

CXXV.—*The Properties of Malonic Anhydride (Carbon Suboxide), C<sub>3</sub>O<sub>2</sub>.*

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A QUANTITY of carbon suboxide has been prepared by the method of Diels and Meyerheim (*Ber.*, 1907, **40**, 359) with a view to the study of the kinetics of its process of polymerisation in the gaseous state. Also, since it was a comparatively simple matter to prepare the oxide in the pure state, the vapour pressure was measured over the range — 62° to 4°.

The oxide in the gaseous state proved to be very stable, even at room temperature, when dry and contained in a glass vessel the surface of which had not been previously contaminated with the polymerised product. On the other hand, it could not be stored over mercury for any length of time, or in the presence of moisture without polymerisation occurring. The dried gas is not appreciably affected by insolation with ultra-violet light.

The polymerisation occurs on the surface of the containing vessel, and from the measurement of the velocity of chemical change, the process is seen to be very complex.

EXPERIMENTAL.

The method of Diels and Meyerheim was adopted with slight modifications. Mixtures of 20 g. of pure malonic acid and 200 g. of powdered phosphorus pentoxide were placed in a 350 c.c. flask of hard glass and, after evacuation by means of a Langmuir pump, heated by suddenly plunging the flask into an oil-bath at 140—

160°. The gases liberated were withdrawn as rapidly as possible from the hot flask and cooled by passage through tubes immersed in a freezing mixture of ice and salt, and in liquid air. A mixture of acetic acid, carbon dioxide and carbon suboxide condensed in the tube immersed in liquid air. The temperature of the mixture was allowed to rise slowly and the bulk of the carbon dioxide evaporated into the air. When a temperature of 7° was reached, the gas was collected in a mercury reservoir; the first fraction was rejected, as it was contaminated with much carbon dioxide, and the second fraction was condensed as rapidly as possible in a 3 c.c. bulb immersed in liquid air. The liquid carbon suboxide was freed from carbon dioxide at -50° by connecting the bulb repeatedly with an evacuated space (10 c.c.) until the liquid gave a constant vapour pressure. The purity of the preparation was shown by the vapour density, which was 34.3.

*Determinations of Vapour Pressure at Various Temperatures.*—About 2 c.c. of carbon suboxide were condensed in a small bulb, to which was attached a mercury manometer by a glass-to-glass connexion. Since the suboxide slowly polymerises on the surface of mercury, the manometer was shut off by a tap except when measurements were being taken. Vapour-pressure determinations were made between -62° and 4°, in a bath of alcohol contained in a Dewar vessel as a thermostat. The alcohol was cooled by means of solid carbon dioxide. After every reading the bulb was placed in liquid air, and the vapour-pressure readings showed that no appreciable decomposition occurred throughout the experiments. In the table are given the readings of the manometer. Those at -62° are the successive values obtained during the removal of carbon dioxide.

*Vapour Pressure Readings.*

Temp. ....	-62°	-62°	-62°	-62°	-62°
Vap. press. (cm.) .....	5.80	3.55	2.85	2.45	2.30
Temp. ....	-62°	-62°	-52°	-44°	-39°
Vap. press. (cm.) .....	2.30	2.30	3.83	6.48	8.67
Temp. ....	-35°	-31°	-27°	-24°	-21°
Vap. press. (cm.) .....	10.97	13.61	16.69	19.34	22.37
Temp. ....	-16°	-11°	-6°	0°	+4°
Vap. press. (cm.) .....	28.47	35.97	44.62	57.52	67.32

From the vapour pressure curve, the boiling point at atmospheric pressure is 6.8°.

The heat of vaporisation was calculated from the above data by means of the expression  $d \log p/dT = -Q/RT^2$ , and the values for the range of temperature -62° to 4° are given below.

*Values of Q for the Different Temperature Ranges.*

Range ...	-62° to -52°	-52° to -44°	-44° to -39°	-39° to -35°
Q (Cal.)...	4.74	6.62	6.16	6.57
Range ...	-35° to -31°	-31° to -27°	-27° to -24°	-24° to -21°
Q (Cal.)...	6.18	6.03	6.02	6.06
Range ...	-21° to -16°	-16° to -11°	-11° to - 6°	- 6° to 0°
Q (Cal.)...	6.22	6.27	6.00	6.14
Range ...	0° to 4°			
Q (Cal.)...	5.93			

The mean value of  $Q$  between  $-31^\circ$  and  $4^\circ$  is 6.08 Cal.

*Velocity of Chemical Change.*—Purified liquid carbon suboxide was vapourised into a glass bulb of 80 c.c. capacity. The bulb had been used previously in an experiment in which a red film of polymerised product had been deposited. This was removed by means of water and chromic acid. The polymerisation was accompanied by a decrease in pressure. The pressure was observed at constant volume and temperature ( $12^\circ$ ). The following readings were obtained for an initial gas pressure of 44.39 cm.

Time (hrs.) .....	0.25	0.75	1.75	2.75	4.75	6.75
Change of press. (cm.) ...	0.55	2.90	3.86	4.08	4.25	4.50

The values of the velocity coefficient,  $k$ , calculated from the above data, on the assumption that from 1 to 6 molecules may be taking part in the change, fall off with time. The reaction is probably a catalytic surface reaction. The fact that the speed of the reaction falls off with time may be explained by the fact that the vapour must diffuse through the layer of decomposed or polymerised product to the surface of the glass before it can undergo change.

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