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CHEMICAL REACTIONS AT HIGH TEMPERATURES AND PRESSURES. III. EQUIPMENT FOR OXIDATION WITH OXYGEN UNDER PRESSURES UP TO 1,500 ATMOSPHERES. STUDY OF THE METHOD OF OXIDATION OF ORGANIC COMPOUNDS.

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AUTHORS' ABSTRACT

Equipment was designed with which oxygen pressures of up to 1500 atm. can be reached. With the aid of this apparatus some experiments of oxidation of cyclohexene at different temperatures were carried out. The temperature at which freshly distilled cyclohexene explodes reaches 150°, and this temperature may be lower when the amount of the starting material is higher or if it is left in contact with oxygen of the air for a long time. This phenomenon is apparently due to accumulation of peroxides accelerating the oxidation.

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Apparatus

Reactions with compressed oxygen reported in the literature were performed at pressures of 100-170 atm. and oxygen was used in mixture with an inert gas (1, 2, 3). Only Finkelnburg et al (4) succeeded in reaching a pressure of 600 atm. in investigating the absorption spectrum of compressed oxygen. Indications were found that under these conditions O_4 molecules may be formed and the intensity of the bands in absortpion spectraascribed to these molecules increased as a quadratic function of pressure.

Absorption spectra of compressed oxygen are under study by one of the present authors in collaboration with A.F.Prikhot'ko; at pressuresof 600-1300 atm. a rapid increase of intensity of the bands with rise of

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pressure is observed. The results justify an assumption that at pressures of 3000 atm. and higher oxygen will be present exclusively in the form of O_4 molecules. Accordingly, work was started on the construction of equipment suitable for the use of oxygen under pressures up to 3000 atm., which will be described in a separate communication.

The design of this apparatus was based on the authors' experience gained in work with oxygen under 1500 atmospheres pressure. In the course of development of this equipment obstacles encountered were solved to varying degrees. One of the difficulties consisted in finding a liquid for transmitting the pressure and at the same time suitable for serving as a lubricant for the moving parts of the high pressure pump, because the use of oil was precluded by the presence of oxygen. A second problem consisted in finding a suitable material for packing, and a third - in removing all traces of fat from the parts of the equipment, while a fourth problem involved sufficient protection from explosion and from fragments should an explosion of the apparatus occur. Other problems of smaller significance were encountered which are not mentioned here.

Mercury could not be used as a fluid for transmitting pressure, as done by many investigators in compressing gases, since some experiments unavoidably lead to explosions and mercury could be blown into the laboratory. Glycerin was selected instead, which was used after two careful vacuum distillations. However, pure glycerin crystallized out in the steel capillaries at about 10° under a pressure of 1500 atm.,

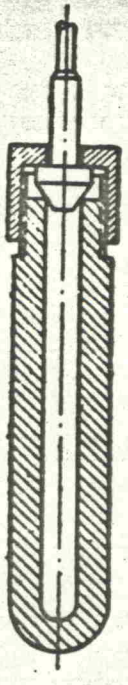


Fig. 1.

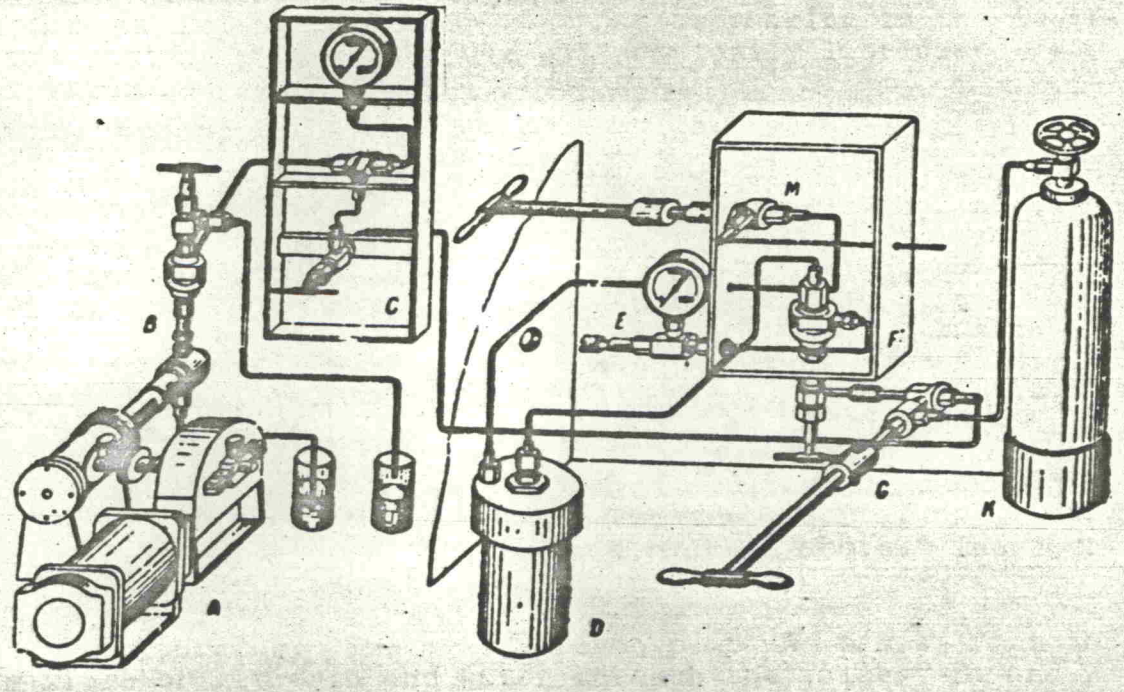


Fig. 2.

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which was rather unexpected because Tammann and co-workers (5) reported great difficulty in crystallizing this compound. On the other hand, under high pressure its melting point increases (for benzene the melting point rises from 5.4° at 1 atm. to 96.6° under 4000 atm. (6)). Accordingly, crystallization of glycerin can easily be explained.

In the further work glycerin was used in the form of a 50 per cent mixture with distilled water; pure water was not desirable, because the corrosion of steel greatly increases in its presence. The oxidation stability of glycerin was also unknown, and the experiments confirmed the theoretically possible further oxidation of this compound. In one experiment a violent explosion took place in the reaction vessel and the shock wave, the pressure of which was assumed by the authors to be of the order of 100,000 atm., passed through the steel capillary into the bomb containing oxygen over glycerin and brought about its partial explosion on the surface with ensuing destruction of the entire apparatus. The temperature developed in the explosion was apparently very high, because the steel of the capillary and the bomb was partly melted by the hot gases. In addition to this phenomenon, a slow oxidation of glycerin to glyceric acid took place at room temperature and 1000-1500 atm. pressure, with consequent extensive corrosion of the equipment. The latter could easily be prevented by frequent changes of the glycerin for transmitting the pressure because accumulation of glyceric acid is slow.

Fat-free asbestos impregnated with pure glycerin was used as packing material. In the high pressure pump which does not come in direct contact with oxygen fat-free leather was used as packing in the stuffing box of the piston. The piston was satisfactorily lubricated with a mixture of water and glycerin.

Special attention was paid to removal of oil from all parts of the equipment. A droplet of oil in one of the valves led to an explosion and destruction of the pipeline. The apparatus was kept in a steel safe with a specially constructed labyrinth for the easy elimination of the sound wave after it had been reflected twice, which removed the danger of tearing off the steel sheets of the safe in case of an explosion. It was found that at the moment of an explosion one could stay close to the safe without danger and even observe the explosion through a plexiglass window. All fragments remain inside the safe.

The safe consisted of a small steel room inside the laboratory and its walls were made of 15 mm. sheet steel. All valves and other equipment could be manipulated from the outside and the observation of the apparatus and manometer through the window mentioned above. The door of the safe was closed throughout the experiment.

Fig. 2 shows the apparatus. The motor-driven pump A passes from the beaker the mixture of glycerin and water through the valves B and C into the receiver D, which constitutes a steel bomb of internal diameter 50 mm. and 400 mm. high. The liquid passing from the pump to the receiver goes through a steel pipe reaching the bottom of the

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receiver. Before starting the pump the receiver and the entire equipment are filled with oxygen from a tank under a pressure of 100-150 atm. After this operation, the bomb is shut off from the rest of the equipment with the aid of the valve G. The manometer E shows the initial pressure in the apparatus. After the pump A is started, the liquid passing into the receiver D compresses the oxygen to the required extent.

A drawback in this method consists in the loss of some oxygen, which is dissolved in the pressure transmitting liquid. The oxygen passes under 1000-1500 atm. through the valve M into the reactor not shown in the figure. The latter is a cylinder of stainless steel, of internal diameter 10 mm., external diameter 30 mm., and 140 mm. high. A general view of it, including the packing, is shown in Fig. 1. For heating it is immersed in an oil bath with the aid of a pulley outside the safe.

The compound to be oxidized was placed into a glass test tube and the latter into a reactor, after which the reactor was closed by screwing on its cap and connected to the valve M with the aid of the steel capillary 0.5 x 5 mm.

Oxidation of cyclohexene.

Exploratory experiments were performed of oxidation of cyclohexene with oxygen under up to 1500 atm. According to literature data, cyclohexene, pure or in solution in acetone, will be oxidized to adipic acid when oxygen is passed through it in the presence of osmium or tellurium. Simultaneously, small amounts of adipaldehyde, cyclohexanol and similar substances are also formed (7). It was recently shown (8, 9) that slow oxidation of cyclohexene involves an intermediate step of formation of peroxides.

Cyclohexene for the experiments under report was prepared by dehydration of cyclohexanol. Its boiling point was 82-83°; n(20/D), 1.4497.

In the first experiment 0.5 g. cyclohexene in a glass tube were subjected to a pressure of 1000 atm. at 12° for 4 hours. No changes were observed and the refractive index remained the same. In the second experiment a similar sample was treated under the same pressure at 50° for 4 hours with no apparent change in the sample. Its refractive index was not affected. Further, an 0.5 g. sample of cyclohexene was heated for 5 hours to 100° under the above pressure, whereupon yellowish crystals were found in the tube. The liquid had an n(20/D) 1.4518. In experiment No. 4 the temperature was raised to 150°, other conditions being the same. After 3 minutes, an explosion took place in the reactor, upon which the product was found to have been carbonized. In the experiment No. 5 the temperature was again reduced to 100° and the pressure left at 1000 atm. After 1 hour the 2.4 g. sample of cyclohexene exploded under these conditions. In the experiment No. 6, 2.4 g. cyclohexene were charged into a glass test tube at -5°

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and heated to 50° under 1000 atm. An explosion took place after 2 hours.

The conclusion which the authors believe to be indicated by these exploratory tests is that cyclohexene is not oxidized by oxygen under pressures up to 1000 atm. until a temperature of 50° is reached. At higher temperatures a very slow oxidation takes place, the rate of which apparently greatly depends upon the presence of peroxides. Accumulation of the latter substantially accelerates the oxidation and leads to an explosion.

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