STUDIES ON THE EXPLOSIONS UNDER HIGH PRESSURES, VI

Considerations on the Explosive Phenomena

under High Pressures

By Hiroshi Teranishi

In the previous papers the author reported on the thermal explosions of acetylene[1,2], tetrafluoroethylene[3], and ethylene[4] mixed with oxygen or air which were observed by means of the "admission" method under the conditions of total pressure up to $100\,kg/cm^2$. In the present paper the author will describe some brief considerations on the explosive phenomena under high pressures based on the results obtained in these experiments.

Summary of the previous experimental results   The results obtained in the previous experiments with acetylene, tetrafluoroethylene and ethylene are summarized as follows:

1) Under a constant temperature, as shown in Fig. 1, the range of explosive composition becomes wider as the total pressure of a combustible gas and oxygen or air mixture becomes higher.
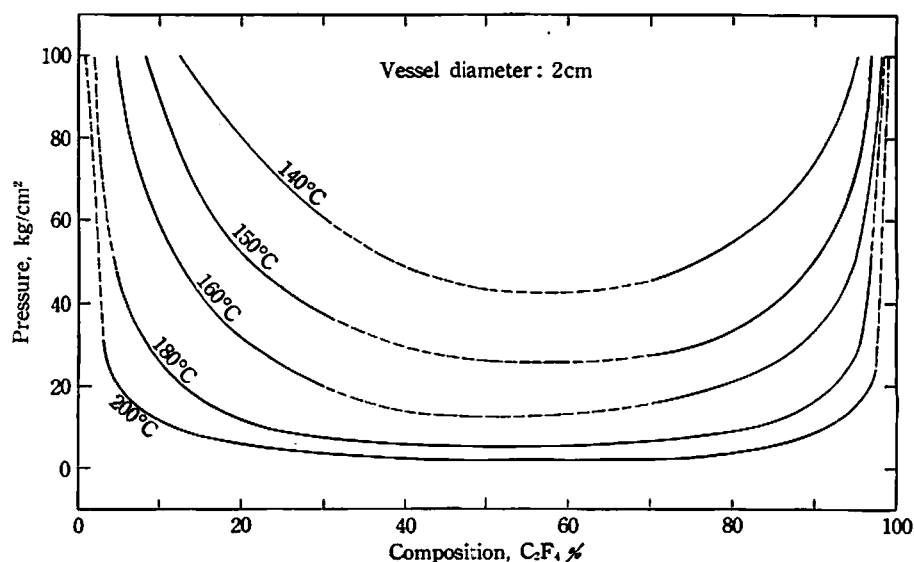

Fig. 1   Relations between pressure and composition of explosion limits
at specified temperatures in C_2F_4—O_2 mixtures

1) R. Kiyama, J. Osugi and H. Teranishi, *This Journal*, 24, 41 (1954)
2) H. Teranishi, *ibid*, 25, 58 (1955)
3) H. Teranishi, *ibid*, 28, 9 (1958)
4) H. Teranishi, *ibid*, 29, 30 (1959)

  2) The isobaric curves of explosion limits shown in the temperature *vs.* composition diagrams, such as Fig. 2, show a tendency that the higher the total pressure, the flatter the bottom of the curve, and the lower the temperature of the bottom.
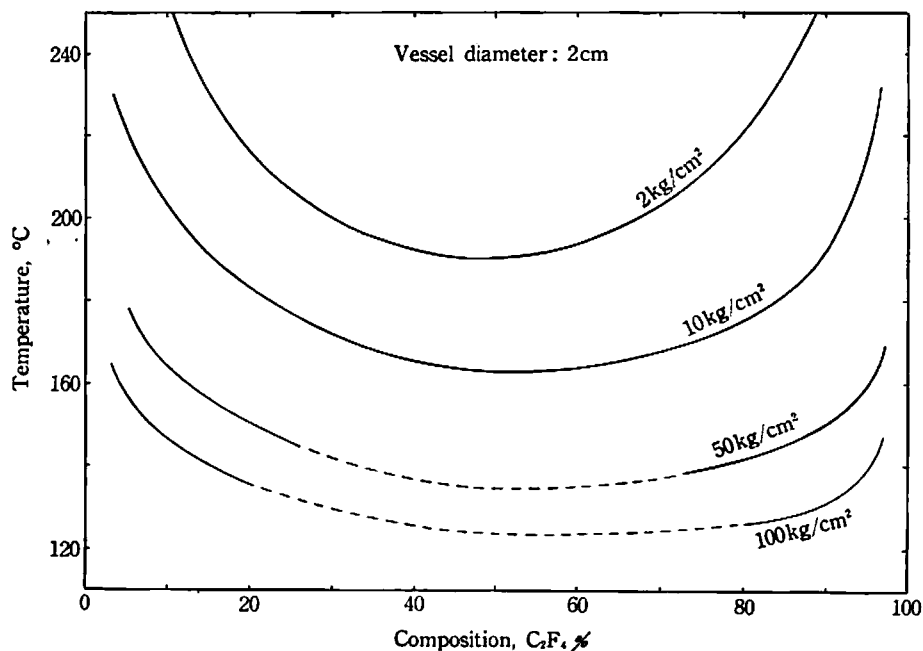

Fig. 2 Relations between temperature and composition of explosion limits
at specified pressures in C_2F_4—O_2 mixtures

  3) The increase in the inner diameter of the reaction vessel (1 cm, 2 cm and 4 cm) causes the explosion temperature to be lower, but it is supposed that even if the vessel having 5 cm or more diameter would be used, the explosion temperature would scarcely be affected, conforming
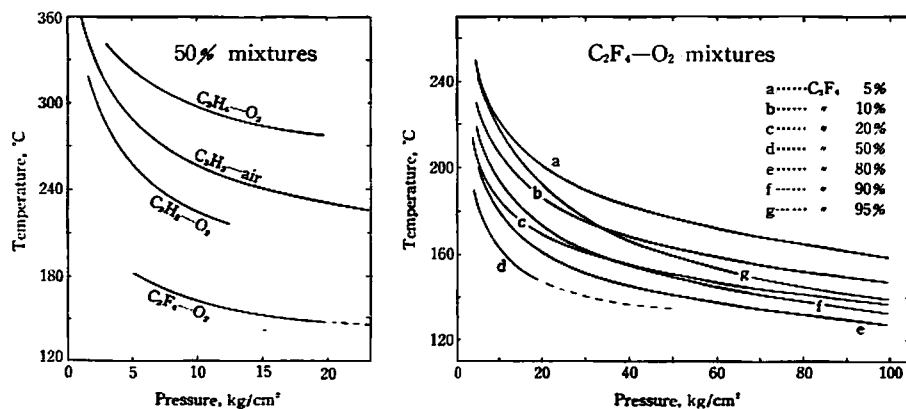

Fig. 3 Relations between temperature and pressure of explosion limits
at specified compositions of combustible gases

H. Teranishi

to the general tendency of explosion phenomena[5].

4) The temperature of the explosion limit for each composition becomes lower as the total pressure of the explosive mixture becomes higher, and the pressure effect on the temperature is shown by a smooth exponential curve on the pressure *vs.* temperature diagram, such as Fig. 3.

5) In the cases of combustible and oxygen mixtures, the explosions are, in general, of violence, but they are comparatively mild under such conditions that the experimental pressure and temperature are near to those of the respective explosion limits. In such cases, as shown in Fig. 4, two or more small explosions happen to take place consecutively or at some intervals of
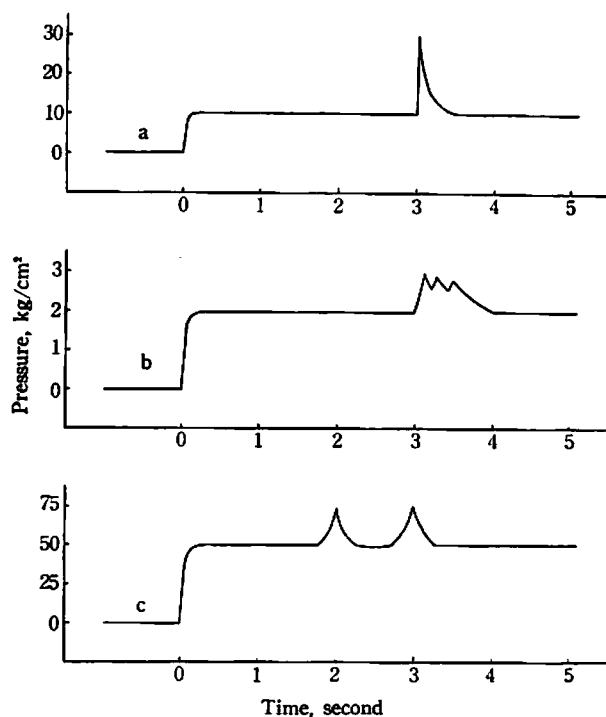

Fig. 4   Typical pressure-time curves of
explosions under high pressures
curve a : normal explosion
curves b and c : mild explosions

time. On the other hand, when the experimental temperatures become over 10 degrees higher than those of respective explosion limits, the explosions of oxygen mixtures become of great violence and often cause detonations which may destroy the experimental apparatus. Calculated from the tensile strength of the steel pipe bursted, the maximum pressure at the instance of these detonations is supposed to be 100 times as high as the initial pressure.

6) Comparing the explosions of each combustible and air mixture with those of respective oxygen mixtures, both minimum temperatures of the explosion limits under the same total pressures differ by no more than 10 dergees but the violence of the explosion of the air mixture is much weaker than that of the oxygen mixture.

Thermal explosion theory   The explosion limits for each combustible gas generally

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

consist of three parts, *i. e.* the first, second and third explosion limits. The first and the second limits, which form the explosion peninshula as its lower and upper pressure limits respectively, are usually observed under such conditions as the pressures are lower than 200 mmHg and the temperatures higher than 450°C.   These limits are elucidated qualitatively or in some cases quantitatively from the stand point of the chain mechanism theory proposed by Semenoff[6] and developed by Hinshelwood[7] and Lewis *et al*[8].   On the other hand, for the explosion limit under higher pressures, that is, the third explosion limits, Semenoff[9] proposed the thermal theory and gave successful explanations to a few kinds of explosive reactions.

In the thermal theory, it is assumed that the explosive gaseous reactions proceed homogeneously in the whole reacting system.   The amount of heat produced per second in the whole system (q_1) will be proportional to the reaction rate and will increase exponentially as the reaction temperature rises.   The heat transferred from the reacting gas to the wall of the vessel (q_2) will be proportional to the temperature difference between the gas (T) and the wall (T_o).   Fig. 5 shows
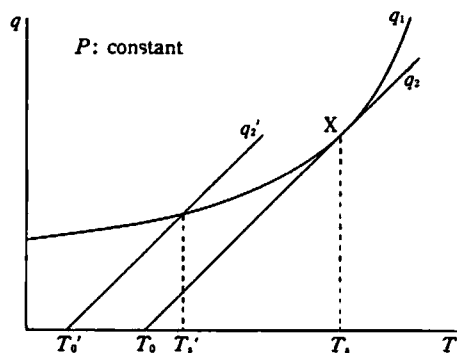

Fig. 5 Relations between temperature of vessel and heat change in the thermal ignition process
q_1: the amount of heat produced per second in the whole gaseous system
q_2: the amount of heat transferred per second from the reacting gas to the wall of the vessel

how q_1 and q_2 vary with temperature at a constant pressure. If the wall is at T_o', the gas heats up until some gas temperature T_s' is reached, but no further heating occurs, because if the gas should somehow become heated above T_s', it will cool back again, since $q_2' > q_1$. Hence this reaction does not lead to explosion. When the wall is at T_o, the curves q_1 and q_2 touch at the point X where a spontaneous explosion would start, and so T_o is the lowest temperature of the vessel to lead the gas to explosion. Hence T_o is considered to be "the thermal explosion limit" and the temperature difference $T_s - T_o$ is defined as "the pre-explosion rise".

Standing on these points of view, Semenoff gave an exact formulation of thermal explosion, and derived the following equations:

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

6) N. N. Semenoff, *Chemical Kinetics and Chain Reactions*, Oxford (1935)
7) C. N. Hinshelwood, *The Kinetics of Chemical Change*, Oxford (1940)
8) B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases*, Academic Press Inc., (1951)
9) N. N. Semenoff, *Z. Physik*, **48**, 571 (1928)

H. Teranishi

$$T_R - T_a \fallingdotseq \frac{RT_o^2}{E} , \qquad\qquad (2)$$

where P is the pressure of the system and E is the apparent activation energy of the explosion reaction. These equations show good applicability to the experimental data on the third limits, for example, explosive decomposition of Cl_2O[10], explosion of H_2—Cl_2 mixture[11], and explosion of C_2H_4—O_2 mixture[12]. In these reactions, all experiments were performed under subatmospheric pressure, and within this pressure range, the basic assumption of the thermal theory, that is, the reactions proceed homogeneously in the whole system, is considered to be applicable.

As described above, it has been considered that the explosion related to the third limits would be of purely thermal type, but Hinshelwood has recently shown in O_2—H_2 explosion that the existence of the third limits can be explained by the behavior of HO_2 radical[13]. Althought it is not certain whether the analogous situation can be applicable to the explosion of hydrocarbon, yet it would be sure that the explosion under higher pressures would also be made by some successive radical reactions containing the chain branching one.   Because in the explosion of hydrocarbon and air mixture "the cool flame region" is often observed under the pressure of $5\sim7$ atm and this fact is supposed to be elucidated only by the radical reaction mechanism.

Local explosion   For the explosions under such high pressures as those in the author's experiment, it is impossible to assume that the explosive gaseous reaction would proceed homogeneously in the whole system. For the higher the pressure, the more difficult the diffusion of molecules or radicals. It is therefore considered by the author that the explosive gaseous mixture made to flow into the heated reaction vessel would become reactive at local zones contacting on some parts of inner surfaces[14] of the vessel, and the number or size of the zone would vary with conditions of the vessel wall, reaction temperature and pressure. The oxidation process started in one of these local zones would elevate the temperature of the zone and hence the oxidation reaction in the zone would be more promoted, and the zone size would rapidly grow large. These processes are explained from the view point of the chain theory, thus: some radicals which behave as the chain carriers would be produced at first in this zone and then chain branching reactions would proceed in the zone. As mentioned above, the higher the pressure, the slower the diffusion velocity of the radical, and so the larger the difference between the radical concentration in and that outside the zone. Hence higher pressure would cause the thermal unbalance near the zone, even though the thermal conductivity of the gas itself would rather be increased by the higher pressure. Therefore it may be supposed that the explosion at first would take place in this local zone before thermal and material balances are attained over the whole gaseous system, and this local explosion* would usually propagate to the whole system.

10)   A. V. Zagulin, *Z. phys. Chem.*, **1**, 275 (1928)

11)   A. V. Zagulin, *ibid.*, **1**, 192 (1928)

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

13)   C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, A **188**, 1, (1946)

14)   R. Goto, *This Journal*, **16**, 101 (1942)

   *   The term "local explosion" employed by the author means the thermal ignition and its propagation within respective local zone where the radical concentration, or the temperature, becomes some-

If it may be supposed that the higher the vessel temperature is than T_o, the larger the number of the local zone, and that the higher the pressure, the smaller the size of each zone, the local explosion in the vessel heated nearly to T_o would not necessarily propagate to the whole system, and the gas mixture would have some probability to explode again being started from the other local zone. These are considered to be the cases shown in Fig. 4.

If the thermal and material homogeneities are assumed within each local zone, the Eqs. (1) and (2) of the thermal theory may be approximately** applicable to the local explosion. These were examined by plotting the measured explosion limits on the $\log P/T_o$ vs. $1/T_o$ diagram. As reported partly in the previous papers and also shown in Fig. 6, these plots for each gas come on a straight line within the experimental pressure ranges of the respective gases.
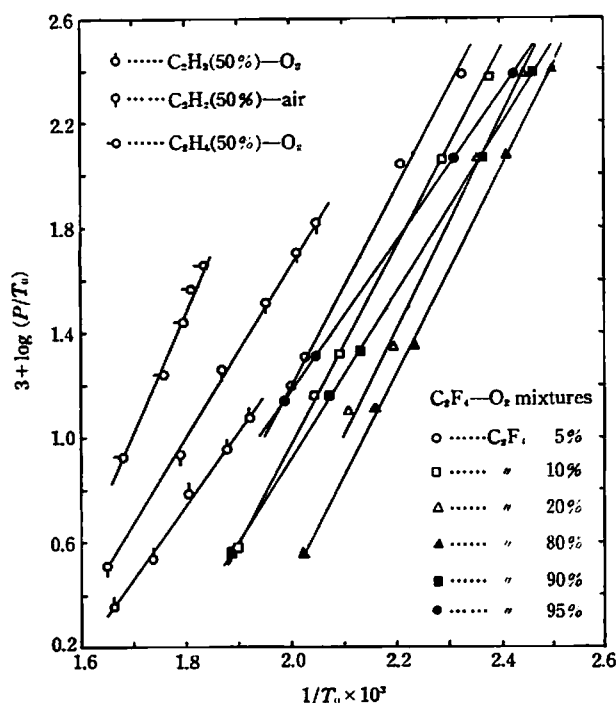

Fig. 6 Relations between $\log(P/T_o)$ and $1/T_o$ of explosion limits at specified compositions of combustible gases

The pre-explosion rise   The apparent activation energy. E and the pre-explosion rise, T_s-T_o, calculated from the slopes of the straight lines in Fig. 6 and Eqs. (1) and (2) are listed in Table 1.

The pre-explosion rise lies within about $10\sim20$ degrees and becomes smaller as the pressure increases. When the reaction vessel is heated to such a temperature as $10\sim20$ degrees higher than T_o, that is near T_s, the temperature where the thermal spontaneous explosion of the respective gas mixture would start, a great number of the local reactive zones would appear and the explosion

what different from that in other larger part by the instance of the ignition.

**   Strictly speaking, the thermal conductivity of the gas is increased as the pressure becomes higher and hence the inclination of the lines for q_2 in Fig. 5 would vary by the pressure.

H. Teranishi

Table 1   Apparent activation energies, E, and pre-explosion rises,
T_s-T_o, at the explosion reactions of combustible gases

Mixtures and vol. % of combustible gases		E kcal/mole	T_s-T_o, degree	
			at 10 kg/cm^2	at 100 kg/cm^2
C_2F_4—O_2	5	34.6	14.7	10.5
	10	34.8	13.8	10.0
	20	37.1	12.0	9.0
	80	35.8	11.5	9.8
	90	29.0	15.8	11.1
	95	26.0	19.5	13.0
C_2H_4—O_2	50	41.5	15.6	
C_2H_2—O_2	50	25.3	20.0	
C_2H_2—air	50	29.7	16.9	

started at the most reactive one would propagate rapidly to the whole vessel without any serious loss of energy. These are considered to correspond to the dangerous detonations which are often observed when the vessel temperatures are about 10 degrees or more higher than the respective T_o. The decrease of the amount of pre-explosion rise with the increase of the pressure is thought to be one of the reasons for danger of combustible gases to be handled under high pressures.

The apparent activation energy   As shown in Table 1, the apparent activation energy for each combustible gas becomes smaller as the composition of the gas mixture leaves from the equimolecular composition. This corresponds to the experimental results described above, that is, as shown in Fig. 2, the higher the pressure, the wider the range of the explosive composition and the flatter the bottom of explosion limits shown in the isobaric curve. Because the smaller activation energy, E, being considered from the principle in deriving Eqs. (1) and (2), means the larger depression of the limiting temperature by a given pressure increase.

Nothing has been reported in literature on the activation energies of explosive combustion of C_2H_2, C_2H_4, and C_2F_4 under high pressures, hence it is impossible to examine the numerical values of E listed in Table 1 by direct comparison. As compared with those obtained by the experiments under an atmospheric or lower pressure, the values of E in Table 1 seem a several kcal higher per mole. Of course, it will be unreasonable to assume that the same chain mechanical steps would be favorable in explosion process under the pressure from subatmospheric one to $50 \sim 100$ atm. If assumed so, however the difference of the activation energies would be ascribed to the following causes.

1) The diffusion velocity becomes slower as the pressure increased and so the apparent activation energy which includes that for the diffusion would become larger.

2) The average values of the temperature ranges where the activation energies under lower pressures are calculated seem about more than 150 degrees higher than those for the E in Table 1.

3) The experiments under lower pressures are in most cases performed by means of glass or quartz vessels whose inner diameter are often 3 cm or longer. The thermal ignition phenomena would be affected by the differences in the materials, inner diameter and capacity of the reaction vessels.

The explosion of combustible-air mixture (The effect of nitrogen)   As described above, the minimum temperature of the explosion limits for combustible-air mixtures differs 10 degrees at most from that for the respective oxygen mixtures under the same total pressure. For example. in group A or B of Table 2, the explosions (b) and (c) show almost same value

Table 2   The effect of nitrogen on the thermal explosion limits, T_o, of the combustible gases and oxygen mixtures

Mixtures and compositions (vol. %)		Partial pressures of the constituents kg/cm^2	Total pressure kg/cm^2	T_o °C
A	a) C_2H_2 (50)–O_2	C_2H_2······ 1.7, O_2······ 1.7	3.4	280
	b) C_2H_2 (50)–O_2	C_2H_2······ 5.0, O_2······ 5.0	10	235
	c) C_2H_2 (17)–air	C_2H_2······ 1.7, O_2······ 1.7 N_2·········· 6.6	10	235
B	a) C_2F_4 (50)–O_2	C_2F_4······ 8.5, O_2······ 8.5	17	155
	b) C_2F_4 (50)–O_2	C_2F_4······25, O_2······25	50	135
	c) C_2F_4 (17)–air	C_2F_4······ 8.5, O_2······ 8.5 N_2 ······ 33	50	140

of T_o for each other.   In these explosive compositions, *i.e.*, equimolecular one of combustible gas and oxygen, the depressions of T_o with the increase of the total pressure are almost equal in both cases of (b) and (c), that is, in the former case the total pressure is increased by combustible gas and oxygen themselves and in the latter case by mixing of nitrogen.   In other words, the temperature of the explosion limits depends on the total pressure and are scarcely affected by the addition of nitrogen so long as the total pressure and the ratio of the content of combustible gas to that of oxygen are kept constant.

It would be presumed from these facts that in the pre-explosion steps the radical reactions of chain branching would scarcely be affected by replaceing a portion of the reactant with nitrogen, and this would be understood in such conditions that the ratio of the number of effective collisions for the reaction to that of total ones is very small, as in the initiating steps at the temperature near the explosion limits.   On the other hand, when the ratio would be pretty large. as in the propagating stpes of the explosion which proceed at very high temperature owing to the heat of reaction of the preeeding ignition step, the mixing of nitrogen would considerably retard the reaction.   It would be considered to coincide with the experimental results that the violence of the explosion of the air mixture [(c) in Table 2] is in general much weaker than that of the respective oxygen mixture [(a) and (b) in Table 2].

The Laboratory of Physical Chemistry,
Kyoto University