

Iodine Oxides

Part I. On $I_2O_3 \cdot SO_3$, $I_2O_3 \cdot 4SO_3 \cdot H_2O$, $I_2O_3 \cdot SeO_3$ 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 $I_2O_3 \cdot SO_3$, $I_2O_3 \cdot 4SO_3 \cdot H_2O$ and $I_2O_3 \cdot SeO_3$ 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.¹ Later both intermediate and final products of this and partially modified reactions have been studied.²⁻²²

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 $I_{10}O_{19}$ by Millon¹ and I_6O_{13} by Kaemmerer² from chemical analysis. The formula $(IO_2)_x$ was confirmed by the analysis of Kappeler⁶ who introduced the notation $I_2O_4 \equiv (IO)(IO_3)$.

The reduction of iodic acid takes place according to Masson and Argument¹¹ 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 Argument¹¹ 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 Waddington¹⁹ could replace sulfuric acid with the homologous selenic acid.

A chemically more different alteration of Millon's¹ original synthesis is reported by Kaemmerer² who claims to have synthesized the intermediate product by reduction of I_2O_5 with dry SO_2 .

The composition of the intermediate product has at times been disputed either because the synthesis after Millons¹ 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 I_2O_3 , I_2O_4 and I_2O_5 added to SO_3 with different amounts of H_2O .^{1-11,13,19}

Although the literature even up to the present day is confused, the correct composition appears to be $I_2O_3 \cdot SO_3$.^{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 $I_2O_3 \cdot SO_3$ is reported to be very hygroscopic. Chrétien⁴ originally proposed the composition $I_2O_3 \cdot SO_3 \cdot \frac{1}{2}H_2O$ ($(IO)_2SO_4 \cdot \frac{1}{2}H_2O$) which was doubted by Bahl and Partington⁸ who gave the composition $I_2O_3 \cdot SO_3 \cdot H_2O$. 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.* $\frac{1}{2}H_2O$, or a monohydrate, *i.e.* one H_2O per formula unit $I_2O_3 \cdot SO_3$.

The chemical and physical properties of the intermediate product $I_2O_3 \cdot SO_3$ and the final product I_2O_4 have only been studied unsystematically. The magnetic properties at room temperature were investigated by Willmarth and Dharmatti,¹² Symons¹⁵ and Arotzky *et al.*²¹, infra-red and visible spectra have been reported by Dasent and Waddington,¹⁹ Wise and Hannan²⁰ and Arotzky *et al.*²¹ Dasent and Waddington suggested the formulae $(IO)_2SO_4$ and $(IO)_2SeO_4$ which, however, should not be interpreted according to an ionic picture but rather as inorganic polymers containing $(IO)_n$ groups linked to SO_4 or SeO_4 tetrahedra. Nevertheless the formulae $I_2O_3 \cdot SO_3$ *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 $I_2O_3 \cdot SO_3$, $I_2O_3 \cdot SeO_3$ and I_2O_4 in any solvent. $I_2O_3 \cdot SO_3$ is indeed soluble in fuming sulfuric acid according to Masson and Argument¹¹ but this process leads to the formation of a new compound $I_2O_3 \cdot 4SO_3 \cdot H_2O$.

A compound with composition $I_2O_5 \cdot 2SO_3$ has been prepared^{3,17} by a reaction between liquid SO_3 and KIO_3 , $Sr(IO_3)_2$ or I_2O_5 at temperatures between 60 and 100°C. At lower temperatures $I_2O_5 \cdot 3SO_3$, *i.e.* a product with a higher SO_3 content, is obtained. According to Lehmann and Hesselbarth¹⁷ symproportion of elementary iodine and I_2O_5 yield an equimolar mixture of $I_2O_3 \cdot 3SO_3$ and $I_2O_5 \cdot 2SO_3$. They also reported the preparation of $I_2O_4 \cdot 3SO_3$ from liquid SO_3 and I_2O_4 .

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 I_2O_4 .

EXPERIMENTAL

Chemicals. Iodine (Jodum resublimatum), iodic acid (Jodsäure für Analyse) and iodine pentoxide (Jodpentoxid für Analyse; Jodsäureanhydrid) of p.a. purity were obtained from Riedel-de Haën A.G. and E. Merck A.G. Sulfuric acid (Schwefelsäure für Analyse, $d_{20} = 1.83$, 95–97% ig), oleum (Schwefelsäure rauchend, etw. 60% SO₃) and selenic acid ($d = 2.9$) were obtained respectively from Riedel-de Haën 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 Masson¹⁰ and Masson and Argument.¹¹ 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.¹ 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.¹¹

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

The selenic acid method used by Dasent and Waddington¹⁹ 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-Recording 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 CuK_α-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 CuK_α₁-radiation. Potassium chloride (Analar, The British Drug Houses, Ltd. $a = 6.2919 \text{ \AA}$ ²³) was added to the specimens as an internal standard.

The density of I₂O₄ was determined by the pycnometric method at 25°C with kerosene as displacement liquid.

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 $I_2O_3 \cdot SO_3$ by the earlier investigators. This composition has been proved by Masson and Arguement¹¹ and confirmed by Dasent and Waddington,¹⁹ 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 $I_2O_3 \cdot SO_3 + {}^3H_2SO_4 \text{ occl}$. 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 $I_2O_3 \cdot SO_3$ cannot be kept in moist air because the substance is decomposed by water. For X-ray characterization the substance was thus sealed into capillaries. $\sin^2\theta$ 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^{15,16,21,22}).

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

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

		I_{obs}		$\sin^2 \Theta \times 10^4$			
SeM		SM		MSM		FMS	
vw	159	vw	158			w	203
vw	258					st	294
				m	307	m	314
		vw	323				
st	359	vw	361			w	345
		vst	372	←m	371	vw	381
				vw	401	m	404
		vw	476			vw	430
st	495	st	504	st	489	m	485
				←vw	510	st	521
vw	573	vw	573			vw	555
				vw	597	w	594
		vw	623	w	616	m	616
m	640			w	683	m	689
						w	757
m	795			m	788	m	792
		vst	833	←vw	831		
st	897			vw	899	vw	852
		vst	919	←m	917	m	914
vw	950						
		w	996	←w	1004	m	950
w	1079	vw	1082	←vw	1071	m	1017
w	1139					w	1071
vw	1153	m	1175				
		vw	1229	←m	1224	w	1249
				vw	1299	w	1317
m	1343	w	1346				
		vw	1394	w	1397	m	1391
m	1431			vw	1443	vw	1434
		m	1474	←w	1487	w	1474
vw	1558	vw	1558	vw	1571	m	1571
				vw	1720	w	1710
				vw	1783	m	1789
w	1803						
w	1874	vst	1887				
				vw	1911		
m	1960					w	1974

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 $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ prepared by the sulfuric acid method. This shows that most of the reflections from the compound $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ are also found in the X-ray diagrams

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 I_2O_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 $I_2O_3 \cdot SO_3$ may according to Masson and Argument¹¹ 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 $I_2O_3 \cdot SO_3$ 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 $I_2O_3 \cdot SO_3$ which gives a blue solution in oleum.²²

The composition of the white product, according to Masson and Argument¹¹ is $I_2O_3 \cdot 4SO_3 \cdot H_2O$. 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 $I_2O_3 \cdot SO_3$ can be seen to be formed first; then this primary product reacts with 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 $I_2O_3 \cdot SO_3$ and $I_2O_3 \cdot 4SO_3 \cdot H_2O$. Corresponding reflections are marked with arrows. The fact that the modified sulfuric acid method gives a mixture of $I_2O_3 \cdot SO_3$ and $I_2O_3 \cdot 4SO_3 \cdot H_2O$ explains the colour, *etc.* of these products. Earlier workers^{1,2,4-11,13} 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 I_2O_3 , I_2O_4 and I_2O_5 were added to SO_3 with different amounts of H_2O . The simple interpretation suggested here is sufficient to explain the earlier conflicting results.

The mixture of $I_2O_3 \cdot SO_3$ and $I_2O_3 \cdot 4SO_3 \cdot H_2O$ is obtained because when iodic acid and sulfuric acid are heated the sulfuric acid decomposes somewhat and produces SO_3 which reacts with $I_2O_3 \cdot SO_3$ to give $I_2O_3 \cdot 4SO_3 \cdot H_2O$. When the period of heating is too short I_2O_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,¹⁹ and the notation $I_2O_3 \cdot SeO_3$ 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_2 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 $I_2O_3 \cdot SeO_3$.

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^{15,16,21,22} on iodine compounds in sulfuric acid and oleum and the recent review by Gillespie and Robinson²⁴ 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 $I_2O_3 \cdot SO_3$ 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 $(IO)^+(HS_2O_7)^-$ ($2(IO)HS_2O_7 = I_2O_3 \cdot 4SO_3 \cdot H_2O$).

(ii) Slow hydrolysis of the intermediate products

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 2θ , 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 $I_2O_3 \cdot SeO_3$ (A) and $I_2O_3 \cdot SO_3$ (B) the intensities

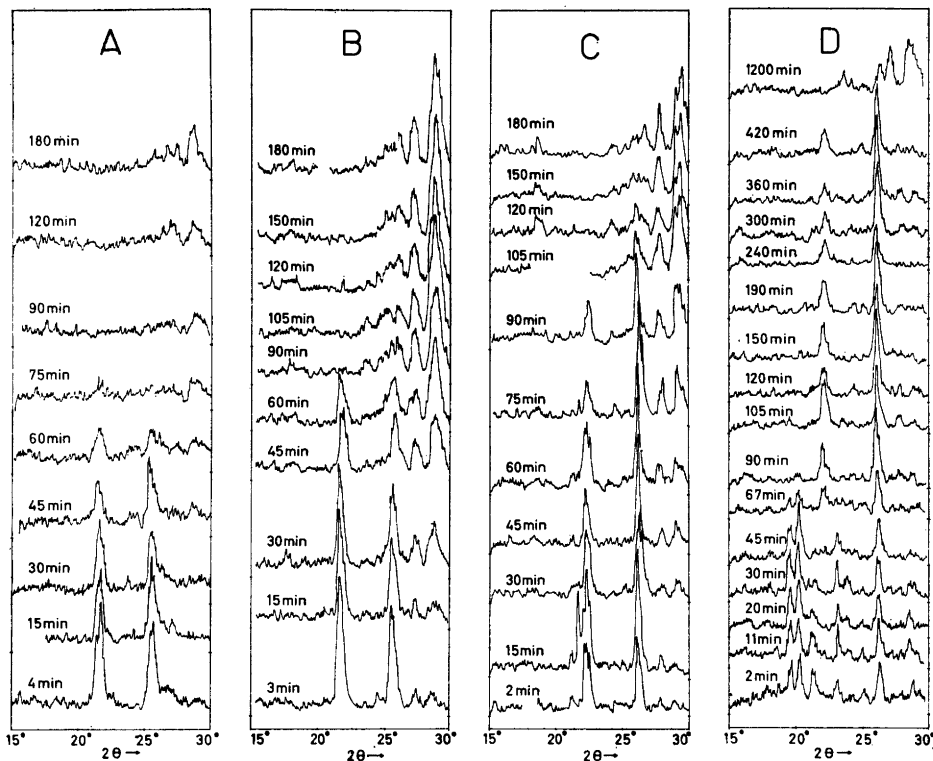


Fig. 1. X-Ray diffraction records of A: $I_2O_3 \cdot SeO_3 + "H_2SeO_4 \text{ occl}"$, B: $I_2O_3 \cdot SO_3 + "H_2SO_4 \text{ occl}"$, C: $I_2O_3 \cdot SO_3 + I_2O_3 \cdot 4SO_3 \cdot H_2O + "H_2SO_4 \text{ occl}"$, D: $I_2O_3 \cdot 4SO_3 \cdot H_2O + "H_2SO_4 \text{ occl}"$ at different time intervals during the decomposition reaction.

of the reflections decreases to vanish finally. For $I_2O_3 \cdot SO_3 + I_2O_3 \cdot 4SO_3 \cdot H_2O$ (C) and $I_2O_3 \cdot 4SO_3 \cdot H_2O$ (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 $I_2O_3 \cdot 4SO_3 \cdot H_2O$ 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 $I_2O_3 \cdot SO_3 + I_2O_3 \cdot 4SO_3 \cdot H_2O$, Fig. 2 C, can in principle be understood by the simultaneous hydrolyses of $I_2O_3 \cdot SO_3$ and $I_2O_3 \cdot 4SO_3 \cdot H_2O$.

The shape of the decomposition curves for $I_2O_3 \cdot SeO_3$ and $I_2O_3 \cdot SO_3$ 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 moist air changes the compound $I_2O_3 \cdot 4SO_3 \cdot H_2O$ to $I_2O_3 \cdot SO_3$. The reflections characterizing $I_2O_3 \cdot SO_3$ will thus first increase in intensity because the amount of $I_2O_3 \cdot SO_3$ increases. At one point all the $I_2O_3 \cdot 4SO_3 \cdot H_2O$

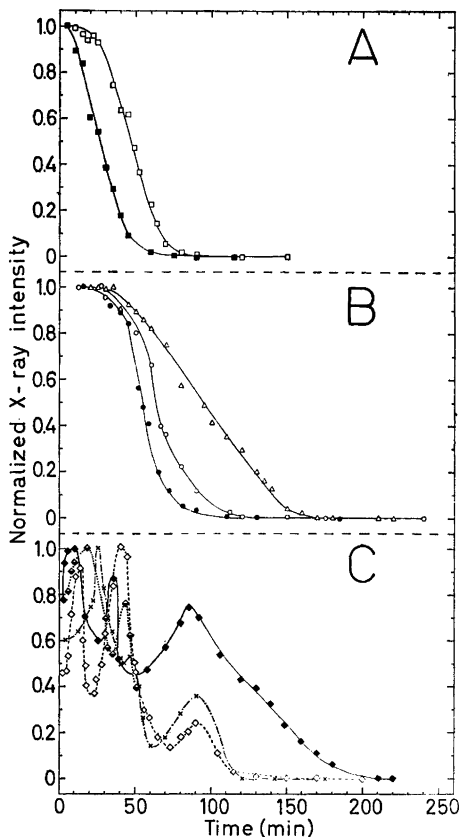


Fig. 2. The slow hydrolysis of

- A: $\text{I}_2\text{O}_3 \cdot \text{SeO}_3 + \text{''H}_2\text{SeO}_4 \text{ occl''}$,
 B: $\text{I}_2\text{O}_3 \cdot \text{SO}_3 + \text{''H}_2\text{SO}_4 \text{ occl''}$,
 C: $\text{I}_2\text{O}_3 \cdot \text{SO}_3 + \text{I}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{H}_2\text{O} + \text{''H}_2\text{SO}_4 \text{ occl''}$, as a function of time.

is converted to $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ and the intensity of the reflections decreases as $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ 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.*

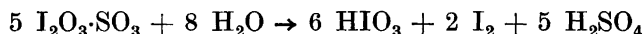
Masson and Argument¹¹ state that the transition from $\text{I}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{H}_2\text{O}$ to $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ is reversible as addition of oleum converts $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ into $\text{I}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{H}_2\text{O}$ while slow dilution with water produces the opposite reaction. Masson and Argument claimed as result of microscopic investigation that the change from $\text{I}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{H}_2\text{O}$ to $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ 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 $\text{I}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot \text{H}_2\text{O}$ to $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ it seems obvious that the reaction depends on the

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 H_2O from moist air $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ decomposes to I_2O_4 . From Masson and Argument¹¹ 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 H_2SO_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.

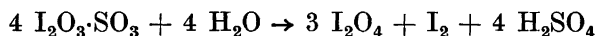
Using more water, $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ decomposes to iodic acid and iodine according to the equation



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 I_2O_4 by moist air, takes place as a oxidation-reduction reaction, and as the valence of iodine increases from + 3 in I_2O_3 to + 4 in I_2O_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 H_2SO_4 or SO_3 is reduced.

The decomposition of $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ taking place as disproportion of I_2O_3 :



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 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-

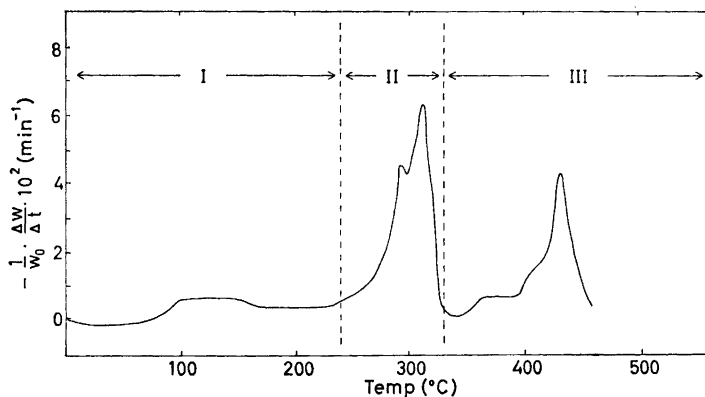
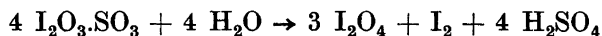


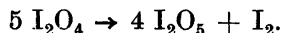
Fig. 3. DTG curve of $\text{I}_2\text{O}_3 \cdot \text{SO}_3 + \text{''H}_2\text{SO}_4 \text{ occl''}$.

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:



Above 190°C the formed iodine tetroxide is decomposed:



II: Temperature range 240–330°C. Observed loss of weight is 52.2 % of total. The compound $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ 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 $\text{I}_2\text{O}_3 \cdot \text{SO}_3$ 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 I_2O_4

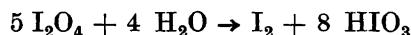
After decomposition the intermediate products give identical final products whether made according to the sulfuric-, the modified sulfuric-, oleum-, or the selenic acid method. X-Ray data from Guinier diagrams of the final products after washing with alcohol and drying, are listed in Table 2. The identity 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 I_2O_4 . The result thus agrees with the formulae given in the literature.^{5-8,19}

Table 2. Guinier photograph data of I_2O_4 obtained by the sulfuric acid method.

I_{obs}	$\sin^2\Theta \times 10^5$	d (Å)	I_{obs}	$\sin^2\Theta \times 10^5$	d (Å)
vw	1214	6.990	m	6187	3.097
w	2423	4.847	st	6343	3.059
w	2530	4.841	m	6536	3.013
vw	2571	4.802	m	8705	2.611
vw	4152	3.779	m	13110	2.127
m	4277	3.724	m	13287	2.113
m	4633	3.578	st	13797	2.073
m	4882	3.485	vw	15532	1.954
m	5047	3.429	vw	19049	1.765
vw	5218	3.372	vw	19431	1.747
w	5283	3.350	vw	20819	1.688
m	5593	3.257	vw	21479	1.662

I_2O_4 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 I_2O_4 according to equation:



The reaction is fast in hot water. It should be noticed that the density of I_2O_4 is found to be 4.97 g/cm^3 at 25°C which is essentially different from the value 4.2 g/cm^3 at 10°C reported by Muir.⁸

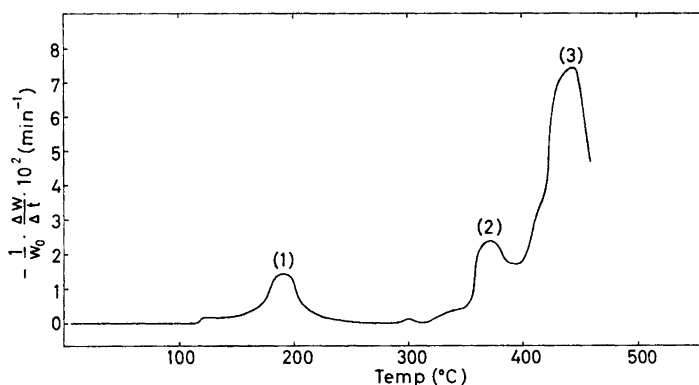
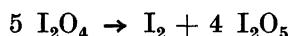


Fig. 4. DTG curve of I_2O_4 .

I_2O_4 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:



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 I_2O_5 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 I_2O_5 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 I_2O_5 into O_2 and I_2 .

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