

SELENIUM IODIDE

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Introduction

EVER since the discovery of selenium by Berzelius¹ attempts have been made to prepare the iodide of the element. Schneider² believed that the iodide could be prepared by fusing together the two elements or by the reaction of selenium bromide with ethyl iodide. Guyot³ stated that the two elements combined in carbon disulphide solution. But investigations on the freezing point curves of binary mixtures of the two elements by Pellini and Pedrina⁴ showed that no compound was produced. Olivari⁵ and Beckmann and co-workers⁶⁻⁹ determined the molecular weight of selenium using iodine, as the cryoscopic solvent. They also used as solvent methylene iodide containing dissolved iodine. They could not obtain any evidence for the existence of selenium iodide. Wright¹⁰ arrived at similar conclusions by his studies on the partial pressures of iodine in equilibrium with fused mixtures of selenium and iodine. Recently, the colour change produced by the addition of selenium to a solution of iodine in carbon tetrachloride, was attributed by McCullough¹¹ to the formation of selenium iodide in the solvent.

The present author showed that sulphur iodide¹² and thionyl iodide¹³ were produced when dilute solutions of the respective chlorides in carbon tetrachloride, were treated with potassium iodide. In this investigation an attempt was made to prepare selenium iodide by employing the same technique. When a dilute solution of selenium monochloride in carbon tetrachloride was shaken up with dry potassium iodide powder, the solution turned yellow in colour; the yellow colour changed to violet within a few seconds of exposure to light; at the same time, tiny crystals of selenium separated from the solution. The yellow colour was suspected to be due to the presence of selenium mono-iodide and a detailed investigation was undertaken.

Experimental

Reagents used.—(1) Carbon tetrachloride: Merck's "Pure" carbon tetrachloride was dried over phosphorus pentoxide and distilled. (2) Potassium iodide: Potassium iodide (Merck's "extra pure") was finely powdered

and dried over phosphorus pentoxide for 24 hours in a vacuum desiccator. (3) Selenium monochloride: Lenher's¹⁴ method was employed to prepare selenium monochloride. Dry chlorine was passed through excess of red amorphous selenium suspended in carbon tetrachloride, till the solution turned orange-red in colour. The excess of chlorine was then removed by a current of dry carbon dioxide. The clear solution was preserved in a bottle from which samples could be removed without contamination with the atmospheric moisture. The selenium content of the solution was estimated by the method suggested by McCullough¹¹ while the chlorine was determined by shaking the solution with potassium iodide and estimating the liberated iodine (by the thiosulphate method). Selenium chloride and potassium iodide had been found to react quantitatively yielding (in presence of light) potassium chloride, selenium and iodine. The selenium chloride solution had 56.0×10^{-6} g. atom of selenium per g. while the chlorine content was 55.6×10^{-6} g. atom per g. of stock solution. This showed that the selenium chloride was quite pure.

Reaction between potassium iodide and selenium chloride.—The estimation of iodine liberated by the decomposition of the selenium iodide constituted an easy method of determining the extent of reaction between potassium iodide and selenium chloride. The reaction between the two substances was very rapid at low temperatures. Thus, at -10°C . the mixture of potassium iodide and selenium chloride solution had to be shaken for a period of only two minutes for the reaction to be complete. At the laboratory temperature (25°C .) however, the mixture had to be shaken for a much longer period (10–15 minutes) before the reaction could be complete. This result was unexpected since the reaction between thionyl chloride and potassium iodide (in the preparation of thionyl iodide¹³) was accelerated by a temperature increase. Further investigations revealed that at higher temperatures, the selenium and iodine (formed during the reaction) were strongly adsorbed by the potassium iodide, and reduced the effective area of the solid. This probably accounted for the retardation of the reaction at the higher temperature.

Hydrolysis of selenium iodide.—Selenium iodide might be expected to react with water in a way analogous to that of selenium chloride with water. On hydrolysis with water, selenium chloride produces selenium, selenious acid and hydrogen chloride. Hence selenium iodide could be expected to react with water yielding selenium, selenious acid and hydrogen iodide. As in the case of sulphur iodide,¹² a portion of the selenium iodide (being highly unstable) might also decompose into selenium and iodine. In experiments on the hydrolysis of selenium iodide, alkali cannot be used (*cf.* sulphur

iodide¹²) since selenium itself reacts with alkali¹⁵ producing the selenide which then gets oxidised by the iodine. Even in neutral solutions, iodine oxidises selenium to selenious acid.¹⁶ Thus when a solution of iodine (0.1 N) in carbon tetrachloride saturated with red selenium is shaken up with water for a period of one hour, the iodine consumed in oxidising the selenium amounts to about 7-8%. It is therefore necessary to conduct a blank experiment in order to determine the amount of iodine consumed in the oxidation of selenium. The following method was adopted to find out the extent of hydrolysis of selenium iodide. Precipitated cadmium carbonate was employed to neutralise the hydrogen iodide liberated during the reaction. Such neutralization was found necessary to avoid the reduction of selenious acid by hydrogen iodide.

A weighed quantity of the stock solution of selenium chloride (2-3 g.) was diluted with carbon tetrachloride (400 g.) and cooled to -14°C . in a freezing mixture. The solution was then shaken up (in the dark) with dry potassium iodide (3-4 g.) for a period of one minute using a shaking machine. The clear liquid was divided into two portions; one portion was immediately shaken up with cadmium carbonate suspension in water for 15 minutes. The other was kept in sunlight to effect complete decomposition of the iodide; the solution was then treated with the aqueous suspension of cadmium carbonate under similar conditions of temperature and shaking. The iodine liberated in both cases was estimated as outlined above. The results are given in Table I.

TABLE I
*Hydrolysis of selenium iodide by water in presence of
cadmium carbonate*

Period of shaking	Iodine got by immediate shaking (g. atom of I per g. solution)	Iodine got by shaking the mixture after exposure to light (g. atom of I per g. solution)	$\frac{\text{Iodine in B}}{\text{Iodine in C}}$
A	B	C	D
1. 15 min.	15.8×10^{-8}	18.1×10^{-8}	0.87
2. 30 "	12.2×10^{-8}	14.4×10^{-8}	0.85
3. 30 "	7.1×10^{-8}	8.5×10^{-8}	0.84

The results indicate that the iodine content of the solution decomposed by light is always greater. When selenium iodide is shaken up with water the

reactions that take place are (1) decomposition and (2) hydrolysis, and can be represented as



When the fresh solution is shaken up with water, a portion of the selenium iodide reacts according to (B), thus reducing the iodine content. But when the solution is exposed to light, the selenium iodide completely decomposes into the elements according to (A). Since no hydrolysis can take place in this case, the iodine content is larger by about 10–15%. In other words, about 10–15% of the selenium iodide hydrolyses with water while the rest merely decomposes. A similar result is also obtained in the hydrolysis of thionyl iodide¹³ in presence of cadmium carbonate where only 3–4% hydrolyses, the rest getting decomposed. It can therefore be concluded that the carbon tetrachloride solution that has not been exposed to light, does contain selenium iodide, a portion of which hydrolyses on shaking with water.

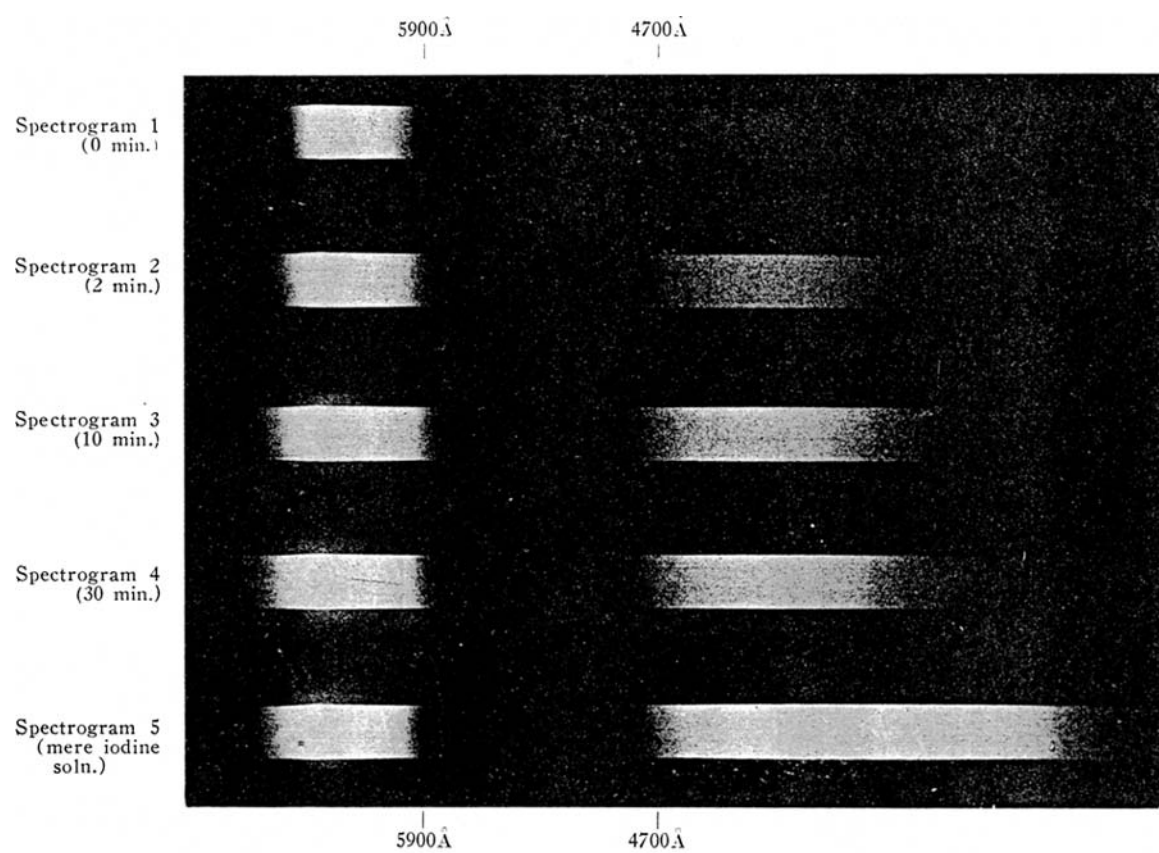
Absorption Spectrum Studies on Selenium Iodide.—The decomposition of selenium iodide can conveniently be followed up by a study of absorption spectra. A Hilger constant-deviation spectrograph was used in the investigations. The intensity of illumination was maintained uniform by passing a constant current through a tungsten filament lamp. The light was rendered parallel and passed through a quartz Baly tube filled with the selenium iodide solution prepared as outlined above. Since selenium iodide is highly photosensitive care has to be taken to avoid unnecessary exposure of the solution to light. Spectrogram 1 was taken with the fresh selenium iodide solution. The period of exposure was 15 seconds in each case. Even during this short interval of exposure to light, perceptible quantities of the selenium iodide were found to decompose. After the first exposure, the solution in the Baly tube was kept illuminated to effect the decomposition of the selenium iodide. Spectrograms 2, 3 and 4 were taken at intervals of 2, 10 and 30 minutes respectively. The last spectrogram is the absorption spectrum taken with a solution of pure iodine in carbon tetrachloride having the same iodine concentration as the decomposed selenium iodide solution.

The following information can be gathered by a study of the absorption spectra. When the selenium iodide solution is fresh (Spectrogram 1) there is practically complete absorption for all wave lengths below 5900 Å. But as the decomposition proceeds, the solution becomes more and more transparent in the violet region. Thus the transmission in the violet region is quite intense in spectrogram 2 and is at its maximum in the spectrograms

3 and 4. This shows that when the solution is exposed to the action of light for 2 minutes, only small quantities of the selenium iodide are left undecomposed. The similarity of spectrograms 3 and 4 indicates that the decomposition of selenium iodide is complete when the solution is exposed to light for a period of 10 minutes. It is of interest to note that light absorption by iodine is markedly affected by the presence of selenium in solution. A comparison of the spectrogram 4 (for a mixture of selenium and iodine in carbon tetrachloride, *i.e.*, the selenium iodide solution after complete decomposition) with spectrogram 5 (for pure iodine in carbon tetrachloride) shows that the absorption in the violet region is increased by the presence of selenium although a solution of selenium itself shows no absorption in this region. As will be pointed out later, this difference in absorption is assumed by McCullough¹¹ to be due to the formation of selenium iodide.

Discussion

The chemical and the spectroscopic evidence presented in this paper shows beyond doubt, that selenium iodide is formed when a dilute solution of selenium chloride is shaken up with dry potassium iodide. The iodide thus produced decomposes very rapidly in presence of light. The colour change when selenium is added to a solution of iodine in carbon tetrachloride (*cf.* Spectrograms 4 and 5) and the increase in solubility of selenium in carbon tetrachloride containing iodine, have been pointed out by McCullough¹¹ as evidence for the formation of selenium iodide in carbon tetrachloride solutions. The colour change might either be due to the formation of a definite compound, *viz.*, selenium iodide or due to the formation of a loose additive product between selenium and iodine. Iodine is known to form such additive products with alcohol, acetone and other liquids^{17,18} in which it dissolves, giving a brown colour. The freezing point experiments also¹⁸ confirm this view. Beckmann and Faust¹⁹ tried similar cryoscopic experiments but could not obtain any evidence for the formation of a compound when selenium and iodine were dissolved in methylene iodide. The increase in solubility of selenium (brought about by the addition of iodine) in carbon tetrachloride cannot be taken as definite evidence in favour of the formation of selenium iodide. For, Amadori²⁰ has found that the solubility of sulphur in benzene and in other liquids is considerably increased by the presence of iodine, although it is definitely established that no sulphur iodide is produced when the two elements are dissolved in common solvents. In view of the high instability of selenium iodide in presence of light, it can be concluded that more experimental work is necessary before one can accept the view that selenium iodide is formed when the two elements are brought together in carbon tetrachloride solution.



Absorption Spectrum of Selenium Iodide solution in carbon tetrachloride

Summary

(1) Selenium moniodide has been shown to be produced when a dilute solution of selenium chloride in carbon tetrachloride, is shaken with dry potassium iodide.

(2) The iodide is highly unstable in presence of light and decomposes into selenium and iodine.

(3) Hydrolysis of selenium iodide by water has been investigated.

(4) Decomposition of selenium iodide has been studied spectroscopically.

(5) The significance of the colour change brought about by the addition of selenium to a solution of iodine in carbon tetrachloride is discussed.

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