STUDIES ON THE EXPLOSIONS UNDER HIGH PRESSURES, V
The Explosions of Ethylene mixed with Oxygen

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Introduction

With the development of petroleum chemistry, ethylene is recently of great industrial importance as a monomer of polyethylene or as a raw material of ethylene oxide or ethylene glycol production. It has become, therefore, necessary to have some knowledge on the explosive nature of ethylene for handling it safely in its industrial polymerization and oxidation processes under high pressures.

On the combustion or explosion of ethylene, as the first member of the olefine series, many works have been reported in literature1, but, most of them have been measured under subatmospheric pressure. On the explosion under high pressures, Kane and Townend2 reported on the thermal explosion limits of a few kinds of ethylene and air mixture which were measured up to 12 atm.

Abbott and Miller3 reported on the explosive phenomena of ethylene, oxygen and nitrogen mixtures under such conditions that the temperature was 300°C and pressure up to 41 atm, but their work was performed in order to observe the cool flames with ethylene and was not satisfactory as the data for the explosion limits of ethylene under high pressures.

Therefore in the present paper, the author will report the results of the experiment performed in order to explain the thermal explosions of ethylene and oxygen mixtures under the conditions of pressure up to 80 kg/cm².

Experimental

Apparatus and procedure In the present experiment, the explosion limits were studied by the "admission method". The experimental apparatus and procedures are the same as described in the previous papers4,5,6. Ethylene and oxygen are mixed at a desired composition* and stored in a steel reservoir, and after complete mixing, a gas mixture, being compressed to a certain pressure, is made to flow into the steel reaction vessel (2 cm in inner diameter and 10 cm in length)

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5) H. Teranishi, ibid., 25, 58 (1955)
6) H. Teranishi, ibid., 28, 9 (1958)
* Throughout this paper, composition will be expressed by volume percentage of ethylene.
which is previously evacuated and heated to an experimental temperature. The occurrences of explosions at given pressures are perceived by their sounds, observed by very rapid and discontinuous displacements of the light spot reflected at the mirror of a membrane pressure gauge and confirmed by the pressure curves recorded by means of a wire resistance strain meter and an oscillograph.

Materials The ethylene $C_2H_4$ used was prepared by the dehydration of ethyl alcohol, purified by passing through a concentrated aqueous solution of sodium hydroxide, concentrated sulfuric acid and silica gel, and compressed into a steel bomb up to about 70 kg/cm$^2$. In the analysis by means of infrared absorption spectrum or gaschromatograph, no impurity but a trace of ethyl ether was observed. The oxygen used was that from commercial bomb having about 99.4 per cent purity.

Results

It was surmised from the report by Kane and Townend that the minimum temperature of thermal explosion limit on ethylene and air mixture was about 310°C under the total pressure of 10 kg/cm$^2$. At the start of the present experiment, the author supposed, from this fact and

![Fig. 1 Relations between temperature and composition of explosion limits at specified pressures in $C_2H_4-O_2$ mixtures](image-url)

Curve a shows the explosion limits for $C_2H_4$-air mixtures under the total pressure of 10 kg/cm$^2$ cited from the data of Kane and Townend.

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the results of his previous works, that the minimum temperature of explosion limit on ethylene and oxygen mixture would fall on 300~310°C under the same total pressure. On these surmises, the measurements on the thermal explosion limits of C₃H₆-O₂ mixtures were performed under various pressures, and the results obtained are shown in Fig. 1.

In the present experiment, the observation of explosion was done for 10 minutes immediately after the admission of the gas mixture, since the relatively longer induction periods were needed than those in the explosions of C₂F₆-O₂ mixtures where the observation for 5 minutes was sufficient to decide the explosion limit.

When the 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 next explosion, but by the evacuation of the vessel for about half an hour after a run, no effect was observed even if the reaction vessel contained some amount of carbon produced in the preceding run.

In Fig. 1, curve a shows the explosion limits for C₃H₆-air mixtures under the total pressure of 10 kg/cm² cited from the data of Kane and Townsend. As shown by each isobaric curve in Fig. 1, the minimum explosion temperature of C₃H₆-O₂ mixture under a constant pressure appears in the case of the composition where C₃H₆ and O₂ are equimolecular, and the temperature under 10 kg/cm² is seemed to be 297°C which comes off but is near the region expected. As the total pressure increases, the corresponding isobaric curve becomes gradually a flat-bottomed shape and at 50 kg/cm² the temperature of the explosion limit shows little difference in the range of composition from 30 to 70 per cent C₃H₆.

In Fig. 2, the explosion limits are shown by isothermal curves on the pressure vs. composition diagram. The range of composition where the mixture would explode becomes wider as the total pressure becomes higher at each constant temperature or as the temperature becomes higher at

![Fig. 2 Relations between pressure and composition of explosion limits at specified temperatures in C₃H₆-O₂ mixtures](image-url)
a constant pressure. The explosion limits for constant compositions when plotted on the pressure vs. temperature diagrams, are shown by the smooth exponential curves like those in Fig. 3. In

![Graph showing relations between temperature and pressure of explosion limits at specified compositions in C₅H₅-O₂ mixtures](image)

Fig. 3 Relations between temperature and pressure of explosion limits at specified compositions in C₅H₅-O₂ mixtures
- curve a: the explosion limits for C₅H₅ (20%)-air mixture cited from the data by Kane and Townend
- curve b: the explosion limits for C₅H₅ (60%)-O₂ mixture cited from the data by Suga

Fig. 3 curve a shows the explosion limits for C₅H₅ (20%)-air mixture cited from the data by Kane and Townend, and curve b for C₅H₅ (60%)-O₂ mixture reported by Suga. Owing to the differences in the material, inner diameter and capacity of the reaction vessel, it is, of course, impossible to discuss quantitatively, but qualitative resemblance of the temperature-pressure relations or roughly suitable coincidence by extrapolation is shown between these curves and those of the present work.

The violence of the explosion of C₅H₅-O₂ mixture is in general somewhat weaker in comparison with those of C₅F₅-O₂ and C₅H₅-O₂ mixtures and no dangerous detonation which would destroy the experimental apparatus was observed throughout the course of present work. However, after several explosions under the higher pressures some amount of plastic deformation was observed with the spring steel disk (2.0~4.0 mm in thickness and 44 mm in effective diameter) which had been used in the membrane pressure gauge. It is supposed from the fact that the maximum pressure at the instance of the explosion would attain to about tenfold of the initial pressure. As observed in the experiments with C₅F₅ and C₅H₅, the higher the pressure, the more violent the explosion of C₅H₅-O₂ mixture, but, when the experimental temperature and pressure are near to those of the limits, relatively weak explosions are observed. Under these conditions the pressure change at the instance of the explosion is small and gradual, and two or more weak explosions happen to be observed, as reported on the case of C₅F₅-O₂ mixture in the previous paper.

Considerations

Kane and Townend considered that the product of the main combustion of ethylene was vinyl alcohol, ethylene oxide and acetaldehyde, and that formaldehyde, which is known to promote the main combustion, was always a product of the pre-flame combustion. Abbott and Miller reported the observation of formaldehyde, acetaldehyde and a small amount of peroxide in the product by the relatively weak explosion with \( \text{C}_2\text{H}_4-\text{O}_2-\text{N}_2 \) system. In the present work nothing has been confirmed as the products but carbon and carbon dioxide, because of the lack of precise analysis, but it would be supposed, from these products, and those from the experiment under subatmospheric pressures\(^9\), that the following reactions would eventually take place, even though each of them would be proceeded by stepwise radical reactions.

\[
\begin{align*}
\text{C}_2\text{H}_4 + \text{O}_2 &= 2\text{CH}_2\text{O}, \\
2\text{C}_2\text{H}_4 + \text{O}_2 &= 2\text{CH}_2 = \text{CH}_2, \\
2\text{CH}_2\text{O} + \text{O}_2 &= 2\text{HCOOH}, \\
2\text{C}_2\text{H}_4 + \text{O}_2 &= 2\text{CH}_3\text{CHO}, \\
\text{C}_2\text{H}_4 &= 2\text{C} + 2\text{H}_2, \\
\text{C}_2\text{H}_4 + 3\text{O}_2 &= 2\text{CO}_2 + 2\text{H}_2\text{O}, \\
\text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} &= (\text{CH}_3\text{OH})_2.
\end{align*}
\]

The weak explosions which take place under such lower pressures as up to 300 mmHg are usually elucidated by the chain mechanism. On the other hand, the explosions under higher pressures are considered to be rather of thermal nature than the radical one, and the tendency would become more evident when the pressure becomes such a higher one as in the present work, since the concentration of the reacting gas becomes larger.

In the explosion processes, the reaction gas would become reactive at the local parts of the reaction vessel heated to the temperature \( T_r \), and then the oxidation processes would take place. The heat evolved by the oxidation reactions would elevate the temperature of the system to \( T_e \) and hence the oxidation reactions would be more promoted. If the rate of heat evolution at \( T_e \) is greater than the rate of heat loss which would be proportional to \( T_e - T_v \), the temperature of the system is more elevated and consequently the system will be introduced to the explosion.

On the thermal explosion, the following relations can be derived\(^10\).

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

and

\[
T_e - T_v \approx \frac{RT_e^2}{E}. \quad (2)
\]

\(^9\) S. Lenher, \textit{J. Am. Chem. Soc.}, 53, 3737, 3752 (1931)

\(^{10}\) N. N. Semenoff, \textit{Z. Physik}, 48, 571 (1928)
where $P$ is the pressure of the system, $E$ the apparent activation energy of the explosion reaction, $T_s$ the temperature where the spontaneous explosion would start and $T_a$ the corresponding temperature of the reaction vessel, that is the temperature measured and discussed in the present paper as "the thermal explosion limit". Assuming that these equations are applicable to the initial oxidation process begun at any locally limited small part in the reaction gases, the explosion limits of $\text{C}_2\text{H}_4-\text{O}_2$ mixtures are plotted on the log $P/T_a$ vs. $1/T_a$ diagram. As shown in Fig. 4,

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Relations between log ($P/T_a$) and $1/T_a$ of explosion limits at specified compositions in $\text{C}_2\text{H}_4-\text{O}_2$ mixtures.}
\end{figure}
\end{center}

the plots for each composition come on a straight line, and the apparent activation energy and the pre-explosion rise ($T_r-T_a$) calculated from the slopes of the straight lines are given in the table. Suga reported 29.10–34.23 kcal on the apparent activation energy for the explosion of $\text{C}_2\text{H}_4-\text{O}_2$ mixtures. The apparent activation energies, $E$, and pre-explosion rises, $T_r-T_a$, at the explosion reaction of the $\text{C}_2\text{H}_4-\text{O}_2$ mixtures are given in the following table:

<table>
<thead>
<tr>
<th>Composition of $\text{C}_2\text{H}_4$</th>
<th>$E$ kcal/mole</th>
<th>$T_r-T_a$ degree at 10 kg/cm$^2$</th>
<th>$T_r-T_a$ degree at 50 kg/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>38.4</td>
<td>18.2</td>
<td>15.1</td>
</tr>
<tr>
<td>20</td>
<td>38.5</td>
<td>17.4</td>
<td>15.4</td>
</tr>
<tr>
<td>50</td>
<td>41.5</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>40.7</td>
<td>16.0</td>
<td>13.4</td>
</tr>
<tr>
<td>80</td>
<td>37.7</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>36.4</td>
<td>18.8</td>
<td>15.4</td>
</tr>
</tbody>
</table>
C₂H₄—O₃ mixtures under subatmospheric pressures, Thompson and Hinselwood(1) 37~43 kcal, Harding and Norrish(2) 26~42 kcal below 450°C on that for ethylene oxidation. Since these data are all based on the experiments under subatmospheric pressure, the quantitative comparison is impossible. Qualitative coincidence, however, is observed between these values and those of E listed in the table.

As mentioned above, the explosion of C₂F₄—O₃ mixture is more violent than that of C₂H₄—O₃ mixture, and the temperatures of the explosion limits for the former are more than 100 degrees lower than those for the latter under the same total pressure.

In the case of C₂F₄—O₂ mixture a considerable amount of octafluorocyclobutane C₄F₈, the dimer of C₂F₄ and carbonyl fluoride, COF₂, were observed in the product of explosion reaction. In the case of C₂H₄—O₂ mixture, however, nothing has been reported on the observation of cyclobutane C₄H₈ or higher polymers in the product of explosion. These facts are considered to be due to following. Owing to the electronegativity of fluorine larger than that of hydrogen, C-F bond in C₂F₄ has larger polarity than C-H bond in C₂H₄ and hence the carbon-carbon double bond in C₂F₄ becomes easier to polymerize itself or to get oxygen attack than that in C₂H₄, and therefore the amount of COF₂ which is supposed to be produced by the decomposition of peroxide is larger than CH₃O, which is regarded as a product of the pre-flame combustion.

The pre-explosion rise (T₂—T₀) is, as listed in the table, 10~20 degrees under the conditions of the present experiment, and the fact that the explosion becomes sever when the vessel temperature is more than 10 degrees higher than the respective limit is surmised to relate to these values of the pre-explosion rise.

Kane and Townend reported that no cool flame was observed in C₂H₄—air mixture, but Abbott and Miller succeeded to observe it, by introducing some amount of nitrogen to C₂H₄—air mixture, but their experimental conditions (300°C and 17~25 atm) are scarcely different from those of Kane and Townend or of the present work. From these facts, addition of nitrogen would be considered, as in the case of C₂F₄—O₂ mixture, to affect scarcely the ignition step but to affect considerably the propagation step of the explosion of C₂H₄—O₂ mixture.

Summary

1. The thermal explosion limits of C₂H₄—O₂ mixtures under the total pressure up to 80 kg/cm² are measured by the admission method.

2. The minimum explosion temperatures at any constant pressures are shown by the mixture where the compositions of C₂H₄ and O₂ are equimolecular.

3. The pressure-temperature relations of the explosion limits are represented by the equation,

\[
\ln \frac{P}{T₀} = \frac{E}{2RT₀} + \text{constant},
\]

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

4. No dangerous detonation has been observed but the maximum pressures at the instance of sever explosion attained to about tenfold of the initial pressure.

5. Two or more successive small explosions were observed under the conditions near explosion limits.

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