RUSSIAN
CHEMICAL
REVIEWS
Uspekhi Khimii

April 1968

U. D. C. 546.151

New Information about Oxygen-containing Compounds of Iodine

M.Dratovský and L.Pačesová

1. INTRODUCTION

The systematic investigation of the oxygen-containing compounds of iodine has been carried out over the last 150 years but their study is far from complete. These compounds differ considerably from the compounds of the other halogens in their composition, nature of the bonding, stability, and other properties. Compared with chlorine and bromine, iodine forms a greater number of compounds, corresponding to the increased stability of the halogen–oxygen bond.

The following stable compounds are known in the solid state: I_2O_4, I_4O_9, I_2O_5, HIO_3, HI_3O_8, IO_3, HIO_4, $H_7I_3O_{14}$, H_5IO_6, and the salts of the acids mentioned. Furthermore, certain polyiodates are also known which have a composition other than that corresponding to tri-iodic acid HI_3O_8. As well as the oxide of composition IO_3 there are also salts which contain iodine(VI) corresponding in composition to the hypothetical acid H_2IO_4 or $H_2I_2O_7$. There have been descriptions of a series of salts which are derivatives of diperiodic acid $H_4I_2O_9$, the existence of which in the free state is disputed, and also salts of the hypothetical meso-periodic acid H_3IO_5.

Information about the oxygen-containing compounds of iodine(V) and also about lower oxides of iodine is given in a series of well-known reviews and monographs on inorganic chemistry. Compounds of iodine(VI) and iodine(VII) have been less studied. Whilst orthoperiodic H_5IO_6 and meta-periodic HIO_4 acids and periodates of various compositions (derivatives of the acids H_5IO_6, H_3IO_5, HIO_4, and $H_4I_1O_9$) have long been known, the existence of triperiodic acid $H_7I_3O_{14}$, one of the products of the thermal decomposition of orthoperiodic acid, has only been shown recently. The oxide of composition IO_3 was recently isolated as a product of the thermal decomposition of periodic acid in a vacuum. Interesting results were also obtained in studying the thermal decomposition of periodates. These investigations led to the discovery of salts of the triperiodic acid mentioned above and of certain iodine(VI) compounds. The latter compounds, which contain iodine in an uncommon valence state also have the character of salts. Compounds of this type are completely unknown for the lighter homologues of iodine.

Recent investigations of the thermal decomposition of periodic acid and periodates have revealed extremely important information about the chemistry of iodine compounds. A considerable part of this review is devoted to this question.

2. LOWER OXIDES OF IODINE

The oxide of the empirical composition I_2O_4 is formed as a yellow powder on heating iodic acid with concentrated sulphuric acid and decomposing the sulphate first formed $(IO)_2SO_4$ with water[1-3]. This oxide is sparingly soluble in water and in organic solvents. At elevated temperatures with water it disproportionates to iodic acid and iodine. At higher temperatures I_2O_4 decomposes with the formation of iodine pentoxide and elemental iodine[4].

The oxide I_2O_4 is often considered as a compound of iodine of mixed valency (ter- and quinque-valent iodine). It is diamagnetic[5] and therefore it cannot be represented as the monomer IO_2. It must be considered as the dimer I_2O_4, or even as a polymer $(IO_2)_x$. Analysis of the infrared spectra indicate that the structure of this oxide in the solid state is a chain of

–O–I–O–I–O–

groups, with which a lattice of IO_3^- anions is bonded. Ideas[8] about the existence in the crystal lattice of simple iodyl cations and discrete molecules $(IO)^+(IO_3)^-$ seem incorrect.

The iodyl group is present in certain other iodine compounds, particularly salts (especially sulphates, selenates, and nitrates)[9,10].

An oxide of composition I_4O_9 is formed by the action of ozone on iodine (in the gas phase at 50°C or in solution in chloroform or carbon tetrachloride) as a yellow product[3,11-13]. By analogy with other iodine(III) salts this oxide is usually considered[14] as iodine iodate $I(IO_3)_3$.

3. IODINE(V) COMPOUNDS

Iodic acid HIO_3 is the most stable oxygen-containing acid of iodine. Together with iodates and iodine pentoxide it was known as early as the first half of the preceding century (Davy, 1815). Ever since, iodine(V) compounds have formed the subject of investigations by many authors.

The basis of the synthesis of iodic acid is oxidation of iodine by various reagents (for example, nitric acid, chlorine, by electrolysis, etc.) or by displacement of iodic acid from its salts by other acids. Iodates are obtained by neutralisation or even the oxidation of iodine in alkaline medium. Iodine pentoxide I_2O_5 can be made by the direct reaction of the constituent elements at elevated temperature or by dehydration of iodic acid (see below).

As well as simple iodates other derivatives of iodic acid, namely, a series of double salts and also salts with a complex cation, are known. For complexes in which iodate anions act as ligands, the preparation and properties of the acids $H_2[Sn(IO_3)_6]$, $H_2[Sn(OH)_2(IO_3)_4]$, and $H_2[Sn(OH)_4(IO_3)_2]$ and their salts have been investigated[15]. These compounds were obtained by the reaction, and subsequent crystallisation, of tin(IV) chloride (or potassium hexachlorostannate) with iodic acid (or with alkali metal iodates) in acid medium. Compounds of titanium(IV)[16], lead(IV)[17], manganese(IV)[18], and uranium(IV)[19] were isolated in a similar manner and investigated. Compounds of niobium and tantalum, have been described in which the iodine coordination number is 6. These can be represented by the formulae[20]: $Nb_2O_5 \cdot 2HIO_3 \cdot 2H_2O$ and $Ta_2O_5 \cdot HIO_3 \cdot 6H_2O$.

Of the compounds which contain a cationic complex, there have been studies of certain iodate salts of hexamminecobalt(II), for example, $[Co(NH_3)_6](IO_3)_2 \cdot 3H_2O$ [21], and of hexamminecobalt(III), for example, $[Co(NH_3)_6](IO_3)_3 \cdot 3HIO_3$, also the iodates of hexammineplatinum(IV), of tetrammineplatinum(II), and tetramminepalladium(II).[22,23] The existence of certain simple iodate salts, their hydrates,, and in particular of a series of double compounds was established in a solubility study of multicomponent systems at various temperatures (Table 1).

Iodic acid is known in two modifications: α and β. Both are orthorhombic and differ only in the ratio of the crystallographic axes. Several early papers dealt with the structure of this compound[50-52]. Later only the α modification interested most authors[53-58]. The structure investigated consists of aggregates of molecules mutually connected by hydrogen bridges, which contain IO_3 groups in the form of deformed octahedra. There are 4 HIO_3 molecules in the unit cell. The presence of O–H–O bonds was confirmed also by the neutron diffraction method[59].

Several papers[51-53,60-66] are devoted to the study of the structure of iodates, particularly the alkali metal salts. These are usually compounds for which a perovskite lattice is characteristic, where the iodine has a coordination number of six. The perovskite-type compounds include potassium, rubidium, caesium, and ammonium iodates. It was found that as the atomic number of the cation is increased the edge of the lattice lengthens. The existence of a perovskite-type crystal lattice for these compounds was also established by the NMR method[67]. The structure of sodium iodate remained unexplained. Some authors assume that it has an antiperovskite-type structure[53,61,65]. For several other iodates, particularly those of silver, copper, calcium, barium, radium, and aluminium, the literature mentions only the system in which they are crystallised[51,52,60,68-72]. The structure of cerium(IV) iodate has been studied in greater detail[73,74]. Table 2 lists iodine(V) compounds, the structure of which has been investigated by X-ray diffraction.

Table 1. Equilibrium systems of compounds of iodine(V).

Equilibrium system	Compounds formed in the system	Reference
1	2	3
$HIO_3 - NH_3 - H_2O$	$NH_4H(IO_3)_2$; $NH_4H_2(IO_3)_3$	24
$HIO_3 - HNO_3 - H_2O$	$HIO_3 \cdot 2HNO_3$	25
$I_2O_5 - HF - H_2O$	$2HIO_3 \cdot 3HF$	26
$I_2O_5 - NaF - H_2O$		27
$I_2O_5 - KF - H_2O$	$KH(IO_3)_2 \cdot H_2O$; $KH(IO_3)_2 \cdot KF \cdot 4H_2O$	27
$NaIO_3 - HIO_3 - H_2O$	$NaIO_3 \cdot 2HIO_3$	28
$NaIO_3 - I_2O_5 - H_2O$	$Na_2O \cdot 2I_2O_5$; $NaIO_3 \cdot 1,5H_2O$	28
$NaIO_3 - NaI - H_2O$	$NaIO_3 \cdot 5H_2O$; $NaIO_3H_2O$	29
	$2NaIO_3 \cdot 3NaI \cdot 20H_2O$ (15; $10H_2O$)	30
	$3NaIO_3 \cdot 4NaI \cdot 23H_2O$	31
$NaIO_3 - NaCl - H_2O$	$2NaIO_3 \cdot 3NaCl \cdot 20H_2O$ (15; $10H_2O$)	30
$NaIO_3 - NaBr - H_2O$	$2NaIO_3 \cdot 3NaBr \cdot 15H_2O$ ($10H_2O$)	30, 42
$NaIO_3 - KIO_3 - H_2O$		32
$NaIO_3 - NaNO_3 - H_2O$	$2NaIO_3 \cdot 3NaNO_3 \cdot 15H_2O$; $NaIO_3 \cdot H_2O$	34, 35
$NaIO_3 - NaClO_3 - H_2O$		36
$NaIO_3 - Na_2SO_4 - H_2O$	$NaIO_3 \cdot 3Na_2SO_4$; $NaIO_3 \cdot 4Na_2SO_4$	37
$NaIO_3 - Na_2CO_3 - H_2O$		38
$NaIO_3 - Na_2C_2O_4 - H_2O$		39
$NaIO_3 - Na_2MoO_4 - H_2O$		40
$KIO_3 - HIO_3 - H_2O$	$KIO_3 \cdot HIO_3$; $KIO_3 \cdot 2HIO_3$	28, 41
$KIO_3 - KCl - H_2O$		32
$KIO_3 - KBr - H_2O$		42
$KIO_3 - KI - H_2O$		31, 43
$KIO_3 - KNO_3 - H_2O$		44
$KIO_3 - KClO_3 - H_2O$		36
$KIO_3 - K_2SO_4 - H_2O$		32
$KIO_3 - K_2MoO_4 - H_2O$		45
$NH_4IO_3 - HIO_3 - H_2O$	$NH_4IO_3 \cdot 2HIO_3$; $NH_4IO_3 \cdot HIO_3$	28, 46
$AgIO_3 - M^IIO_3 - H_2O$ (M^I = Li, Na, K, NH_4)	$KIO_3 \cdot 2HIO_3$	47
$AgIO_3 - I_2O_5 - H_2O$	$AgIO_3 \cdot I_2O_5$	47
$Mg(IO_3)_2 - NaIO_3 - H_2O$	$Mg(IO_3)_2 \cdot 10H_2O(4H_2O)$; $NaIO_3 \cdot 5H_2O(H_2O)$	32
$Mg(IO_3)_2 - Mg(NO_3)_2 - H_2O$	$Mg(IO_3)_2 \cdot 10H_2O$	48
$Ca(IO_3)_2 - NaIO_3 - H_2O$	$Ca(IO_3)_2 \cdot H_2O$	44
$Ba(IO_3)_2 - BaCl_2 - H_2O$	$Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$	49

The structure of iodic acid and of its salts has been studied by various physical methods (mainly spectroscopic and magnetic) both in the solid state and in solution. The nature of the Raman and infrared spectra agrees with the idea that in the solid state and in highly concentrated solutions there is polymerisation of the HIO_3 molecules[75-90]. The presence of $(HIO_3)_3$ trimers is usually assumed but the possible existence of polymers of the type $H_2I_4O_{11}$ etc. has also been discussed[91]. The degree of polymerisation usually drops with decrease in the concentration of the acid in the solution. In dilute solutions there are simple IO_3^- anions. Fonteyne[92] suggests that molecules of the pseudo-acid $HO-IO_2$ are also present. Study of the spectra of

iodates[81,83,93-107] suggests a symmetrical pyramidal structure for the IO_3^- anions. The molecule of iodine pentoxide I_2O_5 is also constructed symmetrically: two IO_2 groups are connected by an oxygen atom[108]. Magnetic susceptibility measurements also support these ideas on the structure of iodic acid molecule and anion[109-119]. The investigation of other properties of iodic acid and the determination of certain physical constants has mainly given way to a tendency to prove the presence of polymerisation of the molecules in concentrated solutions[120-137].

By thermal decomposition of certain hydrated iodates a series of hydrates with less water, and anhydrous salts, were isolated, and the limits of their stability established[105,106,138-150]. Dehydration of iodic acid at elevated temperature[151,152], forms tri-iodic acid HI_3O_8:

$$3HIO_3 \rightarrow HI_3O_8 + H_2O.$$

Table 2. Results of the X-ray studies of the structure of iodine(V) compounds.

Composition of compound	Crystallographic system	Lattice parameters, Å	No. of molecules in unit cell	Interatomic distances	References
1	2	3	4	5	6
HIO_3	o-rh.	$a = 5.520$ $b = 5.855$ $c = 7.715$	4	I — O: 1,80—2,90 O—O: 2,78 H—O—H: 2,68	50, 53, 54, 55 57, 58, 59
$3I_2O_5 \cdot H_2O$	mon.	$a:b:c =$ $0,901:1:$ $:0.891$ $\beta = 112°53'$			154
$LiIO_3$	hex.	$a = 5.469$ $c = 5.155$ (4,05)	2	Li—O=I—O=2,33	61
$NaIO_3$	o-rh.	$a = 5.75$ $b = 6.37$ $c = 8.10$	4	I—O = 1,80; 2,84 (2,05; 2,08; 3,18)	53, 65, 66
KIO_3			4		60, 63, 64, 67, 69
$KH(IO_3)_2$	mon.				51, 52
$KH_2(IO_3)_3$	tric.				51, 52
$CsIO_3$					53, 67
NH_4IO_4	cub. or o-rh.?	$a = 6.41$ $b = 6.38$ $c = 9.25$			62, 65
$AgIO_3$	o-rh.				60
$Cu(IO_3)_2$	mon.				68
$Cu(IO_3)_2 \cdot H_2O$	tric.				68
$Mg(IO_3)_2 \cdot 4H_2O$	mon.				68
$Ca(IO_3)_2$	mon.	$a = 7.18$ $b = 11.38$ $c = 7.32$ $\beta = ?$			69
$Ca(IO_3)_2 \cdot 6H_2O$	o-rh.				51, 52
$Ba(IO_3)_2$	mon.				70
$Sr(IO_3)_2$	tric.				70
$Al(IO_3)_2 \cdot NO_3 \cdot 6H_2O$	trig.				72
$Ce(IO_3)_4 \cdot H_2O$	mon.	$a = 9.57$ $b = 14.92$ $c = 8.00$ $\beta = 97°35'$	4		73, 74

This acid can also be obtained by recrystallisation of iodic acid from concentrated nitric acid. Some authors ascribe the formula $3I_2O_5 \cdot H_2O$ to this compound[153-156]. Oxygen bridges were indicated in the HI_3O_8 molecule by infrared spectra[91,157]. The existence of other transitional hydrates, as, for example, $2I_2O_5 \cdot H_2O$, was not confirmed. According to some results the dehydration of iodic acid takes place directly with the formation of iodine pentoxide[158,159]. Some differences have been observed[160] in the dehydration of the α and β modifications of HIO_3.

By heating an equimolar mixture of potassium (or rubidium) iodate and iodine pentoxide in a sealed ampoule at 170°C, and also by the dehydration of salts of the type $M^IH_2(IO_3)_3$, the salts of tri-iodic acid KI_3O_8 and RbI_3O_8 can be obtained[161]. However, the formation of potassium triiodate in the thermal decomposition of $KH(IO_3)_2$ was not observed[152]—here only a mixture of the iodate and iodine pentoxide is formed.

The structure of the acid iodates and the question of the polymerisation of iodic acid and iodates are still unsolved problems. The acid iodates $M^IH(IO_3)_2$ and $M^IH_2(IO_3)_3$ can be obtained by crystallisation from aqueous solution of an equimolar mixture of iodate and iodic acid. According to early ideas they can be considered[162-165] as double compounds of general formula $M^IIO_3 \cdot HIO_3$ or $M^IIO_3 \cdot 2HIO_3$. The existence of such compounds is confirmed by equilibrium diagrams of multicomponent systems (see Table 1). Starting from the behaviour of iodic acid in solution, its dimer

Table 3. Spectroscopic investigations of iodine(V) compounds.

Compound	Spectroscopic method	Reference	Compound	Spectroscopic method	Reference
I_2O_5	IR	108, 157	$Sr(IO_3)_2 \cdot H_2O$	IR	105, 106
HIO_3	IR	86, 104, 157	$Sr(IO_3)_2$	RS	100
	RS	75—88, 92, 95	$Ba(IO_3)_2 \cdot H_2O$		105, 106
HI_3O_8	RS	91	$Zn(IO_3)_2$		105, 106
$LiIO_3$	IR	105	$Cd(IO_3)_2$		105, 106
	RS	77, 81	$Ni(IO_3)_2$		104, 105, 106
$NaIO_3 \cdot H_2O$	IR	105, 157	$Co(IO_3)_2$	IR	104, 105, 106
	RS	98	$Pb(IO_3)_2$		104, 105, 106
KIO_3	IR	7, 105, 157	$Mn(IO_3)_2$		104
	RS	83, 84, 95	$Fe(IO_3)_3$		104
	X-ray abs. spectra	99	$Th(IO_3)_4$		104
$KIO_3 \cdot HIO_3$	RS	77	$Hg_2(IO_3)_2$		104
	IR	104	$Hg(IO_3)_2$		104
M^IIO_3 (M^I = alkaline metal)	IR	97, 104, 106	$K_2Mn(IO_3)_2$	IR	7, 104
	RS	77, 94, 96, 103, 107	$K_2Pb(IO_3)_6$		104
	UV	101, 102, 137	$K_2Ti(IO_3)_6$		104
$AgIO_3$	IR	104, 105, 106			
$Mg(IO_3)_2 \cdot 4H_2O$	IR	105, 106			
$Ca(IO_3)_2 \cdot 6H_2O$	IR	105, 106			

* IR = infrared absorption spectra; RS = Raman spectra; UV = ultraviolet spectra.

is often considered a dibasic acid and the presence of the anion $I_2O_6^{2-}$ in solution has been suggested[77,92,122,135,166]. In other studies the existence of such an anion has been denied[167,168]. Polyiodates of the type $K_2H_2I_6O_{17}$ and $K_2I_4O_{11} \cdot 2H_2O$ have also been obtained by the thermal decomposition of certain hydrogen iodates. Infrared spectroscopy showed[157] the presence of I—O—I bridges in these polyiodates. Table 3 lists the compounds of iodine(V) the structure of which has been studied by spectroscopic methods.

Iodine dioxide fluoride IO_2F is also an iodine(V) compound. It can be obtained[169] by the action of iodine pentoxide on iodine(V) fluoride or the action of fluorine on iodine pentoxide in anhydrous [hydrogen] fluoride[170]. IO_2F tends to form complexes, for example, the complex arsenate $IO_2[AsF_6]$.

4. THE OXIDE I_2O_7

The existence of the oxide I_2O_7 in the free state cannot be considered as definitely proved. In many attempts to make this substance compounds of another composition were obtained. The following were erroneously taken for the oxide I_2O_7: the product of the reaction of iodine with

oxygen or ozone under the action of a silent discharge[171], the product of the reaction of iodine with chlorine(VII) oxide[172,173], or even the product of the reaction of iodine with iodic acid[174]. Neither could periodic anhydride be obtained by the thermal decomposition of the iodic acid at various temperatures in air or in a vacuum[175]. As a result of the dehydration of orthoperiodic acid by gaseous fluorine[176] only the metaperiodic acid HIO_4, and not periodic anhydride, is formed. Even the metaperiodic acid could not be dehydrated completely by fluorine in anhydrous hydrogen fluoride. As a result of this reaction the iodine(VII) oxide fluoride IO_3F is formed[172]. The most successful was apparently an attempt[177] to dehydrate periodic acid in 65% oleum. The composition of the strongly reactive orange compound obtained differs little from the ultimate analysis of the oxide I_2O_7.

5. PERIODIC ACID

Four solid hydrates of iodine(VII) oxide are known: $I_2O_7.5H_2O$ (H_5IO_6, orthoperiodic acid), $3I_2O_7.7H_2O$ ($H_7I_2O_{14}$, triperiodic acid), $I_2O_7.2H_2O$ ($H_4I_2O_9$, diperiodic acid) and $I_2O_7.H_2O$ (HIO_4 metaperiodic acid).

a. Orthoperiodic acid H_5IO_6 has been known for about 130 years and methods for its preparation and principal chemical properties have been given in well-known monographs. This acid can be prepared by electrolysis[178] or by its displacement from periodates by the action of strong acids (particularly by use of nitric[179] and perchloric[180] acids). Orthoperiodic acid forms the starting point for making all the hydrates of the oxide I_2O_7 poorer in water. As a rule this is done by thermal decomposition of orthoperiodic acid at ordinary pressure or in a vacuum.

Periodic acid can be represented as the ortho-acid H_5IO_6 or as the dihydrate of the meta-acid $HIO_4.2H_2O$. The second formula was proposed on the basis of magnetic measurements[181] according to which the experimental magnetic susceptibility of periodic acid ($\chi = -71.4 \times 10^{-6}$) is close to the value calculated for the dihydrate $HIO_4.2H_2O$ ($\chi = -77.7 \times 10^{-6}$) and slightly different from the value calculated for orthoperiodic acid ($\chi = -55.7 \times 10^{-6}$). Other authors who studied the dehydration of periodic acid in anhydrous pyridine[182] also consider periodic acid to be the dihydrate of the meta-acid. However, the structural measurements show that it is more correct to consider the pentahydrate of the oxide I_2O_7 to be the ortho-acid. The Raman spectrum of periodic acid in the solid state shows the octahedral symmetry of the IO_6 group. In the spectrum of the aqueous solution of periodic acid four lines agree with the frequencies of the metaperiodate anion IO_4^- and three lines correspond with the undissociated H_5IO_6 molecules. It is therefore assumed[183] that in solution the ortho-acid undergoes dehydration:

$$H_5IO_6 \rightleftarrows H^+ + IO_4^- + 2H_2O.$$

In the absorption spectra of periodic acid in the infrared region distinct bands can also be distinguished at 2900 and 2200 cm^{-1}, due to the OH group, and in the 1100–1300 cm^{-1} range there are bands due to the I–OH groups, whereas the bands at 3400 cm^{-1}, typical for water molecules, are absent.

The octahedral structure of the anion IO_6^{5-} also follows from the structure found for orthoperiodic acid[185,186]. This compound is monoclinic with somewhat deformed octahedra of oxygen atoms about the central iodine atoms. Since conclusions based on the direct determination of structure by spectroscopic and X-ray diffraction methods ought to be considered more reliable than those which follow from magnetic measurements and dehydration experiments, it can be assumed that the correct formula for the pentahydrate of I_2O_7 is H_5IO_6, that is, this compound is the ortho-acid.

By heating the orthoperiodic acid in the atmosphere it loses water and is converted into triperiodic and then metaperiodic acid. Above 170°C it undergoes more extensive decomposition into iodine(VII) oxide[187]. The thermal decomposition of this acid in a vacuum is somewhat more complex (see below).

b. Triperiodic acid $H_7I_3O_{14}$ is formed[187] as a primary dehydration product as a result of the thermal decomposition of orthoperiodic acid in the temperature range 121-130°C. This compound was discovered in an attempt to reproduce the diperiodic acid preparation according to Partington and Bahl[188]. The existence of triperiodic acid was proved by thermogravimetric, tensimetric, and X-ray diffraction methods[187]. The decrease in the weight of the specimen observable in the thermogravimetric study of the dehydration of some preparations of orthoperiodic acid (prepared by three different methods) is always less than would correspond with the formation of diperiodic acid. Instead of the expected 1.5 moles water which correspond with the formation of diperiodic acid, the observed loss in weight during the dehydration amounts to 1.33 moles water per 1 mole of the initial acid. Therefore the dehydration can be represented by the equation:

$$3H_5IO_6 = H_7I_3O_{14} + 4H_2O.$$

The formation of triperiodic acid was also confirmed by dehydration in a vacuum on a quartz spiral thermobalance at 60°C. The tensimetric measurements made by Hauptman[187] refute the incorrect conclusions of Partington and Bahl[188] concerning the existence of diperiodic acid $H_4I_2O_9$. The measurements of the latter authors were insufficiently detailed, since they did not record experimental points in the range important for deciding to which composition the break on the tensimetric curve relates ($H_4I_2O_9$ or $H_7I_3O_{14}$).

c. Diperiodic acid $H_4I_2O_9$. The existence of diperiodic acid in the solid state has been noted in only two studies. The first of these is the work of Partington and Bahl already mentioned[188], in which tensimetric measurements were made. As we have already noted, the results obtained by these authors were later refuted by Hauptman[187].

Ripanova and Duca[189] described the isolation of diperiodic acid from aqueous solution. The acid was displaced from barium diperiodate by the action of sulphuric acid of from the silver salt by the action of hydrogen chloride. The acid was separated by crystallisation from the solution obtained. The authors also propose the formation of diperiodic acid in solution, in which orthoperiodic and metaperiodic acids are present in 1 : 1 ratio. From conductometric measurements the authors assume that this acid should be formed on the introduction of carbon dioxide into a solution of orthoperiodic acid. Diperiodic acid should be precipitated, since its solubility is only about one-sixtieth of that of the ortho-acid. However, Hauptman[187] did not succeed in reproducing these extremely unreliable results.

d. Metaperiodic acid HIO_4 was first obtained[190] by dehydrating orthoperiodic acid at reduced pressure at 100°C. Later the formation of this acid was also confirmed by other authors, who investigated the thermal decomposition of the ortho-acid in the air[188,191] in the tem-

perature range 140–170°C and in vacuum[192] at 80°C. Furthermore, it was shown that the sublimate formed as a result of the dehydration of the ortho-acid at reduced pressure is metaperiodic acid. Proof was obtained by the ultimate analysis and by comparison of the X-ray powder patterns of the sublimate and metaperiodic acid[191,193].

Both the well-known hydrates poorer in water, that is, the acids $H_7I_3O_{14}$ and HIO_4, are extremely hygroscopic compounds and therefore they are instantaneously rehydrated to the ortho-acid with atmospheric moisture.

e. The oxide IO_3. In the thermal decomposition of orthoperiodic acid in a vacuum two processes take place in the range 105–117°C: decomposition and simultaneous sublimation. On the colder parts of the apparatus a deposit is formed which according to earlier publications contains only iodine(VII) and is in all probability metaperiodic acid. A yellow substance containing formally sexivalent iodine remains at the bottom of the decomposition tube. According to the ultimate analyses its composition corresponds to the formula IO_3. The X-ray diffraction pattern of the powder also shows the individuality of the compound IO_3. The lines of the powder pattern of the substance were compared with those for HIO_4, I_2O_5, and HI_3O_8. The oxide IO_3 is formed[193] also in the thermal decomposition of the lower hydrates of iodine(VII) oxide ($H_7I_3O_{14}$ and HIO_4) in a vacuum at 115°C. However, the appearance of the sublimate formed by the decomposition of these compounds differs from that of the sublimate obtained in the decomposition of orthoperiodic acid. Because of experimental difficulties (mainly the considerable rehydration of the sublimate under the action of the water liberated) the composition of this product cannot be determined accurately nor is it possible to show whether the decomposition of the lower hydrates of iodine(VII) oxide results in the formation of metaperiodic acid or the anhydrous oxide I_2O_7.[192]

6. SALTS OF PERIODIC ACID

Periodates were discovered[194] in 1833 in the oxidation of a mixture of iodine and sodium carbonate solution with chlorine. Oxidation of various iodine compounds with chlorine in alkaline medium is themain method of preparing alkali metal periodates. Periodates of other metals are obtained from these by double decomposition in aqueous medium (by precipitation). Almost all the known periodates can be divided into four classes according to their composition: the metaperiodates M^IIO_4; mesoperiodates $M^I_3IO_5$ or $M^I_2HIO_5$; the orthoperiodates $M^I_2H_3IO_6$, $M^I_3H_2IO_6$, and $M^I_5IO_6$; and the diperiodates $M^I_4I_2O_9$. In some earlier studies[175,195], periodates of another composition are considered, for example, $M^I_8I_2O_{11}$, etc. Probably the authors isolated basic salts or even mixtures of the metal oxides and the corresponding periodates.

The investigation of the periodates is directed mainly to the preparation of new compounds and the subsequent study of their structure and physical properties. Several papers are also devoted to the investigation of their thermal decomposition.

The preparation of new simple periodates has usually accompanied the detailed study of the metal oxide–iodine(VII) oxide–water ternary system. The formation of new compounds in the ternary systems were established from the solubility curve or from measurements of the pH, etc. With the aid of such a method there has been success in extending considerably the number of known simple and double periodates of lithium[196,197], sodium[198,199], potassium[198,200], beryllium[201], magnesium[202], calcium and barium[203], lead(II)[204], copper(II)[205], silver[206–208], cadmium[209], and iron(III)[210] and observing all the periodates of the corresponding metals which can exist in the range of temperature studied in the presence of water. The systems studied are listed in Table 4.

Table 4. Equilibrium systems of iodine(VII) compounds.

Equilibrium system	Compounds formed in the system	Reference
$Li_2O—I_2O_7—H_2O$	Li_5IO_6, $Li_3H_2IO_6$, $Li_2H_3IO_6$, $LiIO_4·H_2O$	196
$Li_2H_3IO_6—(NH_4)_2H_3IO_6—H_2O$	$NH_4LiHIO_6·3H_2O$	197
$NaIO_4—NaOH—H_2O$	$NaIO_4·3H_2O$, $Na_2H_3IO_6$, $Na_3H_2IO_6$	198
$Na_2H_3IO_6—(NH_4)_2H_3IO_6—H_2O$		199
$KIO_4—KOH—H_2O$	$K_4I_2O_9$, $K_4I_2O_9·9H_2O$	198
$K_4I_2O_9·9H_2O—H_2O—(NH_4)_2H_3IO_6$	$KNH_4H_3IO_6$	200
$Be(OH)_2—H_5IO_6—H_2O$	$Be_5(IO_6)_2·12H_2O$; $Be(IO_4)_2·13H_2O$	201
$Mg(OH)_2—H_5IO_6—H_2O$	$Mg_5I_2O_9·13H_2O$; $Mg(IO_4)_2·8H_2O$	202
$Ca(OH)_2—H_5IO_6—H_2O$	$Ca_3(IO_5)_2·9H_2O$; $Ca_4I_2O_9·9H_2O$ $Ca(IO_4)_2·6H_2O$	203
$Ba(OH)_2—H_5IO_6—H_2O$	$Ba_3(IO_5)_2·2H_2O$; $Ba_4I_2O_9·6H_2O$ $Ba(IO_4)_2·6H_2O$	203
$Pb_3(IO_5)_2·H_2O—H_5IO_6—H_2O$	$Pb_5I_2O_9·3H_2O$	204
$Pb_3(IO_5)_2·H_2O—KOH—H_2O$	$Pb_4I_2O_{11}·5H_2O$	204
$Cu(ClO_4)_2—NaIO_4—NaOH—H_2O$	$Cu_2HIO_6·3H_2O$, $Cu_5(IO_6)_2·5H_2O$ $NaCu_2IO_6$	205
$Ag_2O—I_2O_7—H_2O$	Ag_5IO_6, Ag_3IO_5, Ag_2HIO_6, $Ag_2H_3IO_6$ $AgIO_4$, $AgIO_4·2H_2O$	206, 207 208
$Cd_5(IO_5)_2·3,5H_2O—H_5IO_6—H_2O$	$Cd(IO_4)_2·8H_2O$; $Cd_2I_2O_9·13H_2O$	209
$Fe_2(SO_4)_3—KIO_4—H_2O$	$Fe_5(IO_6)_3$	210

There is considerable interest in those ammonium and alkali metal periodates which can be obtained[211] from aqueous solutions (primarily by precipitation with methanol or by crystallisation at 0°C). These are mainly mesoperiodates, which apparently contain five-coordinate iodine. They are of low stability and are readily converted into the corresponding orthoperiodates with apparently six-coordinated iodine (Table 5).

However, certain orthoperiodates of the $M^I_5IO_6$ type—for example, Na_5IO_6,[212,213] $Ca_5(IO_6)_2$, and $Ba_5(IO_6)_2$[175,203]—can be prepared only by "dry" methods, since in contact with water they undergo partial hydrolysis with the formation of periodates which have a lower metal : iodine ratio.

In the preparation of new periodates special attention has been paid to the investigation of compounds which contain an anionic complex with a metal atom of higher valency as central atom and periodate anions as ligands Mn^{IV}, Fe^{III}, Co^{III}, Ni^{IV}, Cu^{III}, Ag^{III}, and Ce^{IV} are encountered as central atoms in these compounds (the periodate ions stabilise the higher oxidation state of the metal, which is of low stability). In most instances the sodium, potassium, and barium salts of the following hypothetical acids have been obtained:

$H_{11}Mn(IO_6)_3^{214,215}$, $HMnIO_6^{216}$,
$H_3FeIO_6^{217,218}$, $H_3Fe_4(IO_6)_3$, $H_7Fe(IO_6)_2^{219}$,
$H_3Co_4(IO_6)_3^{220,221}$, $H_7Co(IO_6)_2^{215,222}$.
$HNiIO_6^{223}$,
$H_7Cu(IO_6)_2^{224,225}$,
$H_7Ag(IO_6)_2^{226}$,
$H_6Ce(IO_6)_3^{227}$,

The general method of preparing these compounds[228] consists in the addition of an appropriate oxidant (for example, hypochlorite or peroxodisulphate) to a slightly

acid solution of alkali metal periodate and the corresponding salt of the metal to form the central atom, then making the mixture alkaline. Sometimes the crystallisation of the complexes can be brought about by addition of alcohol. The oxidation state of the central metal atom was found by titration with a suitable reductant or by measuring the magnetic susceptibility. These compounds are usually coloured and readily soluble in water. They are more stable in alkaline medium but some of them retain their stability in acid. For example, the free acid $H_7Co(IO_6)_2$ is stable in aqueous solution and it can be obtained by passing a solution of the sodium salt through a suitable cation-exchange resin.

Other complexes with the character of heteropolyacids are more stable in acid medium. They include chiefly compounds of periodic acid with vanadium[229], niobium, and tantalum[20] pentoxides. In these compounds, which contain an anionic complex, the iodine plays the part of central atom and the ligands are oxygen or oxo-anions of the Group Vb elements.

Periodates with a complex cation, the central atom of which is an atom of a metal with a strongly expressed complex-forming ability (for example, Co^{III},[230-233] Cr^{III},[234,235] Pd^{II}, Pt^{II}, Pt^{IV} [23]), are also well known. The ligands most frequently encountered are NH_3 molecules, molecules of organic compounds, Cl^-, Br^-, and SCN^- ions, etc. Periodate anions usually do not enter the coordination sphere of these compounds.

The structure of periodates has been investigated by X-ray diffraction, especially for alkali metal and silver periodates. Table 6 surveys the published information[236-254]. Clearly, most of the anhydrous periodates are tetragonal. They are isostructural with scheelite and their anions form tetrahedra, whereas in the structure of orthoperiodates the IO_6^{5-} anions are arranged in octahedra. The diperiodate anions are also usually made up of two octahedra with one edge in common (that is, two oxygen atoms).

The structure of the ammonium and alkali metal periodates was also studied with the aid of spectroscopic methods. The infrared spectra led to some unexpected results. It was found, for example, that the structure of certain compounds which were thought earlier to be diperiodates or orthoperiodates corresponds to mesoperiodates[184,211]. Table 7 gives the results of these measurements. The infrared spectra of silver periodates[255] and some transition metal periodates[215] were studied rather more systematically.

Table 5. Metastable periodates and their conversion into stable compounds.

Metastable	Stable
$Li_2HIO_5 \cdot 8(4)\,H_2O$	$Li_2H_3IO_6$
$Li_3IO_5 \cdot Li_2HIO_5 \cdot 11\,H_2O$	$Li_2H_3IO_6 + Li_3H_2IO_6$
$Na_2HIO_5 \cdot 4\,H_2O$	$Na_2H_3IO_6$
$Na_3H_2IO_6 \cdot H_2O$	$Na_2H_3IO_6$
$Na_3IO_5 \cdot Na_2HIO_5 \cdot 14\,H_2O$	$Na_2H_3IO_6 + Na_3H_2IO_6$
$(NH_4)_2HIO_5$	$(NH_4)_2H_3IO_6$
$KNH_4HIO_5 \cdot H_2O$.	$KNH_4H_3IO_6$

Table 7. Composition of periodates corresponding to the results of spectroscopic measurements.

Periodates	Li^+	Na^+	K^+	NH_4^+	Rb^+	Cs^+
Meta-		$NaIO_4$	KIO_4	NH_4IO_4	$RbIO_4$	$CsIO_4$
Meso-	$Li_2HIO_5 \cdot 8\,H_2O$ $Li_2HIO_5 \cdot 4\,H_2O$ $Li_3IO_5 \cdot H_2O$ $Li_3IO_5 \cdot Li_2HIO_5 \cdot 11\,H_2O$	$Na_2HIO_5 \cdot 4\,H_2O$ $Na_3IO_5 \cdot Na_2HIO_5 \cdot 14\,H_2O$	$K_2HIO_5 \cdot 4\,H_2O$	$(NH_4)_2HIO_5$ $LiNH_4HIO_5 \cdot 3\,H_2O$ $KNH_4HIO_5 \cdot H_2O$		
Ortho-		$Na_3H_2IO_6 \cdot H_2O$	$K_3H_2IO_6 \cdot 3H_2O$ $K_5IO_6 \cdot 5.5\,H_2O$	$KNH_4H_3IO_6$		

Table 6. Results of the X-ray diffraction investigation of the structure of periodates.

Composition	Crystallographic system	Lattice parameters, Å	No. of molecules in unit cell	Interatomic distance	Reference	Note
$LiIO_4 \cdot 3\,H_2O$	tric.	$a = 6.13$; $\alpha = 93°28'$ $b = 9.43$; $\beta = 107°17'$ $c = 5.01$; $\gamma = 96°16'$	2		236	
$Li_2H_3IO_6$	hex.	$a = 5.31$ $c = 4.61$	1		236	
$NaIO_4$	tetrag.	$a = 5.322$ $c = 11.93$	1		237	
KIO_4	tetrag.	$a = 8.13$ $c = 12.63$			238	
$K_4I_2O_9 \cdot 9\,H_2O$	tric.	$a = 7.06$; $\alpha = 97°47'$ $b = 10.57$; $\beta = 121°30'$ $c = 7.56$; $\gamma = 81°55'$	1	I—I=2.7	239, 240 241	$\left[(OH)O_3I\langle\begin{smallmatrix}O\\O\end{smallmatrix}\rangle IO_3(OH)\right]^{4-}$
$KNH_4H_3IO_6$	mon.	$a = 6.300$; $\beta = 76°14'$ $b = 15.19$ $c = 6.813$	4		242	
$(NH_4)_2H_3IO_6$	hex.	$a = 6.88$ $c = 11.10$		I—O=1.93	243, 244	
$N(CH_3)_4IO_4$	tetrag.	$a = 8.77$ $c = 12.07$			245	
$Al(IO_4)_3 \cdot 12\,H_2O$	cub.	$a = 15.42$	8		246	octahedra IO_6^{5-} and $[Al(H_2O)_6]^{3+}$
$Na_3KH_3Cu(IO_6)_2 \cdot 14\,H_2O$	mon.	$a = 6.12$ $b = 14.84$; $\gamma = 97°38'$ $c = 25.18$	4	I—I=5.84 Cu—I=2.92	247	
$AgIO_4$	tetrag.	$a = 5.37$ $c = 12.07$	4		245, 248	
$Ag_2H_3IO_6$	hex.	$a = 5.31$ $\alpha = 67°38'$	1		249, 250 251	
Ag_2HIO_5					252	
$Na_7H_4Mn(IO_6)_3$	mon.	$a = 16.00$ $b = 19.57$ $c = 10.29$	4	I—Mn=2.97 I—O=1.95 Mn—O=1.90	253, 254	

The structure of periodates has also been determined on the basis of measurements of magnetic properties, especially, magnetic susceptibility[256-259]. The results of these measurements have sometimes enabled complexes to be distinguished from simple compounds.

Ammonium and silver trihydrogen periodates $(NH_4)_2H_3IO_6$ and $Ag_2H_3IO_6$ exhibit anomalous dielectric constants at low temperatures. This can be explained by a transformation to an antiferroelectric phase at low temperatures[244,260-265].

7. BEHAVIOUR OF PERIODATES AT ELEVATED TEMPERATURE

The thermal decomposition of periodates of various compositions is accompanied by loss of water, oxygen, and iodine (in some instances of only one or two of these components). Depending on the composition of the initial periodates, the products of their thermal decomposition are: partly dehydrated periodates, for example[197]:

$$3\,[LiIO_4\cdot 3H_2O]=Li_3H_4I_3O_{14}+7H_2O\,, \qquad (1)$$

or completely dehydrated periodates[200]:

$$K_4I_2O_9\cdot 9H_2O=K_4I_2O_9+9H_2O\uparrow\,, \qquad (2)$$

periodates of another composition, for example[197]:

$$3\,[(NH_4)_2\,Li_2I_2O_9\cdot 7H_2O]=2Li_3\,(NH_4)_2H_2I_3O_{14}+2NH_3+20\,H_2O\,, \qquad (3)$$

or[269]:

$$5Ba\,(IO_4)_2=Ba_5\,(IO_6)_2+4I_2+14O_2\,, \qquad (4)$$

compounds of iodine(VI), for example[270]

$$Na_2H_3IO_6=Na_2IO_4+\frac{3}{2}\,H_2O+\frac{1}{4}\,O_2\,, \qquad (5)$$

iodates[199]:

$$NaIO_4=NaIO_3+\frac{1}{2}\,O_2\,, \qquad (6)$$

or iodides[199]:

$$NaIO_4=NaI+2O_2\,. \qquad (7)$$

In the thermal decomposition of heavy metal periodates, oxides of the corresponding metal[271] or the metal in an elemental state[266,268] can also be formed.

Whereas the products formed as a result of the thermal decomposition of periodates according to Eqns. (2), (4), (6), and (7) are known substances and their formation during the course of these reactions was established long ago, the products obtained as a result of reactions (1), (3), and (5) were identified only recently. According to Eqn. (1), and also (3), in the thermal decomposition of periodates, periodates are formed which on the basis of their composition could be classified as salts of triperiodic acid $H_7I_3O_{14}$ obtained by Hauptman[187]. The substance produced in the partial dehydration of magnesium periodate[202] may also belong to these polyperiodates:

$$Mg\,(IO_4)_2\cdot 8H_2O=Mg\,(IO_4)_2\cdot 1.66\,H_2O+6.33\,H_2O\,,$$
$$3\,[Mg\,(IO_4)_2\cdot 1.66\,H_2O]=Mg_3\,(H_4I_3O_{14})_2\cdot H_2O\,. \qquad (8)$$

Since the structure of triperiodic acid and its salts has not yet been established, it is impossible to explain why triperiodates are formed as a result of the decomposition of periodates of metals of small ionic radius (Li^+, Mg^{2+}).

It was observed recently that iodine(VI) compounds are formed in the thermal decomposition of periodates at 200°C according to the equations:

		Reference
$Li_2H_3IO_6=Li_2IO_4+\frac{3}{2}\,H_2O+\frac{1}{4}\,O_2\,,$	(9)	272
$Na_2H_3IO_6=Na_2IO_4+\frac{3}{2}\,H_2O+\frac{1}{4}\,O_2\,,$	(10)	270
$Be_3\,(IO_5)_2\cdot 12H_2O=Be_3I_2O_9\cdot 4H_2O+8\,H_2O+\frac{1}{2}\,O_2\,,$	(11)	273
$Mg_2I_2O_9\cdot 2{,}5\,H_2O=2\,[MgIO_4\cdot 0{,}5\,H_2O]+\frac{3}{2}\,H_2O+\frac{1}{2}\,O_2\,,$	(12)	202
$Ca_2I_2O_9\cdot 9\,H_2O=2CaIO_4\cdot H_2O+7H_2O+\frac{1}{2}\,O_2\,,$	(13)	274
$Ba_2I_2O_9\cdot 9\,H_2O=2BaIO_4\cdot H_2O+7H_2O+\frac{1}{2}\,O_2\,,$	(14)	269
$2Al\,(IO_4)_3\cdot 12\,H_2O=Al_2\,(I_2O_7)_3\cdot 2H_2O+22\,H_2O+\frac{3}{2}\,O_2\,,$	(15)	275
$Pb_2I_2O_9\cdot 3H_2O=2PbIO_4+3H_2O+\frac{1}{2}\,O_2\,,$	(16)	271
$2Cd_2I_2O_9=4CdIO_4+O_2\,.$	(17)	209

The products of these reactions, which contain iodine(VI), are white or yellow. Most of them are stable over a wide range of temperatures (see Table 8). These compounds are stable in air in the absence of moisture but they react with water to form a mixture of iodic and periodic acids, iodates and periodates. For example, the compound Na_2IO_4 disproportionates in water to form the soluble iodate and insoluble periodate[270] according to Eqn. (18):

$$2Na_2IO_4+H_2O=NaIO_3+Na_3H_2IO_6\,. \qquad (18)$$

Table 8. Thermal stability of iodine(VI) compounds.

Compound	Temperature of formation, °C	Decomposition temperature, °C
Li_2IO_4	180	450
Na_2IO_4	180	370
$Be_2I_2O_9\cdot 4\,H_2O$	150	170
$CaIO_4\cdot H_2O$	180	370
$BaIO_4\cdot H_2O$	220	380
$MgIO_4\cdot 0{,}5\,H_2O$	220	380
$PbIO_4$	220	400
$Al_2(I_2O_7)_3\cdot 2\,H_2O$	90 *	

* In a vacuum at constant temperature.

Table 9. Values of the magnetic susceptibility and magnetic moments of iodine(VI) compounds.

Compound	$10^6\chi$	μ, μ_B
Li_2IO_4	+0.24	0.50
Na_2IO_4	+0.64	0.71
$Be_2I_2O_9\cdot 4\,H_2O$	+4.25	1.63
$CaIO_4\cdot H_2O$	+4.31	1.65
$BaIO_4\cdot H_2O$	+5.21	2.12
$MgIO_4\cdot 0{,}5\,H_2O$	+0.94	0.60
$PbIO_4$	+2.33	1.54
$Al_2(I_2O_7)_3\cdot 2\,H_2O$	+0.17	0.51

† It is impossible to consider as definitely solved the problem whether the dehydration of silver periodate $Ag_4I_2O_9.3H_2O$ (which is usually considered to be the orthoperiodate $Ag_2H_3IO_6$) proceeds by a similar reaction or decomposes more extensively with the liberation of oxygen[266-268].

8. CHARACTERISATION OF IODINE(VI) COMPOUNDS[202-209,269-275]

Although the products of the thermal decomposition of periodates correspond in composition to compounds containing iodine(VI) it could be assumed that they are equimolar mixtures of iodates and periodates or of iodates and peroxides. The latter possibility can be ruled out since the absence of peroxides from these products has been verified by a chemical method and, moreover, it was found that the products react with water to form iodates and periodates. Since peroxide is incapable of oxidising iodate to periodate under any circumstances, the substance which contains the formally sexivalent iodine cannot be a mixture of iodates and peroxides. The problem of whether the thermal decomposition products of periodates are chemical individuals or mixtures of iodates and periodates was solved successfully by magnetic susceptibility measurements. Important results were also obtained by X-ray diffraction studies.

On the basis of the X-ray diffraction results the iodine(VI) compounds obtained by the thermal decomposition of periodates can be roughly classified into three groups:

1. Compounds which do not exhibit X-ray diffraction: $Be_3I_2O_9.4H_2O$, $CaIO_4.H_2O$, $BaIO_4.H_2O$. It has not proved possible to remove the "amorphous to X-rays" nature of these compounds and to being about crystallisation even by prolonged heating at the temperature of their formation.

2. Compounds which exhibit X-ray diffraction analogous to that of the corresponding iodates: Na_2IO_4 and Li_2IO_4 behave analogously to $NaIO_3$ and $LiIO_3$ respectively. These substances are probably also amorphous in the X-ray diffraction sense but under the action of atmospheric moisture they partly decompose into iodate and periodate.

3. Compounds which exhibit a small number of weak lines which are distinguished from the lines of periodates and iodates of the corresponding metal: $MgIO_4.0.5H_2O$, $PbIO_4$, $Al_2(I_2O_7)_3$, $CdIO_4$. Probably the crystal lattice of these compounds is incompletely constructed.

Only the product of the thermal decomposition of silver orthoperiodate and mesoperiodate ($Ag_2H_3IO_6$ and Ag_2HIO_5) of composition Ag_2IO_4 shows X-ray diffraction patterns in which lines coincide with those of the Ag_3IO_5–$AgIO_3$ mixture. Clearly, therefore, the product mentioned is a mixture of mesoperiodate and iodate and cannot be considered chemically distinct[268].

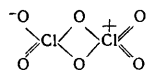
Iodine(VI) compounds are paramagnetic, unlike those of iodates and periodates which are diamagnetic. It has been found that their paramagnetism is not due to impurities but is a property of iodine(VI) compounds. Table 9 gives the values of the mass magnetic susceptibilities of these compounds and the corresponding magnetic moments (calculated from these values).

9. ANALOGUES OF THE COMPOUNDS OF IODINE(VI)

Analogues of the known compounds of iodine(VI) can be found with the lighter homologues of iodine (chlorine and bromine), with its neighbour tellurium, and also its lighter homologue selenium.

As regards chlorine(VI) and bromine(VI), compounds analogous to the iodine (VI) salts of type $M^I_2IO_4$ have not been observed but the oxides Cl_2O_6 (or ClO_3) and Br_2O_6 analogous to the oxide IO_3 are known. These oxides are unstable compounds which are formed as a result of reaction of the corresponding halogen with oxygen or ozone under the action of an electrical discharge[276,277]. An oxide of chlorine(VI) is also formed by the reaction of ozone with the oxide ClO_2 at liquid air temperature[278] or as an intermediate product in the thermal decomposition of perchloric acid[279] and of chlorine(VII) oxide at reduced pressure in the range 100–120°C. It is known[280] also that it is formed as an intermediate product in the reaction of fluorine with potassium iodate at 40–60°C. Chlorine(VI) oxide is a red, oily liquid at ordinary temperature and bromine(VI) oxide a colourless solid.

The presence of a valency of six was demonstrated[281-284] only for chlorine(VI) oxide in the gaseous state: this compound is paramagnetic and consists of ClO_3 molecules. In the liquid state this oxide dimerises. From the Raman spectra the structure of the Cl_2O_6 molecule is analogous to that of the aluminium chloride molecule:



This oxide reacts with water to form chloric and perchloric acids. Therefore some authors suggest[286-288] that it is a compound with the character of a salt $ClO_2^+ClO_4^-$.

For the oxide of bromine(VI) there has been no direct proof of a valency of six for the bromine and there has been no observation of the existence of dimeric molecules Br_2O_6 because of the instability of this compound. Dimerisation can usually be judged only by analogy with the chlorine oxide. However, results were obtained[289,290] which made it possible to rule out the older idea that this oxide is Br_3O_8. With water it gives a solution in which the presence of bromine(V) has been demonstrated. This can be explained by the following reactions:

$$Br_2O_6 + H_2O = HBrO_3 + HBrO_4 ,$$
$$2HBrO_4 = 2HBrO_3 + O_2 .$$

An analogy with the compounds of iodine of higher valency also appears in tellurium compounds. The clearest is the chemical and structural analogy of the compounds of iodine(VII) and tellurium(VI), especially for orthoperiodic and orthotelluric acids. As already noted[183] from the Raman spectra, telluric acid must be considered to be the ortho-acid H_6TeO_6 with an octahedral structure for the anion, as also happens for the periodate anion IO_6^{5-}. The infrared spectra of the two acids are also similar[184,291]. The two acids also form salts analogous in composition—for example, Na_5IO_6, and Na_6TeO_6; or Ag_5IO_6 and Ag_6TeO_6; or $Hg_5(IO_6)_2$ and Hg_3TeO_6, etc.—and in their physical properties (for example, from the solubility of the alkali metal salts). The iodine and tellurium compounds also show an ability to form heteropolyacids of analogous composition (characterised by a ratio of iodine or tellurium to metal atom of 1 : 6), for example, the acids $H_5[I(MoO_4)_6]$, $H_5[I(WO_4)_6]$, and $H_6[Te(MoO_4)_6]$ and $H_6[Te(WO_4)_6]$ respectively.

Analogous composition and properties are shown by certain complexes in which the central metal atom has an unusual valency. A series of salts of diperiodatocopper and diperiodatosilver and respectively ditelluratocopper and ditelluratosilver acids and also periodato- and tellurato-complexes of Co^{III}, Mn^{IV}, Ni^{IV}, Au^{III}, Pd^{IV}, Pt^{IV} has been described[214,217,219,220,224-228,247,253,254,292-295].

In the thermal decomposition of selenium(VI) and tellurium(VI) oxides, telluric acid, and certain tellurates, compounds of selenium(V) and tellurium(V) are formed: Se_2O_5, Te_2O_5, and also the corresponding salts. The tellurium(V) compounds are paramagnetic, like those of iodine(VI).

They are distinguished by this from the diamagnetic tellurates or telluric acid itself. The magnetic properties of the oxide Se_2O_5 have not been measured[296,297].

Siebert has recently published a paper[298] on the chemistry of the periodates.

REFERENCES

1. M.M.P.Muir, J.Chem.Soc., **95**, 656 (1909).
2. H.Kappeler, Ber., **44**, 3496 (1911).
3. R.K.Bahl and J.R.Partington, J.Chem.Soc., 1258 (1935).
4. G.Daehlie and A.Kjekshus, Acta Chem.Scand., **18**, 144 (1964).
5. W.K.Wilmarth and S.S.Dharmatti, J.Amer.Chem.Soc., **72**, 5789 (1950).
6. W.E.Dasent and T.C.Waddington, J.Chem.Soc., 3350 (1960).
7. W.E.Dasent and T.C.Waddington, J.Inorg.Nuclear Chem., **25**, 132 (1963).
8. J.H.Wise and H.H.Hannan, J.Inorg.Nuclear Chem., **23**, 31 (1961).
9. T.Kikindai, Compt.rend., **238**, 1229 (1954); 240, 873 (1955).
10. R.J.Gillespie and J.B.Senior, Inorg.Chem., **3**, 440, 972 (1964).
11. F.Fichter and F.Rohner, Ber., **42**, 4093 (1909).
12. F.Fichter and H.Kappeler, Z.anorg.Chem., **91**, 34 (1915).
13. F.Fichter and H.S.Stern, Helv.Chim.Acta, **11**, 1256 (1928).
14. T.Kikindai, Compt.rend., **240**, 1102 (1955).
15. P.R.Ray and S.N.Ray, Quart.Indian Chem.Soc., **3**, 110 (1925).
16. P.R.Ray and H.Saha, Z.anorg.Chem., **208**, 100 (1932).
17. P.R.Ray and H.Saha, Z.anorg.Chem., **217**, 376 (1934).
18. J.Berg, Compt.rend., **128**, 674 (1899).
19. M.Lobanow, Roczniki Chem., **5**, 437 (1925).
20. P.Ray and D.Sen, J.Indian Chem.Soc., **30**, 250 (1953).
21. K.J.Pedersen, Kgl.danske Videnskab.Selskab, Mat.-fys. Medd., 18, No.12 (1941).
22. N.I.Lobanov, Izv.Sektora Platiny Drug.Blagorod.Metal., Inst.Obshch.Neorg.Khim.Akad.Nauk SSSR, No.28, 277 (1954).
23. N.I.Lobanov, Zhur.Neorg.Khim., 8, 1112 (1963) [Russ.J. Inorg.Chem., 576 (1963)].
24. G.Denigès and J.Borlot, Bull.Soc.chim.France, **27**, 824 (1920).
25. E.Moles and A.P.Vitoria, Anales real Soc.españ, Fis. Quim., **30**, 200 (1932).
26. N.S.Nikolaev and I.V.Buslaev, Zhur.Neorg.Khim., **1**, 1672 (1956).
27. A.A.Opalovskii, Z.M.Kuznetsova, and L.A.Lukyanova, Izv. Sibir.Otd.Akad.Nauk SSSR, 54 (1962).
28. P.Q.Meerburg, Z.anorg.Chem., **45**, 324 (1905).
29. A.E.Hill, H.S.Willson, and J.A.Bishop, J.Amer.Chem. Soc., **55**, 520 (1933).
30. J.E.Ricci, J.Amer.Chem.Soc., **56**, 295 (1934).
31. S.I.Yavorskii, Raboty po Khim.chl.Krym.Otd.Vses.Khim. Obshch.im Mendeleeva, Sbornik, 29 (1960); Chem.Abs., **60**, 11421a (1964).
32. A.E.Hill and J.E.Ricci, J.Amer.Chem.Soc., **53**, 4305 (1931).
33. H.W.Foote and J.E.Vance, Amer.J.Sci., **18**, 375 (1929).
34. A.E.Hill and J.E.Donovan, J.Amer.Chem.Soc., **53**, 934 (1931).
35. E.Cornec and A.Spack, Bull.Soc.chim.France, 49, 582 (1931).
36. J.E.Ricci, J.Amer.Chem.Soc., **60**, 2040 (1938).
37. H.W.Foote and J.E.Vance, Amer.J.Sci., **19**, 203 (1930).
38. H.W.Foote and J.E.Vance, Amer.J.Sci., **25**, 499 (1933).
39. H.W.Foote and J.E.Vance, Amer.J.Sci., **26**, 16 (1933).
40. J.E.Ricci and W.F.Linke, J.Amer.Chem.Soc., **69**, 1080 (1947).
41. B.S.Smith, J.Amer.Chem.Soc., **69**, 2285 (1947).
42. J.E.Ricci, J.Amer.Chem.Soc., **56**, 290 (1934).
43. J.E.Ricci, J.Amer.Chem.Soc., **59**, 866 (1937).
44. A.E.Hill and S.F.Brown, J.Amer.Chem.Soc., **53**, 4316 (1931).
45. J.E.Ricci and F.J.Loprest, J.Amer.Chem.Soc., **75**, 1224 (1953).
46. A.Ditte, Ann.Chim.Phys., **21**, 150, 161 (1890).
47. J.E.Ricci and J.Amron, J.Amer.Chem.Soc., **73**, 3613 (1951).
48. A.E.Hill and S.Moskowitz, J.Amer.Chem.Soc., **53**, 942 (1931).
49. J.E.Ricci, J.Amer.Chem.Soc., **73**, 1375 (1951).
50. C.F.Rammelsberg, Pogg.Ann., **90**, 12 (1853).
51. C.Marignac, Ann.Miner., **9**, 32 (1856).
52. C.Marignac, Ann.Miner., **12**, 66 (1857).
53. W.H.Zachariasen, Skrifter Norske Videnskapsakad Oslo, 8 (1928).
54. A.P.Vitoria and J.Garrido, Anales real Soc.españ.Fis. Quim., **30**, 12 (1932).
55. J.A.Prins and R.Fonteyne, Physica, **2**, 1016 (1935).
56. M.T.Rogers and L.Helmholz, J.Amer.Chem.Soc., **63**, 278 (1941).
57. A.F.Wells, Acta Cryst., **2**, 128 (1949).
58. N.T.Gilfrich and G.M.Urginic, U.S.Nat.Bur.Stand.Circ., No.575 (1955).
59. B.S.Garrett, Diss.Abs., **14**, 1152 (1954); Chem.Abs., **48**, 1249d (1954).
60. A.S.Eakle, Z.Krist., **26**, 569 (1896).
61. W.H.Zachariasen and F.A.Barta, Phys.Rev., **37**, 1626 (1931).
62. J.Garrido, Anales real Soc.españ.Fis.Quim., **30**, 811 (1932).
63. L.Waldbauer and D.C.McCann, J.Chem.Phys., 2, 615 (1934).
64. B.Cioffari, Phys.Rev., **51**, 630 (1937).
65. C.H.McGillavry and C.L.P.Van Eck, Rec.Trav.chim., **62**, 792 (1943).
66. J.Náray-Szabó and J.Neugebauer, J.Amer.Chem.Soc., **69**, 1280 (1947).
67. F.Herlach, H.Gränicher, and D.Itschner, Helv.Phys.Acta, **32**, 473 (1959).
68. A.Granger and A.Schulten, Z.Krist., **42**, 108 (1907).
69. B.Gossner, Z.Krist., **96**, 381 (1937).
70. A.Schulten, Bull.Soc.franc Minéral.Cristallogr., **26**, 107 (1903).
71. G.Denigès, Compt.rend., **171**, 633 (1920).
72. K.Sztrókay, Z.Krist., **90**, 381 (1935).
73. J.A.Ibers, Acta Cryst., **9**, 225 (1956).
74. D.T.Cromer and A.C.Larson, Acta Cryst., **9**, 1015 (1956).
75. R.G.Dickinson and R.T.Dillon, Proc.Nat.Acad.Sci.USA, **15**, 334 (1929).
76. M.R.Nayar and P.Sharma, Z.anorg.Chem., **220**, 169 (1934).
77. C.S.Venkateswaran, Proc.Indian Acad.Sci., **A2**, 119 (1935).
78. C.S.Venkateswaran, Proc.Indian.Acad.Sci., **A4**, 174 (1936).
79. C.S.Venkateswaran, Proc.Indian.Acad.Sci., **A7**, 13 (1938).
80. C.S.Venkateswaran, Nature, **140**, 151 (1937).
81. T.G.Kujumzelis, Z.Physik, **109**, 586 (1938).
82. M.R.Nayar, L.N.Srivastava, A.B.Sen, L.R.Gopal, and P.N.Sharma, Z.anorg.Chem., **240**, 217 (1939).
83. N.R.Rao, Indian J.Phys., **16**, 71 (1942).
84. N.R.Rao, Current Sci., **11**, 429 (1942).
85. L.Couture-Mathieu, and J.P.Mathieu, Compt.rend., **231**, 839 (1950).
86. L.Couture-Mathieu, J.A.A.Katelaar, W.Vedder, and J.Fahrenfort, Physica, **18**, 762 (1952).
87. J.P.Mathieu, Bull.Soc.franc.Minéral.Cristallogr., **77**, 869 (1954).
88. H.Poulet, Ann.Physik, **10**, 908 (1955).

89. K.Nakamoto, M.M.Margoshes, and R.E.Rundle, J.Amer. Chem.Soc., **77**, 6483 (1955).
90. K.Shimomura and N.Inone, J.Phys.Soc.Japan, 14, 86 (1959).
91. T.Dupuis and J.Lecomte, Compt.rend., **252**, 26 (1961).
92. R.Fonteyne, Naturw.Tijdschr.(Ghent), **21**, 141 (1939).
93. C.Schaefer and M.Schubert, Z.Physik, **7**, 309 (1921).
94. C.Schaefer, F.Matossi, and H.Aderhold, Z.Physik, **65**, 289 (1930).
95. P.Krishnamurti, Indian J.Phys., **5**, 633 (1930).
96. S.T.Shen, Y.T.Yao, and T.Y.Wu, Phys.Rev., **51**, 235 (1937).
97. M.Parodi, Compt.rend., **205**, 607 (1937).
98. P.G.N.Nagyar, Proc.Indian Acad.Sci., **A8**, 419 (1938).
99. O.Stelling, Svensk ken.Tidskr., 52, 144 (1950).
100. O.Theimer, Monatsh., **82**, 301 (1950).
101. A.D.Awtrey and R.E.Connick, J.Amer.Chem.Soc., **73**, 1842 (1951).
102. R.P.Buck, S.Singhadeja, and L.B.Rogers, Analyt.Chem., **26**, 1240 (1954).
103. H.Siebert, Z.anorg.Chem., **275**, 225 (1954).
104. W.E.Dassent and T.C.Waddington, J.Chem.Soc., 2429 (1960).
105. C.Rocchiccioli, Compt.rend., **250**, 1232 (1960).
106. C.Rocchiccioli, Ann.Chim.(Italy), **5**, 999, 1013 (1960).
107. G.W.Chantry and R.A.Plane, J.Chem.Phys., **34**, 1268 (1961).
108. C.Duval and J.Lecomte, Rec.Trav.chim., **79**, 519 (1960).
109. P.Pascal, Rev.Gen.Sci., **34**, 388 (1923).
110. A.Shchukarev, Z.phys.Chem., **113**, 452 (1924).
111. A.Shchukarev, Z.phys.Chem., **114**, 500 (1925).
112. F.W.Gray and J.Farquharson, Phil.Mag., **10**, 91 (1930).
113. K.Kido, Sci.Reports Tôhoku Univ., [1], **21**, 869 (1932).
114. S.R.Rao and S.Sriraman, Phil.Mag., **24**, 1025 (1937).
115. S.R.Rao and S.Sriraman, Current Sci., **6**, 54 (1937).
116. V.C.G.Trew, Trans.Faraday Soc., **37**, 476 (1941).
117. P.Pascal, A.Pacault, and C.Jamet, Bull.Soc.chim.France, **15**, 324 (1948).
118. M.Prasad and D.M.Desay, Proc.Nat.Inst.Sci.India, **15**, 145 (1949).
119. M.Prasad, S.S.Dharmatti, and A.K.Ghosse, J.Chem. Phys., **17**, 819 (1949).
120. J.N.Sugden, J.Chem.Soc., 178 (1926).
121. N.R.Dhar, J.Indian Chem.Soc., **5**, 585 (1928).
122. N.R.Dhar and R.N.Mittra, J.Indian.Chem.Soc., **12**, 771 (1935).
123. W.G.Davies and R.T.Lattey, Phil.Mag., **12**, 1135 (1931).
124. G.Steulmann, Z.Physik, **77**, 114 (1932).
125. R.M.Fuoss and A.Kraus, J.Amer.Chem.Soc., **55**, 476 (1933).
126. A.Endrédy, Z.anorg.Chem., **217**, 53 (1934).
127. M.Beauvilain, Ann.Physik, **6**, 502 (1936).
128. J.Martinéz-Cros and L.Boucher, Anales.real Soc.españ. Fis.Quim., **23**, 229 (1935).
129. J.Martinéz-Cros, Anales.real Soc.españ.Fis.Quim., **34**, 72 (1936).
130. J.Lange and E.Herre, Z.Elektrochem., **43**, 592 (1937).
131. J.E.Ricci and T.W.Davis, J.Amer.Chem.Soc., **62**, 407 (1940).
132. M.R.Nayar and N.K.Mundle, Current Sci., **8**, 73 (1939).
133. M.R.Nayar and N.K.Mundle, Current Sci., **10**, 76 (1941).
134. M.R.Nayar and L.N.Srivastava, Phil.Mag., **39**, 800 (1948).
135. J.J.Reimer and D.S.Martin, J.Amer.Chem.Soc., **78**, 1833 (1956).
136. J.F.Harvey, J.P.Redfern, and J.E.Salmon, J.Inorg. Nuclear Chem., **26**, 1326 (1964).
137. A.Mokherji and S.P.Tandon, Indian J.Phys., **38**, 278 (1964).
138. C.F.Rammelsberg, Pogg.Ann., **44**, 548 (1838).
139. A.Ditte and C.F.Rammelsberg, Ann.Chim.Phys., 166 (1890).
140. G.Gore, Phil.Mag., **41**, 310 (1871).
141. F.W.Clarke and H.B.Fullerton, Amer.J.Sci., **14**, 280 (1877).
142. F.Mylius and R.Funk, Ber., **30**, 1721 (1897).
143. A.Meusser, Ber., **34**, 2434 (1901).
144. F.A.Henglein and L.Teichman, Z.anorg.Chem., **188**, 138 (1930).
145. V.Biber, A.A.Vnukova, and N.Konshin, Zhur.Obshch. Khim., **6**, 873 (1936).
146. I.A.Khernikov and T.A.Uspenskaya, Zavod.Lab., **9**, 276 (1940).
147. S.Peltier and C.Duval, Analyt.Chim.Acta, **1**, 345, 355, 360 (1947).
148. S.S.Roginskii and M.I.Yanovskii, Dokl.Akad.Nauk SSSR, **65**, 879 (1949).
149. Y.Marin and C.Duval, Analyt.Chim.Acta, **6**, 47 (1952).
150. C.Duval, Analyt.Chim.Acta, **15**, 223 (1956).
151. E.Moles and A.P.Vitoria, Anales.real Soc.españ.Fis. Quim., **30**, 99 (1932).
152. C.Duval, Analyt.Chim.Acta, **16**, 224, 546 (1957).
153. E.Moles and A.Parc, Anales.real Soc.españ.Fis.Quim., **31**, 618 (1933).
154. J.Garrido, Anales.real.Soc.españ.Fis.Quim., **31**, 616 (1933).
155. A.P.Vitoria, Anales.real.Soc.españ.Fis.Quim., **33**, 795 (1935).
156. E.Moles and P.Villau, Anales.real.Soc.españ.Fis.Quim., **34**, 787 (1936).
157. T.Dupuis, Mikrochim.Acta, 289 (1962).
158. A.B.Lamb, W.C.Bray, and W.J.Geldard, J.Amer.Chem. Soc., **42**, 1636 (1920).
159. N.P.Komar, Materiali Nauch.-Issled.Rabot.Ukrain.Inst. Sov.Torg., 1939 (1940).
160. A.Halász, A.Jánosi, and K.Labdi, Veszpremi Vegyip. Egyet.Kozlemen., **4**, 159 (1960).
161. U.Groatto and G.Bryk, Gazzetta, **71**, 590 (1941).
162. G.S.Serullas, Ann.Chim.Phys., **45**, 61 (1831).
163. E.Millon, Ann.Chim.Phys., **9**, 408, 422 (1843).
164. A.Ditte, Ann.Chim.Phys., **21**, 50 (1870).
165. C.W.Blomstrand, J.prakt.Chem., **40**, 305 (1889).
166. A.Rosenheim and O.Liebknecht, Analyt.Chem., **308**, 40 (1891).
167. L.Malaprade, Bull.Soc.chim.France, **39**, 325 (1926).
168. M.R.Nayar and T.R.Gairola, Z.anorg.Chem., **220**, 163 (1934).
169. E.E.Aynsley and P.L.Robinson, J.Chem.Soc., 623 (1953).
170. M.Schmeisser and K.Lang, Angew.Chem., **67**, 156 (1955).
171. J.Ogier, Compt.rend., **86**, 222 (1878).
172. A.Michael and W.T.Conn, Amer.Chem.J., **23**, 446 (1900).
173. A.Michael and W.T.Conn, Amer.Chem.J., **25**, 89 (1901).
174. C.F.Roberts, Amer.Chem.J., **48**, 157 (1894).
175. C.F.Rammelsberg, Ber., **1A**, 70 (1868).
176. G.H.Rohrback and G.H.Cady, J.Amer.Chem.Soc., **70**, 2603 (1948).
177. H.C.Mishra and M.C.R.Symons, J.Chem.Soc., 1194 (1962).
178. H.H.Willard and R.R.Ralston, Trans.Amer.Electrochem. Soc., **62**, 249 (1932).
179. H.H.Willard, Inorg.Synth., **1**, 172 (1939).
180. U.Braendli, Elektrochemie Turgi, Ger.1, 111, 156 (20th July 1961); Chem.Abs., 56, 13796h (1962).
181. S.L.Aggarwal and S.Singh, J.Indian.Chem.Soc., **22**, 158 (1945).
182. K.V.Astakhov, A.I.Elitsur, and N.E.Nikolaev, Zhur. Obshch.Khim., **21**, 1753 (1951).
183. H.Siebert, Z.anorg.Chem., **273**, 21 (1953).

184. H.Siebert, Z.anorg.Chem., **303**, 162 (1960).
185. O.Jarchow, Chem.Zvesti, **13**, 741 (1959).
186. Y.D.Feikema, Acta Cryst., **14**, 315 (1961).
187. Z.Hauptman, Coll.Czech.Chem.Comm., **24**, 2132 (1959).
188. J.R.Partington and R.K.Bahl, J.Chem.Soc., 1088 (1934).
189. R.Ripanova and A.Duca, Analele Acad.Rep.Populare Romane, Sect.Stiinte Mat.Fiz.Chim., [A], 11 (1949).
190. A.B.Lamb, J.Amer.Chem.Soc., **27**, 134 (1902).
191. Z.Hauptman, Coll.Czech.Chem.Comm., **24**, 2673 (1959).
192. L.Pačesová, Candidate's Thesis, Prague, 1963.
193. L.Pačesova and Z.Hauptman, Z.anorg.Chem., **325**, 325 (1963).
194. F.Ammermüller and G.Magnus, Ann.Chim.Phys., **53**, 92 (1833).
195. C.F.Rammelsberg, Ber., **2**, 149 (1869).
196. A.Hessaby and P.Souchay, Bull.Soc.chim.France, **20**, 606 (1953).
197. M.Drátovský, Coll.Czech.Chem.Comm., **26**, 636 (1961).
198. A.E.Hill, J.Amer.Chem.Soc., **50**, 2678 (1928).
199. M.Drátovský and J.Turnwald, Coll.Czech.Chem.Comm., **25**, 2503 (1960).
200. M.Drátovský, Coll.Czech.Chem.Comm., **24**, 2340 (1959).
201. M.Drátovský and J.Prejzková, Coll.Czech.Chem.Comm., **28**, 1280 (1963).
202. M.Drátovský and J.Košlerová, Coll.Czech.Chem.Comm., **31**, 4375 (1966).
203. M.Drátovský and Z.Ternbach, Chem.Zvesti, 18, 241 (1964).
204. M.Drátovský and J.Matějčková, Chem.Zvesti, **19**, 447 (1965).
205. R.Näsänen, Acta.Chem.Scand., 8, 1587 (1954).
206. P.P.Gyani, J.Indian Chem.Soc., **27**, 5 (1950).
207. P.P.Gyani, J.Phys.Colloid Chem., **55**, 1111 (1951).
208. P.Souchay and A.Hessaby, Bull.Soc.chim.France, **20**, 599 (1953).
209. E.Bohanesová and L.Pačesová, Coll.Czech.Chem.Comm., in the press.
210 G.B.Seifer, Zhur.Neorg.Khim., **3**, 2309 (1958).
211. H.Siebert, Z.anorg.Chem., **304**, 266 (1960).
212. E.Zintl and W.Morawietz, Z.anorg.Chem., **238**, 372 (1938).
213. E.Zintl and W.Morawietz, Z.anorg.Chem., **245**, 20 (1940).
214. M.W.Lister and Y.Yoshino, Canad.J.Chem., **38**, 1291 (1960).
215. Y.Yoshino, T.Takeuchi, and H.Konoshita, J.Chem.Soc. Japan, **86**, 978 (1965); Chem.Abs., **64**, 10 738g (1966).
216. J.Reimer and M.W.Lister, Canad.J.Chem., **39**, 2431 (1961).
217. L.Malatesta, Gazzetta, **71**, 467 (1941).
218. O.Pročke and A.Šlouf, Coll.Czech.Chem.Comm., **11**, 273 (1939).
219. N.J.M.Campbell and C.J.Nyman, Inorg.Chem., **1**, 842 (1962).
220. L.Malaprade, Compt.rend., **210**, 504 (1940).
221. L.Malaprade, Compt.rend., **204**, 979 (1937).
222. M.W.Lister and Y.Yoshino, Canad.J.Chem., **38**, 45 (1960).
223. P.Ray and B.Sarma, J.Indian Chem.Soc., **25**, 205 (1948).
224. M.W.Lister, Canad.J.Chem., **31**, 638 (1953).
225. L.Jenšovský, Z.anorg.Chem., **307**, 208 (1961).
226. L.Jenšovský and M.Skála, Z.anorg.Chem., **312**, 26 (1961).
227. I.P.Alimarin, I.V.Puzdrenkova, and O.A.Shiryaeva, Vestnik Moskov.Gos.Univ., **17**, 61 (1962).
228. M.W.Lister, Canad.J.Chem., **39**, 2330 (1961).
229. A.Rosenheim and K.H.Yang, Z.anorg.Chem., **129**, 181 (1923).
230. J.Soos, C.Varhelyi, and E.S.Stoivici, Studii si Cercetari Sti.Chim.(Fil.) Iasi, **11**, 249 (1960); Chem.Abs., **57**, 8170g (1962).
231. J.Soos, C.Varhelyi, and J.Treiber, Studia Univ.Babes-Bolyai, Ser.1, 1, 85 (1960); Chem.Abs., 57, 8070i (1962).
232. N.I.Lobanov, Zhur.Neorg.Khim., **5**, 565 (1960) [Russ.J. Inorg.Chem., 271 (1960)].
233. N.I.Lobanov, Zhur.Neorg.Khim., **6**, 870 (1961) [Russ.J. Inorg.Chem., 442 (1961)].
234. J.Soos and C.Varhelyi, Studia Univ.Babes-Bolyai, Ser.1, **1**, 95 (1960); Chem.Abs., **57**, 11 167 (1962).
235. R.Ripanova, J.Soos, and C.Varhelyi, Studia Univ.Babes-Bolyai, Ser.1, 1, 53 (1961); Chem.Abs., 57, 8171c (1962).
236. A.Ferrari, A.Braibanti, and A.Tiripicchio, Gazzetta, **92**, 29 (1962).
237. L.M.Kirkpatrick and R.G.Dickinson, J.Amer.Chem.Soc., **48**, 2328 (1926).
238. E.Hylleraas, Z.Physik, **39**, 308 (1926).
239. A.Ferrari, A.Braibanti, and A.Tiripicchio, Acta Cryst., **19**, 629 (1965).
240. A.Ferrari, A.Braibanti, and A.Tiripicchio, Cazzetta, **92**, 17 (1965).
241. H.Siebert and H.Wedemeyer, Angew.Chem., **77**, 507 (1965).
242. V.K.Trunov and M.Drátovský, Vestnik Moskov.Gos.Univ., Ser.2, 49 (1964).
243. L.Helmholtz, J.Amer.Chem.Soc., **59**, 2036 (1937).
244. D.Aboav, H.Gränicher, and W.Petter, Helv.Phys.Acta, **28**, 299 (1955).
245. A.Ferrari, A.Braibanti, and A.Tiripicchio, Gazzetta, **92**, 22 (1962).
246. A.Ferrari, A.Braibanti, and A.Tiripicchio, Gazzetta, **91**, 77 (1961).
247. J.Hadinec, L.Jenšovský, A.Linek, and V.Syneček, Česk. Casopis Fys., **10**, 693 (1960); Naturwiss., **47**, 377 (1960).
248. L.Birkenbach and F.Buschendorf, Z.Phys.Chem., **B16**, 102 (1933).
249. A.Ferrari, R.Curti, and L.Cavalca, Gazzetta, **74**, 43 (1958).
250. V.Riganti and S.Locchi, Ann.Chim.(Italy), **48**, 1249 (1958); Chem.Abs., **53**, 10 891a (1959).
251. E.R.Peterson, Washington State Univ., Pullman, Dis.Abs., **25**, 5588 (1965); Chem.Abs., **63**, 5051a (1965).
252. R.Curti, S.Locchi, and V.V.Riganti, Chima (Switz.), 15, 557 (1961).
253. J.Hadinec and A.Linek, Česk.Časopis Fys., **B12**, 489 (1962).
254. A.Linek, Česk.Časopis Fys., **13**, 398 (1963).
255. J.R.Kyriki, Suomen Kem., **38**, 129 (1965); Chem.Abs., **64**, 5944b (1966).
256. R.C.Sahney, S.L.Aggarwal, and M.Singh, J.Indian Chem. Soc., **23**, 177 (1946).
257. R.C.Sahney, S.L.Aggarwal, and M.Singh, J.Indian Chem. Soc., **24**, 193 (1947).
258. M.Rálek and L.Jenšovský, Coll.Czech.Chem.Comm., **24**, 3495 (1959).
259. R.Blinc, J.Chem.Phys., **31**, 849 (1959).
260. C.C.Stephenson, J.Chem.Phys., **9**, 379 (1941).
261. P.Baertschi, Helv.Phys.Acta, **16**, 218 (1943).
262. P.Baertschi, Helv.Phys.Acta, **18**, 267 (1945).
263. G.Busch, W.Känzig, and W.M.Meier, Helv.Phys.Acta, **26**, 385 (1953).
264. H.Gränicher, W.M.Meier, and W.Petter, Helv.Phys.Acta, **27**, 216 (1954).
265. W.Schurter and H.Gränicher, Helv.Phys.Acta, 29, 209 (1956).
266. J.R.Partington and R.K.Bahl, J.Chem.Soc., 1086 (1934).
267. R.Curti and M.Coggiola, Gazzetta, **71**, 487 (1941).
268. I.Jonáš and L.Pačesová, Coll.Czech.Chem.Comm., **31**, 4385, 4718 (1966).
269. M.Drátovský, Z.anorg.Chem., **334**, 169 (1964).
270. M.Drátovský, Zhur.Neorg.Khim., **8**, 2434 (1963) [Russ.J. Inorg.Chem., 1276 (1963)].
271. M.Drátovský and J.Matějčková, Chem.Zvesti, **19**, 604 (1965).
272. M.Drátovský, Coll.Czech.Chem.Comm., **29**, 579 (1964).

273. M.Drátovský, Coll.Czech.Chem.Comm., **29**, 1710 (1964).
274. M.Drátovský, Zhur.Neorg.Khim., **8**, 1792 (1963) [Russ.J. Inorg.Chem., 931 (1963)].
275. J.Matějček and L.Pačesová, Coll.Czech.Chem.Comm., **31**, 190 (1966).
276. M.Bodenstein, P.Harteck, and E.Padelt, Z.anorg.Chem., **147**, 233 (1925).
277. B.Lewis and J.J.Schumacher, Z.anorg.Chem., **182**, 182 (1929).
278. H.J.Schumacher and G.Stieger, Z.anorg.Chem., **184**, 272 (1929).
279. V.P.Babaeva and A.A.Zinov'eva, Dokl.Akad.Nauk SSSR, **149**, 592 (1963).
280. H.Bode and E.Klesper, Z.anorg.Chem., **266**, 275 (1951).
281. J.Farquanson, C.F.Goodeve, and F.D.Richardson, Trans. Faraday Soc., **32**, 790 (1936).
282. C.F.Goodeve and F.A.Todd, Nature, **132**, 514 (1933).
283. C.F.Goodeve and F.D.Richardson, Trans.Faraday Soc., **33**, 453 (1937).
284. C.F.Goodeve and F.D.Richardson, J.Chem.Soc., 294 (1937).
285. H.C.Longuet-Higgins, Nature, **153**, 408 (1944).
286. E.Colloccia, R.V.Figini, and H.J.Schumacher, Angew. Chem., **68**, 492 (1956).
287. R.V.Figini, E.Colloccia, and H.J.Schumacher, Z.Phys. Chem., **14**, 32 (1958).
288. H.A.Lehman and G.Krüger, Z.anorg.Chem., **274**, 141 (1953).
289. A.Pflugmacherova, A.J.Rabben, and H.Dahmen, Z.anorg. Chem., **279**, 313 (1955).
290. A.Pflugmacherova, Z.anorg.Chem., **298**, 9 (1958).
291. H.Siebert, Z.anorg.Chem., **301**, 161 (1959).
292. L.Jenšovský and M.Rálek, Z.anorg.Chem., **314**, 76 (1962).
293. M.W.Lister and P.McLeod, Canad.J.Chem., **43**, 1720 (1965).
294. N.G.Vannerberg and I.Blockhammar, Acta Chem.Scand., **19**, 875 (1965).
295. L.Jenšovský, Rev.Roumaine Chim., 293 (1966).
296. H.G.Jerschkewitz and K.Menning, Z.anorg.Chem., **319**, 82 (1962).
297. J.Rosický, J.Loub, and J.Pavel, Z.anorg.Chem., **334**, 312 (1965).
298. H.Siebert, Fortschr.Chem.Forsch., 8, 470 (1967).

Faculty of Natural Sciences, Karlov University, Prague, Czechoslovakia

U.D.C. 547.481

γ-Formyl Acids

V.M.Andreev, G.P.Kugatova-Shemyakina, and S.A.Kazaryan

CONTENTS

I. Introduction 254
II. Methods of preparing γ-formyl acids 254
1. Aromatic and heterocyclic γ-formyl acids 254
2. β-Formylpropionic acids 255
3. β-Formylacrylic and β-formylcrotonic acids 256
III. Reactions of γ-formyl acids 256
IV. Investigation of the structure of γ-formyl acids by physical methods 259
V. Alicyclic γ-formyl acids 260

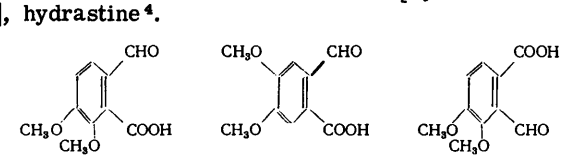
I. INTRODUCTION

The chemistry of γ-formyl acids and especially the problem of their structure has occupied the minds of many eminent investigators for over a century. It is sufficient to mention that Liebig and Wöhler, Gabriel and Libermann, Hans Meyer and Wilslicenus, Alder and Grove worked fruitfully in this field. The Soviet scientists V. M. Rodionov and M. M. Shemyakin also made a significant contribution to the study of the γ-formyl acids. Nevertheless the overwhelming majority of the studies completed up to the present time have been devoted to only an extremely limited number of γ-formyl acids, since the number of known representatives of this class of compound is generally small. They include principally the opianic and 2-formylbenzoic acids and their derivatives, halogenomucic acids, and β-formylpropionic and β-formylacrylic acids. We therefore did not set ourselves the aim of compiling an exhaustive review of all the investigations related to this problem, but have used from them only that part which, in our opinion, allows the contemporary state of the problem to be given with sufficient completeness.

II. METHODS OF PREPARING γ-FORMYL ACIDS

1. Aromatic and Heterocyclic γ-Formyl Acids

The first representative of the class of γ-formyl acids —opianic acid (I) was obtained as long ago as 1842 by Liebig and Wöhler[1-3] in oxidising one of the opium alkaloids—narcotine. Opianic acid (I) is also formed in the oxidation of the alkaloid of Canadian golden seal [*Hydrastis canadensis*], hydrastine[4].



(I) (II) (III)

The structure of opianic acid was established by the work of Matthiessen and his coworkers (for example, see Ref. 5).

As well as opianic acid, γ-formyl acids isomeric with it are known: metaopianic (II)[6-8], which is formed in the