Some Experiments on the Explosive Reaction between Liquid Oxygen and Acetylene : Preliminary Research on Explosion of Liquid Oxygen

Some Experiments on the Explosive Reaction between Liquid Oxygen and Acetylene.——Preliminary Research on Explosion of Liquid Oxygen*

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I. Introduction.

Many accidental explosions of air liquifying oxygen plants have been reported, and in almost all cases the explosion took place in the part of evaporators of liquid oxygen in liquid air rectifying apparatuses. Various kinds of reaction are supposed to be the cause of the explosion. The following two reactions are considered rather provable as the explosion initiating reaction, 1) formation and explosive decomposion of copper acetylide in the air rectifying apparatus, or 2) reaction between ozone and acetylene both contaminating in liquid oxygen. However the formation of copper acetylide from metalic copper and acetylene at room temperature is almost impossible and the experimental evidence of reaction between acetylene and ozonized oxygen at low temperature has scarcely been known[1]. The present authors tried the various experiments to ascertain the possibility of explosive reactions between acetylene and ozonized oxygen at very low temperatures.

II. Experimental.

Liquid oxygen which was used in the following experiments was prepared by the air liquifying oxygen plant in the authors' institute, and acetylene gas was prepared by addition of water to calcium carbide and purified by passing through concentric sulphuric acid and caustic potash solution.

Experiment 1. Acetylene gas was blown into liquid oxygen of about 300 cc. in a Dewar flask. This experiment was done three times on different days, but no explosion occurred.

Experiment 2. To ascertain the view of "copper acetylide", the following experiments were tried. Acetylene gas was blown into the liquid oxygen in a Dewar flask containing copper powder and a copper net which had in advance been soaked in ammoniacal copper chloride solution. The whole system was stirred with a glass rod, but no explosion occurerd.

Experiment 3. Oxygen gas containing ozone prepared by passing through ozonizer B was condensed in the test tube C which was cooled by liquid nitrogen in Dewar flask A in Fig. 1.

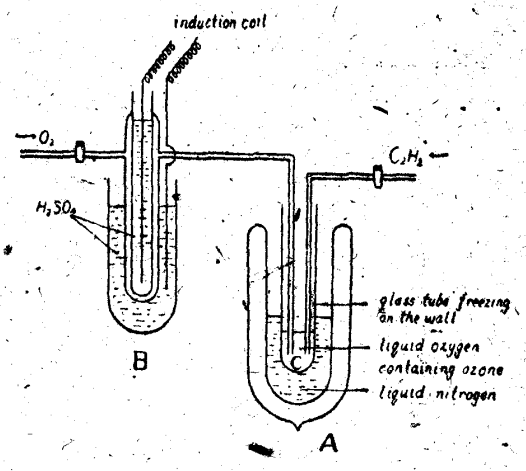

Fig. 1.

Then acetylene gas was flowed into it. During this procedure no explosion occurred. However, a violent explosion occurred at the moment when we tried to draw out the glass tube which freezed on the inner wall of the test tube, and the Dewar flask was broken

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to pieces. It was certain that, at the moment of the explosion, there was liquid nitrogen in the Dewar flask and liquid oxygen containing ozone in the test tube. However it was not certain that the explosion took place at the part of such low temperature of the apparatus, but it might initiate at the place of higher temperature. In any case, it was supposed that, in addition to the existence of both ozone and acetylene, some slight stimulus such as mechanical stirring or friction is necessary for the initiation or the explosion.

Experiment 4. Acetylene was condensed to solid in the glass bulb D (Fig. 2.) cooled by liquid nitrogen. Liquidous pure ozone was obtained in the ozonizer E which was also cooled by liquid nitrogen. D and E was connected with a breakable joint C. This joint was broken by a weight hanging by a fine wire which was cut by electric current. Such a remote operation was used to seek refuge from a danger of explosion if it would occur. When ozon vapour flowed into the bulb D no explosion occurred. Then the Dewar vessel B was removed and the temperature of D was raised gradually. Explosion occurred when the temperature was raised to about $-140°$ C.

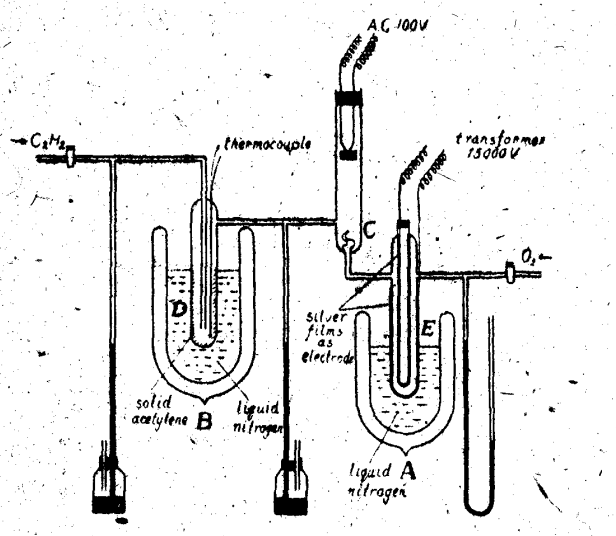

Fig. 2.

Experiment 5. The beakable joint C of Fig. 2 was removed. D and E was connected directly. Ozonized oxygen flowed into the bulb B where solid acetylene was condensed. An explosion occurred.

III. Detection of acetylene and ozone.

The proceeding experiments show the existence of both of acetylene and ozone in an air liquifier may cause an explosive reaction, although the reaction mechanism is not clear. The detection of acetylene and ozone in an air liquifier is one of the necessary procedures for the prevention of the explosion.

Acetylene in liquid oxygen can be detected in the usual way. All of the liquid oxygen for test is evaporated and introduced into an ammoniacal silver nitrate solution. If acetylene is contained in a sample, silver acetylide is precipitated.

Trace of ozone in liquid oxygen can be detected by the following procedure by which Paneth and Edger[2] determined ozone in the atomspheric air. About 1/2 litre of sample liquid oxygen from the air liquifier is received in a Dewar flask. The whole sample is gradually evaporated and passed through silica gel cooled by liquid oxygen. The silica gel being heated and evacuated in advance adsorbs ozone quantitatively. The gas adsorbed by silica gel is now desorbed by warming the adsorbent and allowed to act upon potassium iobide and starch solution. The solution colours blue when the sample of liquified oxygen is ozonized even feebly, but the liquid oxygen from the air liquifier of the authors' institute scarcely showed sign of ozone.

IV. Discussion.

The scientific researches of accidental explosions are generally very difficult as the evidence and witness have been almost damaged or injured by the accident. In the case of so called "explosion of liquid oxygen" it is certain that no heating is necessary for initiating the reaction and the rapid reaction begins at very low temperature near that of liquid oxygen. A certain kind of activation other than thermal one is expected to exist for such a remarkable reaction at very low temperature. A reaction of very small activation energy is also supposed in the whole reaction. In this case some special kinds of reactant such as an atomic one or some active particles are supposed to play an important role. In any way a manner of activation must exist in the process of liquifaction and rectification of air. A supposed manner of activation in this process is the discharge between particles whose

charge originated from triboelectricity. In air liquifiers compressed air or liquified air expands through a valve in jet including some particles of ice, oil and carbon dioxide which has escaped from a trapping apparatus. The violent stream of air through the valve will cause the so called triboelectricity. If the electric charge is accumulated on some insulating materials, discharge will take place between them. This discharge will suffice for the activation of reaction to form some active reactants[3]. Ozone or atomic oxygen will be formed by the discharge reaction in the liquid air. Formation of ozone is favoured by the low temperature. But experimental evidence has not yet been obtained in the present research. The present work only shows that explosive reaction is possible to occur at a low temperature near the boiling point of oxygen if acetylene and ozone were present in a vessel. Formation of ozone or atomic oxygen in liquid oxygen is supposed to result from the above mentioned discharge. But the formation or the existence of ozone in the air liquifier is not always free from questions. Ozone has a very characteristic odour and is identifieded even if its content is very small in the atomospheric air. Still there is no smell of ozone in the evaporating gas from liquid oxygen. The experimental research on the formation of ozone or atomic oxygen in the air liquifier will be carried on by the present authors.

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References

(1) Flyeman, J. Soc. Chem. Ind., (Transact. and Abstracts), **42** (1923), 37.

(2) Paneth and Edger, Natur, **142** (1938), 112.

(3) It has been reported that a jet of compressed gas caused some explosive reaction. For example W. Nusselt reported on the selfinflammation of hydrogen in jet, see Z. V. D. I., 66 (1922), 203.