THIONYL IODIDE

Part II. Rate of Decomposition and Spectroscopic Studies

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Received February 6, 1940

[Communicated by Prof. B. Sanjiva Rao, M.A., Ph.D. (Lond.), F.A.Sc.]

Introduction

It has been shown in the previous paper (Part I) that a solution of thionyl iodide could be prepared by shaking a mixture of thionyl chloride solution (in carbon tetrachloride) with solid potassium iodide. The stability of thionyl iodide at different temperatures is of interest since it gives us the optimum conditions for the preparation of the compound. A study of the rate of decomposition at different temperatures was therefore undertaken.

Experimental

Time of reaction between thionyl chloride and potassium iodide at different temperatures.—It has been stated in Part I that the surface of potassium iodide catalyses the decomposition of thionyl iodide. In order to get a maximum yield of the iodide, the mixture of potassium iodide and thionyl chloride should be shaken for an interval just sufficient to complete the reaction of the chloride with potassium iodide. A study of the time required for complete reaction was therefore undertaken.

The reagents used were prepared in the manner described in Part I. The thionyl chloride had $106{\cdot}2 \times 10^{-6}$ mole of the chloride per gm. of the solution. The time for complete reaction between potassium iodide and thionyl chloride was determined in the following way at 0° C. The stock solution of thionyl chloride (18 gm.) was diluted with carbon tetrachloride (1500 gm.) and shaken with potassium iodide at 0° C. in the dark. At intervals, samples of the reaction mixture were transferred to dry bottles. The thionyl iodide present in these samples was allowed to decompose completely by exposing them to sunlight. The iodine liberated was then estimated colorimetrically as outlined in Part I. The experimental data were used to calculate the percentage reaction of thionyl chloride for different intervals of shaking. In order to determine the effect of temperature on the rate of reaction, the above experiment was repeated at 30° and 50° C. and the results are presented in the following table:

TABLE I

Effect of temperature on the rate of reaction between thionyl chloride and potassium iodide

Time of shaking in minutes ..	3	6	10	20	40	60	120
% $SOCl_2$ reacted at 50° C. ..	47	68	81	100	100	..	..
,, at 30° C. ..	28	40	52	75	100	100	..
,, at 0° C. ..	..	..	..	..	27	41	75

The results indicate that the reaction between thionyl chloride and potassium iodide is extremely slow at lower temperatures. Further experiments showed that the reaction between the two substances was complete within 15 minutes at 50° and within 35 minutes at 30° C.

Percentage of undecomposed thionyl iodide in the samples obtained at different temperatures.—Samples of thionyl iodide were prepared at 30° and 50° C. by shaking the mixture of thionyl chloride and potassium iodide for the minimum interval required to complete the reaction. The samples were then subjected to hydrolysis with 2 N alkali. The results were employed to calculate the extent of decomposition of thionyl iodide as described in Part I. It was noticed that the decomposition of the iodide at 30° amounted to only 46%, while that at 50° was as high as 56%. A sample of thionyl iodide prepared by shaking the reaction mixture at 0° C. for a period of 120 minutes, was hydrolysed in presence of alkali. The results indicated that 50% of the iodide formed had decomposed. Thus it can be concluded that a temperature of 30° C. is best suited for the preparation of thionyl iodide.

Rate of decomposition of thionyl iodide at different temperatures.—Thionyl iodide solutions used to study the rate of decomposition at 30° and 0° C. were prepared by shaking dilute solutions of thionyl chloride (18 gm. of the stock thionyl chloride solution diluted with 1600 gm. of carbon tetrachloride) with potassium iodide for the minimum period as described already. The extent of decomposition of the iodide could be determined by finding out the amount of free sulphur formed during the decomposition (equation A, Part I). The free sulphur was determined in two ways: In the first method, the thionyl iodide solution was treated with 2 N alkali and the carbon tetrachloride layer was analysed for the dissolved sulphur. In the second method the free sulphur was got indirectly by estimating the total sulphur compounds in the alkali layer ($BaSO_4$ method, Part I), and subtracting this value from the total sulphur started with. It may be pointed out, however, that during

the preparation of the thionyl iodide solution, part of the iodide had decomposed. A portion of the sulphur dioxide and sulphur thus formed, is found to be adsorbed on potassium iodide. This should be taken into account in the calculations. To estimate the amount of adsorbed free sulphur and sulphur dioxide, the potassium iodide used for the preparation of thionyl iodide, was washed with carbon tetrachloride and dissolved in 100 c.c. of water. Aliquots were used for the determination of free sulphur and sulphur dioxide as described in Part I.

The following procedure was adopted to study the rate of decomposition of thionyl iodide at 0° C. Approximately equal quantities of the iodide solution were transferred in the dark, to dry bottles and the weight of these solutions quickly determined. The bottles were then kept in an ice-bath in the dark room. The extent of decomposition of the thionyl iodide at different intervals was determined by shaking the iodide samples with 2 N alkali and analysing the products of hydrolysis as described already. In some of the samples, it was noticed that a small quantity of free sulphur got deposited on the glass walls, which did not go into solution with carbon tetrachloride. In such cases, the value for free sulphur could be calculated by the second method outlined above. As pointed in Part I, twice the value of free sulphur represented the amount of thionyl iodide decomposed. A similar procedure was adopted to determine the rate of decomposition at 30° C. An air thermostat was used to maintain the temperature constant. The following results were obtained:

TABLE II (*a*)

Rate of decomposition of thionyl iodide at 30° *C.*

Time in hours ..	0	2	7	24	50
% Decomposition.. ..	44·7	61·2	77·5	91·8	95·3

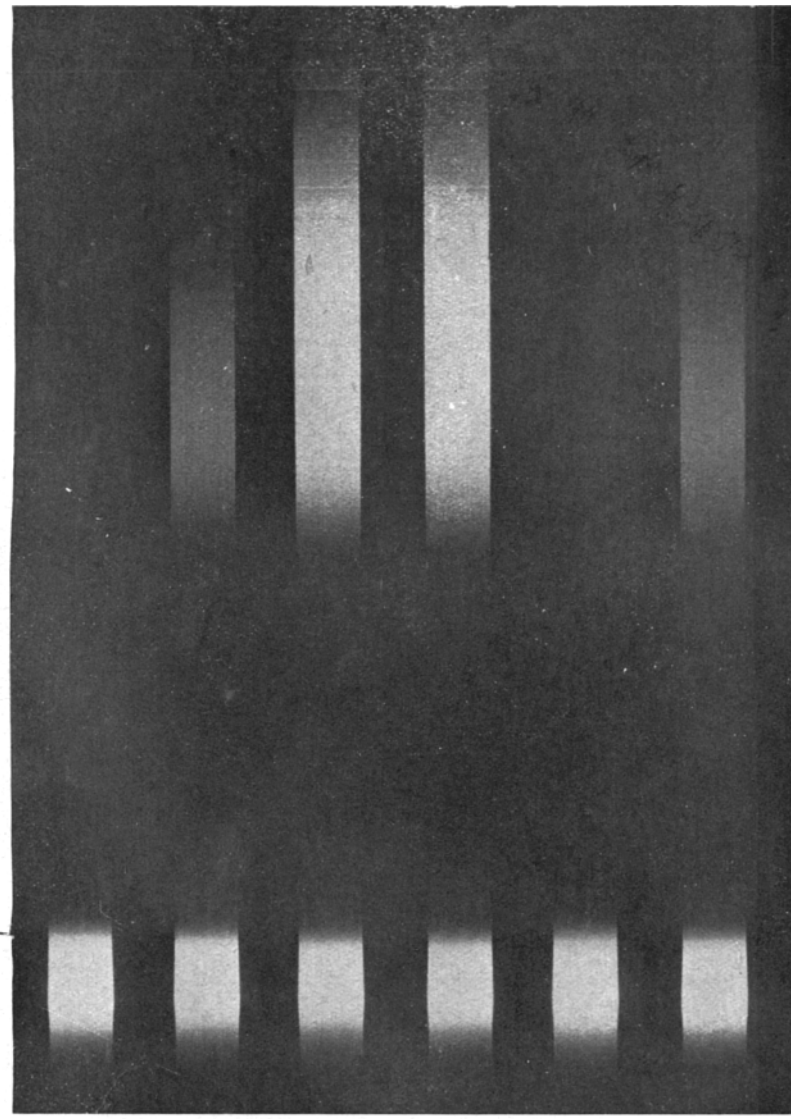
TABLE II (*b*)

Rate of decomposition of thionyl iodide at 0° *C.*

Time in hours	0	13	37	64	96
% Decomposition	44·1	52·7	65·0	77·2	87·0

The results indicate that the rate of decomposition is very much less at 0° than at 30° C.

Spectroscopic studies on thionyl iodide.—Thionyl iodide in carbon tetrachloride solutions, gives a characteristic absorption spectrum. The decomposition of thionyl iodide can therefore be conveniently studied spectroscopically. The Hilger Constant-deviation Spectrograph was used in the investigations. Light from a pointolite lamp was rendered parallel and passed through the iodide solution in a quartz Baly tube. The intensity of illumination was kept uniform by passing a constant current through the lamp. The thionyl iodide solution used was prepared by shaking a mixture of 10 gm. of potassium iodide with 300 gm. of carbon tetrachloride containing 8 gm. of the stock solution of thionyl chloride. The Baly tube was filled with the solution to a depth of 8 cm. and the absorption spectrum (spectrogram 1, Plate X) was immediately taken. The period of exposure in each case was 20 seconds. The Baly tube was then kept illuminated (by means of a 50 c.p. electric lamp) when there was a rapid decomposition of the iodide. Spectrograms 2 and 3 were taken after the solution had been exposed to light for a period of 5 and 10 minutes respectively. At the end of 10 minutes, it was noticed that the solution did not have any yellow tinge. This indicated that the thionyl iodide had completely decomposed. Spectrogram 4 was taken with a solution of iodine, sulphur and sulphur dioxide (in carbon tetrachloride) having the same concentration as the decomposed thionyl iodide. A sample of the thionyl iodide solution preserved in the dark, was used in the spectrograms 5 and 6 at the end of 8 and 24 hours respectively. The following conclusions can be drawn by a study of Plate X. When the concentration of thionyl iodide is at its highest value (spectrogram 1), there is complete absorption of light for all wave-lengths below 5930 Å. But as the decomposition proceeds (spectrogram 2), transmission of light occurs in the violet region of the spectrum. The transmission increases as the decomposition proceeds as shown by a comparison of the spectrograms 2 and 3. Thus under similar conditions, the intensity of the spectrum in the violet region gives one, an idea of the thionyl iodide concentration. When the decomposition of the iodide is complete (spectrogram 3), the absorption band extends from 5930 Å to 4400 Å. Spectrograms 3 and 4 are practically identical in intensity. This shows that complete decomposition of the iodide takes place when the solution is allowed to remain in light for a period of 10 minutes. In the two spectrograms 5 and 6, the intensity of transmission in the violet region is less than that of the spectrogram 3. This shows conclusively that even after keeping for 24 hours in the dark, the thionyl iodide has not completely decomposed while in presence of light a period of 10 minutes is sufficient to bring about the complete decomposition.



Effect of light on the decomposition of thionyl iodide

Spectrograms at 30°

(1) Interval 0 hrs.

(2) „ 4 „

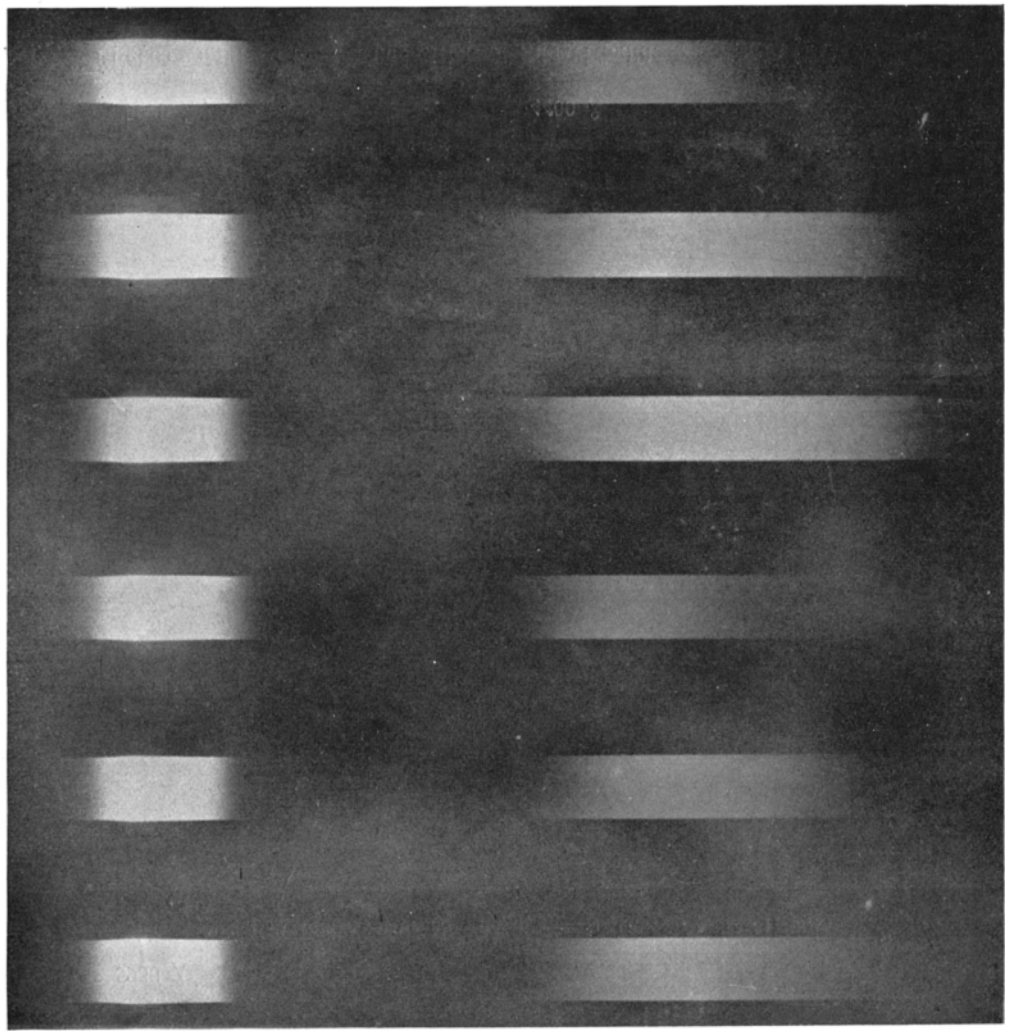
(3) „ 8 „

Spectrograms at 0°

(4) Interval 0 hrs.

(5) „ 12 „

(6) „ 24 „



Effect of temperature on the decomposition of thionyl iodide

Effect of temperature on the rate of decomposition studied spectroscopically.—In studying the effect of temperature, the thionyl iodide solution prepared at 30° C. was divided into two portions. One of these was kept in the dark in an air thermostat at 30°C. while the other portion was kept at 0°C. in the dark room. The spectrograms are given in Plate XI. Spectrograms, 1, 2 and 3 were taken with the thionyl iodide solution kept at 30°C. at the intervals 0, 4 and 8 hours respectively, filling the Baly tube to a depth of 4 cm. in each case. Similarly, the spectrograms 4, 5 and 6 were taken with the solution at the intervals 0, 12 and 24 hours respectively. A comparison of the intensities of the spectrograms indicates that there is far less of decomposition at 0° C. than at 30° C. This is quite in conformity with the analytical data presented in Table II.

Summary

(1) The rate of decomposition of thionyl iodide in carbon tetrachloride solutions has been studied at 30° and 0° C.

(2) In presence of light, the iodide decomposes far more rapidly than in the dark. The dark reaction is found to have a high temperature coefficient.

(3) The absorption spectrum of thionyl iodide in carbon tetrachloride solutions has been studied. With the iodide solution, a complete absorption for all wave-lengths below 5930 Å is noticed. The spectroscopic investigations on the instability of the iodide are in conformity with the analytical data.

Acknowledgment

The author wishes to express his thanks to Prof. B. Sanjiva Rao and to Dr. K. S. G. Doss for their keen interest in the work.