THE INTERACTION OF CHLORINE AND SULPHUR MONOCHLORIDE. PREPARATION OF SULPHUR DICHLORIDE: USE OF ANTIMONY PENTA-CHLORIDE AS CATALYST.

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It was observed by $Aten^{1}$ that chlorine and sulphur monochloride combine only very slowly at room temperature, the yellow liquid gradually changing to red. The process may be expedited by cooling the reaction vessel in ice; also by the addition of certain catalysts.

In 1918 Pope and Heycock² stated that by the addition to the sulphur monochloride of 1 per cent. by weight of "absorbent charcoal" the reaction may be accelerated, and that "this material is considerably superior to the catalysts hitherto proposed to be used for the purpose in view;" but they do not say how the charcoal was prepared, nor do they give any quantitative data as to the acceleration.

In the course of some experiments carried out by the author, antimony

¹ Aten, Z. physikal Chem., 1906, 54, 72. ² Pope and Heycock, (B.P. No. 142879).

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pentachloride was found to be a very efficient catalyst for the reaction $S_2Cl_2 + Cl_2 = 2SCl_2$, the addition of 0.5 per cent. by weight causing the absorption of the theoretical quantity of chlorine in about an hour at atmospheric temperature (19°-curve C).

 \therefore A larger proportion (1-2 per cent.) of the catalyst caused no further acceleration. In the absence of a catalyst (at 16°) only about one-fifth of the theoretical quantity of chlorine had been absorbed in 5 hours (curve A); and even when the reaction vessel was cooled in ice 5 hours were required for completion of the reaction (curve B).

n The dotted horizontal line in the figure indicates the theoretical quantity of chlorine required for the complete conversion into sulphur



A. Pure S₂Cl₂ at 16° C. B. Pure S₂Cl₂ at 0° C. C. 0.5 per cent. SbCl₅ present, at 19° C. D. Pure S₂Cl₂ at 0° C. in bright sunlight. FIG. 1.

dichloride (SCl₂) of the amount of sulphur monochloride employed. All volumes are reduced to $N.T.P.^3$

The antimony pentachloride dissolves readily in the sulphur monochloride, but on passing chlorine through the solution a colourless precipitate is formed, presumably the compound SbCl₅SCl₄, obtained by Ruff

³ In experiments carried out at room temperature absorption of chlorine ceased when the liquid contained about 70 per cent. Cl ($SCl_2 = 68.9$ per cent. Cl). At o°, however, absorption proceeded beyond this point.

The nature of the product SCl₂ is not discussed (cf. Ruff and Fischer, Ber., 1903, **36**, 418; Aten, Z. physikal. Chem., 1906, **54**, 55; Bergmann and Bloch, Ber., 1920, **53**, 977; Lowry, McHatton, and Jones, F. Chem. Soc., 1927, 746.

and Fischer⁴ by adding SCl₂ to a cold solution of antimony pentachloride in sulphuryl chloride.

The curves A and B for pure sulphur monochloride show that after the first 20 minutes or so there is a period of quiescence during which no absorption of chlorine occurs. At the beginning of this period the liquid is yellow, but towards the end it gradually becomes red; absorption is then renewed, and proceeds continuously. These observations agree with those of Aten,¹ the initial absorption being presumably a physical solution of chlorine in sulphur monochloride.

The occurrence of a period of induction suggested that the reaction might be a photochemical one, as are many reactions of chlorine, e.g., chlorine and hydrogen; 5 and as all the experiments described above were carried out in dull diffused daylight, the effect of exposure to direct sunlight was examined, the reaction vessel being cooled in ice as in B. A comparison of the results (curve D) with those obtained at o° in dull diffused daylight (curve B) shows that the period of induction is shorter, and the absorption, when renewed, proceeds more rapidly, than is the case in dull diffused daylight; the time required for completion of the reaction in the former case is less than half of that required in the latter.

Experimental.

Fig. 2 shows the apparatus employed. Chlorine, washed with water (B), and dried with sulphuric acid (C and D), was passed into the graduated

cylinder G, which was filled with concentrated sulphuric acid saturated with chlorine,⁶ until most of the acid had been driven over into K. The taps L and P were then opened, and the current of gas continued through \mathbf{M} and N until all air had been expelled, when F and P were closed. By raising or lowering K the gas in G and N was brought under atmospheric pressure, and the level of acid in G was noted.



A measured quantity (3 c.c.) of pure sulphur monochloride,⁷ or of the sulphur monochloride containing a known weight of antimony pentachloride, was then introduced into Q, and by momentarily opening P, was allowed to

⁴ Ruff and Fischer, Ber., 1904, 37, 4515.
⁵ Cf. Bunsen and Roscoe, Phil. Trans., 1857, 147, 381; Burgess and Chapman,
⁵ C. Chem. Soc., 1906, 89, 1399; Norrish, J., *ibid.*, 1925, 127, 2323.
⁶ In order to fill G with acid the tube F was disconnected at E from the chlorine

supply and connected to a water-pump, by means of which the acid was drawn in through H from K, which was raised on a level with G.

7 Cf. Mann, Pope and Vernon, J. Chem. Soc., 1921, 119, 636.

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run into N, which was surrounded by a glass basin O, for containing ice when necessary. N was gently agitated from time to time. As absorption proceeded, K was slowly raised so as to keep the gas under atmospheric pressure during the whole experiment.

Before beginning the series of quantitative experiments the cylinder G was filled with chlorine and allowed to stand for about a week, the chlorine being renewed every day, in order to "season" the rubber cork.

Summary.

The effect of the addition of antimony pentachloride on the rate of chlorination of sulphur monochloride has been measured.

Evidence is furnished that the reaction between chlorine and sulphur monochloride is a photochemical reaction.

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