THE CHEMICAL CHANGE OF CARBON DISULPHIDE UNDER ELECTRODELESS DISCHARGE.*

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There have been many investigations to prepare carbon monosulphide,(1) among which the work by J. Dewar and H. O. Jones appears to be the most important. They decomposed the vapour of carbon disulphide at a low pressure of about 15 mm. under silent discharge in an ozonizer.

The present author decomposed the vapour of carbon disulphide under electrodeless discharge and examined the change. The vapour was passed through a discharge apparatus, and to attain a pressure sufficiently low to effect electrodeless discharge, a bulb containing carbon disulphide was connected with the reaction vessel by means of a long capillary tube with a diameter of about 0.1 mm., and the vapour coming out of the reaction vessel was condensed by cooling with liquid air, so that carbon disulphide distilled continuously through the reaction vessel. Further details of the apparatus are shown in Fig. 1.

Electrodeless discharge was effected by connecting two annular copper stripes on the reaction vessel to a supply of an alternating current of a frequency of approximately 10^7 cycles per second, which was generated from an alternating current of 200 cycles per second and about 2000–3000 volts by using a small transmitting valve. The circuit is shown diagramatically in Fig. 2.

To purify carbon disulphide (from Hopkin and William Co., Ltd.), it was first distilled at about 46°, shaken with concentrated sulphuric acid, then with mercury, and finally with lime, and redistilled at 46°. When carbon disulphide (50 c.c.) was placed in bulb A and the bulb was cooled in ice, the

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* Cf. J. J. Thomson, The Electrodeless Discharge through Gases, *Phil. Mag.*, Nov. 1927; J. S. Townsend and R. H. Donaldson, Electrodeless Discharge, *Phil. Mag.*, Jan. 1928; G. Mierdel, Untersuchungen über den Elektrodenlosen Ringstrom. *Ann. Physik*, Nr. 5, 1928; S. B. Bhatnager and Rama Krishna Sharma, Chemical Reaction under Electrodeless Discharge, *J. Indian Chem. Soc.*, June, 1928.

(1) M. Berthelot, *Ann. chim. phys.*, (3), **53** (1858), 142; A. W. Hofmann, *Ber.*, **3** (1870), 197; T. Sidot, *Compt. rend.*, **69** (1869), 1303; S. M. Losanitsch, *Ber.*, **30** (1897), 135; **40** (1907), 4656; J. Thomsen, *Z. anorg. Chem.*, **34** (1903), 187; A. Deninger, *J. prak. Chem.*, **51** (1895), 346; J. Dewar and H. O. Jones, *Proc. Roy. Soc.*, A, **83** (1910), 408, 526; **85** (1911), 574. Further cf. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VI, p. 94.

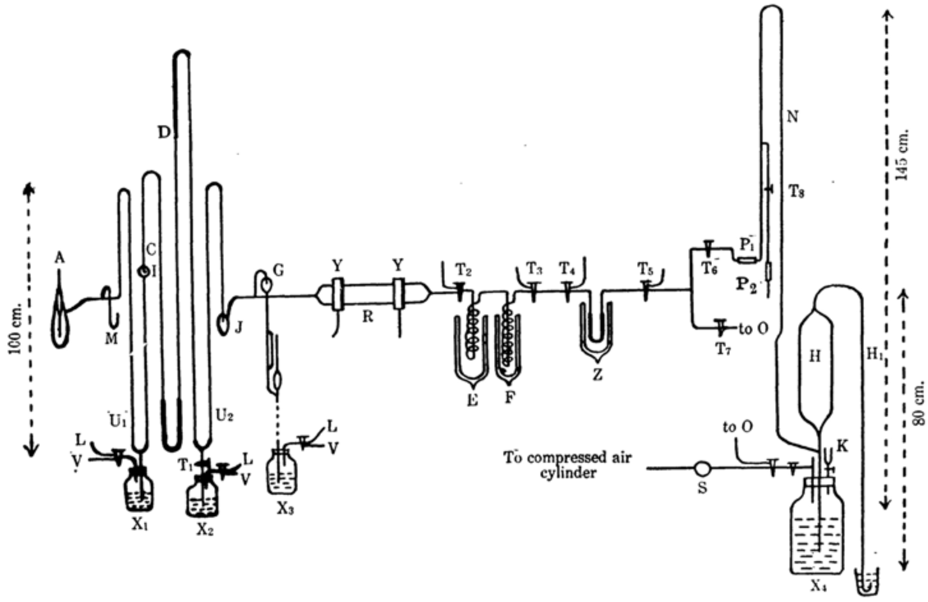

Fig. 1. A : bulb containing carbon disulphide. M : manometer. CD : capillary tube. I and J : traps for mercury. GX$_3$: McLeod guage. R : reaction vessel (about 250 c.c.). Y : annular copper stripes. E and F : condensers. Z : spare condenser. T_1, T_2, T_3, T_4, T_5, T_6, T_7 and T_8 : taps. Condensed carbon disulphide is removed from T_2, T_3, T_4 and T_5. The vapour of carbon disulphide attacks tap grease, and hence it is necessary to grease the taps frequently to avoid leaks. HX$_4$: Toepler pump to drive the gas from H into capillary tube H_1. X_1, X_2, X_3 and X_4 : mercury reservoirs. K : funnel for supplying mercury to keep the mercury level of X_4 constant. S : safety valve. O : Cenco Hyvac pump. It is necessary to apply a pressure of about 600 mm., and tube N extends to about 145 cm. above the mercury level in X_4. Compressed air is used to expel the gas from cylinder H, the pressure being controlled to about 0.8 atmosphere by safety valve S. U_1 and U_2 : long glass U-tubes for controlling the flow of the gas. L's : air is supplied by L's. The air is dried with $CaCl_2$, conc. H_2SO_4, potash, and finally with P_2O_5. V's : The air in the reservoirs is sucked from V's. Mercury goes up to the bottom of U_1 or U_2 and stop the flow of the gas when air is allowed from L, and goes down into the reservoir when air is sucked from V. P_1 and P_2 : tubes for drying the gas and the air flowing to Toepler pump respectively.

vapour pressure was found 128 mm. mercury, which was higher than the values obtained by H. V. Siemens (127 mm.) and by Henning and Stock (127.25 mm.).

To fill bulb A with carbon disulphide, the bulb was communicated with a Cenco Hyvac pump through a phosphorus pentoxide tube, evacuated, and dried, and liquid carbon disulphide was put in. After carbon disulphide having been frozen by cooling in liquid air, the bulb was evacuated through the phosphorus pentoxide tube as far as possible, and then sealed off.

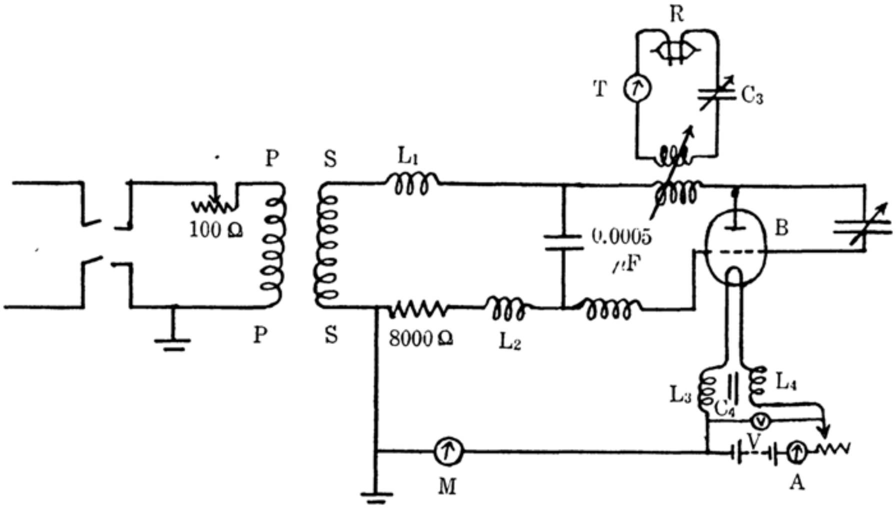

Fig. 2. L_1, L_2: pyrex tubes of 2′ 6″ length and $1\frac{1''}{8} - 1\frac{1''}{4}$ diameter, 2′ being wound with D.S.C. copper wire of 32 S.W.G. L_3, L_4: one pyrex tube of $1\frac{1''}{2}$ diameter and 16″ length, wound doubly with D.C.C. copper wire of 16 S.W.G. C_4: glass tube with copper foil on its inner wall to slide inside the tube of L_3 and L_4. C_2, C_3: variable condensers, each consisting of two copper sheets of $4''\times4''\times\frac{1''}{16}$, mounted on pillars so that the space between them can be adjusted. M: milliammeter (0—30 m.a.). T: thermoammeter (0—12 amp.). B: Marconi valve (12.5 volts, 5.5 amp.). P: primary coil of the transformer. S: secondary coil of the transformer. R: reaction vessel. A: ammeter (0—10 amp.). V: voltmeter (0—15 volts).

U_1, U_2, T_2, T_3, T_4, T_5 and T_6 were then all communicated with the Toepler pump, and condenser E was placed in liquid air, and thus the vapour of carbon disulphide was allowed to flow from bulb A and to carry any residual air with it, the pump removing continuously the carried air. It took a long time (about two days) to expel air from the apparatus because of the slowness of the flow of the gas.

The vapour of carbon disulphide in the apparatus was tested on purity in the following manner. U_1 and U_2 were shut, condenser E previously evacuated as highly as possible was placed in liquid air, and taps T_2 and T_3 were then shut. The mercury in the McLeod guage was allowed to rise by adjusting the pressure in the mercury reservoir X_3 to the atmospheric pressure. U_1 and U_2 were then opened; in 5 minutes the mercury fell by 50 mm., and then U_1 was shut and T_2 opened. In about 10 minutes U_2 was shut and the pressure was read on the guage during about half an hour, and found constant at 0.005 mm. The initial pressure of the carbon disulphide in the reaction vessel being 50 mm., the ratio of the pressure of air to that of carbon disulphide can not be greater than 0.005/50, that is 0.01 per cent.

The pressure of the vapour of carbon disulphide in the reaction vessel in the steady state was determined in the following manner. The whole apparatus was evacuated to about 0.005 mm., and the vapour of carbon disulphide was allowed to flow from bulb A cooled in ice (the vapour pressure being 128 mm. here) into the apparatus. Condenser E was then cooled in liquid air and the pressure was read, Table 1.

Table 1.

Time (min.)	Pressure (mm.)
0	0.08
5	,,
10	,,
15	,,
20	,,
25	,,
35	,,

Table 2.

Time (min.)	Pressure (mm.)	Time (min.)	Pressure (mm.)	Time (min.)	Pressure (mm.)
0	0.085	30	0.0925	60	0.075
4	,,	35	,,	65	,,
9	,,	40	,,	72	,,
15	0.0925	45	,,	80	,,
20	,,	50	0.075	88	,,
25	,,	55	,,	90	,,

When the pressure in the apparatus was steady (0.08 mm.), condenser F as well as E was cooled in liquid air, and the vapour of carbon disulphide was subjected to the action of electrodeless discharge. The pressure was read continually, Table 2. The pressure fell to 0.075 mm. in fifty minutes and stayed steady there.

When electrodeless discharge was stopped, the whole wall of the reaction vessel was found to be covered with brown solid, and the narrow necks with dark solid. On removing liquid air from condenser E, instantaneous detonation took place with a flash, and the upper part of the condenser was covered with a dark lustrous solid mass, and the bottom with a dark brown powder, while no liquid was found.

A part of the deposit on the wall of the reaction vessel was dissolved in carbon disulphide, when a brown solution resulted. On adding a drop of concentrated sulphuric acid to this solution, a brown precipitate was formed. The deposit on the bottom of condenser E was dissolved in carbon disulphide to a purplish brown solution, which gave a purple precipitate on adding a drop of concentrated sulphuric acid. These solid substances appear to be the polymers of gaseous carbon monosulphide in different degrees of polymerization.

The black lustrous substance on the wall of the reaction vessel may probably be a polymer of carbon ditrita-sulphide $(C_3S_2)_X$ which might be formed together with the polymers of monosulphide. It seems that mercury also deposited on the wall of the condenser.

It can not be said that carbon monosulphide CS existed as a stable gas. It is very interesting that Dewar and Jones, too, reported the formation of a brown mass accompanied by a flash and detonation. More precise and quantitative investigation will further be made.

In conclusion the author wishes to express his hearty thanks to Prof. F. G. Donnan of the University College, London, where this investigation was made by virtue of his kind suggestion and encouragement, and to acknowledge the kind advice and great help rendered by Dr. R. W. Lunt during the course of the experiments.