205. *The Effect of Solvent on the Reaction between Iodine and Hydrogen Sulphide.*

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THE reaction between iodine and hydrogen sulphide, with ether containing different amounts of water as solvent, has been studied by Parsons (*J. Amer. Chem. Soc.*, 1925, **47**, 1820). He found that in pure ether the reaction was very slow but went to completion, whereas in the moist solvent reaction was comparatively rapid but incomplete. He therefore suggested the formation of sulphurous acid ($3H_2O + 3I_2 \rightleftharpoons 6HI + 3O$, $3O + H_2S \rightleftharpoons H_2SO_3$), which was assumed to react reversibly with the hydrogen iodide: $H_2SO_3 + 6HI \rightleftharpoons 3H_2O + H_2S + 6I$; but he was unable to isolate the products of the reaction.

In the investigations now described, ether, carbon tetrachloride, and their mixtures with certain reagents were employed to elucidate the effect of a solvent on the same reaction.

EXPERIMENTAL.

In view of Parsons's observation that oxygen affects the reaction, rigorous precautions were taken to exclude this gas from the reaction vessel. By attaching to the vessel a tube into which the solution could be transferred, colour changes due to loss of iodine could be measured without exposure of the solution to the atmosphere. The reaction vessel (see fig.) consisted of a bulb *A* of about 50 c.c. capacity, to which the side tube *C* was attached for measurement of colour due to unreacted iodine. The narrow tube *D* had a scratch made at *E* so that it could be broken by suitably dropping on to it the glass rod *S*, thus admitting the solution from the bulb *A* into the flask *B* containing hydrogen sulphide.

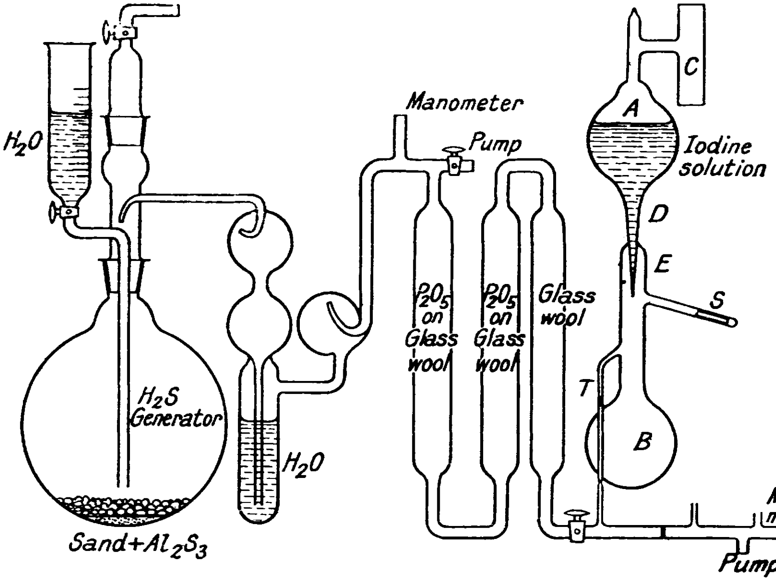
Before being sealed to the hydrogen sulphide generator, the reaction vessel was kept at 300° in a vacuum. The bulb *A* was then filled with carbon dioxide (dried over phosphoric oxide), the requisite amount of iodine solution poured in, and the end sealed off. The vessel was then sealed to the generator, and after the assemblage was complete, all the vessels were again dried for two days under vacuum in contact with phosphoric oxide.

The ether and carbon tetrachloride were purified by standard methods. Finally, the ether was refluxed over sodium for two days and distilled. Phosphoric oxide was employed for drying the carbon tetrachloride.

The hydrogen sulphide was prepared by the action of water on aluminium sulphide, obtained from pure aluminium and sulphur by ignition as in the thermite process.

The iodine concentration in all the bulbs was 0·0062 g.-atom per l. of solution. The volume of solution in each of the bulbs was so adjusted that in all the reaction vessels the ratio of hydrogen sulphide to iodine was identical.

The following solvents were employed : (1) dry ether, (2) dry carbon tetrachloride, (3) ether containing (*a*) 5·4, (*b*) 52·0, and (*c*) 211·0 millimols. of water per l., (4) carbon tetrachloride containing a small quantity of water, (5) carbon tetrachloride with varying quantities of ether, (6) 50 c.c. of carbon tetrachloride with 1 c.c. of pyridine, (7) 50 c.c. of carbon tetrachloride with 1 c.c. of absolute alcohol.



After the requisite amount of carefully dried hydrogen sulphide had been introduced into the reaction vessels, they were sealed off from the generator. The capillary ends of the bulbs containing the liquids were then broken, and the liquids allowed to come into contact with the hydrogen sulphide. The loss in colour of the iodine solution in each of the vessels was determined from time to time by comparison with standard solutions of iodine in the appropriate solvent. The experimental error in most of the colorimetric measurements was about 5%. In some instances colour comparisons could not be satisfactorily made.

Results.

The colour of iodine in the dry ether disappeared slowly and the liquid was very pale at the end of 3 months. In dry carbon tetrachloride solutions, however, there was no detectable loss of colour even at the end of this period.

With ethereal solutions containing various amounts of water, we obtained results which in general confirm those of Parsons, though equilibrium was not attained so readily in our experiments, as can be seen from the table, which shows the ratio, *R*, of the intensity of the colour of the solution in the reaction vessel to that in the original solution after the given number of days.

Rate of reaction between iodine and hydrogen sulphide in ethereal solutions containing small quantities of water.

Initial concn. of iodine 0·0062*N*; hydrogen sulphide was in large excess (*ca.* 12-fold).

H_2O, millimols. per l. of Et_2O.	*R*, after (days).							Iodine consumed.
	1.	12.	32.	47.	57.	72.	90.	
0·0	0·8	0·5	0·25	0·22	0·18	0·16	0·16	0·84
5·4	0·8	0·4	0·35	0·33	0·33	0·33	0·33	0·67
52·0	0·8	0·65	0·55	0·55	0·55	0·55	0·55	0·45
211·0	0·9	0·65	0·55	0·40	0·40	0·40	0·40	0·60

Carbon tetrachloride solutions containing pyridine gave an instantaneous decolorisation of iodine with the production of a white precipitate of pyridine hydriodide. In carbon tetrachloride solutions containing small quantities of ether, there was a slow reaction, the extent of which was roughly proportional to the concentration of ether in the solution.

Iodine and hydrogen sulphide reacted to a slight extent in carbon tetrachloride containing small quantities of water, but the solubility of water was so low that a very limited variation in water content was practicable. In carbon tetrachloride solutions containing alcohol there was fairly rapid reaction, but the solutions were not completely decolorised, there being finally a pale yellow colour.

In ethereal solutions, after the slight reaction, ethyl iodide and mercaptan were detected. To test for the former the ether was shaken with an aqueous suspension of calcium carbonate; the colour due to iodine disappeared, and the ethereal layer was separated, washed several times with water, and then treated with alcoholic ammonia. A few crystals of silver nitrate were added, the precipitate obtained was filtered off, washed, and digested with boiling nitric acid (to remove silver sulphide), silver iodide remaining.

DISCUSSION.

Thermochemical data show that normally very little reaction between hydrogen sulphide and iodine is possible (Neumann, *Ber.*, 1876, **9**, 1574); but if sufficient heat is developed by the solution of the hydrogen iodide formed, the reaction could proceed farther, giving, *e.g.*, in aqueous solution a concentration of *ca.* 25% of hydrogen iodide (Friend, "Text Book of Inorganic Chemistry," Vol. 7, Part 2, p. 58). Reaction can also take place if the hydrogen iodide formed is removed, as shown by the fact that addition of pyridine caused rapid and complete reaction in carbon tetrachloride, the insoluble hydriodide of the base being formed.

The feeble reaction in dry ether was probably due, therefore, to a very slow removal of hydrogen iodide to form ethyl iodide, the mercaptan being produced by interaction of ethyl iodide with hydrogen sulphide (this, however, would regenerate hydrogen iodide). Direct combination of the ether with hydrogen iodide is also a possible factor.

Since the production of ethyl iodide would be accompanied by that of alcohol, which would in turn react with hydrogen iodide yielding ethyl iodide and water, we have to take into account the effect of this water on the main reaction. Although we find that traces of water appear to retard the reaction in ether, yet the presence of larger quantities would undoubtedly cause it to proceed to a greater extent for the reasons advanced above.

The explanation now advanced for the nature of the reaction in moist ether makes Parsons's postulated formation of sulphurous acid improbable, especially as he was unable to obtain any direct evidence in support of this mechanism.

SUMMARY.

Iodine and hydrogen sulphide do not react together in dry carbon tetrachloride solution, but addition of pyridine causes rapid and complete reaction. A slow and incomplete reaction occurs if small quantities of water or alcohol are present in the solvent.

The slow but nearly complete reaction in dry ethereal solutions seems to be due to the removal of hydrogen iodide by its reaction with ether to form ethyl iodide. The

incompleteness of the reaction in moist ethereal solutions and the effect of varying water concentrations can be satisfactorily explained.

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