

Iodine Oxides

Part II.* On the System $H_2O-I_2O_5$

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The phase relationships of the $H_2O-I_2O_5$ system have been studied by thermal decomposition of α - HIO_3 and by recrystallization from aqueous solutions with various degrees of acidity. The only iodine containing compounds, α - HIO_3 , HI_3O_8 , and I_2O_5 have been isolated and identified by a combination of X-ray diffraction, density, infra-red spectroscopic, proton magnetic resonance, differential thermal analyses, and thermogravimetric measurements. Commercial products of iodic acid and iodine pentoxide from several manufacturers have been tested.

The oxides and oxo-acids of iodine have been the subject of numerous investigations over a period of time extending back to the early history of chemistry. The literature covering this field has become so voluminous that any survey of reasonable size is bound to give a very incomplete picture of all the work done. However, despite all this research effort the present knowledge of the chemical and physical properties of these substances is rather fragmentary and uncertain, the ambiguities being emphasized in recent textbooks and reference sources, see *e.g.* Cotton and Wilkinson¹ and Pascal.² Even the existence or composition of many of the compounds previously reported is an open question. The oxides I_2O_4 and I_2O_5 and the oxo-acids HI_3O_8 , α - HIO_3 , HIO_4 , ($H_4I_2O_9$?), and H_5IO_6 appear to be properly established whereas the existence of compounds with formulae *e.g.* I_2O_3 , I_4O_9 , IO_3 , I_2O_7 , IO_4 , $H_2I_4O_{11}$, $H_{10}I_{12}O_{35}$, β - HIO_3 , and H_3IO_5 (these formulae occur frequently in the literature) is associated with a considerable degree of uncertainty. Most of these uncertainties seem to be connected with the fact that too little emphasis has been put on the use of sensitive and accurate methods for the physical characterization of the samples and determinations of their homogeneity. In particular, insufficient attention has been given to the stability of these substances in relation to moisture and heat treatment. Determinations of crystal structures are, so far, limited to those of Rogers and Helmholtz³ and

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Garrett⁴ for α -HIO₃, that for HI₃O₈ by Feikema and Vos,⁵ and that for H₅IO₆ by Feikema.^{6,7} Tentative information concerning the structural arrangements of I₂O₄ and I₂O₅ has also been published^{8,9} on the basis of their infra-red (IR) spectra.

The present investigation has been carried out with the main purpose of establishing the existence of stable compounds in the H₂O—I₂O₅ system, using a combination of X-ray, IR, and proton magnetic resonance (PMR) methods for their characterization. Differential thermogravimetric (DTG) and differential thermal analyses (DTA) have been used to study the thermal decomposition of α -HIO₃, references to the contributions by Duval^{10,11} being relevant in this connection.

MATERIALS AND METHODS

Chemicals. Iodine (*Jodum resublimatum*), nitric acid (Salpetersäure min. 65 % zur Analyse, $d_{20}=1.40$), fuming nitric acid (Salpetersäure rauchend 100 % zur Analyse, $d_{20}=1.52$), sulphuric acid (Schwefelsäure 95–97 % zur Analyse, $d_{20}=1.84$), *ortho*-phosphoric acid (*ortho*-Phosphorsäure min. 85 % zur Analyse, $d=1.71$), and hydrochloric acid (Salzsäure min. 32 % zur Analyse, $d_{20}=1.16$) of *p.a.* purity were supplied by E. Merck AG. and *ortho*-periodic acid (Überjodsäure, krist.) by Riedel-de Haën AG., whereas iodic acid and iodine pentoxide were obtained from various manufacturers (see Table 1).

Syntheses. Commercial products of iodic acid and iodine pentoxide were recrystallized from:

(i) unsaturated aqueous solutions by slow evaporation of all water at room temperature;

Table 1. Estimated compositions of the commercial reagents of iodic acid and iodine pentoxide.

Manufacturer	Reagent	Composition (%)			
		α -HIO ₃	HI ₃ O ₈	I ₂ O ₅	β -HIO ₃ (?)
The British Drug Houses, Ltd. Fisher Scientific Company Fluka AG. Hopkin & Williams Ltd. K & K Laboratories, Inc. May & Baker Ltd. E. Merck AG. E. Merck AG. Riedel-de Haën AG.	Iodic acid "Analar"	60	40		
	Certified iodic acid	50	50		
	Jodsäure ≥ 98 % purum	80	20		
	Iodic acid "Analar"	100			
	Iodic acid		100		
	Iodic acid "R"	70			30
	Jodsäure krist. zur Analyse	50	50		
Jodsäure krist. zur Analyse	100				
Jodsäure für Analyse	60	40			
Allied Chemical The British Drug Houses, Ltd. Hopkin & Williams Ltd. K & K Laboratories, Inc. E. Merck AG. Riedel-de Haën AG. Carl Roth OHG.	Iodine pentoxide "B & A"		60	40	
	Iodine pentoxide		100		
	Iodine pentoxide		100		
	Iodine pentoxide		100		
	<i>di</i> -Jodpentoxid, gekörnt		100		
	Jodpentoxid für Analyse		100		
	Jodpentoxyd, granuliert	50	50		

(ii) aqueous solutions which were boiled down to saturation at 70–80°C, after which the crystals were allowed to deposit at room temperature, followed by filtering, and finally drying at room temperature;

(iii) acidic solutions of HNO₃, H₂SO₄, and HCl. The procedure followed in these preparations is essentially that described by Brauer,¹² but modifications are introduced in some of the experiments. Following Brauer HIO₃ (or I₂O₅) was dissolved in a mixture of equal volumes of conc. HNO₃ and water, whose total volume was reduced to 1/3 by boiling, and the solution was then cooled to room temperature. The crystals so formed were filtered from the mother-liquor and finally dried at room temperature.

A variety of thermal decomposition experiments were carried out in open crucibles at temperatures between 20 and 300°C. The recorded temperatures were kept constant to within ±5°C.

Following the procedure of Moles and Parts¹³ iodine was oxidized with fuming nitric acid at room temperature in an Erlenmeyer-flask with ground-glass stopper. The mixture was stirred by a magnetic stirrer.

Ozonization of saturated solutions of I₂ in CCl₄ was performed with ozone (delivery 1.9 g/l) from a model T-23 laboratory ozonator from Projecting A.B. (Sweden).

I₂O₄ was prepared by the sulphuric acid method.¹⁴

X-Ray photographs of the powdered samples were taken in a Guinier type focusing camera of 80 mm diameter with monochromatized CuKα₁-radiation (λ=1.54050 Å) using KCl (a=6.2919 Å¹⁵) as internal standard. The lattice dimensions were refined by applying the method of least squares to the Guinier photographic data.

X-Ray photographs of I₂O₅ single crystals were taken with a Weissenberg camera of 57.3 mm diameter using Mo-radiation.

DTG and DTA analyses were accomplished with a Mettler Recording Vacuum Thermo-analyzer using 50–70 mg samples and Al₂O₃ crucibles. The heating rate was 2°C/min, the atmosphere was air with a flow rate of 5 l/h, and kaolin (37.0 mg) was used as reference material for DTA.

PMR spectra of the powdered compounds were recorded on a DP-60 Varian Associate NMR Spectrometer operating at a frequency of 60 MHz. The sample holder was of the LP-4331 type and field sweep was carried out with a Varian field-dial unit.

Five PMR spectra were taken of each sample, the data were averaged, and experimental second moments were evaluated and corrected for modulation. Calculated second moments were deduced from the formula

$$M_2 = \frac{1}{n} \sum_{i=1}^n \left(358.07 \sum_j r_{ij}^{-6} + 74.31 \sum_k r_{ik}^{-6} \right)$$

where the first term gives the proton-proton contribution and the second the proton-iodine contribution, *n* is the number of protons in the asymmetric unit of the cell, and *r_{ij}* (*r_{ik}*) is the distance from a proton *i* (within the asymmetric unit) to another nucleus *j* (*k*).

IR spectra were recorded on a Perkin-Elmer Infra-red Spectrophotometer Model 21 (NaCl or CsBr prisms) with the samples suspended in KBr or waterfree paraffin, the latter suspensions being pressed between NaCl slices.

Density measurements (of I₂O₄ and I₂O₅) were carried out pycnometrically at 25°C with kerosene as displacement liquid.

RESULTS

(i) *Iodic acid*. Pure iodic acid was obtained by recrystallization of the commercial products of HIO₃ and I₂O₅ from aqueous solutions at room temperature. The Guinier photographic data of such samples confirmed identity with α-HIO₃, the composition of which had been proved by its complete crystal structure determination by Garrett.⁴ All reflections on the X-ray photographs could be accounted for by indexing, and the unit cell dimensions of α-HIO₃

Table 2. Unit cell dimensions and pycnometric densities for I_2O_4 , I_2O_5 , HI_3O_8 , α - HIO_3 , and H_5IO_6 . The error limits correspond to the standard deviations as obtained by the least squares refinements.

Compound	a (Å)	b (Å)	c (Å)	β (°)	d_{pycn} (g cm ⁻³)
I_2O_4	8.487 ± 0.008	6.706 ± 0.003	8.338 ± 0.005	124.65 ± 0.05	5.21
I_2O_5	11.036 ± 0.003	5.063 ± 0.001	8.135 ± 0.002	107.18 ± 0.02	5.08
$HI_3O_8^{a,b}$	7.580 ± 0.002	7.713 ± 0.002	11.407 ± 0.003	90.15 ± 0.02	4.97^5
α - HIO_3	5.538 ± 0.002	5.876 ± 0.002	7.735 ± 0.002		4.63^4
$H_5IO_6^a$	5.313 ± 0.002	18.355 ± 0.005	4.961 ± 0.002	111.83 ± 0.03	3.39^6

^a The setting of the unit cell is based on the unconventional space group $P2_1/n$ rather than $P2_1/b$ as listed in *International Tables*. In an attempt to avoid confusion we have decided to adopt the same space group ($P2_1/n$) as previously used by Feikema and Vos⁵ and Feikema.^{6,7} The transformation matrix for axes and indices from $P2_1/n$ to $P2_1/b$ is 100/010/101.

^b In terms of space group $P2_1/n$ the hydrogen atoms in the crystal structure of HI_3O_8 are most probably located in $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ with $x = 0.9069$, $y = 0.4463$, $z = 0.1323$.

listed in Table 2 are in close agreement with those of Rogers and Helmholtz³ and Garrett.⁴

The present IR data for α - HIO_3 confirmed those of Dupuis and Lecomte¹⁶ (see also Wise and Hannan¹⁷) and a presentation in this paper is hardly justified. The PMR spectra unequivocally confirm the presence of hydrogen in α - HIO_3 and the comparison of observed and calculated second moments (Table 3) show that the PMR data are consistent with the structural data of Garrett.⁴

Table 3. Comparison of observed and calculated PMR second moments for α - HIO_3 , HI_3O_8 , and H_5IO_6 .

Compound	Second moment (G)	
	obs	calc
α - HIO_3	1.7 ± 0.1	1.50
HI_3O_8	0.9 ± 0.1	0.92
H_5IO_6	7.9 ± 0.3	7.21

The DTG and DTA curves in Fig. 1 show that α - HIO_3 decomposes to HI_3O_8 at 100–130°C. Prolonged heat treatments of α - HIO_3 at constant temperatures demonstrate that the onset of the decomposition reaction takes place at $\sim 80^\circ\text{C}$. Thus, in order to avoid partial decomposition during drying, it is suggested that α - HIO_3 should be dehydrated below 50°C, and preferably dried at room temperature under vacuum. The pure α - HIO_3 thus obtained

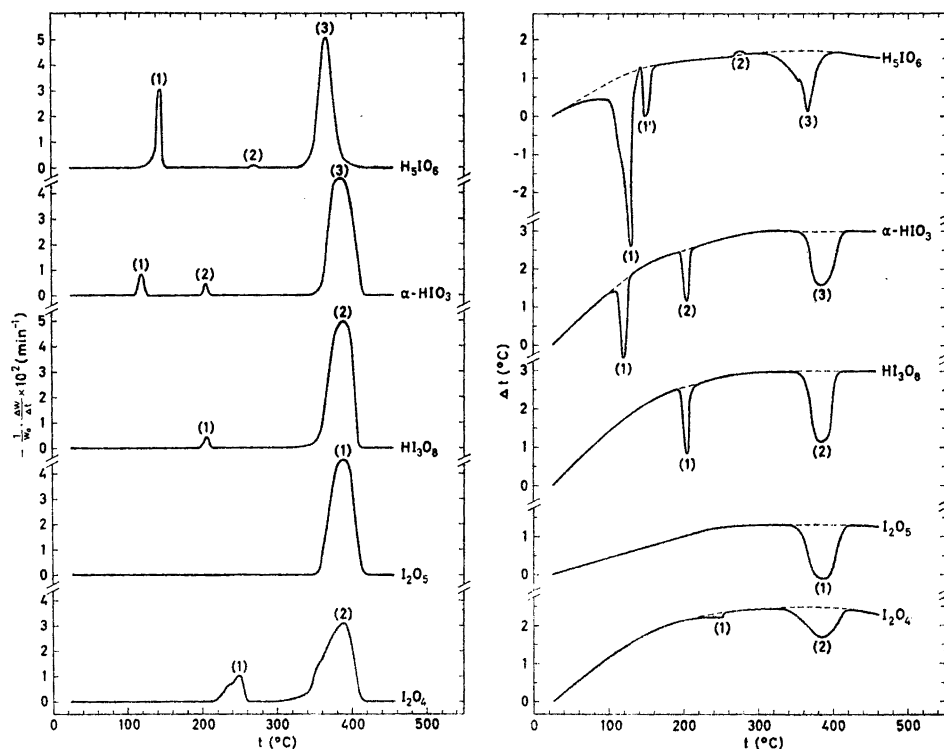


Fig. 1. DTG and DTA curves for I_2O_4 , I_2O_5 , HI_3O_8 , $\alpha-HIO_3$, and H_5IO_6 .

can, however, be stored at room temperature for an indefinite period without any special precautions.

The modification of iodic acid described above carries the designation $\alpha-HIO_3$, which implies the existence of a β -modification. A careful search of the literature shows that the existence of $\beta-HIO_3$ has been inferred in 1906 by Groth¹⁸ on the basis of goniometric data from 1853–1857. Later investigations of iodic acid have apparently not confirmed the occurrence of more than one modification of this compound which might indicate that the prefix to its formula is superfluous. However, on the Guinier photographs of one of the commercial products of HIO_3 (see section iv) and those of about 3% of our recrystallized samples there occur some additional reflections which definitely do not belong to $\alpha-HIO_3$. Despite numerous attempts we have been unable to obtain this phase in a pure state, its preparational conditions being apparently highly irreproducible. The possible existence of $\beta-HIO_3$ is therefore still an open question which must be subjected to further examination.

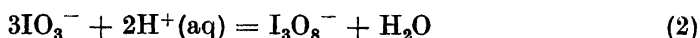
(ii) *Anhydro iodic acid*. Pure anhydro iodic acid was prepared by two different methods:

(a) Thermal decomposition of α -HIO₃ at temperatures between 100 and 150°C gives HI₃O₈ according to the equation:



The DTG data (Fig. 1 and Table 4) confirm eqn. 1 and accordingly also the formula HI₃O₈. Several decomposition experiments at constant temperatures (100–150°C) gave also perfect agreement between observed and calculated (from eqn. 1) weight losses.

(b) Recrystallization of α -HIO₃ (or I₂O₅) from acidic solutions produces HI₃O₈, resulting from the reaction:



Aqueous solutions of HNO₃ have been used in most of the present experiments, but other strong acids, *i.e.* HCl, H₂SO₄, *etc.*, give the same result.

Both methods give identical products of HI₃O₈ according to the X-ray IR, and PMR data. All reflections on the X-ray photographs are indexed and the good agreement between the lattice dimensions in Table 2 and those of Feikema and Vos⁵ confirms identity between the two studies. The values in Table 2 refer to HI₃O₈ prepared according to method (b). Although the unit cell dimensions obtained from the products of the two methods are in excellent agreement, method (b) appears to give the most well formed crystal samples, judging from the sharpness of the X-ray reflections. This feature is also reflected in the calculated standard deviations, those of the samples of method (a) being generally about twice the corresponding values in Table 2.

The structural data of Feikema and Vos⁵ confirm the composition of HI₃O₈ with respect to iodine and oxygen, but their investigation gave no direct information on the hydrogen atom and its location in the crystal structure. The PMR spectra definitely prove, however, that hydrogen is present in the crystal lattice of HI₃O₈. Following the general trends for hydrogen bonding in relation to interatomic distances (*cf.*, *e.g.*, Pauling¹⁹ where further references are included) and the tentative suggestion by Feikema and Vos concerning HI₃O₈, the hydrogen atom is placed as shown in the footnote to Table 2. The value for the second moment calculated on the basis of these hydrogen and iodine positions is in excellent agreement with the observed value (Table 3), which accordingly places some confidence in the hydrogen coordinates. The second moment is somewhat insensitive, however, to the numerical values of these parameters.

The IR spectra of HI₃O₈ agree with those published by Dupuis and Lecomte¹⁶ and these data are accordingly not repeated here. The interpretation of the IR data given by these authors is furthermore fully consistent with the structural data.

The DTG and DTA results (Fig. 1 and Table 4) demonstrate that HI₃O₈ decomposes to I₂O₅ at 195–220°C, but the onset of the reaction is appreciable at ~170°C when HI₃O₈ is subjected to prolonged heat treatment at constant temperature. The stability of HI₃O₈ at room temperature depends on the particle size of the sample and the humidity of the surrounding atmosphere.

Table 4. DTG and DTA data (extracted from Fig. 1) for I_2O_4 , I_2O_5 , HI_3O_8 , α - HIO_3 , and H_5IO_6 . The comparisons of observed and calculated weight losses refer to reactions discussed in the text; the eqn. nos. being listed in the ultimate column.

Compound	Peak No.	Decomp. temp. from DTA (°C)	Decomp. temp. from DTG ($\Delta w/w_0 \neq 0$) (°C)	$-(\Delta w/w_0)$ obs	$-(\Delta w/w_0)$ calc	Eqn. No.
I_2O_4	1	210–260	215–260	0.17	0.160	4
	2	300–420	300–415	0.82	0.840	8
I_2O_5	1	350–420	355–420	0.99	1.000	8
HI_3O_8	1	200–220	200–215	0.01 ₉	0.018	3
	2	340–410	320–410	0.97	0.982	8
α - HIO_3	1	100–130	105–130	0.03 ₈	0.034	1
	2	195–215	195–210	0.01 ₇	0.017	3
	3	350–415	345–415	0.94	0.949	8
H_5IO_6	1(1')	40–160	85–155	0.25	}0.268	6 & 7
	2	265–285	265–280	0.00 ₇		
	3	300–400	330–420	0.72	0.732	8

Coarse crystalline HI_3O_8 can apparently be stored in open vessels for an indefinite period independent of the humidity of the air, and the same result is also obtained for fine-powdered samples provided the humidity is low. On the other hand, fine-powdered samples of HI_3O_8 placed in a closed system with moist air are completely converted into α - HIO_3 after 1 day.

(iii) *Iodine pentoxide*. Pure iodine pentoxide is obtained by several methods:

(a) HI_3O_8 undergoes thermal decomposition to I_2O_5 in the temperature range 190–250°C. The reaction



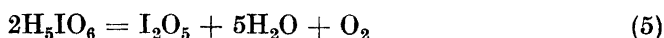
is verified by the DTG data (Fig. 1 and Table 4). Excellent agreement between observed and calculated weight losses was also obtained in numerous decomposition experiments carried out at constant temperatures (190–250°C). However, it should be noted that I_2O_5 readily undergoes sublimation, the sublimation rate depending on such factors as the previous history of the sample and its particle size, the temperature, the shape of the crucible, the surrounding atmosphere, etc. When, e.g., fine-powdered I_2O_5 is heated in open crucibles at 250°C there appears to be an initiation period of about 3 h in which no weight change of the sample is registered, i.e. the sample is in apparent thermodynamical equilibrium. Thereafter follows the sublimation period in which the weight loss of the sample is proportional to the time, the first visible sublimate being detected after 15–20 h. Guinier photographs confirm that the sublimate and the residuum of the samples are identical, i.e. I_2O_5 .

(b) I_2O_4 decomposes irreversibly to I_2O_5 on heating at 125–250°C according to the equation:

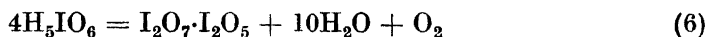


The course of the reaction is confirmed by the DTG data (Fig. 1 and Table 4), the composition of I_2O_4 having been verified previously.¹⁴ The PMR technique was used to prove that the I_2O_4 samples were completely waterfree and the redetermined unit cell dimensions²⁰ and density¹⁴ are included in Table 2 for the purpose of identification.

(c) Thermal decomposition of H_5IO_6 at 170–250°C evolves H_2O and O_2 and produces I_2O_5 according to the reaction:



The observed losses of weight during numerous decomposition experiments at constant temperatures (170–250°C) were 27 ± 1 % of the total weights, which show that eqn. 5 is correct. It has on the other hand been difficult to give an entirely satisfactory explanation of the present DTG data for H_5IO_6 . The data in Fig. 1 and Table 4 may be essentially consistent with the formation of the intermediate product $I_2O_7 \cdot I_2O_5$ ($\equiv 4IO_3$) reported by Pačesová and Hauptman²¹



which is followed by the reaction



Detailed experiments are now being carried out in order to check the validity of eqns. 6 and 7, and these results will be published in a forthcoming paper.

The H_5IO_6 samples used in this study were checked by X-ray and PMR methods prior to use. The present values for the lattice dimensions of H_5IO_6 (Table 2) are in good agreement with those of Feikema⁶ and the comparison of observed and calculated second moments (Table 3) show that the PMR data may be essentially consistent with the positional parameters for hydrogen and iodine given by the latter author.^{6,7}

(d) α - HIO_3 (and HI_3O_8) is chemically dehydrated to I_2O_5 by treatment with conc. H_2SO_4 or $H_4P_2O_7$. Although this method is quick and simple it has the drawback that it is difficult to remove the last traces of these acids from the samples even after repeated treatments on porous porcelain and careful washing with absolute alcohol. (Note that the least trace of water in the alcohol produces a corresponding amount of HI_3O_8 in the sample.)

Fichter and Kappeler²² have claimed that the treatment of HIO_3 in boiling $H_4P_2O_7$ gives an oxide with composition I_4O_9 . None of our numerous experiments according to their procedure has confirmed this result, I_2O_5 invariably being obtained as the only reaction product. The evidences of Fichter and Kappeler were mainly based on chemical analyses, and the analytical difficulties in distinguishing between the formulae I_2O_5 and I_4O_9 must be appreciated in view of the amounts of $H_4P_2O_7$ which may have been contained in their samples.

(e) Iodine is easily oxidized to I_2O_5 by fuming nitric acid at room temperature. The oxidizing agent is afterwards easily removed by centrifuging, treatment on porous porcelain, washing with absolute alcohol, and finally, drying under vacuum.

The present result is in complete accordance with that derived by Bahl and Partington²³ from chemical analyses. On reading the paper by Feikema and Vos⁵ one may perhaps get the impression that they have obtained HI_3O_8 according to the above procedure, but these authors have, however, recrystallized their samples from aqueous solutions of nitric acid (see section ii).

(f) Ozonization of iodine dissolved in waterfree CCl_4 gives I_2O_5 as the only stable product. Despite numerous attempts we have been unable to verify the existence of the ozonide I_4O_9 previously reported by, *e.g.*, Bahl and Partington.²³ It should be emphasized, however, that the present finding does not exclude the possibility of other compounds being formed as intermediate products of the reaction or even, *e.g.*, I_4O_9 being the end product of the reaction before the ozone containing atmosphere and the dissolvent (CCl_4) are removed. In fact, the quantitative measurements of the amounts of ozone required for complete ozonization in the various experiments may suggest that I_4O_9 exists at room temperature under these conditions. It is finally worth mentioning that the present observations show that the reaction between iodine and ozone takes place in the CCl_4 solution rather than in the gaseous phase as opposed to the previous suggestions of Berger²⁴ and Kikindai.²⁵

The final products of the various methods (a)–(f) are proved to be identical by means of X-ray and IR methods. Pure I_2O_5 is best characterized by the X-ray diffraction data listed in Table 5, its composition being established in

Table 5. Guinier photographic data of I_2O_5 taken with monochromatized $CuK\alpha_1$ -radiation.

I_{obs}	$\sin^2\theta \times 10^5$		hkl	I_{obs}	$\sin^2\theta \times 10^5$		hkl
	obs	calc			obs	calc	
vw	2129	2134	200	vw	7117	7117	310
vw	2842	2849	110	w	7630	7632	112
st	3408	3403	11 $\bar{1}$	vw	7772	7773	202
m	3598	3607	10 $\bar{2}$	m	8477	8479	31 $\bar{2}$
vst	3934	3928	002	st	8543	8538	400
w	4349	4351	20 $\bar{2}$	st	9050	9044	40 $\bar{2}$
vst	4460	4449	210	vw	9789	9793	120
st	4575	4576	21 $\bar{1}$	m	10089	10088	212
m	5316	5317	102	st	10242	10241	021
m	5925	5922	11 $\bar{2}$	st	10404	10405	11 $\bar{3}$
m	6168	6164	30 $\bar{2}$	w	11200	11203	121
m	6246	6243	012	vw	11291	11296	302
st	6286	6286	211	vw	11358	11359	41 $\bar{2}$
m	6673	6666	21 $\bar{2}$	w	12863	12866	12 $\bar{2}$
vw	6808	6816	31 $\bar{1}$	w	12971	12971	113

the various decomposition experiments described above and also confirmed by chemical analyses. The PMR spectra of cautiously treated samples show that I_2O_5 does definitely not contain hydrogen, and the IR data concur with this result provided the interpretations given by Duval and Lecomte⁹ and Dupuis and Lecomte¹⁶ are accepted as correct.

I_2O_5 is extremely hygroscopic and access to moist air rapidly converts it into HI_3O_8 . The rate at which moisture is taken up by a sample depends primarily on the size of its surface area and for preparations according to methods (d)–(f) also on its previous history, other important factors being humidity, temperature, etc. The coarsest particle size of I_2O_5 is obtained in the sublimates (*vide supra*), but even in this case the advancing disintegration can be watched under a microscope. The present findings imply that greater care should be taken in the storage and handling of I_2O_5 than previously realized.

When I_2O_5 is subjected to heat treatment above 280°C it decomposes irreversibly into the elements



The decomposition temperatures obtained from the DTG and DTA data (Fig. 1 and Table 4) are somewhat higher than 280°C since these experiments were performed under non-equilibrium conditions.

Well formed, needle shaped single crystals of I_2O_5 are easily obtained by sublimation (*vide supra*). Due to their hygroscopic property it is difficult to mount and seal a crystal in the thin-walled boron-lithium-glass capillaries before it is partially or completely disintegrated. However, after some unsuccessful attempts a nearly perfect I_2O_5 crystal was mounted. The oscillation and Weissenberg photographs showed that I_2O_5 crystallizes monoclinically with the diad axis along the needle axis. The Guinier photographic data (Table 5) were easily indexed on the basis of the single crystal data and the unit cell dimensions are listed in Table 2. The pycnometric density (Table 2) shows that the unit cell contains 4 I_2O_5 -groups ($Z_c = 3.98$). The only systematically missing reflections in the X-ray photographs were of the type $(h0l)$ absent when $l = 2n + 1$ and the most probable space group is accordingly $P2/c$. The determination of the crystal structure of I_2O_5 will be reported in a forthcoming paper.

(iv) *Commercial products.* The present study concludes that there exist only three iodine-containing compounds in the $H_2O-I_2O_5$ system, *i.e.* $\alpha-HIO_2$, HI_3O_8 , and I_2O_5 , this conclusion being in complete accordance with that of Duval.^{10,11} Any of these compounds are easily obtained in the pure state following an appropriate method as outlined above, but checking of the samples by physical methods is required in order to ascertain their homogeneity. However, even the most cautiously prepared samples can easily be spoiled by improper handling and/or negligent storage.

Iodic acid and iodine pentoxide should be available as commercial reagents according to the catalogues published by the manufacturers. However, already at a preliminary stage of this study it became evident that the contents of

the bottles supplied by such well-known manufacturers as E. Merck AG. and Riedel-de Haën AG. differed from the announcements on their labels. These findings encouraged us to examine also commercial reagents from other sources in order to be able to draw a more general conclusion. The results of this investigation are presented in Table 1 which comprise products from the majority of the manufacturers of these reagents. The percentage compositions of the reagents have been estimated from Guinier photographic data by comparisons with those of standard mixtures of the pure compounds. (The seals on the bottles were broken immediately before the experiments and great care was taken in order to avoid contamination prior to use.)

The commercially available iodic acid proved in most cases to consist of a mixture of α -HIO₃ and HI₃O₈, excepting the reagent of Hopkin & Williams, Ltd. and one of the batches of E. Merck AG. which contained pure α -HIO₃ (cf. Table 1). Another exception must be made for the product of May & Baker, Ltd. which may contain α - and β -HIO₃. According to the results presented in section (i) it is suggested that most of the manufacturers have chosen a too high drying temperature for their products.

None of the reagents sold under the label iodine pentoxide contain the pure anhydride, on the contrary most of those tested by us proved to be pure HI₃O₈ (Table 1). The reason for this failure is almost certainly to be attributed to the extremely hygroscopic property of I₂O₅ (see iii). In order to overcome this problem we suggest that the manufacturers supply their reagents in evacuated and sealed glass capsules.

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