Different Routes in the Synthesis of $(IO)_2(SO_4)_{1-x}(SeO_4)_x$

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The reaction between I_2 and I_2O_5 in mixtures of conc. H_2SO_4 and H_2SeO_4 results in a regular solid solution phase $(IO)_2(SO_4)_{1-x}(SeO_4)_x$, covering the entire range $0.00 \leq x \leq 1.00$. Improvements have been introduced·in the washing–drying procedure for this product. The contours of a reaction mechanism are discussed. $(IO)_2(SO_4)_{1-x}(SeO_4)_x$ can also be prepared virtually pure by means of I_2O_5 and $X =$ S, Se, P, As, Ge and Sn instead of elementary iodine. With $X =$ Bi and Pb the reaction follows an entirely different course, and for the former element a 'double' solid solution phase, $(IO)_{2-t}(BiO)_t(SO_4)_{1-x}(SeO_4)_x$, is obtained as the reaction product. For $X =$ Te and Pb, the reaction products contain $Te_2O_3SO_4$ and $PbSO_4$, respectively, in addition to $(IO)_2(SO_4)_{1-x}(SeO_4)_x$. For $X =$ Sb, the reaction product is an amorphous phase, not yet identified. No reaction can be initiated between $X =$ Si and I_2O_5 in conc. $H_2SO_4(+ H_2SeO_4)$. The findings are discussed on the basis of the standard reduction potentials for HIO_3 and the elements concerned.

The reaction between iodic acid and hot concentrated sulfuric acid was described by Millon[1] in 1844. Since then, the intermediate and the final products of this reaction and of partly modified reactions, have been frequently studied, and a brief historical survey up to 1964 is given in Ref. 2. It may be relevant to recapitulate certain milestones in the development. Analytical proof for $(IO_2)_n$ as the composition of the *final* product was provided by Kappeler[3] in 1911, and the same author also introduced the notation $I_2O_4 = (IO)(IO_3)$. After several years of dispute within the literature as to the water content of the intermediate product, in 1938 Masson and Argument[4] provided the correct formula $(IO)_2SO_4$ (analytically $I_2O_3 \cdot SO_3$). The latter authors also simplified the synthesis by showing that heating is not needed if I_2 and I_2O_5 are mixed in the right proportion in concentrated H_2SO_4, thereby eliminating a rather uncontrollable step in the procedure, and a nearly 100% yield could be obtained. Based on the improved procedure, Dasent and Waddington[5] showed in 1960 that replacement of sulfuric acid by concentrated H_2SeO_4 leads to the analogous selenium intermediate, whereas the final product is still I_2O_4. Dasent and Waddington[5] argued for $(IO)_2SO_4$ and $(IO)_2SeO_4$ as inorganic polymers on the basis of spectroscopic evidence. The subsequent structure determination of $(IO)_2SO_4$ by Furuseth et al.[6] in 1974 confirmed this prediction. The $(IO)_2SO_4$ structure consists of polymeric $(IO)_n$ units linked to SO_4 tetrahedra. Based on the

bonding situation in $(IO)_2SO_4$ and the inferred isostructurality between $(IO)_2SO_4$ and $(IO)_2SeO_4$ (Refs. 6 and 7), it is pertinent to ask what would appear as the product if concentrated acid mixture were introduced into the synthesis rather than pure H_2SO_4 or H_2SeO_4. This question is addressed in this communication. Related questions originate from the fact that a new, quite different compound $(IO_2)_3HSO_4$ has recently been obtained by Rehr and Jansen[8] as a result of more extensive changes in the synthesis procedure. This communication also addresses the possibility of retaining $(IO)_2SO_4$ and $(IO)_2SeO_4$ as intermediate reaction products for various appreciably modified synthesis routes.

Experimental

All reagents used in this study were of selected pure quality (variously designated purum, puriss, reagent grade, 99%, 5N etc., depending on the scheme of the manufacturer).

The preparational procedure for $(IO)_2SO_4$ outlined in Ref. 2 was followed with certain modifications described below. 0.010 mol I_2 and 0.015 mol I_2O_5 were added to ca. 0.45 mol conc. H_2SO_4 (95–97%), conc. H_2SeO_4 (ca. 95%) or to a mixture of these acids in a round-bottomed flask with a glass stopper. The content of I_2O_5 can be replaced by 0.030 mol of, say, HIO_3 or KIO_3. The mixtures were stirred by a magnetic stirrer for 1–5 d until the yellow precipitate was deposited in a clear solution. In

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the initial experiments the decantation and drying on porous porcelain sequence of Ref. 2 was followed, but this was later replaced by an improved washing procedure. Here the yellow product was filtered off through a sintered glass funnel, transferred to a beaker containing ca. 150 ml of cold glacial acid, stirred for a few minutes, and then filtered off. The precipitate was subsequently washed quickly with acetone, and thereafter with cold acetone and finally with cold diethylether (stored at $-25°C$). The $(IO)_2(SO_4)_1 {}_x(SeO_4)_x$ samples were kept in a dry-ice container until the characterization by powder X-ray diffraction (PXD) was performed.

In another series of experiments, the elementary iodine was replaced by other main group elements: $X = S$, Se, Te, P, As, Sb, Bi, Si, Ge, Sn or Pb. The same molar amounts of I_2O_5 and concentrated acids (in most cases pure H_2SO_4) were used, 0.015 mol of X was normally introduced (in some cases varied between 0.05 and 0.010 mol), and the procedure followed the same route as described above for the synthesis with iodine. For some elements, irregularities in the reaction scheme were noticed. For $X = Si$, no reaction was observed even after heating. For $X = Ge$, heating (to ca. $120°C$) was required for ca. 15 min in order to initiate the reaction. In the case of $X = Pb$, the reaction was faster than otherwise and was completed within 5 h. Also, the course of the reaction differed in that the solution remained light brown, turning into a viscous, gel-like state at a certain stage before the rapid precipitation of the yellow reaction product. In the case of $X = Sb$, neither a distinct yellow precipitate nor a clear solution could be obtained. Also for $X = Bi$, special features were observed. Here the solution never turned brown or dark, but remained rather clear during the progressing precipitation of the yellow product. A brown/dark colouring of the solution occurred by heating during the reaction, but the solution became colourless again upon cooling.

All samples were characterized by PXD using Guinier–Hägg cameras, Cu$K\alpha_1$ radiation and Si as internal standard. Additional PXD data were collected with a Guinier–Simon camera (Enraf–Nonius) operating in the low-temperature mode at a fixed temperature of $-60°C$. For the latter recordings, the samples were sealed into thin-walled boron-lithium glass capillaries. Positions and integrated intensities of the Bragg reflections were obtained from the films by means of a Nicolet L18 film scanner using the SCANPI program system.[9] Unit-cell dimensions were deduced by least-squares refinements,[10] including only unambiguously indexable lines.

Results and discussion

Immediately after mixing I_2 and I_2O_5 (alternatively HIO_3 and IO_3^-) into the concentrated acid mixture (hereafter termed acid whenever the explicit emphasis on concentrated acid mixture is renounced) the onset of the reaction

is manifested as a brown colouring of the liquid. The colour turns very quickly darker, and the liquid becomes completely black before the end of this first phase of the reaction. Following Masson,[11] Arotsky *et al.*[12] and Garrett *et al.*,[13] these observations signalize the formation of gradually increasing amounts of I_3^+ according to the following redox reaction:

$$7 \ I_2(solv) + HIO_3(solv) + 8 \ H_2SO_4 \rightarrow 5 \ I_3^+(solv)$$
$$+ 3 \ H_3O^+(solv) + 8 \ HSO_4^-(solv) \qquad (1)$$
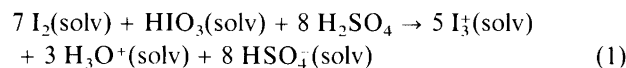
We are reasonably confident that $I_2(solv)$ is the correct species, but less certain that HIO_3 is the *active* agent. However, we prefer $HIO_3(solv)$ brought about by

$$I_2O_5(s) + H_2O(solv) \rightarrow 2 \ HIO_3(solv) \qquad (2)$$

instead of $I_2O_5(solv)$ or IO_3^- (solv). It was, on the other hand, verified that on suspension in conc. H_2SO_4, I_2O_5 remains as the solid oxide within the PXD detection limit. The spontaneous onset of the I_3^+ formation indicates that the process is in principle fast, but the gradually increasing amount of I_3^+ with time shows that the reaction is slowed down by a certain limiting factor. From experiments where I_2 and I_2O_5 were separately treated with H_2SO_4, it became evident that the solubility of $I_2(s)$ and, in particular, $I_2O_5(s)$ in H_2SO_4 is low and that the dissolving processes are also apparently slow. Access to $I_2(solv)$ and/or $HIO_3(solv)$ is accordingly proclaimed to be limiting factors of eqn. (1).

Some 10 wt% H_2O is the maximum amount of water which is tolerated in the concentrated acid mixture in order to allow the reaction [eqns. (1) and (2)] to take place.

Fig. 1 attempts to visualize schematically the progressing reaction according to eqn. (1) in the first phase of the synthesis of $(IO)_2SO_4$ $[(IO)_2(SO_4)_1 {}_x(SeO_4)_x]$. It should now be noted that the relative amounts of I_2 and I_2O_5 involved in eqns. (1) and (2) are different from those
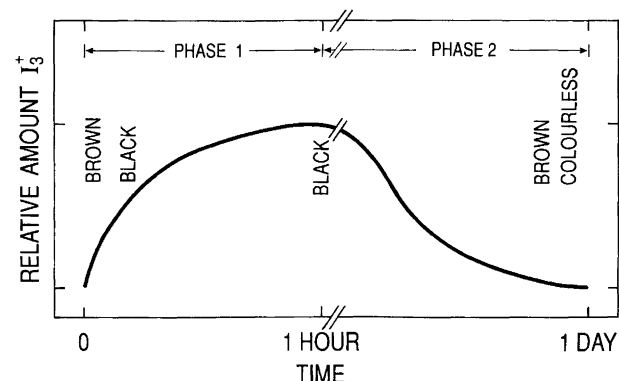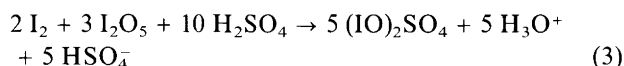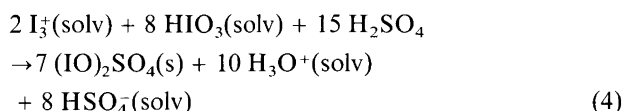

Fig. 1. Schematic representation of time variation in I_3^+ amount during synthesis of $(IO)_2(SO_4)_{1-x}(SeO_4)_x$ from I_2 and I_2O_5. For reaction equations, see text. The colour of the solution at various stages in the progressing reaction is indicated.

required for the synthesis of $(IO)_2SO_4$ according to the overall reaction:

$$2 I_2 + 3 I_2O_5 + 10 H_2SO_4 \rightarrow 5 (IO)_2SO_4 + 5 H_3O^+ + 5 HSO_4^- \tag{3}$$

The fact that the overall reaction [eqn. (3)] proceeds through eqns. (1) and (2), and that the formation of I_3^+ is *essentially completed before* the succeeding redox reaction:

$$2 I_3^+(solv) + 8 HIO_3(solv) + 15 H_2SO_4$$
$$\rightarrow 7 (IO)_2SO_4(s) + 10 H_3O^+(solv)$$
$$+ 8 HSO_4^-(solv) \tag{4}$$

sets in, shows that eqn. (1) has preference over eqn. (4). The reaction mechanism is clearly more complex than indicated by eqn. (4), since the formal IO^+ units are a part of an infinite (polymeric) spiral chain in the $(IO)_2SO_4$ structure.[6] In addition to the polymerization reaction, the dissolving of $I_2O_5(s)$ in H_2SO_4 is a limiting factor in the second phase of the $(IO)_2SO_4$ synthesis. As seen from Fig. 1, the second phase is much more time-consuming than the first, which we believe is a consequence of the polymerization process.

Fig. 2 demonstrates that there is a complete range of solid solubility between $(IO)_2SO_4$ and $(IO)_2SeO_4$. The diffraction data confirm that the 'sulfate' and 'selenate' units are randomly distributed and that the $(IO)_2(SO_4)_{1-x}(SeO_4)_x$ solid solution system is accordingly of the regular substitutional type. (A minor line broadening was noted for some of the samples.)

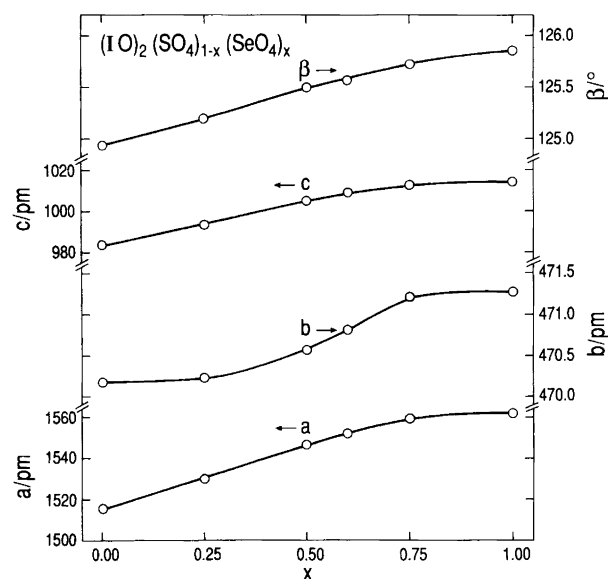The results from the experiments in which I_2 was replaced by other main group elements (X) are sum-

Fig. 2. Unit cell data at 295 K for $(IO)_2(SO_4)_{1-x}(SeO_4)_x$ as function of composition parameter x. Size of symbols is at least five times the *calculated* standard deviation. Note the expanded scale for b.

marized in Table 1. In most cases $(IO)_2SO_4$ [$(IO)_2(SO_4)_{1-x}(SeO_4)_x$ in a few cases where H_2SO_4 and H_2SeO_4 mixtures were used] appeared as the main or only crystalline reaction product. The exceptions are noted in Table 1 and are considered below. Aside from $X = Si$, which showed no sign of reaction with I_2O_5 even after prolonged heating, all the other X elements were shown to reduce I_2O_5 in conc. H_2SO_4. According to tabulated[14] *standard* reduction potentials, it is thermodynamically conceivable to reduce HIO_3 to I_2 with all these X elements (including Si). However, there are serious problems in the extrapolation of a chemical reaction from an H^+ activity of 1.00 under standard conditions to the situation in a concentrated acid: (i) It may be difficult even under standard conditions to select the proper oxidation half-reaction for X. In a concentrated acid this may be further complicated by the possibility of new half-reactions, whereas others may no longer be allowed. (ii) Even when the situation under standard conditions is clear, extrapolation to a concentrated acidic medium is dubious, not only owing to the new alternatives mentioned in (i), but because key concepts such as reduction potential and H^+ activity are not defined in concentrated acids. (iii) As an extension of (i), we recall that a thermodynamically possible reaction may not occur due to kinetic or related factors. This is precisely the case when one attempts to reduce HIO_3 to I_2 by X under standard conditions (or in addition, subjected to heating). Unlike the situation in conc. H_2SO_4, only $X = S$, Se, Te and P proved able to reduce HIO_3 to I_2 in a 1 M H^+ sulfuric acid solution.

As seen from Table 1, the oxidation products of X have only been unambiguously established in the cases of $X = Te$ (Bi; see below) and Pb, where the crystalline phases $Te_2O_3SO_4$ and $PbSO_4$, respectively, occur as roughly half of the products. The present unit-cell data for $Te_2O_3SO_4$ [$a = 466.3(6)$, $b = 692.0(1)$ and $c = 887.0(9)$ pm] are in close agreement with Ref. 15, and accordingly differ somewhat from those in Ref. 16. The corresponding data for $PbSO_4$ [$a = 847.4(1)$, $b = 540.20(7)$ and $c = 695.95(9)$ pm] concur with those compiled in Ref. 17. For $X = S$, Se, P, As, Ge and Sn, the oxidation products most likely remain dissolved in the virtually colourless sulfuric acid mother liquor. No attempt was made to determine the dissolved oxidation products, partly because the identification of non-metal species in conc. H_2SO_4 was considered futile and partly because such species are likely to change on dilution with water.
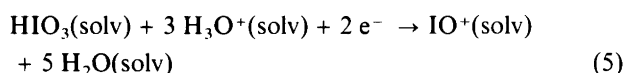
The possibility of minor amounts of another crystalline phase in addition to $(IO)_2SO_4$ cannot be ruled out for $X = As$. Except for $X = Sb$, a larger-scale formation of amorphous products can be ruled out, both from visual inspection of the product and from PXD data. For $X = Sb$, an amorphous product is obtained. [Trace amounts of $(IO)_2SO_4$ were formed on the bottle neck.] When this amorphous product was subjected to heat treatment in a sealed glass capsule for 20 d at 200°C, some water and iodine was given off, and the amorphous

Table 1. Unit-cell data for $(IO)_2SO_4$ prepared by reaction between a main group element X (including data for the reference compound obtained from $X=I$, viz. I_2) and I_2O_5 in conc. H_2SO_4.
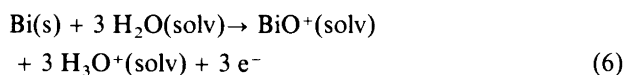
X	a/pm		b/pm	c/pm	$\beta/^\circ$	$V/10^6$ pm^3	Comment
I	1515.16	(7)	470.17 (2)	984.02 (7)	124.937 (5)	574.6 (1)	
S	1515.8	(1)	470.28 (3)	984.3 (1)	124.945 (8)	575.1 (1)	
Se	1515.3	(2)	470.27 (4)	984.1 (1)	124.929 (8)	574.9 (1)	
Te	1515.0	(8)	469.8 (3)	983.6 (9)	125.03 (5)	573.2 (8)	Mixed with $Te_2O_3SO_4$ (see text)
P	1515.28	(9)	470.11 (3)	983.92 (8)	124.939 (6)	574.5 (1)	
As	1517.5	(8)	470.7 (2)	985.2 (6)	124.98 (3)	576.5 (6)	Some PXD lines broadened; impurity?
Sb							Amorphous product
Bi	1515.4	(2)	470.20 (2)	984.2 (2)	124.90 (1)	575.2 (2)	Some PXD lines broadened; $(IO)_{2-y}(BiO)_y SO_4$ (see text)
Si							No reaction with I_2O_5
Ge	1515.9	(2)	470.30 (6)	985.6 (1)	124.92 (1)	576.1 (2)	
Sn	1515.3	(2)	470.24 (4)	987.3 (1)	124.88 (1)	577.0 (1)	
Pb	1516.1	(4)	470.6 (1)	985.5 (5)	125.04 (2)	575.7 (3)	Mixed with $PbSO_4$ (see text)

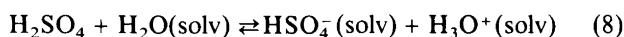phase was converted into a yet unidentified, crystalline phase.

As noted in the experimental section, the heaviest X elements Bi and Pb show different reaction courses than the other X elements. This is shown by the lack of appreciable I_3^+ formation (no, or only light brown, colouring of the solvent phase) during the reaction. This observation led us to postulate that the reaction with $X =$ Bi and Pb proceeds through a direct reduction of HIO_3(solv) to IO^+(solv):

$$HIO_3(\text{solv}) + 3\ H_3O^+(\text{solv}) + 2\ e^- \rightarrow IO^+(\text{solv})$$
$$+\ 5\ H_2O(\text{solv}) \tag{5}$$

with the parallel oxidation reactions (6) and (7):

$$Bi(s) + 3\ H_2O(\text{solv}) \rightarrow BiO^+(\text{solv})$$
$$+\ 3\ H_3O^+(\text{solv}) + 3\ e^- \tag{6}$$

$$Pb(s) \rightarrow Pb^{2+}(\text{solv}) + 2\ e^- \tag{7}$$

neglecting the equilibrium (8) in eqns. (5) and (6):

$$H_2SO_4 + H_2O(\text{solv}) \rightleftharpoons HSO_4^-(\text{solv}) + H_3O^+(\text{solv}) \tag{8}$$

Traditional qualitative analysis confirmed that the yellow reaction product obtained for $X =$ Bi did contain appreciable amounts of bismuth. Hence, we are led to conclude that the reaction with $X =$ Bi results in a regular, substitutional solid solution phase $(IO)_{2-y}(BiO)_ySO_4$ [or for mixed acids $(IO)_{2-y}(BiO)_y(SO_4)_{1-x}(SeO_4)_x$], structural aspects of which are addressed in a forthcoming paper.[18] Additional support for our conclusion comes from the fact that the reaction products are contaminated by Bi or I_2O_5 when the molar proportion of the reactants differed from that prescribed by eqns. (5) and (6), and from the different end hydrolysis products obtained from $(IO)_{2-y}(BiO)_ySO_4$.[18]

Although the reactions with $X =$ Bi and Pb have eqn. (5) in common, there are notable distinctions, originating from the disparity of the oxidation products BiO^+(solv)

and Pb^{2+}(solv) [eqns. (6) and (7)]. A first, direct consequence is that (within the detection limit of traditional qualitative analysis) no lead is incorporated into the $(IO)_2SO_4$ lattice. It is well established[19] that freshly precipitated $PbSO_4$ from aqueous solutions appears in a gel-like, amorphous or poorly microcrystalline state, and that this product subsequently undergoes recrystallization (aging)[19] over a period of 1 d at room temperature. We established the same behaviour when 1 M Pb^{2+}(aq) is subjected to precipitation in conc. H_2SO_4. This explains the gel-like state during the reaction with $X =$ Pb. Moreover, it is tempting to suggest that polymerization of the IO^+ species formed according to eqn. (5) is catalyzed by the presence of the $PbSO_4$ gel-like product, thereby accounting for the observed enhanced reaction rate. The redox reaction according to eqns. (5) and (7) is exothermic (as is probably also the case for the reactions with some other X elements). The heat gradually evolved during the progressing reaction is believed to give rise to a partial decomposition of IO^+ to I_3^+ and HIO_3 [the reverse of eqn. (4); see also the experimental section] and in turn to account for the light brown colouring of the solution in the reaction with $X =$ Pb.

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