Syntheses and Crystal Structures of Titanium Oxide Sulfates

M. A. K. Ahmed, H. Fjellvåg and A. Kjekshus†

Department of Chemistry, University of Oslo, N-0315 Oslo, Norway


When titanium dioxide, metatitanic acid or iron titanate (ilmenite) is heated with 65–95 wt% H₂SO₄, TiOSO₄ or TiOSO₄·H₂O is formed depending on the water content of the sulfuric acid. The contours of reaction mechanisms are discussed. TiOSO₄ and TiOSO₄·H₂O dissolve slightly in cold or hot water during short-term treatment. On longer contact with water the solubility becomes more appreciable. The undissolved remainder, as well as the dissolved fraction after removal of the water phase, proves to have been converted into X-ray amorphous products with composition TiOSO₄·xH₂O, x ≈ 1. The crystal structure of TiOSO₄·xH₂O is determined on the basis of powder X-ray diffraction data. The structure of TiOSO₄·H₂O has been reetermined. Both structures contain zigzag chains with short Ti–O distances. The chains are connected via sulfate groups, and the structures probably suffer from some disorder. For both structures the possibility of deviations from the centrosymmetric space group Pnma is discussed. The close structural relationship between TiOSO₄ and TiOSO₄·H₂O is discussed. On heating, TiOSO₄ undergoes a reversible phase transition at around 330 °C and decomposes into TiO₂ (anatase) at ca. 525 °C. TiOSO₄·H₂O loses its crystal water at ca. 310 °C. However, liberation of SO₃ starts at about 40 °C lower temperature than for TiOSO₄, and the decomposition shows a two-step character in TG, DTG and DTA. Attempts to isolate intermediate decomposition products have so far not been successful.

The use of concentrated H₂SO₄ (in this context 60–95 wt% H₂SO₄) as a solvent has long traditions in pure and industrial chemistry. Nevertheless, reactions in and with conc. H₂SO₄ are little systematically explored and understood. It can not be denied that working with conc. H₂SO₄ has certain disadvantages, some of which are of a psychological nature owing to the risk of damaging living organisms or materials coming into contact with the acid. The high viscosity, some 25 times that of water, introduces experimental difficulties: solutes dissolve and crystallize more slowly, adhered H₂SO₄ may be difficult to remove from the reaction product and concentration fluctuations may be present. However, for many purposes the advantages of conc. H₂SO₄ may be more important: extreme acidobasic differentiating power combined with weakly developed redox properties. Its dielectric constant is higher than that of water, making it a good solvent for ionic substances and leading to extensive ionic crystallization.

The situation for titanium oxide sulfate, TiOSO₄, may serve to illustrate the points mentioned above. TiOSO₄ and/or its hydrates are dealt with in textbooks,3 reference books,4 original5–6 and patent7 literature, and are also involved in industrial processes for the manufacture of titanium compounds (cf. Ref. 2 and references therein). Yet limited completely reliable information on the titanium oxide sulfates is available apart from the crystal structure determination of TiOSO₄·H₂O,4 and the approximate unit-cell dimensions for TiOSO₄.6 The present work, which has its origin in interest in gaining insight into the numerous possible reactions in conc. H₂SO₄ (cf. Ref. 8), will hopefully contribute to rectifying this situation.

Experimental

TiO₂ (Aldrich; > 99.9%, anatase [TiO₂-a, a = 378.41(3), c = 951.2(2) pm]), ilmenite (Egersund, Norway; pure mineral specimen of FeTiO₃) and conc. H₂SO₄ (Merck; 95–97 wt%, the former value being used throughout this paper) were used as starting chemicals for the syntheses. Concentrated H₂SO₄ in the range 60–95 wt% H₂SO₄ was made by diluting the as-purchased acid with distilled H₂O. Owing to the virtually lacking reactivity of the as-purchased TiO₂-a in 60 wt% H₂SO₄, a parallel series of syntheses made use of metatitanic acid (cf. Refs. 2–4) as
an intermediate in a two-step reaction. [In the first step, metatitanic acid was obtained: TiO₂ was dissolved in H₂SO₄ (vide infra), the solution cooled to room temperature, whereafter conc. NH₃ was added slowly under cooling until the liquid became weakly basic. The resulting deposit was then filtered, carefully washed, dried, crushed, and washed and dried once more. The metatitanic acid thus obtained (TiO₂·xH₂O) was virtually X-ray amorphous (am)].

Four parallel series of syntheses were performed, using either the as-purchased TiO₂-a, the rutile [TiO₂-r, a = 459.30(5) and c = 295.63(5) pm] modification (converted from TiO₂ at 1000°C), FeTiO₃ (limonite) or TiO₂·xH₂O-am as the titanium oxide source. TiO₂ or Fe-TiO₂ (0.02 mol) was added to 20 ml conc. H₂SO₄ (60–95 wt %) in a round-bottomed flask with either a glass stopper (90–95 wt % H₂SO₄) or a reflux cooler (60–85 wt % H₂SO₄). The mixtures were heated to boiling under stirring until all titanium oxide material (for the successful syntheses) had dissolved, and a clear yellow to dark-brown solution was obtained. The stirring was then stopped, but the heating was continued. After a few minutes (up to 30 min) with clear solution, the liquid turned cloudy and a white precipitate began to deposit. The heating was maintained for another 5 min before being stopped. During the cooling and the storing at room temperature, the precipitation continued. The reaction vessel was kept untouched until the precipitate was well separated from the H₂SO₄ mother liquor. The liquid phase was removed by decantation, the precipitate was transferred to a beaker containing ca. 100 ml of glacial acetic acid, stirred for 10 min, filtered off, washed with acetic acid, acetone, diethyl ether and dried in a desiccator.

All samples were characterized by powder X-ray diffraction (PXD) using Guinier–Hägg cameras, Cr Kα, or Cu Kα, radiation and Si as internal standard. High-temperature PXD data were collected with a Guinier–Simon camera (Enraf–Nonius) between 20 and 500°C at a heating rate of 25°C h⁻¹. The samples were contained in open silica-glass capillaries. The positions of the Bragg reflections were obtained from the films by means of a Nicolet L18 scanner using the SCAPNI program system. The diffraction pattern of TiOSO₄ was indexed with the help of the TREOR program. Unit-cell dimensions were obtained from least-squares refinements using the CELLKANT program.

PXD intensity data for the crystal structure determination and/or refinements of TiOSO₄ and TiOSO₄·H₂O were collected with a Siemens D500 diffractometer, using monochromatic Cu Kα radiation. The data were recorded in steps of 0.02° in 2θ between 10 and 110°, and the counting time for each setting was 30 s; flat plate in reflection mode geometry (Bragg–Brentano), 1 and 1° slits in front of the sample, 1 and 0.18° in front of the scintillation counter. The fine powders were pressed into a standard sample holder. In addition, powder neutron diffraction data for TiOSO₄ were collected with the OPUS III two-axis diffractometer at the JEEP II reactor, Kjeller. Data corrections, deconvolution, structure determination and profile refinements were performed with the ALLHKL, SIPOW and DBW3.2S programs.

Differential scanning calorimetry (DSC) measurements were made between 20 and 600°C with a Mettler TA 3000 system. Open Al₂O₃ crucibles were used for the 15–25 mg samples, nitrogen was used as atmosphere and the heating/cooling rate was 5–10°C min⁻¹. Thermogravimetric (TG) and differential thermal (DTA) analyses were performed between 20 and 1000°C with a Perkin Elmer TGA 7 and 7TA 7 system, respectively. The 15–25 mg samples were placed in Al₂O₃ crucibles, nitrogen was used as an atmosphere and the heating rate was 10°C min⁻¹.

Results and discussion

(i) Synthesis of TiOSO₄ and TiOSO₄·H₂O. The progressing reactions between TiO₂-a/r, TiO₂·xH₂O-am or Fe-TiO₂ and 65–95 wt % H₂SO₄ are evidenced by the dissolution of the solids and the colouring of the liquid phase. No detectable reaction was found for any of the solid reactants in 60 wt % H₂SO₄. The fact that two-phase mixtures of TiOSO₄ and TiOSO₄·H₂O are obtained in the intermediate concentration range around 75 wt % H₂SO₄ (Table 1) is attributed to kinetics. In line with the polymeric nature of the Ti–O framework in TiOSO₄ and TiOSO₄·H₂O (see ii), these compounds are very difficult to redissolve in H₂SO₄ once they are formed.

As seen from Table 1, TiOSO₄ and TiOSO₄·H₂O are the only solid compounds obtained from TiO₂-a/r and TiO₂·xH₂O-am in 65–95 wt % H₂SO₄. Hence, the exist-

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<table>
<thead>
<tr>
<th>TiO₂ reactant</th>
<th>TiOSO₄·H₂O → Two-phase → TiOSO₄</th>
</tr>
</thead>
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<tr>
<td>TiO₂-a/r</td>
<td>TiOSO₄·H₂O → Two-phase → TiOSO₄</td>
</tr>
<tr>
<td>TiO₂·xH₂O-am</td>
<td>TiOSO₄·H₂O → Two-phase → TiOSO₄</td>
</tr>
<tr>
<td>FeTiO₃</td>
<td>TiOSO₄·H₂O → Two-phase → TiOSO₄</td>
</tr>
</tbody>
</table>

Table 1. Products resulting from the reaction of TiO₂-a/r, TiO₂·xH₂O-am or FeTiO₃ (limonite) with 60–95 wt % H₂SO₄. Yields for TiO₂-a/r series are 85–95% of the calculated amount and for TiO₂·xH₂O-am series some 30%, whereas yields are not determined for FeTiO₃ series.

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* No reaction. † Mixture of TiOSO₄ and TiOSO₄·H₂O. ‡ Not tested. § Unidentified products. ¶ Also for 84 wt %.
ence of TiOSO₄·2H₂O claimed in Refs. 2, 3 and 5 could not be confirmed by our method. The findings concur, on the other hand, with Refs. 4, 6 and 7. The yields of the syntheses are very good (85–95% of the calculated amount) when TiO₂·a/r is used as reagent, but decrease generally with decreasing concentration of sulfuric acid. With TiO₂·xH₂O-am as reactant, the yields become much poorer (some 30%).

TiOSO₄ and TiOSO₄·H₂O were characterized by PXD (see Refs. 4 and 6 and Section ii). Their compositions were verified by quantitative chemical analysis (S determined as BaSO₄; for TiOSO₄, obs. 20.5% S, calc. 20.0% S; for TiOSO₄·H₂O, see Ref. 4), from the crystal structure determinations (see Ref. 4 and Section ii) and from TG measurements (see Section iv).

The course of the reaction between TiO₂·a/r and H₂SO₄ has certain features (a period with a clear, light-yellow coloured solution followed by rapid precipitation of the polymerized product in common with that between Bi₂O₃·H₂O and H₂SO₄). This leads us to postulate a three-step reaction mechanism:

\[
\text{TiO}_2(s) + H_2SO_4 \rightarrow TiO^{2+} \text{(solv)} + SO_4^{2-} \text{(solv)} + H_2O \text{(solv)}
\]  
(1)

followed by the polymerization:

\[
nTiO^{2+} \text{(solv)} \rightarrow (TiO)_n^{2n+} \text{(solv)}
\]  
(2)

and finally the precipitation:

\[
(TiO)^{2n+} \text{(solv)} + nSO_4^{2-} \text{(solv)} \rightarrow n \text{TiOSO}_4(s)
\]  
(3)

The reaction with FeTiO₃ proceeds almost certainly quite similarly; however, the presence of the iron component prevents ascertainment of the colouring of the solution resulting from step (1). A very dark colouring is a distinguishing mark when TiO₂·xH₂O-am rather than TiO₂·a/r is used as reactant in combination with the most concentrated sulfuric acid solutions studied (black for 95 wt% H₂SO₄; virtually colourless at 70 wt% H₂SO₄). The essential difference between TiO₂·xH₂O-am and TiO₂·a/r (and FeTiO₃) is the amorphous state of the former. The amount of water introduced from TiO₂·xH₂O-am is considered too small to play a major role. On this basis we suggest that the dark colour represents intermediated sized (TiO)ₙ²⁺ (solv) species, say, with n of the order of 10 and with different configurations of the ...Ti–O... chains than when formed according to the steps (1) and (2).

When TiOSO₄ and TiOSO₄·H₂O are treated with cold or hot 60–95 wt% H₂SO₄, H₂O or 1 M NH₃ for a short period of time, no or very limited solubility is observed, and water may in fact be used as washing agent. Similar behaviour is observed for cold 1 M HCl and 1 M H₂SO₄, whereas both compounds are readily dissolved when treated with hot, diluted acids.

When TiOSO₄ and TiOSO₄·H₂O are kept in contact with H₂O at room temperature for a prolonged time, the solubility proves to be more appreciable, with a saturation value of ca. 1 g dissolved in 100 ml H₂O after one week with intermediate stirrings. The thus obtained diluted aqueous solutions of TiOSO₄ are colourless, but on gradual evaporation the colour turns yellowish and finally a distinctly yellow, transparent, glassy material is obtained. The crushed, off-white powder obtained from the glassy material appears X-ray amorphous. On heating the yellowish glassy material at 150°C, it turns into a nearly black glassy material. Probably the colour change is introduced by the changed disorder consequent on removal of included water. At first sight it is surprising that the undissolved, major remains after TiOSO₄ and TiOSO₄·H₂O (white powders) are also converted into amorphous materials after prolonged contact with water. However, the complete conversion of the bulk phase is merely a consequence of the equilibrium situation between dissolved and undissolved titanium oxide sulfates. The converted bulk product shows no colour change on heating.

On heating (see also Section iv), the amorphous products, here termed TiOSO₄·xH₂O-am, gradually give off included and crystal water, and at some 350°C (according to fixed temperature experiments, not observed by DSC) a major dehydration occurs together with crystalization of TiOSO₄.

(ii) Crystal structure determination and refinements. The crystal structure of TiOSO₄ was solved from scratch on the basis of PXD data. (The combined single crystal and PXD determination of unit-cell dimensions and probable space group for TiOSO₄ was pointed out to us by one of the referees. However, both the unit-cell dimensions and the indexing in Ref. 6 are slightly, yet significantly, incorrect.)

Data from Guinier photographs were subjected to trial-and-error indexing by the TREOR program.¹⁹ This gave an orthorhombic unit cell with the dimensions a = 1095.3(3), b = 515.2(1) and c = 642.6(1) pm [V = 362.6(2) x 10⁶ pm³; all 32 reflections indexed; figure of merit¹⁵ M(20) = 21].

The (probable) systematic extinctions in the PXD data, 0kl absent when k + l = 2n + 1 and hkl absent when h = 2n + 1, leaves a choice between the space groups Pnma and Pn2₁a. Both space groups were tested out during the structure refinements, see below. The observed density, 2.89 ± 0.04 g cm⁻³ at 25.00 ± 0.01°C, shows that the unit-cell content is four (Z_{obs} = 3.95) TiOSO₄ formula units.

The observed PXD profiles (Fig. 1) were deconvoluted by means of the ALLHKL program, and the obtained set of F_{obs}² was, together with unit-cell dimensions, space group and unit-cell content used as input parameters for the direct methods program SIRPOW.¹³ This treatment gave a proposal for the crystal structure of TiOSO₄ with very reasonable coordinates for titanium and sulfur, but with various possible locations for the four non-equiva-
dent oxygen atoms. At this stage, the observed PXD pattern was subjected to Rietveld analysis by the program DBW3.2S\textsuperscript{14} with parameters for the trial structure, the scale factor, the counter zero point and the half-width parameters (pseudo-Voigt function) as variables. From variation of occupation numbers, the correct choice for the location of oxygen atoms was settled, and the structure determination was continued with regular least squares Rietveld refinements (246–257 reflections, 4000–5000 data points, 27 variables). At this stage, bond valence\textsuperscript{16} calculations (see Section iii) suggested that certain details were not completely resolved. For this reason, PND data were collected and refined, but without providing more satisfactory bond valence data (for both Ti and S).

Four means to modify the data analyses were tried in order to identify possible sources for the non-satisfactory results; taking the possibility of preferred orientation into account, removal of the (small) low-angle part of the PXD diagram with very strong reflections, turning to anisotropic description of the atoms with the largest temperature factors, and refinements in the non-centrosymmetric space group \textit{Pn}2\textsubscript{1}a (No. 33). In accordance with the fact that the samples of TiOSO\textsubscript{4} and TiOSO\textsubscript{4}·H\textsubscript{2}O were agglomerates of very small particles, introduction of preferred orientation parameters had no significant effects on the refinements. Excluding the region 10–30° in 2θ (i.e. shutting out 11 reflections; Fig. 1) gave minor improvements. Turning to an anisotropic temperature factor description for the atoms O(1) and O(4), which could simulate disorder for these atoms, gave hardly any significant improvement in terms of reliability factors, but gave atomic coordinates which in turn resulted in somewhat more reasonable bond valences (see Section iii). For the refinements according to the non-centrosymmetric space group \textit{Pn}2\textsubscript{1}a, the O(1) atoms, which occupy an eight-fold position according to \textit{Pnma}, were split in two four-fold positions, whereas all other parameters were constrained at the values prescribed by \textit{Pnma}. As a next step, the γ-parameters were entered as variables (γ\textsubscript{1}, fixed at 0.25). However, the improvements in the reliability factors were not significant, and hence \textit{Pn}2\textsubscript{1}a hardly provides any better description of the structure than \textit{Pnma}. The observed and difference (observed – calculated) plots for the PXD profiles in Fig. 1 leave no doubt that the main features are well described according to the higher symmetric space group. The resulting final values for the positional parameters according to \textit{Pnma} are listed in Table 2. On the other hand, the use of anisotropic temperature factor descriptions for O(1) and O(4) gave large B\textsubscript{12} components which may indicate that the true symmetry is lower than concluded here (see also Ref. 6).

Although the crystal structure of TiOSO\textsubscript{4}·H\textsubscript{2}O reported in Ref. 4 appears to be correct to a large extent, it needs refinement for three reasons. First, there is a space group ambiguity in that Ref. 4 claims that the real symmetry is \textit{P2}\textsubscript{1}2\textsubscript{1}2\textsubscript{1}, yet the refinements are performed according to \textit{Pnma}. Second, the refinements in Ref. 4 kept some of the variable oxygen parameters effectively fixed. Third, the large scatter in the S–O distances (124–157 pm) and the improbable Ti and S valences which follow from the Ti–O and S–O distances are in themselves good reasons for renewed refinements.

The present refinements of the TiOSO\textsubscript{4}·H\textsubscript{2}O structure were carried out for PXD data collected for a sample synthesized from TiO\textsubscript{2}·H\textsubscript{2}O-am and 65 wt\% H\textsubscript{2}SO\textsubscript{4} (Section i). The obtained unit-cell data a = 982.8(1), b = 513.4(1), c = 861.3(1) pm and V = 434.6(2) × 10\textsuperscript{6} pm\textsuperscript{3} are in fair agreement with results presented in Ref. 4. The refinements were carried out as described for TiOSO\textsubscript{4} (297–309 reflections, 4000–5000 data points; 30–34 variables). For TiOSO\textsubscript{4}·H\textsubscript{2}O, the removal of the region 10–30° in 2θ reduced R\textsubscript{wp} from 14.8 to 10.8. Also for TiOSO\textsubscript{4}·H\textsubscript{2}O, problems with unexpected large deviations

Table 2. Positional parameters and temperature factors with calculated standard deviations in parentheses for the crystal structure of TiOSO\textsubscript{4} as derived form PXD data [space group \textit{Pnma}, 246 reflections, R\textsubscript{R} = 6.72, R\textsubscript{wp} = 8.66, goodness of fit, GOF = 1.72; see text concerning anisotropic temperature factor description for O(1) and O(4)].

<table>
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<tr>
<th>Atom</th>
<th>Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B\textsubscript{11}/10\textsuperscript{4} pm\textsuperscript{2}</th>
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<tr>
<td>S</td>
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<td>1/4</td>
<td>0.4778(7)</td>
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<tr>
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<td>0.6709(17)</td>
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Table 3. Positional parameters with calculated standard deviations in parentheses for the crystal structure of TiOSO$_4$·H$_2$O as derived from PXD data (space group Pnma, 300 reflections, $R_s=7.74$, $R_{ave}=10.60$, goodness of fit, $GOF=2.41$; see text concerning anisotropic temperature factor description for O(1) and O(4); $B_{an}=0.4-0.6 \times 10^4$ pm$^2$ for Ti and S, $0.5-1.5 \times 10^4$ pm$^2$ for O). Corresponding values from Ref. 4 are included (below) for comparison. Numbering of atoms follows Ref. 4.

<table>
<thead>
<tr>
<th>Atom</th>
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<td></td>
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<td>0.5064(16)</td>
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<td>0.572</td>
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in calculated valences were found (Section iii). More satisfactory distances were achieved by adopting anisotropic temperature factors for O(1) and O(4) (viz. compensating some kind of structural disorder or symmetry reduction by giving large $B_{2}$ and $B_{11}$ components, respectively). Slight such improvements were further achieved for refinements according to the non-centrosymmetric space group Pn$\bar{2}a$ where the eight-fold position is split up in two four-fold positions. Introduction of more free variables (e.g. $\gamma$-parameters according to Pn$\bar{2}a$ or P2$_1$/a, as suggested by Lundgren) was considered meaningless on the basis of the quality of the present data. In summary, it is concluded that the most correct picture is presently achieved by adopting Pnma and an anisotropic temperature factor description for O(1) and O(4) (Table 3). Attention should be drawn to the fact that the reaction mechanism (Section i) which rules the syntheses of these compounds makes it quite likely that there exists some disorder between sulfate groups in TiOSO$_4$ as well as between sulfate and/or water groups in TiOSO$_4$·H$_2$O.

(iii) A closer look at the crystal structures of TiOSO$_4$ and TiOSO$_4$·H$_2$O. Relevant interatomic distances in the crystal structures of TiOSO$_4$ and TiOSO$_4$·H$_2$O are listed in Table 4, and projections and perspective views of the structures are shown in Fig. 2. The infinite ...Ti-O-... zigzag chains, which are very distinctive features of both structures, run horizontally (along $\delta$) in the projections. The interchain Ti-O distances are about of equal length, 179 pm in TiOSO$_4$ versus 182 pm TiOSO$_4$·H$_2$O. These distances are notably very short compared with the expected value for a normal Ti-O bond (around 195 pm). The structures contain slightly distorted tetrahedral SO$_4$ groups (S-O distances of 144-150 pm in TiOSO$_4$ and 148-150 pm in TiOSO$_4$·H$_2$O) as can easily be recognized in Fig. 2. In TiOSO$_4$ the oxygen atoms of the SO$_4$ groups are connected to four different titanium atoms at distances of 188-201 pm. In TiOSO$_4$·H$_2$O only three of the oxygen atoms of the SO$_4$ group are bonded to titanium atoms at distances of 198-203 pm. The fourth oxygen atom of the SO$_4$ group, O(2), is directed towards the open channel where the water molecules are found (Fig. 2D). In this channel, the six oxygen-oxygen distances between the oxygen of the water molecule and surrounding oxygens [O(1), O(2) and O(4)] are around 270-290 pm, which are in the typical range for O···H–O hydrogen bonds in hydrates.

The details of the actual structures (Fig. 2) tend to blur the essential differences between TiOSO$_4$ and TiOSO$_4$·H$_2$O. Therefore, simplified and idealized projective representations of the two structures are given in Fig. 3, which immediately focuses the attention on the different arrangement of the ...-Ti-O-... chains. In TiOSO$_4$ (Fig. 3A) the chains run completely parallel, whereas they are related by mirror imaging in TiOSO$_4$·H$_2$O (Fig. 3B; the relation may alternatively be described as displacement along the chain direction between successive chains). The different ways of joining the SO$_4$ groups to the two ...-Ti-O-... chains is a result of the different chain arrangements and the incorporated crystal water in TiOSO$_4$·H$_2$O.

Despite the close structural relationship between TiOSO$_4$ and TiOSO$_4$·H$_2$O, the structural changes which are involved in converting one into the other of these compounds must be classified as major. The removal of crystal water from TiOSO$_4$·H$_2$O is easily accomplished through thermal decomposition (onset at ca. 340°C, Section iv), but the rather rough treatment introduces additional disorder which causes the obtained TiOSO$_4$ product to perform somewhat differently from that prepared by direct synthesis. Hydration of TiOSO$_4$ is on the other hand impossible at normal conditions (inter alia long-range refluxing in boiling 65 wt% H$_2$SO$_4$). The only path from TiOSO$_4$ to TiOSO$_4$·H$_2$O appears to go via decomposition of the former into TiO$_2$-H$_2$O (or conversion into TiO$_2$·H$_2$O-am) and completely repeated synthesis in 65-75 wt% H$_2$SO$_4$ (Section i). The reluctance to allow H$_2$O to enter the TiOSO$_4$ structure directly is understandable on the basis of the required structural rearrangements.

Figure 3 also serves to bring out structural relationships between TiOSO$_4$, TiOSO$_4$·H$_2$O and (IO)$_2$SO$_4$ (see Refs. 17 and 18). The dominating feature of the three structures are ...X-O-... zigzag chains. The different connections of the SO$_4$ groups to the chains may be regarded as reflections of the chemical formulae (or vice versa), but notably, iodine is four-coordinated whereas titanium in six-coordinated. The differences in bonding situation and crystal structure are manifest in strikingly different reactivity with water. (IO)$_2$SO$_4$ undergoes rapid hydrolysis into I$_2$O when exposed to moisture, whereas TiOSO$_4$ and TiOSO$_4$·H$_2$O are much more water resis-
Fig. 2. The crystal structure of (A) TiOSO$_4$ and (B) TiOSO$_4\cdot$H$_2$O projected along [001] and [100], respectively, and in perspective views along [010] for (C) TiOSO$_4$ and (D) TiOSO$_4\cdot$H$_2$O. The numbering of crystallographic non-equivalent atoms is shown on the illustrations. Oxygen [O(5)] of the crystal water in B and D are marked by larger circles, hydrogen positions are not determined.

tant (Section i). The sulfates are only the first examples of a large class of compounds comprised of ...,O..., zigzag chains. Representatives are further found among main group metalloids (e.g. Bi and Te), transition metals (e.g. V), and furthermore, the SO$_4$ may be exchanged by other anionic groups (e.g. SeO$_4$ etc.). Compounds like KTiOPO$_4$ and CsTiOAsO$_4$ also have some features in common with the titanium oxide sulfates. Their structures comprise tetrahedral PO$_4$ and AsO$_4$ groups, and the titanium atoms are connected in ...,Ti-,O..., chains with
short Ti–O distances (171.6–173.3 pm for KTiOPO$_4$). KTiOPO$_4$ and CsTiOAsO$_4$ have very interesting non-linear optical properties rooted in their non-centrosymmetric crystal structures (space group $Pna_2_1$). The optical properties of TiOSO$_4$ and TiOSO$_4$·H$_2$O are not known, but in view of the space group ambiguities discussed above, they are certainly candidates for an examination.

It may be instructive to calculate bond valencies ($V_j$) from the observed distances ($d_{ij}$/100 pm; Table 4) according to the expression:$$V_j = \sum \exp \left(\frac{(D_{ij} - d_j)/b}{b}\right)$$

where $D_{ij}$ is the bond-valence parameter for the particular bond concerned and $b = 0.37$. For Ti$^{IV}$–O and S$^{VI}$–O bonds, Ref. 16 lists $D_{ij} = 1.815$ and 1.624, respectively. The calculations gave $V_{Ti-O} = 4.89$ and $V_{S-O} = 6.06$ for TiOSO$_4$ and $V_{Ti-O} = 4.43$ and $V_{S-O} = 5.75$ for TiOSO$_4$·H$_2$O, values which deviate unsatisfactorily much from the expected values of 4 and 6, respectively. The significant discrepancies may either reflect crystal disorder or lower symmetry than used during the refinements (see Refs. 4 and 6).

(iv) Effects of heat treatment on TiOSO$_4$ and TiOSO$_4$·H$_2$O.

Lundgren made use of the two-step decomposition of TiOSO$_4$·H$_2$O to analyse its composition. In the present study, TG, DTG and DTA have been utilized more systematically to explore the effects of heat treatment on TiOSO$_4$ and TiOSO$_4$·H$_2$O.

TiOSO$_4$ represents the simplest case. When single phase, carefully washed and dried TiOSO$_4$ is subjected to TG, a one-step thermal decomposition occurs:

$$\text{TiOSO}_4(s) \rightarrow \text{TiO}_2(s) + \text{SO}_3(g) \quad (4)$$

(Fig. 4A; onset at 525°C, maximum at ca. 675°C and completion at ca. 720°C for 10°C min$^{-1}$ heating rate and N$_2$ atmosphere). The observed, relative weight loss, $\Delta m/m_0 = 0.4988$, is in excellent agreement with the calculated value (0.5005) according to eqn. (4). Careful washing and drying is required to achieve such an excellent result, and TG is actually a valuable technique to design optimum conditions for the drying procedure. The final, solid product is TiO$_2$·a.

Inspection of the DTA curve for TiOSO$_4$ reveals a small, endothermic peak at 320–420°C which has no counterpart in TG. This is caused by a structural phase transition. When heating a TiOSO$_4$ sample at ca. 350°C, the colour turns light lemon yellow, whereas it reverts to white on cooling. This appears to be an effect of the phase transition, and is probably related to charge-transfer ex-
Fig. 4. TG, DTG and DTA data for (A) TiOSO$_4$, (B) TiOSO$_4$·H$_2$O and (C) TiOSO$_4$·xH$_2$O. The DTA scans are adjusted to constant background signal.

Fig. 5. Variation of unit-cell dimensions with temperature for TiOSO$_4$. Transition TiOSO$_4$(II) $\rightarrow$ TiOSO$_4$(III) at 350±10°C, decomposition of TiOSO$_4$(II) at 500±20°C. Thermal expansion coefficients 20–250°C (in 10$^{-5}$ K$^{-1}$): $\alpha_a$=2.4, $\alpha_b$=2.0, $\alpha_c$=2.3, $\gamma$=7.8. [Thermal expansion coefficients for TiOSO$_4$·H$_2$O at 20–250°C (in 10$^{-5}$ K$^{-1}$): $\alpha_a$=4.8, $\alpha_b$=1.9, $\alpha_c$=0.0, $\gamma$=6.6.]

nor. However, the distinct line splitting for TiOSO$_4$(II) clearly proves that the symmetry changes from orthorhombic to monoclinic on heating, which is somewhat surprising for a temperature-induced transition.

TG, DTG and DTA data for a good quality (requires cautious washing and drying) sample of TiOSO$_4$·H$_2$O are shown in Fig. 4B. In comparison to TiOSO$_4$, the monohydrate undergoes the additional decomposition:

\[
\text{TiOSO}_4\cdot\text{H}_2\text{O}(s) \rightarrow \text{TiOSO}_4(s) + \text{H}_2\text{O}(g)
\]  
(6)

(onset at ca. 310°C, maximum at ca. 400°C and completion at ca. 485°C for 10°C min$^{-1}$ heating rate and N$_2$ atmosphere). The observed relative weight loss, $\Delta m/m_0 = 0.0997$, is in good agreement with 0.1012 as calculated for the dehydratization reaction (6). The dehydratization of TiOSO$_4$·H$_2$O takes place in the same temperature interval as the phase transition (5) in the anhydrate. Although the overall, observed relative weight
loss \((\Delta m/m_0 = 0.4982)\) for the subsequent decomposition of \(\text{TiOSO}_4\) formed according to reaction (5) into \(\text{TiO}_2\)-a composites with reaction (4), some essential details differ. First, the onset and completion temperatures in Fig. 4B are lowered by some 40°C compared with Fig. 4A. Second, and more remarkable, is to find that reaction (4) is composed of two steps in Fig. 4B. The characteristic features of one and two steps decompositions in TG, DTG and DTA were found for all synthesized samples of \(\text{TiOSO}_4\) and \(\text{TiOSO}_4\cdot\text{H}_2\text{O}\).

The composite character of the \(\text{TiOSO}_4\) to \(\text{TiO}_2\)-a reaction in Fig. 4B shows striking resemblance with corresponding recordings for \(\text{CuSO}_4\cdot5\text{H}_2\text{O}\), where the terminal step from \(\text{CuSO}_4\) to \(\text{Cu}_2\text{O}\) also occurs in two stages.\(^{21}\) By careful regulation of the decomposition temperature, the intermediate \(\text{Cu}_2\text{OSO}_4\) could be successfully isolated.\(^{21}\) Inspired by Ref. 21, the TG apparatus was used in an attempt to perform analogous partial decomposition of \(\text{TiOSO}_4\) [formed according to reaction (6)] at 520°C. However, despite numerous attempts, these experiments have so far not been successful.

TG, DTG and DTA data for \(\text{TiOSO}_4\cdot\text{H}_2\text{O}-\text{am}\) are presented in Fig. 4C. The results are chosen for a sample which with luck in washing and drying gave a total weight loss \((\text{TiOSO}_4\cdot\text{H}_2\text{O to TiO}_2-t)\) well on the way to matching that in Fig. 4B. Although Figs. 4B and C have features in common, the details differ. \(\text{TiOSO}_4\cdot\text{H}_2\text{O}-\text{am}\) starts to loose weight (water) already below 100°C, and the dehydratization [the analogogue of reaction (6)] goes more or less continuously into the liberation of \(\text{SO}_3\) according to reaction (4). The distinct features in Fig. 4B are hence more smeared out in Fig. 4C. The lack of distinct thermoanalytical responses are just as expected when amorphous phases are involved, as is also the observation of a certain degree of irreproducibility between experiments on different samples of \(\text{TiOSO}_4\cdot\text{H}_2\text{O}-\text{am}\).

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