Iodine Oxides

Part I. On $I_2O_3\cdot SO_3$, $I_2O_5\cdot 4SO_3\cdot H_2O$, $I_2O_5\cdot SeO_3$ and $I_2O_4$

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The reaction between iodine and iodine pentoxide has been studied in concentrated sulfuric acid, oleum, and selenic acid. The intermediate compounds $I_2O_3\cdot SO_3$, $I_2O_5\cdot 4SO_3\cdot H_2O$ and $I_2O_5\cdot SeO_3$ have been isolated and identified. The relationship between these compounds is investigated as well as their slow hydrolysis to $I_2O_4$.

A reaction between iodic acid and hot concentrated sulfuric acid was first observed by Millon. Later both intermediate and final products of this and partially modified reactions have been studied.

The reaction can be divided into two stages of which the first consists of the isolation of intermediate products and the second of the decomposition of these intermediate products into iodine oxides.

The composition of the final product was designated $I_{19}O_{19}$ by Millon and $I_6O_{13}$ by Kaemmerer from chemical analysis. The formula $(IO_2)_x$ was confirmed by the analysis of Kappeler who introduced the notation $I_2O_4 = (IO)(IO_3)$.

The reduction of iodic acid takes place according to Masson and Argument as a partial thermal decomposition. The $I_2$ first formed reacts with $I_2O_5$ (i.e. dehydrated HIO$_3$) to give $I_2O_3$. This then forms a compound with SO$_3$ from sulfuric acid. This knowledge about the reaction mechanism enabled Masson and Argument to suggest a simplification of the synthesis. This consists of using a mixture of $I_2$ and $I_2O_5$ in the right proportion in excess of sulfuric acid. By this method the reaction is reported to be more easily controlled and a better defined intermediate product can be obtained. Using this method Dasent and Waddington could replace sulfuric acid with the homologous selenic acid.

A chemically more different alteration of Millons' original synthesis is reported by Kaemmerer who claims to have synthesized the intermediate product by reduction of $I_2O_5$ with dry SO$_2$.

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The composition of the intermediate product has at times been disputed either because the synthesis after Millons' procedure is difficult to control or because the applied analytical methods have not been suitable for accurate determination. The intermediate product prepared by this method is said to consist of variable amounts of the iodine oxides I₂O₃, I₂O₄ and I₄O₅ added to SO₃ with different amounts of H₂O.⁵⁻¹³,¹⁹

Although the literature even up to the present day is confused, the correct composition appears to be I₂O₅·SO₃.¹⁰,¹¹ The water content has been particularly disputed both because the analytical determination (by difference) of water in small amounts is uncertain and also because the compound I₂O₅·SO₃ is reported to be very hygroscopic. Chrétien⁴ originally proposed the composition I₂O₅·SO₃·½H₂O ((IO)₂SO₄·½H₂O) which was doubted by Bahl and Partridge⁸ who gave the composition I₂O₅·SO₃·H₂O. Fichter and Dinger⁹ came to the conclusion that the lower water content suggested by Chrétien was correct, whereas Kikindai¹³ would not take an attitude as to whether the water content corresponds to a hemihydrate, i.e. ½H₂O, or a monohydrate, i.e. one H₂O per formula unit I₂O₅·SO₃.

The chemical and physical properties of the intermediate product I₂O₅·SO₃ and the final product I₂O₄ have only been studied unsystematically. The magnetic properties at room temperature were investigated by Willmarth and Dharmatti,¹² Symons¹⁵ and Arotsky et al.,¹⁰ infra-red and visible spectra have been reported by Dasent and Waddington,¹⁹ Wise and Hanman and Arotsky et al.¹¹ Dasent and Waddington suggested the formulae (IO)₂SO₄ and (IO)₂SeO₄ which, however, should not be interpreted according to an ionic picture but rather as inorganic polymers containing (IO)₅ groups linked to SO₄ or SeO₄ tetrahedra. Nevertheless the formulae I₂O₅·SO₃ etc. are used in this paper as they are much more convenient for comparing the formulae of the various compounds.

With regard to the chemical properties it is of interest to notice that Dasent and Waddington¹⁹ report that they cannot dissolve without decomposition I₂O₅·SO₃, I₂O₅·SeO₃ and I₂O₄ in any solvent. I₂O₅·SO₃ is indeed soluble in fuming sulfuric acid according to Masson and Argument¹¹ but this process leads to the formation of a new compound I₂O₅·4SO₃·H₂O.

A compound with composition I₂O₅·2SO₃ has been prepared³,¹⁷ by a reaction between liquid SO₃ and KIO₅, Sr(IO₃)₂ or I₂O₅ at temperatures between 50 and 100°C. At lower temperatures I₂O₅·3SO₃, i.e. a product with a higher SO₃ content, is obtained. According to Lehmann and Hesselbarth¹⁷ symproportion of elementary iodine and I₂O₅ yield an equimolar mixture of I₂O₅·3SO₃ and I₂O₅·2SO₃. They also reported the preparation of I₂O₄·3SO₃ from liquid SO₃ and I₂O₄.

The aim of the present investigation was to study the reaction between iodine and iodine pentoxide in concentrated sulfuric acid, oleum, and selenic acid, and furthermore to isolate and investigate the relationships between the intermediate reaction products and study the slow hydrolysis of these intermediate products to I₂O₄.

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EXPERIMENTAL

*Chemicals.* Iodine (Jodum rosullimatum), iodic acid (Jodsaure fur Analyse) and iodine pentoxide (Jodpentoxid fur Analyse; Jodsaureanhidrid) of p.a. purity were obtained from Riedel-de Haen A.G. and E. Merck A.G. Sulfuric acid (Schwefelsaure fur Analyse, d<sub>42</sub> = 1.83, 95–97% ig), oleum (Schwefelsaure rauchend, etw. 60%, SO<sub>3</sub>) and selenium acid (d = 2.9) were obtained respectively from Riedel-de Haen A.G., E. Merck A.G. and The British Drug Houses Ltd.

*Syntheses.* Syntheses according to the sulfuric acid method were carried out as earlier described by Masson and Masson and Argument. Iodine (2.54 g = 0.010 mole) and iodine pentoxide (5.00 g = 0.15 mole) were mixed with concentrated sulfuric acid (43.4 ml = 0.45 mole) in an Erlenmeyer-flask with ground-glass stopper. The mixture was stirred by a magnetic stirrer. After one day a yellow product was seen to separate. The reaction was stopped when the iodine colour disappeared and all iodine pentoxide appeared to be converted to this yellow product. The liquid was then decanted and the reaction product dried on porous porcelain in a desiccator.

The modified sulfuric acid method is a repetition of the method first described by Millon. Finely ground iodic acid (6 g = 0.34 mole) and sulfuric acid (10.8 ml 97% = 0.11 mole) are heated in an evaporating dish. The liquid gradually assumes a darker colour (turning from yellow through brown to nearly black) and finally iodine vapour is observed. At his stage the heating is stopped and the dish is transferred to a desiccator for cooling. The liquid was removed by decantation and the product then dried on porous porcelain in a desiccator.

A parallel to the sulfuric acid method is the oleum method by which the amounts of iodine and iodine pentoxide are the same as in the sulfuric acid method, and 60 ml of fuming acid is added. Also the yellow product obtained by the sulfuric acid method was treated with oleum as described by Masson and Argument.

To remove mother-liquor the product was dried on porous porcelain after decantation.

The selenic acid method used by Daeent and Waddington is parallel to the sulfuric acid method with selenic acid instead of sulfuric acid. The amounts of iodine and iodine pentoxide are kept constant and the volume of selenic acid (50 ml) is equivalent to the amount of sulfuric acid in the sulfuric acid method. The product was dried on porous porcelain.

The intermediate products, after removal of most of the occluded sulfuric, or selenic acid, were exposed to moist air for about 3 h. During this treatment the samples were left on porous porcelain. The final products were washed with alcohol and dried in a vacuum desiccator.

*Apparatus.* Thermogravimetric analysis was carried out with a Stanton Thermo-Scanning Balance of 1 mg sensitivity. An approximate linear rate of temperature increase, 4.2°C/min, was maintained over the entire temperature range. Samples (0.4–1.0 g) were weighed on an ordinary analytical balance. Automatic arresting of the thermobalance at 5 min intervals recorded the time scale on the weight curve. Weight changes as a function of time with prolonged heating at constant temperature were also studied. These experiments were carried out with 1 g samples using ordinary analytical crucibles, furnace and balance.

The X-ray diffraction investigation of the intermediate products was carried out in powder cameras with 114.6 mm effective diameter, using filtered CuKα-radiation. The samples were sealed in thin-walled boron-lithium-glass capillaries. The decomposition of the intermediate products was studied with a Philips wide angle X-ray diffraction unit. The samples were mounted on a self-made, modified, specimen holder of porous porcelain fixed with Araldite to the original holder. Both strip-chart recording and timer/counter combination were used to register the experimental data. Final products were crushed and X-ray photographs were taken with Guinier focusing camera of 80 mm diameter with strictly monochromatized CuKα-radiation. Potassium chloride (Analar, The British Drug Houses, Ltd. a = 6.2919 Å) was added to the specimens as an internal standard.

The density of IO₃ was determined by the pycnometric method at 25°C with kerosene as displacement liquid.

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RESULTS

In presenting the experimental results it has been convenient to use terms which refer to the synthesis method rather than to the actual composition of the samples. Lacking better notation the following terms have been used: The sulfuric acid method, the modified sulfuric acid method, the oleum method, and the selenic acid method.

(i) Formation of intermediate products

The reaction between iodine, iodine pentoxide and sulfuric acid starts soon after the mixing of the chemicals. This can be seen from the darkening of the sulfuric acid immediately after mixing. When the mixture is shaken a yellow substance is seen after a short time on the wall of the Erlenmeyer flask, and continued shaking gives rise to more of the yellow product often showing a dirty colour from the dark mother-liquor. After a washing process which consisted of successive exchange of the dark coloured sulfuric acid with pure, concentrated sulfuric acid, a lemon coloured product was obtained.

The reaction product is shown to have the composition \( \text{I}_2\text{O}_3\cdot\text{SO}_3 \) by the earlier investigators. This composition has been proved by Masson and Argument and confirmed by Dasent and Waddington, and no quantitative analysis was carried out in the present study to confirm this composition. As it is impossible to obtain the compound completely free from mother-liquor (even after careful treatment on porous porcelain), the composition of the product should be written as \( \text{I}_2\text{O}_3\cdot\text{SO}_3 + \text{H}_2\text{SO}_4 \text{ occl} \). In the following text this notation will, however, only be used when it is important for the understanding of the properties of the substance.

The compound \( \text{I}_2\text{O}_3\cdot\text{SO}_3 \) cannot be kept in most air because the substance is decomposed by water. For X-ray characterization the substance was thus sealed into capillaries. Sin2\( \Theta \) values for the characteristic low angle reflections are listed in Table 1. It has been observed that the same product is obtained when iodic acid or soluble iodates instead of iodine pentoxide are mixed with iodine in sulfuric acid. The reaction will not take place at room temperature unless both iodine and iodine pentoxide are present. When iodine is absent iodic acid and iodates form iodine pentoxide when treated with sulfuric acid. It is also of some interest to notice that the solubility of iodine in sulfuric acid is affected by the presence of iodine pentoxide (cf. Symons and coworkers).

On changing the temperature to the boiling point of sulfuric acid, the presence of iodine is not necessary. The reaction which thus takes place according to the modified sulfuric acid method may qualitatively be divided into several stages.

When iodic acid is heated in sulfuric acid the first stage is that of the liquid turning yellow just before the iodic acid is completely dissolved. The appearance of yellow colour is accompanied by gas liberation. Continued heating at the boiling point of sulfuric acid (\( \sim 330^\circ\text{C} \)) produces a darker colour. When the solution is dark brown, or nearly black, iodine vapour is seen. This occurs about 1 min after complete solution. The reaction product crystallizes.

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Table 1. Powder photograph data (CuK-radiation) of products obtained by the selenic (SeM), sulfuric (SM), modified sulfuric (MSM) and oleum (FMS) method.

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when the heating is stopped. The compound is yellow-white and cannot be kept in moist air.

X-Ray diagrams, cf. Table 1, of the compound were compared with that of $I_2O_3$-SO$_3$ prepared by the sulfuric acid method. This shows that most of the reflections from the compound $I_2O_3$-SO$_3$ are also found in the X-ray diagrams

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of the reaction product of the modified sulfuric acid method. In addition there are many new reflections on the powder diagram of the latter specimens. If the heating-time is too short reflections from \( \text{I}_2\text{O}_5 \) are also found on the diagrams. The sulfuric and the modified sulfuric acid method thus do not give identical reaction products.

It is furthermore of interest to remark that the modified sulfuric acid synthesis proceeds similarly if iodic acid is exchanged with iodine pentoxide or a soluble iodate.

The yellow addition compound \( \text{I}_2\text{O}_5\cdot\text{SO}_3 \) may according to Masson and Argument \(^{11}\) be reversibly transformed into a white addition compound by treatment with oleum.

If oleum is added to the freshly made yellow addition compound a white compound is obtained. A limited amount of oleum must be used because the white product is soluble in excess. Using \( \text{I}_2\text{O}_5\cdot\text{SO}_3 \) which has been dried and kept for a while, the result is less good as the reaction product then obtains a blue-green colour. It is reasonable to believe that the colour is due to some free iodine in \( \text{I}_2\text{O}_5\cdot\text{SO}_3 \) which gives a blue solution in oleum.\(^{22}\)

The composition of the white product, according to Masson and Argument \(^{11}\) is \( \text{I}_2\text{O}_5\cdot4\text{SO}_3\cdot\text{H}_2\text{O} \). No analysis has been carried out to confirm the composition, as this formula is regarded as proved by Masson and Argument. It should be noticed that Masson and Argument have doubts of whether the water content is correct, but a new examination with the available experimental equipment will probably not solve the problem either. It is for example not possible even with careful treatment on porous porcelain to remove all mother-liquor.

A direct synthesis of the white compound starting from iodine and iodine pentoxide in oleum was also attempted. With care the yellow \( \text{I}_2\text{O}_5\cdot\text{SO}_3 \) can be seen to be formed first; then this primary product reacts with \( \text{SO}_3 \) and gives a gradually whiter product.

At this stage the X-ray diagrams from reaction products of the three sulfuric acid methods are compared. From Table 1 it is seen that the reflections from samples prepared by the modified sulfuric acid method can be explained as a superposition of reflections from the compounds \( \text{I}_2\text{O}_5\cdot\text{SO}_3 \) and \( \text{I}_2\text{O}_5\cdot4\text{SO}_3\cdot\text{H}_2\text{O} \). Corresponding reflections are marked with arrows. The fact that the modified sulfuric acid method gives a mixture of \( \text{I}_2\text{O}_5\cdot\text{SO}_3 \) and \( \text{I}_2\text{O}_5\cdot4\text{SO}_3\cdot\text{H}_2\text{O} \) explains the colour, etc. of these products. Earlier workers \(^{1,2,4-11,12}\) have reported conflicting and confusing compositions for products of the modified sulfuric acid method. It had been thought that the composition was variable because different amounts of the iodine oxides \( \text{I}_2\text{O}_3, \text{I}_2\text{O}_4 \) and \( \text{I}_2\text{O}_5 \) were added to \( \text{SO}_3 \) with different amounts of \( \text{H}_2\text{O} \). The simple interpretation suggested here is sufficient to explain the earlier conflicting results.

The mixture of \( \text{I}_2\text{O}_5\cdot\text{SO}_3 \) and \( \text{I}_2\text{O}_5\cdot4\text{SO}_3\cdot\text{H}_2\text{O} \) is obtained because when iodic acid and sulfuric acid are heated the sulfuric acid decomposes somewhat and produces \( \text{SO}_3 \) which reacts with \( \text{I}_2\text{O}_5\cdot\text{SO}_3 \) to give \( \text{I}_2\text{O}_5\cdot4\text{SO}_3\cdot\text{H}_2\text{O} \). When the period of heating is too short \( \text{I}_2\text{O}_5 \) is also present. Taking into consideration the variable amounts of sulfuric acid present on the surface of the products, the interpretation of earlier analytical data is almost impossible.
Mixing iodine, iodine pentoxide and selenic acid, the mixture seems to turn dark more quickly than with sulfuric acid. However, the reaction seems to need more time before the yellow compound crystallizes.

X-Ray data for characterization are reported in Table 1.

Comparing the powder diagram of the intermediate products from the sulfuric and the selenic acid method it seems that the two compounds may be described as isotypic as suggested by Dasent and Waddington,\textsuperscript{15} and the notation $I_2O_3.SeO_3$ is therefore used.

It was also tried to modify the selenic acid method by changing the reaction temperature. The reaction proceeded at first as in the modified sulfuric acid method, the solution turning yellow just before the iodic acid dissolved in the selenic acid. On further warming the solution turned darker, but no evaporation of iodine was seen. When the reaction was stopped a white compound crystallized which was shown to be iodine pentoxide. The reason for this result is undoubtedly the lower boiling point of selenic acid (260°C) compared with that of sulfuric acid (330°C). The decomposition of iodic acid to $O_3$ and $I_2$ occurs at 300—350°C (i.e. above the boiling point of selenic acid) and iodine is essential for the production of $I_2O_3.SeO_3$.

A detailed discussion of the mechanism for the formation of these compounds cannot be given at present. Reference can, however, be made to the papers by Symons and coworkers\textsuperscript{15,16,21,22} on iodine compounds in sulfuric acid and oleum and the recent review by Gillespie and Robinson\textsuperscript{24} on reactions in concentrated sulfuric acid. Attention should be drawn to the evidence produced for the existence of $(IO)HSO_4$ in the yellow nonconducting solutions of $I_2O_3.SO_3$ in 100 % $H_2SO_4$. Conductivity measurements in 65 % oleum, however, suggest the formation of strongly solvated $(IO)^+$ ions in this medium. The colourless solid obtained from these solutions may possibly be regarded as $(IO)^+(HS_2O_4)^-(2(IO)HS_2O_7 = I_2O_3-4SO_3.H_2O)$.

(ii) S low h ydroly sis o f t h e i n t e r m e di a t e p ro d u c t s

As earlier mentioned the intermediate products can be decomposed by water. In this work the slow, controlled, decomposition was produced by moist air. When these compounds under such conditions are exposed to moist air the advancing hydrolysis can be seen by eye. The compounds were kept on porous porcelain during the hydrolysis, a technique used by earlier investigators.

The slow hydrolysis was followed by X-ray diffraction methods at different times during the reaction. The conditions during the hydrolysis were kept almost identical to those of earlier studies.

To show the gradual change of the compounds, diffraction records were taken in the region $2\theta$, 15—30°, at different time intervals over a period of 3 h. This is shown in Fig. 1. With the present speed the diffractometer takes 8 min to scan an angle of 15°, i.e. the sample is not identical at the beginning and the end of each record. This inaccuracy is not corrected for. Background or reflections resulting from the sample holder are unimportant.

Comparing the curves A—D by looking at the reflection at $2\theta \approx 22^\circ$, it is found that in the case of $I_2O_3.SeO_3$ (A) and $I_2O_3.SO_3$ (B) the intensities.

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Fig. 1. X-Ray diffraction records of A: I₂O₅·SeO₃ + "H₂SeO₄ occl", B: I₂O₅·SO₄ + "H₂SO₄ occl", C: I₂O₅·SO₄ + I₂O₅·4SO₃·H₂O + "H₂SO₄ occl", D: I₂O₅·4SO₃·H₂O + "H₂SO₄ occl" at different time intervals during the decomposition reaction.

of the reflections decreases to vanish finally. For I₂O₅·SO₃ + I₂O₅·4SO₃·H₂O (C) and I₂O₅·4SO₃·H₂O (D) there is, however, an increase in intensity at first, then a decrease finally to vanishing point.

In Fig. 2 the intensity of the same reflection is plotted as a function of time. The result for I₂O₅·4SO₃·H₂O is omitted, because although the diagram reflects the observation in Fig. 1 D and resembles the curves shown in Fig. 2 C, there is a larger scatter in experimental points due to a general low counting rate. The oscillations in the decomposition curves of I₂O₅·SO₃ + I₂O₅·4SO₃·H₂O, Fig. 2 C, can in principle be understood by the simultaneous hydrolysises of I₂O₅·SO₃ and I₂O₅·4SO₃·H₂O.

The shape of the decomposition curves for I₂O₅·SeO₃ and I₂O₅·SO₃ as shown in Fig. 2 A, B, looks like typical curves for reactions, whose rate is determined by the size of the surface area.

Treatment in most air changes the compound I₂O₅·4SO₃·H₂O to I₂O₅·SO₃. The reflections characterizing I₂O₅·SO₃ will thus first increase in intensity because the amount of I₂O₅·SO₃ increases. At one point all the I₂O₅·4SO₃·H₂O

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is converted to $I_2O_3\cdot SO_3$ and the intensity of the reflections decreases as $I_2O_3\cdot SO_3$ hydrolyses to $I_2O_4$. The end product of these processes is identical, i.e. the compound $I_2O_4$.

The difference between the pairs of corresponding curves in Fig. 2 is probably due to external conditions like previous history of the samples, temperature, humidity, particle size etc.

Masson and Argument\textsuperscript{11} state that the transition from $I_2O_3\cdot 4SO_3\cdot H_2O$ to $I_2O_3\cdot SO_3$ is reversible as addition of oleum converts $I_2O_2\cdot SO_3$ into $I_2O_3\cdot 4SO_3\cdot H_2O$ while slow dilution with water produces the opposite reaction. Masson and Argument claimed as result of microscopic investigation that the change from $I_2O_3\cdot 4SO_3\cdot H_2O$ to $I_2O_3\cdot SO_3$ takes place through an intermediate stage of iodine (and probably iodate ion). The present work has neither with certainty confirmed nor disproved this theory. Indeed, local growth of iodine can be distinctly seen when the reaction is followed under a microscope. This may, however, be explained by assuming local variations in the concentration.

Without any knowledge of the detailed mechanism for transition from $I_2O_3\cdot 4SO_3\cdot H_2O$ to $I_2O_3\cdot SO_3$ it seems obvious that the reaction depends on the

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ratio $\text{H}_2\text{O}:\text{SO}_3$. Only when water is added slowly, e.g. as vapour, the decomposition is slow enough to prevent further decomposition.

On further reaction with $\text{H}_2\text{O}$ from moist air $\text{I}_2\text{O}_3\cdot\text{SO}_3$ decomposes to $\text{I}_2\text{O}_4$. From Masson and Argument\textsuperscript{11} the condition for $\text{I}_2\text{O}_3\cdot\text{SO}_3$ to be stable in sulfuric acid is $\text{H}_2\text{SO}_4:\text{H}_2\text{O} > 1$. Experiments at present, have not given results to disprove this condition. However, the compound $\text{I}_2\text{O}_3\cdot\text{SO}_3$ is less hygroscopic than $\text{H}_2\text{SO}_4$, it is even possible that $\text{I}_2\text{O}_3\cdot\text{SO}_3$ is hygroscopic only as a result of occluded sulfuric acid.

Using more water, $\text{I}_2\text{O}_3\cdot\text{SO}_3$ decomposes to iodic acid and iodine according to the equation

$$5 \text{I}_2\text{O}_3\cdot\text{SO}_3 + 8 \text{H}_2\text{O} \rightarrow 6 \text{HIO}_3 + 2 \text{I}_2 + 5 \text{H}_2\text{SO}_4$$

The decomposition of the compounds $\text{I}_2\text{O}_3\cdot\text{SO}_3$ and $\text{I}_2\text{O}_3\cdot\text{SeO}_3$ to $\text{I}_2\text{O}_4$ by moist air, takes place as a oxidation-reduction reaction, and as the valence of iodine increases from $+3$ in $\text{I}_2\text{O}_3$ to $+4$ in $\text{I}_2\text{O}_4$, a simultaneous reduction has to take place.

One hypothesis is that oxidation of iodine goes on simultaneously with reduction of water. $\text{I}_2\text{O}_3\cdot\text{SO}_3$ placed in a closed system with moist air, would evolve enough hydrogen to be measured on a gas manometer if water was reduced. This was not confirmed by experiment. It is possible but not probable that $\text{H}_2\text{SO}_4$ or $\text{SO}_3$ is reduced.

The decomposition of $\text{I}_2\text{O}_3\cdot\text{SO}_3$ taking place as disproportion of $\text{I}_2\text{O}_3$:

$$4 \text{I}_2\text{O}_3\cdot\text{SO}_3 + 4 \text{H}_2\text{O} \rightarrow 3 \text{I}_2\text{O}_4 + \text{I}_2 + 4 \text{H}_2\text{SO}_4$$

is very probable because early in the reaction darkening of the substance is seen.

An experiment was carried out in which the iodine produced was extracted with $\text{CCl}_4$. When the extinction of the solution was measured this indeed gave the expected amount of iodine.

In further studies of the decomposition, the thermal decomposition of the compound $\text{I}_2\text{O}_3\cdot\text{SO}_3$ was studied by thermogravimetric analysis. As an explana-

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**Fig. 3.** DTG curve of $\text{I}_2\text{O}_3\cdot\text{SO}_3 + \text{"H}_2\text{SO}_4\text{ occl"}$.  

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tion of the DTG curve in Fig. 3, one may suggest (as the figure is divided into three parts):

I: Temperature range 20—240°C. Observed loss of weight is 16.8 % of total. Iodine is evolved and sublimed:

\[ 4 \text{I}_2\text{O}_5\text{SO}_3 + 4 \text{H}_2\text{O} \rightarrow 3 \text{I}_2\text{O}_4 + \text{I}_2 + 4 \text{H}_2\text{SO}_4 \]

Above 190°C the formed iodine tetroxide is decomposed:

\[ 5 \text{I}_2\text{O}_4 \rightarrow 4 \text{I}_2\text{O}_5 + \text{I}_2. \]

II: Temperature range 240—330°C. Observed loss of weight is 52.2 % of total. The compound I_O3 SO3 continues to hydrolyse. The sulfuric acid is partly driven off.

III: Temperature range 330—480°C. Observed loss of weight is 31.0 % of total. Iodine pentoxide decomposes. The rest of the sulfuric acid is driven off.

To give a simple explanation of the DTG curve of I2O3 SO3 is difficult because of the many simultaneous reactions taking place without reaching equilibrium on account of the rapid heating and also because the original compound had sulfuric acid occluded.

(iii) The compound I2O4

After decomposition the intermediate products give identical final products whether made according to the sulfuric-, the modified sulfuric-, oleum-, or the selenic acid method. X-Ray data from Guinier diagrams of the final products after washing with alcohol and drying, are listed in Table 2. The identity of the final products is also proved by infra-red spectroscopy.

The composition of the final products was checked by quantitative analysis. After carefully washing with absolute alcohol and cautious drying at 70°C a number of examined products gave the composition I2O4. The result thus agrees with the formulae given in the literature.5–8,19

Table 2. Guinier photograph data of I2O4 obtained by the sulfuric acid method.

<table>
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<tr>
<th>Iobs</th>
<th>(\sin^2\Theta \times 10^4)</th>
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<th>Iobs</th>
<th>(\sin^2\Theta \times 10^4)</th>
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I₂O₄ has a brownish colour which is also dependent on the particle size. It is not decomposed by light or moist air. Prolonged treatment in excess of water decomposes I₂O₄ according to equation:

$$5 \text{I}_2\text{O}_4 + 4 \text{H}_2\text{O} \rightarrow \text{I}_2 + 8 \text{HIO}_3$$

The reaction is fast in hot water. It should be noticed that the density of I₂O₄ is found to be 4.97 g/cm³ at 25°C which is essentially different from the value 4.2 g/cm³ at 10°C reported by Muir.⁸

![Fig. 4. DTG curve of I₂O₄.](image)

I₂O₄ decomposes on heating as shown by the DTG curve in Fig. 4. From the figure it is also seen that the decomposition takes place between 100 and 230°C. The relative loss of weight represented by peak (1) can be explained according to a decomposition:

$$5 \text{I}_2\text{O}_4 \rightarrow \text{I}_2 + 4 \text{I}_2\text{O}_5$$

assuming that the iodine is sublimed. The observed value \((\Delta w/w) = -0.149 \pm 0.004\) corresponds very well to the calculated \((\Delta w/w) = -0.159\) on the basis of above equation.

Between approximately 220 and 300°C the stable decomposition product is I₂O₅ which also has been confirmed by taking a Guinier diagram of it.

On further heating the DTG curve gives peak (2) which may indicate a partial decomposition of I₂O₅ before the total decomposition in the range 340—460°C. However, no intermediate product was observed when an experimental decomposition was carried out at 370°C. Peak (2 + 3) thus represents the total decomposition of I₂O₅ into O₂ and I₂.

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REFERENCES


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