CCLXIX.—*The Reaction between Acetylene and Sulphur at Temperatures up to 650°.*

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MEYER and SANDMEYER (*Ber.*, 1883, **16**, 2176) obtained material, regarded as thiophen and giving the indophenin reaction, by heating sulphur in acetylene, but it is not stated that the substance was isolated. Capelle (*Bull. Soc. chim.*, 1908, **4**, 150) and de Coninck (*Bull. Acad. roy. Belg.*, 1908, 305) state that only carbon disulphide, thiophten, and a material with a garlic-like odour is present. Recent work (Briscoe and Peel, this vol., p. 1741) has indicated that thiophen is probably produced, and this work sought to determine roughly the composition of the liquid condensed at laboratory temperatures. The main reaction appears to yield carbon disulphide and hydrogen sulphide, but 77% of the sulphur at most is in the condensate, the rest probably converting the acetylene into carbon and hydrogen sulphide. Small quantities of thiophen and thiophten are formed at all the temperatures employed, 500° being the optimum, but benzene and naphthalene are entirely absent.

EXPERIMENTAL.

Preliminary.—Sulphur was heated in an ordinary distillation-flask, clamped horizontally, at the centre of which acetylene was delivered, and the products were passed through the side-limb into a bottle cooled in water and fitted with a reflux condenser. The phenomena observed were similar to those noted by Capelle (*loc. cit.*): the reaction, initiated by a dense yellow flame which deposited carbon, appeared to take place between the vapour and the gas at a temperature below the boiling point of sulphur; later, when there was a sufficiently constant supply of vapour, the acetylene burned steadily. The brown oily liquid from several runs was distilled through a spiral column until no further distillate could be obtained at 150°. The boiling point of the distillate gradually rose to a maximum of about 65°. The residue was distilled under reduced pressure and gave an orange liquid, b. p. 110—115°/20 mm., which on redistillation at the ordinary pressure gave a liquid, b. p. 210—220°, with the reactions of thiophten. The lighter fraction, when fractionated through a bead-filled column 4 feet long, yielded a large head fraction of carbon disulphide, b. p. 46·7°, and a fraction, amounting to 5%, b. p. 84·0°/760·5 mm. This proved to be thiophen, giving the indophenin and other reactions characteristic of that substance (Found: C, 57·1; H, 4·5. Calc.: C, 57·1; H, 4·8%). The carbon disulphide contained a trace of material with a

garlic-like odour which even the careful fractionation employed failed to isolate.

Addition of 5% of iron or 1% of iodine to the sulphur had little effect on the course of the reaction, the proportion of thiophen in the lighter fractions being 6% and 5% respectively.

In order to ascertain the lowest temperature at which the reaction began, the flask was surrounded by a double-walled air-bath, closed at the top with asbestos board, carrying a thermometer, and suitably cut for the neck of the flask. Ignition invariably took place at 275°, but after the first flash, if the temperature continued to be raised, no further flame formation took place even up to 325°. If, however, the flask were cooled below 275° and again raised above that point, flashing was once more observed. Below 300° the rate of reaction was inconveniently slow.

Reaction at about 325°.—Acetylene was led below the surface of the molten sulphur, the object being to obtain material at the lowest temperature (325° ± 5°) at which there was a reasonable rate of reaction. About 38% of the sulphur was converted into a brown oil which yielded CS_2 77%, C_4H_4S 9%, $C_6H_4S_2$ 6%.

Reaction at about 500°.—A convenient apparatus consisted of a Pyrex tube 22″ × 1·5″ heated to the required temperature in a cylindrical electric furnace 12″ long. The closed end of the tube which protruded 5″ from the furnace was charged with 50 g. of sulphur and a rapid stream of acetylene was delivered about the centre of the heated zone. About 74% of the sulphur was converted into a brown oil containing CS_2 77%, C_4H_4S 12%, $C_6H_4S_2$ 6%.

Reaction at about 650°.—It was clear that a definite change had taken place in the course of the reaction at this temperature, resulting in the production of more carbon which caused constant trouble by choking the end of the tube delivering acetylene. About 77% of sulphur was converted into a liquid containing CS_2 83%, C_4H_4S 5%, $C_6H_4S_2$ 3%.

Previous determinations of the density (Schiff, *Ber.*, 1885, **18**, 1601) and surface tension of thiophen are somewhat old, and these properties have been redetermined on the material (analysed above) after three further fractionations, glass pyknometers of about 10 c.c. capacity and a pair of carefully calibrated capillary tubes being used; $d_{4°}^{20°} = 1·0615$ and $\gamma = 32·58$ at 20°. These data give a molecular parachor of 189·0, from which may be deduced the parachor of sulphur, 46·5 (value for double bond = 23·2, C = 4·8, H = 17·1, five-membered ring = 8·5). This is in close agreement with the mean value, 46·3, derived from the data for carbon disulphide (Ramsay and Shields, J., 1893, **63**, 1089; Morgan and Thomssen, *J. Amer. Chem. Soc.*, 1911, **33**, 657; Harkins, Clark, and

Roberts, *ibid.*, 1920, **42**, 700) but differs appreciably from the value 50·7 obtained with ethyl mercaptan (Morgan and Chazal, *ibid.*, 1913, **35**, 1821).

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