. The temperatures where the detonations took place were 9 or more degrees higher than those of the explosion limits. As observed from Photo. 4, the steel pipe (6.0 mm and 1.6 mm in outer and inner diameters respectively) was bursted, starting from its screwed part, and so, regarding the diameters as 4.6 mm (diameter at the root of the thread) and 1.6 mm, the bursting pressure P_b was calculated by Faupel's, Lamè's[7] and Leinss'[8] formulas. Although the accurate values of yield stress σ_y and ultimate tensile stress σ_u of the material are not measured, yet their values are thought to be within those listed in Table 3 respectively. On the other hand, on plastic deformation and bursting of a steel disk like the membrane, no exact formula of stress and strain is found, but as shown in Table 4,

Table 3   Calculated bursting pressure of the steel pipes
$$\left(\begin{array}{l}\text{outer diameter at screwed part, } r_o = 4.6 \text{ mm} \\ \text{inner diameter, } r_i = 1.6 \text{ mm}\end{array}\right)$$

σ_y kg/cm²	σ_u kg/cm²	Bursting pressure, P_b, kg/cm²		
		Faupel formula $\frac{2}{\sqrt{3}}\sigma_y\left[2-\frac{\sigma_y}{\sigma_u}\right]\ln K$	Lamè formula $\sigma_u\left[\frac{K^2-1}{K^2+1}\right]$	Leinns formula $\frac{\sigma_u}{[\alpha/(K-1)]+\beta}$
2000	3500	3484	2745	3456
⟨	⟨	⟨	⟨	⟨
3800	7500	6919	5881	7407

σ_y: yield stress σ_u: ultimate tensile stress
K: ratio of outer to inner diameter, r_o/r_i
α, β: parameters independent of K ($\alpha = 1.023$, $\beta = 0.467$ [8])

the observed remained strains f_{obs} (the extent of the plastic deformation at the center of membrane) attain to those over f_e, the deviation of the center corresponding to the elastic limit stress σ_e, and so the pressures acting on the membrane are recognized to be much higher than P_e, the limiting pressure corresponding to the σ_e. The changes of properties of the material due to the explosion pressure are shown in Photos. 7 and 8 and Table 1, and the material of membrane is considered to get some work hardening by the explosion pressure.

As calculated and shown in Table 2, the pressure of the detonation under the initial pressures of 50 and 100 kg/cm² would attain to several thousands kg/cm², that is, about 100-fold as high as the initial pressure, and also as shown in Photo. 3, the spindles of valves were melted and abraded by the high temperature and high pressure of the detonation and by the high temperature gas flow behind the shock wave.

7) J. H. Faupel, *Trans. ASME*, **78**, 1031 (1956)
    E. W. Comings, *High Pressure Technology*, Chap. 6, McGraw-Hill, New York (1956)
8) H. G. David, *Austral. J. app. Sci.*, **7**, 327 (1956)
    H. Leinss, *Engineering*, **180**, 132 (1955)
    S. D. Hamann, *Physico-Chemical Effects of Pressure*, p. 10, Butterworths, London (1957)

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Table 4   Plastic deformations of the steel membranes
(radius, $r=22$ mm)

l mm	P_e kg/cm^2	f_e mm	f_{obs} mm	Initial pressure* kg/cm^2
1.2	32.90	0.324	2.4	10
2.0	91.38	0.194	1.3	10
3.0	205.6	0.130	4.7 ruptured	50
4.5	462.6	0.086	2.1	50, 100

l: thickness of the membrane σ_e: elastic limit stress, $\sigma_e=8293$ kg/cm^2

P_e: pressure corresponding to σ_e, $P_e=\dfrac{4l^2}{3r^2}\sigma_e$

f_e: extent of deviation at the center of the membrane corresponding to σ_e,

$\quad f_e=\dfrac{3}{16}\dfrac{P_e r^4}{Em^2 l^3}(m^2-1)$ E: coefficient of elasticity, $E=2\times10^6$ kg/cm^2
$\qquad\qquad\qquad\qquad\qquad$ m: reciprocal Poisson's ratio, $m=3$

f_{obs}: the extent of the plastic deformation at the center of membrane

*   initial pressure of the gas mixture exploded

Therefore in the present experiment, the explosion limits under such severe conditions that the pressure is over 50 kg/cm^2 and the composition of C_2F_4 is between 30 and 70%, were not observed because of the dangerous detonation, but the reasonably presumed values are shown by the dotted lines in Figs. 3~6.

c) Explosion of tetrafluoroethylene-air mixtures

The explosion limits were detemined for tetrafluoroethylene-air mixtures by the same method as in the cases of C_2F_4–O_2 mixtures. The results of the measurements using the reaction vessels of 1 cm and 4 cm diameters, under the pressures of 10 kg/cm^2 and 50 kg/cm^2 are shown in Fig. 8. In the figure, the curve a is cited from the previous report[2] and shows the explosion limits under the pressure of 70 mmHg in the glass vessel. The minimum temperature of each curve is observed at the composition of about 20% C_2F_4. In this composition the partial pressure ratio of C_2F_4 to O_2 is 1/0.84. In the explosion of C_2F_4–O_2 mixtures, the minimum temperature at constant pressure are also observed at about this ratio, and both minimum temperatures for C_2F_4–O_2 and C_2F_4–air mixtures under the same pressure coincide within about 10 deg.

The effects of the vessel diameter on the explosion limits of C_2F_4–air mixtures are qualitatively analogous to those in the cases of C_2F_4–O_2 mixtures, but the effects are thought to be smaller than in the cases of the latter.

The violence of the explosion of C_2F_4–air mixture is much weaker than that of C_2F_4–O_2 mixture and even under the severest composition, that is, compositions of C_2F_4 and O_2 are equal to one another, the explosions can be observed without any damage to the apparatus.

As the reaction products of explosion of C_2F_4 and O_2 or air mixtures, a large amount of carbon was produced, especially from C_2F_4 rich mixtures, C_4F_8 (dimer of C_2F_4) was observed in the gas phase by means of infrared spectrum analysis, and white products were formed on the inner wall of a glass tube through which the reaction gases were cooled and pumped out from the reaction vessel. The reaction gas has a stimulating offensive odor and is toxic to the larynx.
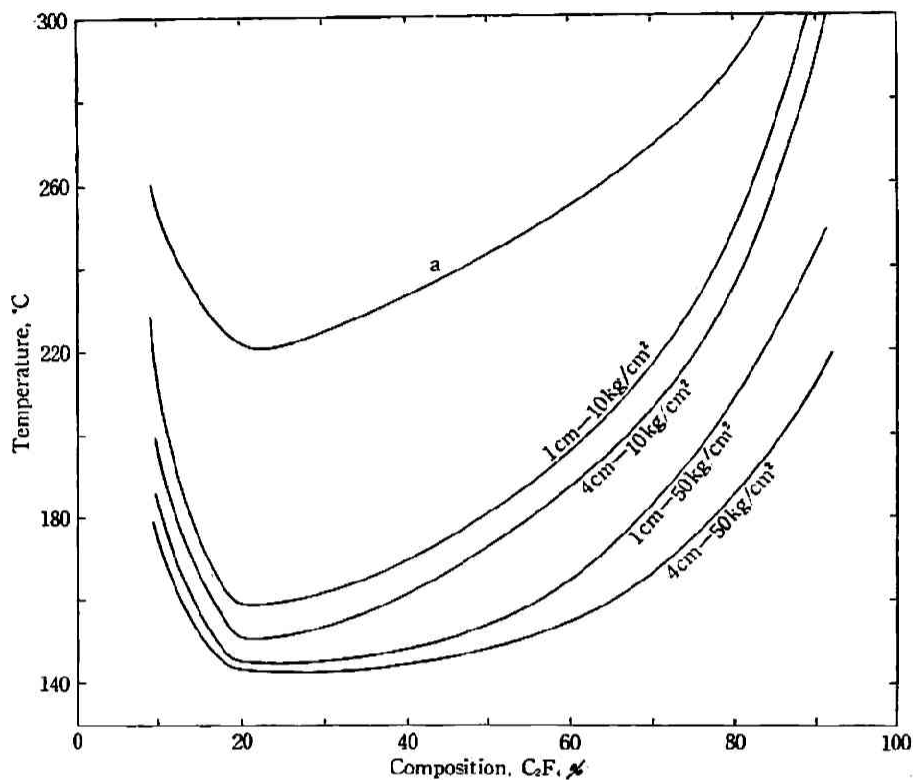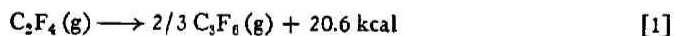
Fig. 8 Relations between temperature and composition of explosion limits at
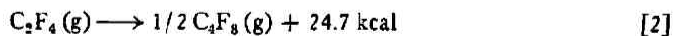specified pressures in C_2F_4–air mixtures

*Curve a shows the explosion limits under 70mmHg pressure in the
glass vessel of 3cm diameter reported in the previous paper[2].*
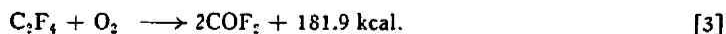
Considerations

As described above, C_2F_4 gas is converted into a higher polymer through the exothermic
polymerization reaction, and on the heat of polymerization of C_2F_4 at 25°C. Duus has reported
as follows[9] :

$$C_2F_4 \,(g) \longrightarrow 2/3 \, C_3F_6 \,(g) + 20.6 \text{ kcal} \qquad [1]$$

and

$$C_2F_4 \,(g) \longrightarrow 1/2 \, C_4F_8 \,(g) + 24.7 \text{ kcal} \qquad [2]$$
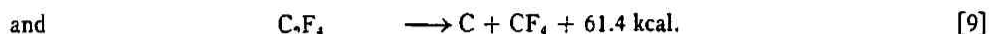
The oxidation and decomposition reactions of C_2F_4 which would take place in the explosion
processes and the heat of reactions (at 25°C) accompanied by these reactions are considered to be
as follows :

$$C_2F_4 + O_2 \longrightarrow 2COF_2 + 181.9 \text{ kcal.} \qquad [3]$$

$$C_2F_4 + O_2 \longrightarrow COF_2 + CO + F_2 + 41.9 \text{ kcal.} \qquad [4]$$

$$CO + F_2 \longrightarrow COF_2 + 140.0 \text{ kcal.} \qquad [5]$$

9) H. G. Duus, *Ind. Eng. Chem.*, **47**, 1445 (1955)

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$$2CO + O_2 \longrightarrow 2CO_2 + 135.2 \text{ kcal}, \qquad\qquad [6]$$

$$C_2F_4 + O_2 \longrightarrow CO_2 + CF_4 + 155.6 \text{ kcal}, \qquad\qquad [7]$$

$$CO_2 + CF_4 \longrightarrow 2COF_2 + 26.3 \text{ kcal}, \qquad\qquad [8]$$

and
$$C_2F_4 \longrightarrow C + CF_4 + 61.4 \text{ kcal}. \qquad\qquad [9]$$
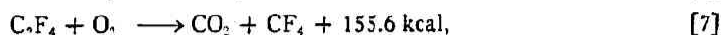
In the explosion processes, reaction gas would become reactive at the local zone of the reaction vessel heated to the temperature T_v, and then the oxidation process [3], [4] or [7] would take place. The heat evolved by the oxidation reactions would elevate the temperature of the system to T_s, and so the oxidation reactions would be more promoted. If the rate of heat evolution at T_s is greater than the rate of heat loss (which would be proportional to $T_s - T_v$), the temperature of the system is more elevated and consequently the system will be introduced to the explosion. When the rate of heat evolution at T_s is equal to that of heat loss, the temperature T_s is defined as "spontaneous ignition temperature" and the corresponding temperature of the reaction vessel (denoted by T_o) is considered to be "thermal explosion limit", that is, those measured and discussed in the present paper.

On the thermal explosion, the following relations can be derived [10].

$$\ln \frac{P}{T_o} = \frac{E}{2RT_o} + \text{constant}, \qquad\qquad (1)$$

and
$$T_s \doteqdot T_o + \frac{RT_o^2}{E}. \qquad\qquad (2)$$

where P is the pressure of the system, and E is the activation energy of the explosion reaction. Assuming that these equations are applicable to the initial oxidation (and also the polymerization) process begun at any locally limited small part in the reaction gases, the explosion limits of C_2F_4–O_2 mixtures are plotted on the $\log P/T$ vs. $1/T$ diagram. As shown in Fig. 9, the plots for each composition come on a straight line for the wide range of the pressure, and the activation energies calculated from the slopes of the straight lines are given in Table 5. The activation energy for each composition is nearly constant independent of the diameter of the reaction vessel, and as the composition of the mixture approaches to the equimolecular one, the activation energy becomes larger. In the previous paper[2], the activation energies were reported to be $17.6 \sim 22.6$ kcal under sub-atmospheric pressure, but the energy showed increasing as the pressure increased. The activation energies listed in Table 5 are, therefore, thought to reasonably coincide with the previous one. Lacher, Tompkin and Park[11] have reported on the activation energy of the polymerization process as follows:

$$2C_2F_4 \longrightarrow \begin{array}{c} CF_2 - CF_2 \\ | \qquad | \\ CF_2 - CF_2 \end{array} \qquad E = 26.299 \text{ kcal/mole}.$$

10) N. Semenoff. Z. physik, 48, 571 (1928)

11) J. R. Lacher, G. W. Tompkin and J. D. Park, J. Am. Chem. Soc., 74, 1693 (1952)

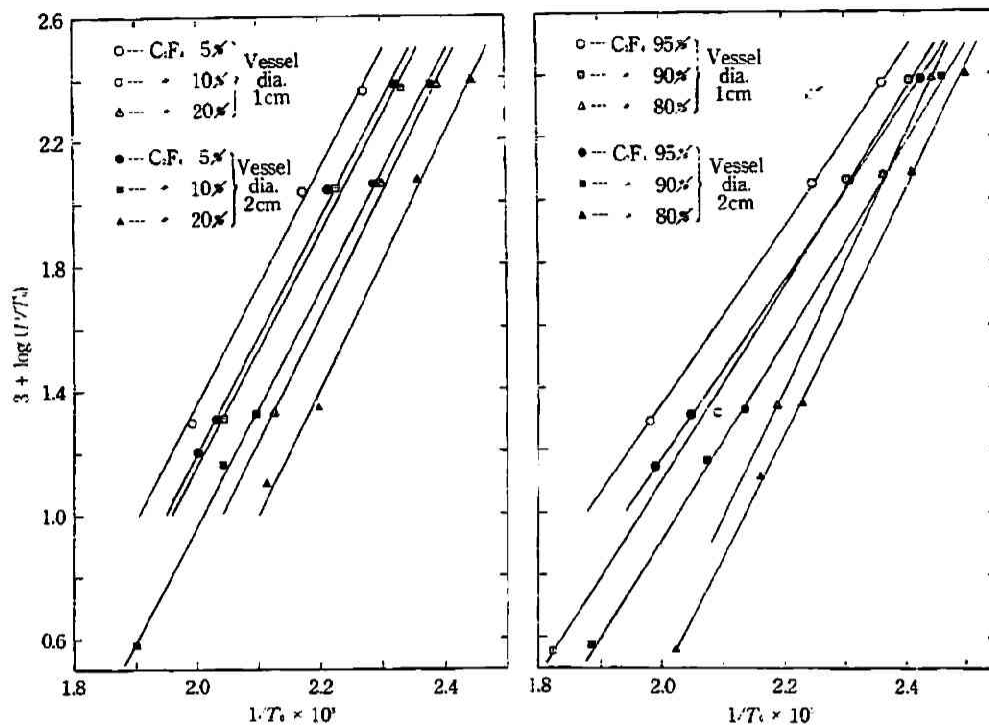Studies on the Explosions under High Pressures, IV

Fig. 9 Relations between log (P/T_0) and $1/T_0$ of explosion limits at
specified compositions in $C_2F_4-O_2$ mixtures

Table 5 Activation energies of the explosion reaction of the $C_2F_4-O_2$ mixtures

Composition C_2F_4 %	Activation energies, E. k cal/mole	
	Vessel dia. 1 cm	Vessel dia. 2 cm
95	25.9	26.0
90	28.5	29.0
80	37.2	35.8
20	36.6	37.1
10	34.1	34.8
5	34.3	34.6

and Atkinson and Trenwith[12] reported 25.4 kcal for the same reaction. If it is assumed that in the explosion processes, the polymerization reactions [2] or [1] take place concurrently with the oxidation reactions and that in the C_2F_4 rich mixtures, the contribution of the polymerization reaction to make the system explode becomes larger, it would be of interest that the present results on the activation energy for the mixture of C_2F_4 95% is comparable with those of the polymerization described above.

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12) B. Atkinson and A. B. Trenwith, *J. Chem. Soc.*, 2082 (1953)

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In the equation (2), if E is a constant, T_s is a function of T_o only and can be calculated using the present experimental results on explosion limits and the values of E in Table 5. The relations thus obtained are shown in Fig. 10. If the reaction vessel is heated to a temperature between T_o and T_s and if near T_o, the explosion initiated at a local high temperature zone of the reaction vessel would have some probability to lose its energy for propagation during passing through the unactivated part. On the other hand, when the vessel has a temperature near T_s, probability of the heat loss would be decreased and consequently the propagation would become severer. This is verified by the fact that as shown in Table 2 and Fig. 10, each detonation observed took place near or over the respective T_s.
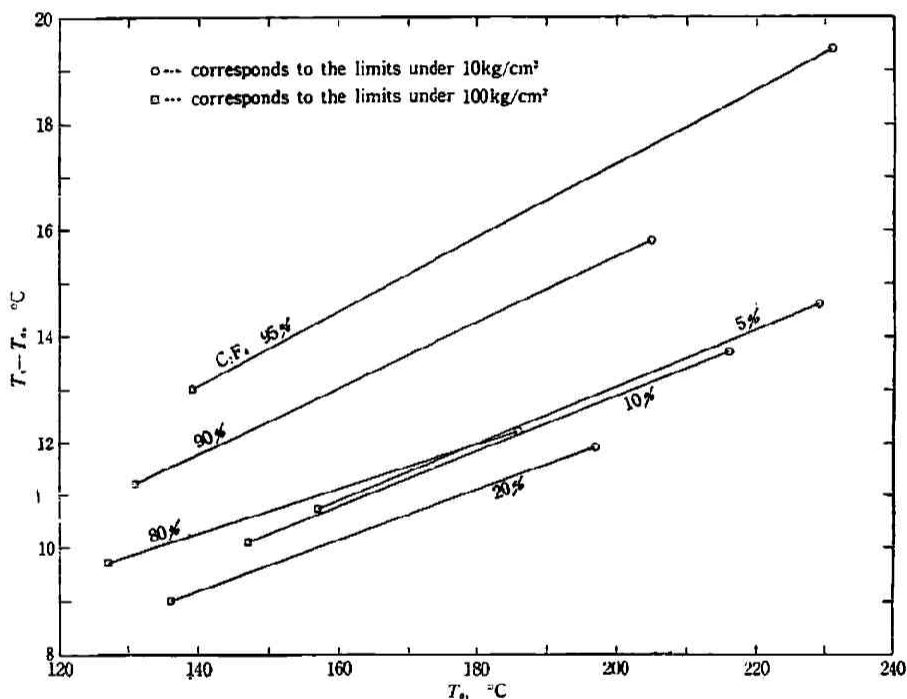

Fig. 10 Relations between T_s and T_o at specified compositions in C_2F_4–O_2 mixtures

On the explosion of C_2F_4–air mixtures, it is impossible to discuss the activation energy accurately because of the meagreness of the experimental data, and by rough estimation their values, however, seem to fall between 30 and 60 kcal/mole, that is, several kcal higher than those of C_2F_4–O_2 mixtures. As described above, the minimum explosion temperature and the compositions of C_2F_4 and O_2 corresponding to it show only a little difference from those in the case of C_2F_4–O_2 mixtures under the same total pressure, so it would be considered that the mixing of N_2 can scarcely affect the retarding of the initiating process of the explosion (on the explosion under low pressure, the N_2 mixed showed rather some promoting effect). On the other hand, considering from the fact that the explosion of C_2F_4–air mixture is much weaker than that of C_2F_4–O_2 mixture,

the mixed N_2 would retard the propagation of the explosion, resembling those in the cases of acetylene-oxygen and -air mixtures[4, 5].

As described above and also in the previous report[2], the white product (mainly the dimer, C_4F_8) and carbon are observed in the reaction products, the latter especially in the C_2F_4 rich mixture, and the reaction gas has a stimulating odor which probably be due to the carbonyl fluoride, COF_2. Considering from these facts, in the O_2 rich mixtures, the reactions [2], [3], [7] and [8], and in the C_2F_4 rich mixtures, the reactions [2], [3] and [9] would principally take place.

Summary

1. The thermal explosion limits of C_2F_4–O_2 and C_2F_4–air mixtures under the total pressures of $2 \sim 100 \, kg/cm^2$ are measured by the admission method.

2. In both cases of C_2F_4–O_2 and C_2F_4–air mixtures, the minimum explosion temperatures at a constant pressure are shown by the mixtures where the compositions of C_2F_4 and O_2 are equimolecular, that is, in the case of C_2F_4–air mixture, the composition of about 20% C_2F_4.

3. The pressure-temperature relations of the explosion limits for C_2F_4–O_2 mixtures are represented by the equation,

$$\ln \frac{P}{T_0} = \frac{E}{2RT_0} + \text{constant},$$

and the activation energy, E is tabulated for a several compositions.

4. The maximum pressures attained at the explosion of C_2F_4–O_2 mixtures are about twofold of the initial pressures in the normal explosion and about more than 100-fold in the detonation.

5. The temperature where the dangerous detonation may take place (T_s) is shown, in the figure, as a function of the limiting temperature of the thermal explosion (T_0).

6. The mixing of N_2 can scarcely affect the retarding of the initiating process, but would retard considerably the propagation process of the explosion.

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