SULPHURYL IODIDE

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Received July 24, 1940

(Communicated by Prof. B. Sanjiva Rao)

Introduction

Attempts to prepare sulphuryl iodide have not hitherto met with any success. Odling[1] claims that the iodide is formed by the slow combination of sulphur dioxide and iodine in sunlight. But Schulze[2] has definitely established that the compound is not produced either by Odling's method or by the action of hydrogen iodide on sulphuryl chloride. The recent investigations of the present author on sulphur iodide[3] and thionyl iodide[4] have shown that these two substances are produced, when carbon tetrachloride solutions of the respective chlorides are treated with dry potassium iodide. A similar technique has now been adopted in the preparation of sulphuryl iodide.

Experimental

Reagents used.—(1) Sulphuryl chloride: Kahlbaum's 'purest quality was used without further treatment. (2) Carbon disulphide (c.p. quality) was dried over phosphorus pentoxide and distilled. (3) Potassium iodide (Merck's extra pure) was finely powdered and dried over phosphorus pentoxide for 24 hours in a vacuum desiccator.

When a dilute solution of sulphuryl chloride in carbon tetrachloride (0·0005 molar) was shaken up (in the dark) with dry potassium iodide powder, the two reacted; but spectroscopic investigations indicated that sulphuryl iodide was not produced. The resulting solution was merely a mixture of iodine and sulphur dioxide. No evidence for the existence of sulphuryl iodide was obtained even when the experiment was tried at − 10° C. The reaction between sulphuryl chloride and potassium iodide was therefore tried at much lower temperatures. Carbon disulphide had to be used as solvent since carbon tetrachloride would freeze at temperatures below − 23° C.

The solution of sulphuryl chloride in carbon disulphide (0·0005 molar) was cooled to − 70° C. in a mixture of alcohol and solid carbon dioxide. The solution was then shaken up with potassium iodide in the dark for

2–3 minutes. Even at this low temperature, sulphuryl chloride and potassium iodide reacted giving rise to a violet solution. The solution was decanted free of potassium iodide and transferred quickly to two similar test-tubes. One of them was kept surrounded by the cooling bath while the other was allowed to attain the laboratory temperature. The violet colour deepened considerably in the latter. On keeping the test-tube back in the cooling mixture, the higher intensity of the violet colour persisted. This indicated that the carbon disulphide solution had some undecomposed sulphuryl iodide to start with which, however, decomposed into sulphur dioxide and iodine on raising the temperature. But when cooled again, the iodine and the sulphur dioxide did not recombine; hence the decomposed solution was deeper in violet colour. Since the fresh solution was only pale violet, it could be concluded that sulphuryl iodide was practically a colourless substance, like its chlorine analogue.

Spectroscopic Studies

The observations mentioned above were further confirmed by spectroscopic investigations. A Hilger Constant deviation spectrograph was used to obtain the absorption spectrum. The intensity of illumination and the period of exposure were maintained constant during each exposure. Spectrogram 1 was taken with a fresh solution of sulphuryl iodide (freed from potassium idoide) prepared at – 70° C. as described above. Maintaining the absorption cell in the same position, the cooling bath was removed and the solution was kept at the laboratory temperature for 15 minutes. During this period, the violet colour became more intense. The absorption cell was cooled again to –70° C. and spectrogram 2 was then taken. Spectrogram 3 represents the absorption spectrum (at –70° C.) for a solution of iodine and sulphur dioxide in carbon disulphide which had the same concentration as the decomposed sulphuryl iodide solution.

A comparison of spectrograms 1 and 2 indicates that the intensity of transmission (in the violet region) is greater in the first spectrogram. This cannot be due to any temperature effect since both the solutions are kept at the same temperature. Hence it can be concluded that the iodine content of the solution when freshly prepared (spectrogram 1) is less than that of the same solution when the temperature is raised and the solution recooled (spectrogram 2). Spectrograms 2 and 3 are practically identical. This shows that after decomposition, the sulphuryl iodide solution is identical with that of a solution of iodine and sulphur dioxide. It is therefore to be concluded that the fresh solution contains both sulphuryl iodide and its products of decomposition (iodine and sulphur dioxide). On raising the termperature however, sulphuryl iodide decomposes but the products of decomposition do not reunite on cooling. Hence the solution after decomposition contains more of iodine than the fresh solution.

Discussion

The spectroscopic evidence presented in this paper shows that sulphuryl iodide is formed on treatment of sulphuryl chloride solution (in carbon disulphide) with potassium iodide at − 70° C. The iodide decomposes rapidly when the temperature is raised, the products of decomposition being sulphur dioxide and iodine. Since the decomposition of sulphuryl iodide is irreversible, earlier reports about the combination of iodine with sulphur dioxide,[1] can hardly be correct. In proving the existence of sulphur iodide[3] and thionyl iodide,[4] the author has tried the action of sodium hydroxide solution on these two iodides. But this procedure cannot be employed to prove the formation of sulphuryl iodide since the products of reaction of sulphuryl iodide with alkali are identical with those of a mixture of sulphur dioxide and iodine when similarly treated.

Summary

(1) Spectroscopic investigations show that sulphuryl iodide is produced by the action of potassium iodide on a dilute solution of sulphuryl chloride in carbon disulphide at − 70° C.

(2) At the laboratory temperature, the iodide decomposes almost immediately into sulphur dioxide and iodine which on cooling do not recombine.

Acknowledgment

The author takes this opportunity to express his sincere thanks to Professor B. Sanjiva Rao, for his keen interest in the work.

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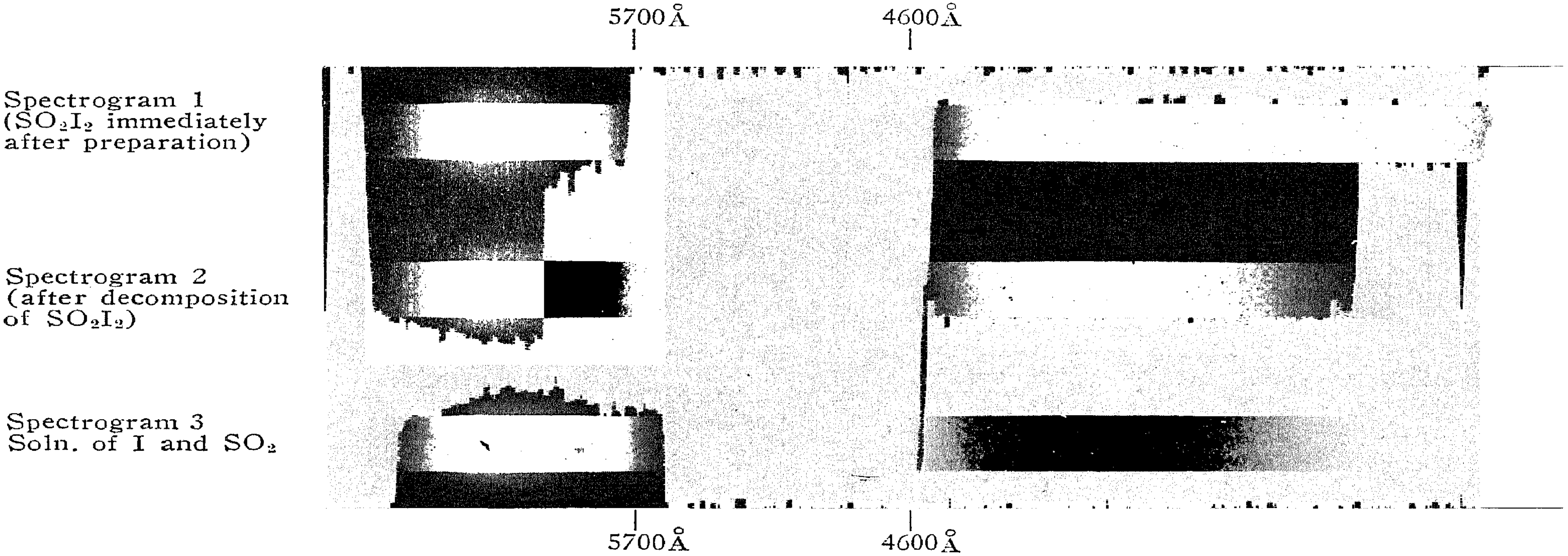

Absorption Spectrum of Sulphuryl Iodide solution in carbon disulphide