ZINC PERIODATES

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Dedicated to Professor S. Škramovský on the occasion of his 75th birthday.

By precipitating sodium periodate and zinc sulphate with sodium hydroxide in an aqueous solution, and by studying the solubility in the three-component system $Zn_2HIO_6.H_2O$–H_5IO_6–H_2O, three zinc periodates were proved to exist at room temperature. The following constitution formulas were proposed on the basis of their infra-red spectra: $Zn_2HIO_6.H_2O$, $Zn_2H_2I_2O_{10}.6\,H_2O$, and $Zn(IO_4)_2.8\,H_2O$. Efforts to verify the existence of $Zn_5(IO_6)_2$ described previously by its preparation at laboratory temperature or as a product of thermal decomposition of the zinc periodates under study, failed.

The existence of a series of zinc periodates of various ratios of zinc to iodine has been reported in the literature[1–11]; the most simple atomic ratios (Zn : I = 2 : 1 and 1 : 1) have compounds described as $4\,ZnO.I_2O_7.H_2O$ (ref.[1–3]), $4\,ZnO.I_2O_7.5\,H_2O$ (ref.[7]) and $Zn_2I_2O_9.6\,H_2O$ (ref.[4–6]). According to the literature, the only anhydrous species of the formula $Zn_5(IO_6)_2$ is obtained by precipitation at pH within 6·2–6·6, and it may be employed for gravimetric determinations of both zinc and iodine[8–11]. Some of the literary data, however, lack support or even veracity.

Infra-red spectra of crystalline periodates were interpreted by Siebert[12–14] and other authors[15–17]. Literary data on dissociation, hydration, and polymeration equilibria of periodic acid and its salts in an aqueous medium are in mutual agreement in the case of the dissociation constant of periodic acid[18–21], but data on hydration and polymeration of various types of anions are at variance[14,22–26].

The present paper forms a part of a series of earlier communications devoted to periodic acid and its salts[15,27–30]; it was aimed at furnishing supplementary data concerning the structure of periodate anions in the solid state and of the products of their thermal decomposition.

EXPERIMENTAL

Chemicals and analytical methods used. All chemicals were of A.R. grade. Deuterated pentahydrogenperiodic acid was prepared by a fourfold recrystallization of H_5IO_6 from D_2O in a va-

cuum evaporator. Deuterated zinc periodates were prepared from anhydrous Na_2CO_3 and $ZnSO_4$ and from deuterated pentahydrogenperiodic acid in solutions of D_2O.

The content of iodine in the compounds under study was determined after reducing it to iodide by argentometric titration with a potentiometric indication. The oxidation number of iodine was determined by iodometry. In samples, whose iodine oxidation numbers were beyond doubt, iodometry was a tool for determining the amount of iodine. The content of zinc was determined after reducing periodate to iodide by titration with Chelatone III to eriochromiumblack T in a Schwarzenbach buffer medium. The water content was obtained from the difference to 100 per cent. All analytical data given in the tables are averages of two to three parallel determinations.

RESULTS

Acidimetric precipitation titrations and calculation of the solubility product. Measurements were made with a PHM Radiometer (Denmark) with a glass indication electrode and a saturated calomel reference electrode. The electrode system was calibrated with the aid of standard buffers (Lachema, Brno).

The above method was used to study the existence of zinc periodates in a pH range 2·5–9·5. A solution of 50 ml of 0·125M-$ZnSO_4$ and 0·05M-$NaIO_4$ was titrated with 1M-NaOH. The course of the titration is given in Fig. 1; the curve exhibits two well-defined plateaus at pH 2·6–3·1 and 6·1–7·15. The first plateau corresponds to the precipitation of a compound of the ratio Zn : I = 2 : 1 and the formula $4\,ZnO.I_2O_7.3\,H_2O$ (analysis 1 in Table I). The second plateau belongs to the precipitation of a species without periodate – probably $Zn(OH)_2$. Values corresponding to points on the titration curves were used for calculating the solubility product of the forming zinc periodate by the method employed previously in calculations of other metal periodates[18,27,31].

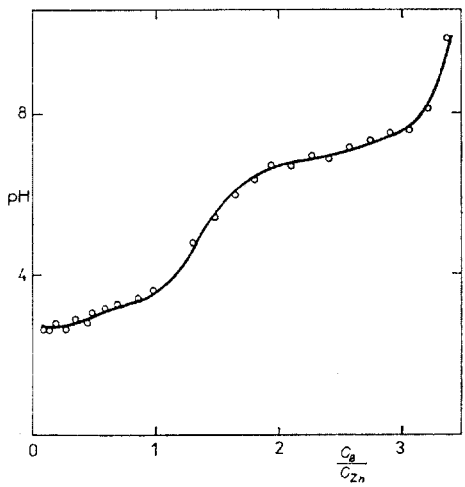

FIG. 1

Titration Curve of 50 ml of 0·125M-$ZnSO_4$ and 0·05M-$NaIO_4$ with 1M-NaOH

c_B, c_{Zn} overall concentrations of NaOH and $ZnSO_4$.

It is evident from the dissociation constants of periodic acid[18,20,21] that undissociated periodic acid and anions resulting from its dissociation to the first degree exist in the solution within pH 2·6–3·1. The formation of the compound may be expressed as

$$2\,Zn^{2+} + H_4IO_6^- + H_2O = Zn_2HIO_6.H_2O + 3\,H^+ . \qquad (1)$$

After rearrangement to

$$Zn^{2+} + 0{\cdot}5H_4IO_6^- + 1{\cdot}5\,OH^- = Zn(OH)_{1.5}(H_4IO_6)_{0.5}$$

the following value for the solubility product is obtained:

$$K_s = [Zn^{2+}].[OH^-]^{1.5}.[H_4IO_6^-]^{0.5} . \qquad (2)$$

Hydration equilibria of periodate anions do not affect the solubility product and need not therefore be considered. The overall concentration of periodate in the reaction system is given by the relation

$$c_{IO_4^-} = [H_4IO_6^-] + [H_5IO_6] + (c_{IO_4^-})_{ppt.} , \qquad (3)$$

where the first two terms on the right-hand side stand for the concentration of the respective particles in the solution and $(c_{IO_4^-})_{ppt.}$ is the concentration of periodate ions in the precipitate. Substituting for this term from equation (2) we obtain

$$(c_{IO_4^-})_{ppt.} = 1/3\,[OH^-] = 1/3(c_B + [H_5IO_6] + [H^+]) . \qquad (4)$$

TABLE I

Analyses of Initial Zinc Periodate $4\,ZnO.I_2O_7.3\,H_2O$

Sample	% I_2O_7	% ZnO	% H_2O	ZnO : I_2O_7 : H_2O
1	49·42	43·65	6·93	3·97 : 1·00 : 2·85
2	49·23	43·69	7·08	3·98 : 1·00 : 2·92
3	48·97	43·47	7·56	3·99 : 1·00 : 3·13
4	48·85	43·42	7·73	4·00 : 1·00 : 3·21
Calculated	49·07	43·66	7·27	4·00 : 1.00 : 3·00

Aside from the analytical concentration of sodium hydroxide (c_B) there are hydroxide ions formed by the dissociation of water present in the solution. Their concentration is equal to the sum of the concentration of hydrogen ions remaining in the solution $[H^+]$ and of the concentration of hydrogen ions consumed to suppress the dissociation of periodic acid, *i.e.* $[H_5IO_6]$. By combining equations (*3*) and (*4*) and expressing $[H_5IO_6]$ by the dissociation constant of H_5IO_6 to the 1st degree (K_1), the concentration of periodate ions in the solution may be expressed with the aid of values which are accessible to determination:

$$[H_4IO_6^-] = [c_{IO_4^-} - 1/3(c_B + [H^+])]/(1 + 4[H^+]/3K_1)\,. \qquad (5)$$

By an analogical process, the expression for the concentration of zinc ions in the solution may be obtained:

$$\begin{aligned} [Zn^{2+}] &= c_{Zn^{2+}} - (c_{Zn^{2+}})_{ppt.}\,, \\ (c_{Zn^{2+}})_{ppt.} &= 2[H_4IO_6^-]_{ppt.} = 2(c_{IO_4^-} - [H_4IO_6^-] - [H_5IO_6])\,, \\ [Zn^{2+}] &= c_{Zn^{2+}} - 2c_{IO_4^-} + 2[H_4IO_6^-]\,(1 + [H^+]/K_1)\,. \end{aligned}$$

The concentration of hydroxide ions in the solution $[OH^-]$ is calculated from the pH values obtained and from the ionic product of water. By measuring pH, however, the activities of hydrogen ions only are obtained. For this reason, the hydrogen ion concentrations $[H^+]$ were replaced with activities in the first calculations (Table II). To verify this approximation, the ion concentration values obtained by the first calculations were used for calculating the ionic strength of solution (I). Then the

TABLE II

Solubility Product of Zinc Periodate $4\,ZnO.I_2O_7.3\,H_2O$

pH	First calculation				Second calculation		
	K_s	pK_s[a]	I	γH^+	K_s	pK_s	I
2·65	$1·67 . 10^{-19}$	18·78	0·50	0·70	$9·34 . 10^{-20}$	19·03	0·50
2·69	$1·83 . 10^{-19}$	18·74	0·49	0·70	—	—	—
2·71	$1·79 . 10^{-19}$	18·75	0·48	0·70	—	—	—
2·80	$2·03 . 10^{-19}$	18·69	0·46	0·70	—	—	—
2·82	$1·59 . 10^{-19}$	18·80	0·43	0·71	—	—	—
2·98	$2·28 . 10^{-19}$	18·64	0·42	0·71	—	—	—
3·10	$2·21 . 10^{-19}$	18·66	0·40	0·71	$1·31 . 10^{-19}$	18·88	0·40

[a] Average 18·72.

activity coefficient γ_{H^+} for hydrogen ions and their concentrations was calculated using Davies' equation:

$$-\log \gamma_{H^+} = 0{\cdot}509[I^{1/2}(1 + I^{1/2})^{-1} - 0{\cdot}21] .$$

By inserting the values of $[H^+]$ so obtained into the above equations, the solubility product K_s was again calculated for the first and the last pH values employed for the first calculations. The values obtained by the first and second calculations were of the same order of magnitude; further calculations could, therefore, be omitted. The value of $K_1 = 6{\cdot}90 \,.\, 10^{-2}$, *i.e.* the most trustworthy literary value[31] was then used.

Efforts to prepare $Zn_5(IO_6)_2$. All efforts to prepare a zinc periodate with a ratio Zn : I above 2 : 1 from an aqueous solution failed. According to the literature[8-11], several efforts were made for preparing $Zn_5(IO_6)_2$ but only $4\,ZnO.I_2O_7.3\,H_2O$ (Table I, samples 2 and 3) were obtained. Even when precipitating potassium zincate with a solution of potassium periodate at pH 12, only a compound with the ratio Zn : I = 2 : 1 is formed (Table I, sample 4).

Measurement of solubility in the three-component system $4\,ZnO.I_2O_7.3\,H_2O$–H_5IO_6–H_2O. Samples for measuring the solubility were prepared in such a way that aqueous solutions of periodic acid of a concentration varying from a very diluted up to a saturated one were saturated with the other component (zinc periodate $4\,ZnO.I_2O_7.3\,H_2O$) up to a solid phase precipitation. The samples were then closed into plastic vials and shaken at 24°C until equilibrium was established (two weeks). The establishment of the equilibrium was controlled iodometrically by determining I_2O_7 in the liquid phase of each sample. Both phases were separated on fritted glass mounted in the cuvette of a centrifuge.

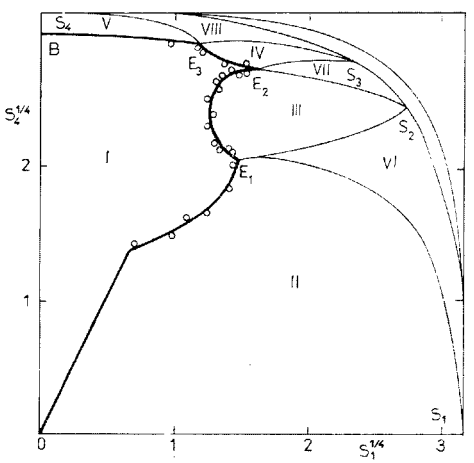

FIG. 2

Solubility in the Three-Component System $4\,ZnO.I_2O_7.3\,H_2O$–H_5IO_6–H_2O at 24°C

Concentrations S_1 and S_4 are expressed in per cent.

The results of the analyses are given in Fig. 2 and Table III. Since solubility diagrams giving concentrations of components on a linear scale are poorly illustrative (the solubility curve is close to one side of the diagram) the fourth roots of the component concentration values were plotted on the axes of a cartesian system[28].

There are four crystalline compounds in the system studied: $4\ ZnO.I_2O_7.3\ H_2O$ (S_1), $2\ ZnO.I_2O_7.7\ H_2O$ (S_2), $ZnO.I_2O_7.8\ H_2O$ (S_3) and H_5IO_6 (S_4). The plot consists of eight fields. I is a one-phase field and corresponds to unsaturated solutions. II, III, IV, and V are two-phase fields, and correspond to equilibria between crystalline phases S_1, S_2, S_3, and S_4, and their saturated solutions, respectively. Three-phase

TABLE III

Solubility in the Three-Component System $4\ ZnO.I_2O_7.3\ H_2O$–H_5IO_6–H_2O at 24°C

Sample	Liquid phase		Solid phase			Compound
	% ZnO	% I_2O_7	% ZnO	% I_2O_7	ZnO : I_2O_7	
1	0·13	3·54	43·54	48·87	4·00	
2	0·78	7·12	43·76	48·95	4·01	$4\ ZnO.I_2O_7.$
3	1·21	10·22	43·58	49·10	3·99	$.3\ H_2O$
4	1·42	10·22	43·69	49·12	4·00	
5	1·89	14·15	43·78	49·19	4·00	(S_1)
6	1·97	16·32	43·40	48·76	4·00	
7	1·83	17·14	24·81	55·54	2·00	
8	1·42	18·73	24·62	55·96	1·98	
9	1·26	20·13	25·12	55·73	2·03	
10	1·24	23·47	24·56	55·82	1·98	
11	1·32	25·29	24·87	55·41	2·02	
12	1·22	29·18	24·93	55·67	2·01	$2\ ZnO.I_2O_7.$
13	1·24	31·56	25·01	55·97	2·03	$.7\ H_2O$
14	1·29	35·14	24·96	55·92	2·01	
15	1·32	38·21	24·87	55·71	2·01	
16	1·12	41·42	25·23	55·42	2·05	(S_2)
17	1·67	43·56	24·81	55·67	2·00	
18	2·01	46·32	24·72	55·44	2·00	
19	2·90	48·28	24·55	55·81	1·98	
20	2·32	48·76	13·65	61·69	0·99	
21	1·51	50·53	13·60	61·82	0·99	$ZnO.I_2O_7.$
22	0·89	52·72	13·78	62·29	0·99	$.8\ H_2O$
23	0·54	57·58	14·03	62·02	1·02	(S_3)
24	0·82	58·34	0·73	80·14	0·04	H_5IO_6
25	0·00	60·82	0·00	80·23	0·00	(S_4)

fields VI, VII, and VIII stand for equilibria between crystalline phases S_1 and S_2 and the solution of a composition E_1, between crystalline phases S_2 and S_3 and solution E_2, and between crystalline phases S_3 and S_4 and solution E_3, respectively. Branch $O-E_1$ on the solubility curve corresponds to the formation of crystalline compound S_1, branch E_1-E_2 to the formation of crystalline compound S_2, branch E_2-E_3 to the formation of crystalline compound S_3, and branch E_3-B to the formation of compound S_4.

Thermal decomposition. Decompositions under raising temperature were made on a Derivatograph (Hungary) or on a statmograph constructed at our institute[32]. Stationary decompositions were made in an air thermostat.

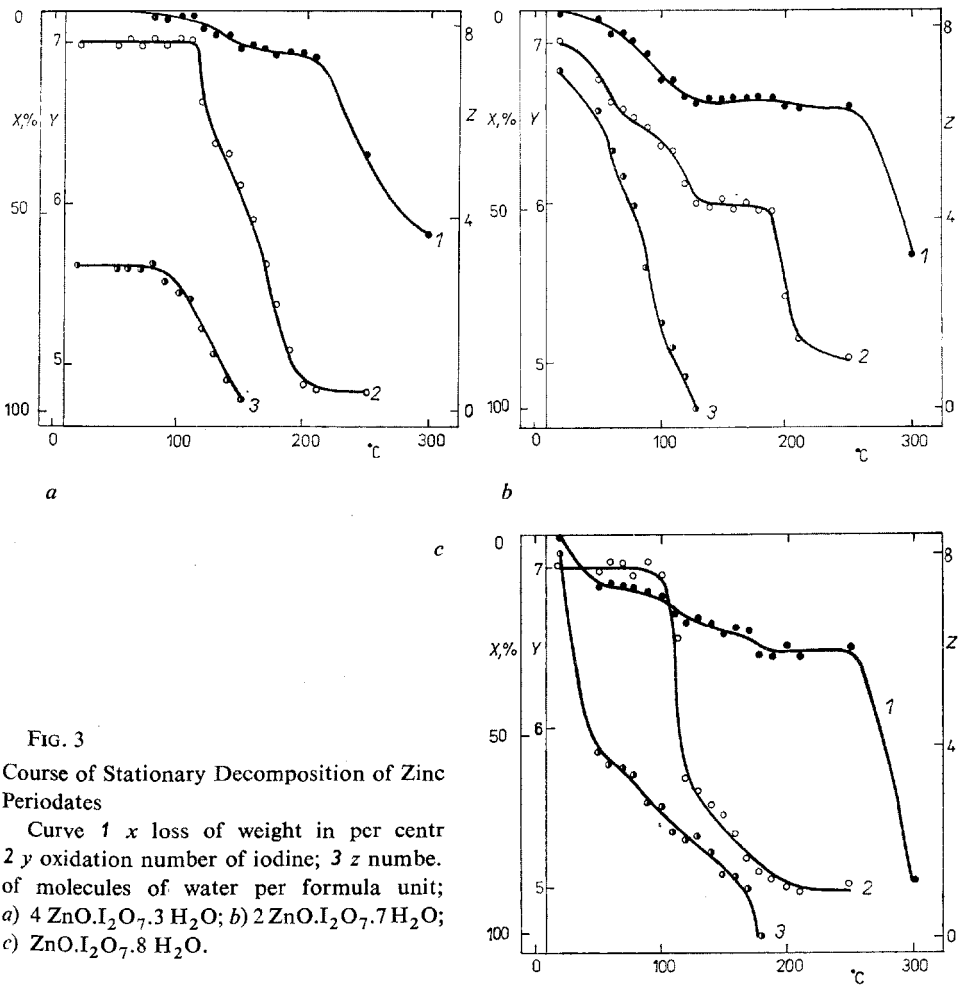

FIG. 3

Course of Stationary Decomposition of Zinc Periodates

Curve *1* *x* loss of weight in per centr *2* *y* oxidation number of iodine; *3* *z* numbe. of molecules of water per formula unit; *a*) $4\ ZnO.I_2O_7.3\ H_2O$; *b*) $2\ ZnO.I_2O_7.7\ H_2O$; *c*) $ZnO.I_2O_7.8\ H_2O$.

Thermal decomposition was studied in compounds denoted by S_1, S_2, and S_3 by the method of stationary decomposition up to 300°C and under raising temperature up to 600°C. The results of the stationary decompositions are given in Fig. 3, and important intermediary products of the decompositions are brought together in Table IV.

X-ray powder photographs were taken with a Mikrometa camera combined with chambers Chirana and Siemens (⌀ 57·3 mm). Radiation CuK_α (λ = 1·5418 Å) was passed through a nickel foil filter.

All the three zinc periodates (S_1, S_2, S_3), some of their thermal decomposition products listed in Table IV, and pentahydrogenperiodic acid (S_4) were analysed. Compounds denoted by S_1, S_2, and S_3 were found to be chemical individuals with characteristic crystal structures. The lower hydrate $ZnO.I_2O_7.4\ H_2O$ has a structure which is slightly different from the initial periodate whereas the product $4\ ZnO.I_2O_7.2{\cdot}5\ H_2O$ has lines coinciding with those of the higher hydrate $4\ ZnO.I_2O_7.3\ H_2O$, by partial decomposition of which it is formed. The product $ZnIO_4$ with the average oxidation number of iodine + VI has most of its lines coinciding with those of the iodate $Zn(IO_3)_2$ (ref.[33]). As for the decomposition products with the oxidation number of iodine + V, in the case of products of compounds S_1 and S_2 it is a mixture of $ZnO + Zn(IO_3)_2$, and in the case of compound S_3 it is a pure $Zn(IO_3)_2$ whose values of d are in agreement with literary data[33].

TABLE IV

Products of Thermal Decomposition of Zinc Periodates

Initial compound	Temperature of decomposition, °C	Product of thermal decomposition	Loss of weight	
			calc.	exptl.
$4\ ZnO.I_2O_7.3\ H_2O$ (S_1)	100	$4\ ZnO.I_2O_7.2{\cdot}5\ H_2O$	1·21	1·47
	210	$4\ ZnO.I_2O_5$	11·54	12·05
	350	ZnO	56·34	56·17
$2\ ZnO.I_2O_7.7\ H_2O$ (S_2)	170	$2\ ZnO.I_2O_6$	21·70	21·04
	250	$2\ ZnO.I_2O_5$	24·15	23·80
	350	ZnO	75·14	74·97
$ZnO.I_2O_7.8\ H_2O$ (S_3)	50	$ZnO.I_2O_7.4\ H_2O$	12·18	11·50
	200	$ZnO.I_2O_5$	29·78	28·36
	350	ZnO	86·24	86·14

Infra-red spectra were run on a double beam IR spectrophotometer UR 20 (Carl Zeiss, Jena) within 400–4000 cm^{-1}. The samples were suspended in Nujol in a potassium bromide cuvette. Spectra of all three zinc periodates S_1, S_2, S_3, their deuterated analogues, and two thermal decomposition products of the formula $ZnO.I_2O_7.4\ H_2O$ and $ZnIO_4$ were obtained. A survey of absorption bands assigned to them according to literary data[12,15,17] is brought together in Table V.

DISCUSSION

It was proved by measuring the solubility in three-component systems, by acidimetric titration, and by efforts to prepare $Zn_5(IO_6)_2$ that only three different zinc periodates may be obtained from aqueous solutions at room temperature, namely $4\ ZnO.I_2O_7.3\ H_2O$ (S_1), $2\ ZnO.I_2O_7.7\ H_2O$ (S_2) and $ZnO.I_2O_7.8\ H_2O$ (S_3). Compounds denoted by S_2 and S_3 are incongruently soluble. Compound S_1 is probably congruently soluble, and the value of its solubility product shows that it could be used for gravimetric determinations (when carefully dried below 50°C – Fig. 3*a*). By some authors, it was erroneously held for the compound $Zn_5(IO_6)_2$. None of the three salts described above is identical with any one of the zinc periodates quoted in the literature. Compounds S_1 and S_2 differ in hydration, compound S_3 also in the ratio Zn : I.

TABLE IV
(*Continued*)

Composition of thermal decomposition products							
% ZnO		% I		I oxidn. no.		% H_2O	
calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.
44·20	44·33	34·46	34·30	7·00	7·0	6·13	6·21
49·37	50·56	38·50	37·94	5·00	5·02	—	—
100·00	98·42	—	—	—	—	—	—
31·75	32·62	49·52	49·26	6·00	6·01	—	—
32·77	32·21	51·12	51·14	5·00	4·99	—	—
100·00	98·57	—	—	—	—	—	—
15·67	15·25	48·88	49·00	7·00	7·01	13·88	14·09
19·60	19·75	61·13	60·91	5·00	5·03	—	—
100·00	97·52	—	—	—	—	—	—

TABLE V

Survey of Assignment of Absorption Bands Encountered in Infra-Red Spectra of Iodates and Periodates

Frequency, cm^{-1}	Vibration type
400— 460	δ I—O—I bridge
400— 500	δ O—I—O
515— 645	ν I—O—I bridge
550— 800	ν I—O
790— 850	ν I—O (in IO_4^-)
750, 840—950	τ I—OH at short H-bonds
850— 970	δ I—O—D
1 070—1 300	δ I—O—H
1 200—1 240	δ D_2O
1 600—1 635	δ H_2O
1 600—1 750	ν O—D···O shorter D-bonds
1 950—2 110	
2 200—2 400	ν O—H···O shorter H-bonds
2 700—2 900	
2 250—2 480	O—D···O longer D-bonds
2 400—2 610	ν O—D
3 100—3 400	ν O—H···O longer H-bonds
3 300—3 585	ν O—H

Thermal decompositions of zinc periodates proceed roughly in three steps. Compounds denoted by S_1 and S_3 partly dehydrate in the first step under formation of lower hydrates, whereas S_2 liberates all water and part of the oxygen yielding a product of the overall composition $ZnIO_4$ with the average oxidation number of iodine + VI. In the second step, all the compounds liberate part of the oxygen and/or the rest of the water under formation of the anhydrous iodate $Zn(IO_3)_2$ or its mixture with zinc oxide. In the third step, all three species liberate iodine and further oxygen under formation of zinc oxide. The course of the thermal decompositions testifies that in no case, not even at an elevated temperature, a periodate of the composition $Zn_5(IO_6)_2$ is formed from any one of the compounds S_1, S_2, or S_3.

Compounds S_1, S_2, and S_3 equally as the lower hydrate $ZnO.I_2O_7.4\,H_2O$ were confirmed as chemical individuals by X-ray analysis. Compound S_1 having the same X-ray plot as has the product of partial dehydration containing 2·5 mol of water, it may be assumed that the hydrate with 2·5 mol of H_2O is a metastable species forming during the dehydration of S_1 preceding the breakdown of its crystal structure. According to its X-ray plot, the decomposition product of S_2 with the formula $ZnIO_4$ should contain the iodate $Zn(IO_3)_2$, and should therefore be its mixture

with periodate of the formula $Zn_3(IO_5)_2$. A periodate of this formula has however not been reported.

For interpreting IR spectra, the bands characteristic of the presence of crystal water, hydrogen bonds, I—OH groups and/or I—O—I bond are important. Bands assigned to valency vibrations I—O are presented in all periodates but their position depends on the number of oxygen atoms bonded to iodine atoms[12] which may also be a guideline for establishing the structure of the compounds studied.

The spectrum of compound S_1 ($4\ ZnO.I_2O_7.3\ H_2O$) is characterized by only a slight hint of absorption at 1630 cm^{-1} corresponding to the presence of crystal water; a little more distinct bands at 1070, 1170 and 1310 cm^{-1} were assigned to deformation vibrations of groups I—O—H, and well-defined wide bands at 2400, 2700 and 3200 cm^{-1} correspond to hydrogen bonds. The spectrum of the deuterated species exhibits a diminuition in the intensity of the above bands, and at the same time, a shift to lower frequency values occurs. This suggests that the deuteration was not complete but the shifts are all the same sufficiently clear to permit a conclusive assignment to be made. The frequency 730 cm^{-1} of the most intensive band of the valency vibration I—O is sufficiently low to correspond to coordination of 6 atoms of oxygen around one atom of iodine. As for the absorption bands below 600 cm^{-1}, no definite decision could be made as to whether they belong to the deformation vibrations O—I—O or to the I—O—I bond linking the iodine atoms in a potential polyanion. The presence of the groups I—O—H, however, is evidently in favour of the formulation $Zn_2HIO_6.H_2O$ and not $Zn_4I_2O_{11}.3\ H_2O$.

The spectrum of compound S_2 ($2\ ZnO.I_2O_7.7\ H_2O$) is characterised by well-defined absorption bands at 1610 and 3555 cm^{-1} corresponding to the presence of crystal water; in deuterated compounds, the bands are shifted to 1200 and 2630 cm^{-1}, respectively. The spectrum further contains a distinct band at 2405 cm^{-1}, a wide shoulder at 2730 cm^{-1}, and a wide well-defined band at 3180 cm^{-1} corresponding to hydrogen bonds; in deuterated compounds they are shifted to 1790, 2200, and 2400 cm^{-1}, respectively. The band belonging to the δI—O—H vibrations at 1220 cm^{-1} (in deuterated compounds at 900 cm^{-1}) is also clearly defined. The shoulder at 840 cm^{-1} was assigned to torsion vibrations I—O—H as it disappears on deuteration probably because it is covered with a strong band of the valency vibration I—O. The frequency of the distinct split band of the valency vibration I—O at 705–760 cm^{-1} is sufficiently low to be able to correspond to coordination of 6 atoms of oxygen around one atom of iodine[12]. The splitting of the band may be caused by a decrease in symmetry due to the presence of several groups I—O—H besides groups I—O, or else it may have been caused by the dimerization of the anion. The band of a medium width at 625 cm^{-1} was assigned to the valency vibrations I—O(H) since its position changes only slightly by deuteration. A very intensive band at 565 cm^{-1} might perhaps be assigned to vibrations of the bond I—O—I because, from analogy with other metal periodates[12] with an equal ratio metal to iodine, the presence of a di-

anion may be expected. The analysis of the spectra shows that the compound contains crystal water, groups I—O—H and bridges I—O—I. The requirements are best met by the formula $Zn_2H_2I_2O_{10}.6\,H_2O$ with the anion $H_2I_2O_{10}^{4-}$ which is also encountered in periodates of other metals[12,15].

The spectrum of compound S_3 ($ZnO.I_2O_7.8H_2O$) has well-defined bands at 3500 and 1640 cm^{-1} which, especially the later corresponding to deformation vibrations of water, suggest that OH groups are not present as IOH but in the form of crystal water molecules. This conclusion is further supported by the absence of more distinct bands belonging to vibrations of IOH groups. In deuterated samples, marked isotopic shifts of these bands to values 2640 and 1210 cm^{-1} were observed. The intensive sharp band at 850 cm^{-1} characterises the valence vibrations I—O in the tetrahedral anion IO_4^- (ref.[12]). For this reason, the composition of compound S_3 may best be expressed by the formula $Zn(IO_4)_2.8\,H_2O$. It is one of the few hydrated periodates with a tetrahedral anion[12] IO_4^-. This compound is stable only in a strongly acid medium and when being isolated it can easily hydrolyse on the crystal surface, and the anion IO_4^- may be converted into another periodate anion. This may also explain the slight hint of bands at 1220 and 1065 cm^{-1} caused by the deformation vibrations I—O—H and also of the poorly distinct bands at 735 cm^{-1} caused by the valency vibrations I—O in a periodate with a number of oxygen atoms above four.

The periodate $Zn(IO_4)_2.8\,H_2O$ is at 50°C partly dehydrated to $ZnO.I_2O_7.4\,H_2O$. In the spectrum of this compound, there is no longer the sharp band at 850 cm^{-1} which is characteristic of the anion IO_4^-. There are well-defined bands here at 1630 and 3400 cm^{-1} pointing to the presence of crystal water; consequently, the formula $Zn(H_4IO_6)_2$ does not hold. Several distinct bands in the region 1100–1300 cm^{-1}, however, point to the presence of groups I—O—H. Considering these facts, the composition of the compound may be expressed as $Zn(H_2IO_5)_2.2\,H_2O$ with a single anion or by one of the formulas $ZnH_2I_2O_9.3\,H_2O$, $ZnH_4I_2O_{10}.2\,H_2O$, $ZnH_2I_2O_{11}.$ $.H_2O$ with dianions. None of these has, however, been found in periodates studied either by X-ray or by molecular spectroscopy, and it is consequently difficult to interpret the data obtained on the basis of analogical compounds. The intensive band at 790 cm^{-1} corresponding to the valency vibrations I—O, would, by its high frequency, correspond to coordination number 5, *i.e.* to a monomeric anion or a dianion with one oxygen bridge. The proof of the presence of the bridge I—O—I is not unequivocal, the frequency 660 cm^{-1} being rather high to permit assignment of the respective intensive bands to the vibration of the I—O—I bond and at lower frequencies there are no more distinct bands in the spectrum.

The product of thermal decomposition of compound S_2 with the formula $ZnIO_4$ has in its spectrum no distinct sharp band corresponding to the tetrahedral anion IO_4^{2-}. In the region of the valency vibrations I—O (650–850 cm^{-1}), an intensive split band appears which points to the presence of various anions *e.g.* IO_3^-, IO_5^{3-}, *etc.* Intensive bands below 650 cm^{-1} suggest the presence of bonds I—O—I connecting

various oxo-anions of iodine. In agreement with analysis, the spectrum does not testify to the presence of crystal water or groups I—O—H. The product of the composition $ZnIO_4$ has probably polymerised oxoanions of a different type linked by oxygen bonds in such a way that the average oxidation number of iodine + VI is obtained. The IR spectrum of this product, similarly as its X-ray plot, does not clearly solve the problem of its chemical individuality.

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