THE INFLUENCE OF METALS ON THE EXPLOSION LIMIT
OF ETHYLENE MIXED WITH AIR*

BY MASAO SUGA**

In the previous papers1-2), the explosion limit of ethylene mixed with oxygen and that with air were determined by the "admission method", and it was shown that the explosion peninsula appeared on the isochor for the explosion limit.

On the other hand, the explosion reaction is a chemical reaction which involves the two processes, i.e. initiation and propagation, and so far as the conditions of initiation are concerned, it is permitted that the explosion and the combustion are the same3). Also, studies of the spontaneous ignition are simplified by the elimination of factors related to the ignition energy source. Therefore, the spontaneous ignition has been conveniently regarded as the explosion and the critical pressure-temperature relationship for the spontaneous ignition (the isochor of the explosion limit), the ignition delay (the induction period of the explosion) at a specified temperature and pressure, and the effect of gas composition, etc., have been determined.

Many investigations of the flammability of combustibles-oxidant mixtures have been made from the practical problem of handling combustibles, and on the experimental evaluation of flammability limits, an electric spark or an electric coil heater is usually employed as a local ignition source4). Moreover, for the investigations of the explosion phenomena at high pressure, the metal vessel has been employed5). In any case, it is fundamentally necessary to study the influence of metals on the explosion.

From these standpoints, the effect of various metals (Pt, Ag, Cu, Al, Fe and W) on the explosion limit of mainly 5% and supplementarily 20% ethylene mixed with air has been studied.

** Experimental

Materials The ethylene employed in the present experiment was prepared by the dehydration of absolute alcohol and purified by the method described in the previous papers. The air was employed after being passed through a train consisting of two bottles containing a concentrated aqueous solution of sodium hydroxide, concentrated sulphuric acid. Before use, gases

---

* The present investigation was presented at the Eleventh Annual Meeting of the Chemical Society of Japan, Tokyo, April, 3, 1958.
** Department of Chemistry, Faculty of Science and Literature, Ehime University, Matsuyama
2) M. Suga, ibid., 32, No. 7 (1959)
5) H. Teranishi, This Journal, 28, 9 (1958)
were dried with phosphorus pentoxide.

The metals employed were commercial Pt, Ag, Fe, Al, Cu, and W wires 1mm in diameter. Those were cut into 10cm long and the two pieces, in the form of lines, were inserted into the reaction vessel.

Fig. 1 Explosion limit of 5% ethylene with air in the presence of the various metals (Induction periods in seconds indicated by numbers beside observation points. Also, broken lines represent the data in the absence of the metals.)
The Influence of Metals on the Explosion Limit of Ethylene mixed with Air

The metals were polished mechanically with sand paper and dried cloth before each experimental run, and were employed several times.

Apparatus and procedure The apparatus used was the same as in the previous papers. Also, the procedure used was the same described in the previous paper except the inserting of the metal lines into reaction vessels.

Results and Considerations

Observation The determination of the occurrence of explosion was made directly by naked eye. The results of observation are classified as the following.
1) After the lapse of various induction periods, luminous flames (blue and yellow flames) were observed.
2) After the lapse of the relatively long induction periods, pale blue flames were observed in the dark room.
3) No flame could be found even in the dark room.

Cases 1), 2) and 3) indicate ◯, ○ and × respectively in Fig. 1. It is interesting to mention that in each case flames spread from the metals inserted.

The effect of the metals on explosion limit Fig. 1 demonstrates respectively the effect of various metals (i.e. Pt, Ag, Al, W, Fe and Cu) on the isochor for explosion limit of 5% ethylene mixed with air. It is noticed that the explosion peninsula tends to disappear, in the presence of the metals in the reaction vessels and especially in the presence of Cu and Fe, the explosion peninsula disappeared completely.

Fig. 2 shows summarily the effect of the metals on the isochor for explosion limit of 20% ethylene with air in the presence of the various metals (Broken line represents the data in the absence of the metals.)
ethylene mixed with air. The metals inserted into the reaction vessels generally cause the narrowing of the explosion region as well as in Fig. 1. It is interesting that the metals lower the level of the isochors for explosion limit of 20% ethylene mixed with air as shown in Fig. 2 in the order of Cu, Fe, Al, W, Ag and Pt. In the cases where Cu and Fe were inserted, it was found after experimental runs that the surfaces of these metals were covered with black materials which were possibly presumed their oxides. Therefore, as will be seen later, it is considered that the metals inserted into the reaction vessels have also a direct reaction with the reaction mixture. The work of Burgoyne and Neale has been experimented on spontaneous ignition limit* of ethylene in air at 650°C. The isotherms for explosion limit of ethylene-air mixtures at 650°C, are given in Fig. 3, where the results are compared with. As the results of Burgoyne and Neale were determined by the apparatus which could determine the flammability, the metals of the ignition source are thought to have been inserted into the reaction vessels. It can be thought, therefore, that the results of Burgoyne and Neale and the present work are much the same.

The effect of the metals on the induction periods. The results of the experiment with regard to the induction periods are shown by the number beside the observation points in Fig. 1. The induction periods were measured by means of a stopwatch, and the admission time requiring more than 0.6 sec., the induction periods could not always be measured by means of a stopwatch with accuracy, except the longer induction periods in the explosion peninsula. The results are at most semiquantitative and there is, in fact, a certain scattering of results, but this does not alter the main characteristics. In Table 1 is shown the data of the induction periods in the absence of the metals which is cited from the previous paper. From these results, it can be concluded that the metals cause to prolong the induction periods at the same conditions (temperature and pressure). But the role of the metals in the explosion process cannot be considered

---

* As described above, the spontaneous ignition limit has been considered the explosion limit in the present work.

The Influence of Metals on the Explosion Limit of Ethylene mixed with Air

Table 1 The induction periods at the definite pressures and temperatures for 5% ethylene with air in the absence of the metals

<table>
<thead>
<tr>
<th>$T^\circ C$</th>
<th>560</th>
<th>570</th>
<th>580</th>
<th>590</th>
<th>600</th>
<th>610</th>
<th>620</th>
<th>640</th>
<th>660</th>
<th>680</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$(mmHg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>7.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>X</td>
<td>X</td>
<td>3.5</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td></td>
<td>X</td>
<td>4.6</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>X</td>
<td>6.0</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>3.9</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td>2.5</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>2.1</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>3.8</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>18.6</td>
<td>10.0</td>
</tr>
<tr>
<td>100</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>89.5</td>
<td>55.6</td>
<td>40.8</td>
<td>29.5</td>
<td>15.0</td>
<td>4.0</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>X</td>
<td>X</td>
<td>419.6</td>
<td>256.0</td>
<td>144.0</td>
<td>90.2</td>
<td>56.1</td>
<td>24.2</td>
<td>8.0</td>
<td>2.0</td>
<td>0.8</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td>X</td>
<td>879.6</td>
<td>391.2</td>
<td>239.7</td>
<td>140.1</td>
<td>87.3</td>
<td>37.5</td>
<td>10.3</td>
<td>3.3</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
<td>164.3</td>
<td>90.1</td>
<td>23.7</td>
<td>12.8</td>
</tr>
</tbody>
</table>

Unit: sec. X: non-explosion

as cleared up in the present experiment.

Summary

The effect of various metals (Pt, Ag, Cu, Al, Fe, and W) on the explosion limit of 5% and 20% ethylene mixed with air, has been studied. The results are proved by the following:

1) Inserting the metals generally caused the narrowing of the explosion region in the order of Cu, Fe, Al, W, Ag and Pt. Also, it is remarkable that the explosion peninsula tends to disappear.

2) After an experimental run, the oxide was found on the surface of the metals and the explosion limit moved from lower to higher ethylene content.

3) It is recognized that, in the case of the inserted metals, the induction periods is prolonged.

After all, it is considered that the metals inserted into the reaction vessels are considered to have a decisive influence on the explosion reaction, even if its mechanism can not be proved.

The author wishes to thank the late Prof. R. Kiyama and Dr. J. Osugi for their kind advice and encouragement throughout this work. He is also grateful to Mr. T. Ogura and Mr. Y. Takasuga for their assistance of the observation in part of the present experiment.