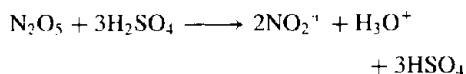
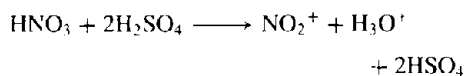


(d) Dehydration reactions:

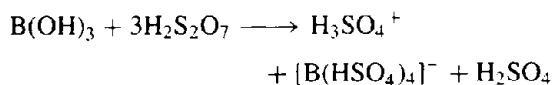


The reaction with  $\text{HNO}_3$  is quantitative, and the presence of large concentrations of the nitronium ion,  $\text{NO}_2^+$ , in solutions of  $\text{HNO}_3$ ,  $\text{MNO}_3$  and  $\text{N}_2\text{O}_5$  in  $\text{H}_2\text{SO}_4$  enable a detailed interpretation to be given of the nitration of aromatic hydrocarbons by these solutions.

Because of the high acidity of  $\text{H}_2\text{SO}_4$  itself, bases form the largest class of electrolytes and only few acids (proton donors) are known in this solvent system. As noted above,  $\text{H}_2\text{S}_2\text{O}_7$  acts as a proton donor to  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_3\text{F}$  is also a weak acid:



One of the few strong acids is tetra(hydrogen sulfato)boric acid  $\text{B}(\text{HSO}_4)_4$ ; solutions of this can be obtained by dissolving boric acid in oleum:



Other strong acids are  $\text{H}_2\text{Sn}(\text{HSO}_4)_6$  and  $\text{H}_2\text{Pb}(\text{HSO}_4)_6$ .

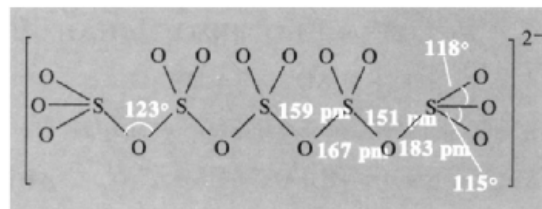
Sulfuric acid forms salts (sulfates and hydrogen sulfates) with many metals. These are frequently very stable and, indeed, they are the most important mineral compounds of several of the more electropositive elements. They have been discussed in detail under the appropriate elements. Sulfates can be prepared by:

- dissolution of metals in aqueous  $\text{H}_2\text{SO}_4$  (e.g. Fe);
- neutralization of aqueous  $\text{H}_2\text{SO}_4$  with metal oxides or hydroxides (e.g.  $\text{MOH}$ );
- decomposition of salts of volatile acids (e.g. carbonates) with aqueous  $\text{H}_2\text{SO}_4$ ;

- metathesis between a soluble sulfate and a soluble salt of the metal whose (insoluble) sulfate is required (e.g.  $\text{BaSO}_4$ );
- oxidation of metal sulfides or sulfites.

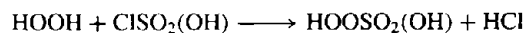
The sulfate ion is tetrahedral ( $\text{S}-\text{O}$  149 pm) and can act as a monodentate, bidentate (chelating) or bridging ligand. Examples are in Fig. 15.29. Vibrational spectroscopy is a useful diagnostic, as the progressive reduction in local symmetry of the  $\text{SO}_4$  group from  $T_d$  to  $C_{3v}$  and eventually  $C_{2v}$  increases the number of infrared active modes from 2 to 6 and 8 respectively, and the number of Raman active modes from 4 to 6 and 9.<sup>(193)</sup> (The effects of crystal symmetry and the overlapping of bands complicates the analysis but correct assignments are frequently still possible.)

Pairs of corner-shared  $\text{SO}_4$  tetrahedra are found in the disulfates,  $\text{S}_2\text{O}_7^{2-}$  ( $\text{S}-\text{O}_\mu-\text{S}$  124°,  $\text{S}-\text{O}_\mu$  164.5 pm,  $\text{S}-\text{O}_t$  144 pm); they are made by thermal dehydration of  $\text{MHSO}_4$ . Likewise the trisulfate ion  $\text{S}_3\text{O}_{10}^{2-}$  is known and also the pentasulfate ion,  $\text{S}_5\text{O}_{16}^{2-}$  whose structure indicates an alternation of  $\text{S}-\text{O}$  interatomic distances and very long  $\text{O}-\text{S}$  distances to the almost planar terminal  $\text{SO}_3$  groups:

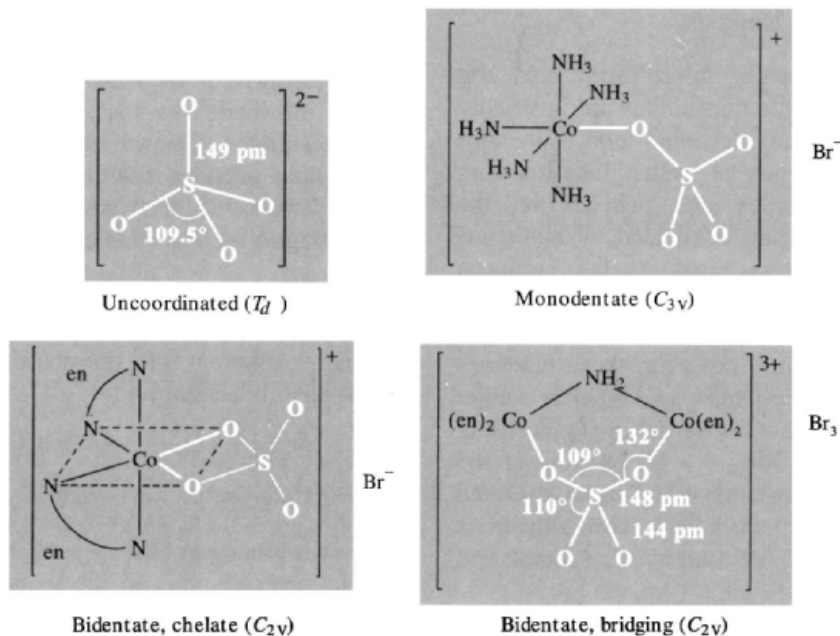


### Peroxosulfuric acids, $\text{H}_2\text{SO}_5$ and $\text{H}_2\text{S}_2\text{O}_8$

Anhydrous peroxomonosulfuric acid (Caro's acid) can be prepared by reacting chlorosulfuric acid with anhydrous  $\text{H}_2\text{O}_2$



<sup>193</sup> K. NAKAMOTO, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd edn., Wiley, New York, 1970, 338 pp. (See also *J. Am. Chem. Soc.* **79**, 4904-8 (1957) for detailed correlation table.)



**Figure 15.29** Examples of  $\text{SO}_4^{2-}$  as a ligand.

It is colourless, beautifully crystalline, and melts at  $45^\circ$ , but should be handled carefully because of the danger of explosions. It can also be made by the action of conc  $\text{H}_2\text{SO}_4$  on peroxydisulfates and is formed as a byproduct during the preparation of  $\text{H}_2\text{S}_2\text{O}_8$  by electrolysis of aqueous  $\text{H}_2\text{SO}_4$  (N. Caro, 1898). Its salts, which are preferably called trioxoperoxosulfates(2-) rather than peroxomonosulfates,<sup>(194)</sup> are unstable and the compound has few uses except those dependent on the formation of the  $\text{H}_2\text{O}_2$  during its decomposition. The structure of the anion  $[\text{HOOSO}_3]^-$ , which is the active principle of Caro's acid, has been determined by X-ray analysis of the hydrated salt  $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ ; selected dimensions are O-O 140.0, S-O<sub>2</sub> 163.2, S-O<sub>1</sub> 143.5–144.4 pm, angle OOS  $109.4^\circ$ .<sup>(195)</sup>

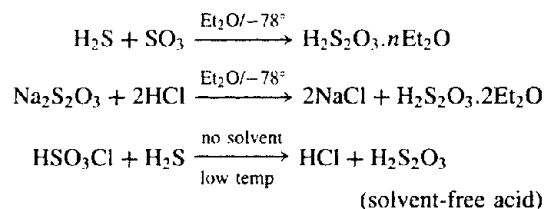
Peroxydisulfuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , is a colourless solid mp  $65^\circ$  (with decomposition). The acid is soluble in water in all proportions and its most important salts,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{K}_2\text{S}_2\text{O}_8$ , are also freely soluble. These salts are, in fact, easier to prepare than the acid and both are made on an industrial scale by anodic oxidation of the corresponding sulfates under carefully controlled conditions (high current density,  $T < 30^\circ$ , bright Pt electrodes, protected cathode). The structure of the peroxydisulfate ion [now preferably called hexaoxo- $\mu$ -peroxydisulfate(2-)]<sup>(194)</sup> is  $\text{O}_3\text{SOOSO}_3^{2-}$  with O-O 131 pm and S-O 150 pm. The compounds are used as oxidizing and bleaching agents. Thus, as can be seen from Table 15.19, the standard reduction potential  $\text{S}_2\text{O}_8^{2-}/\text{HSO}_4^-$  is 2.123 V, and  $E^\circ(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-})$  is similar (2.010 V); these are more positive than for any other aqueous couples except  $\text{H}_2\text{N}_2\text{O}_2$ ,  $2\text{H}^+/\text{N}_2$ ,  $2\text{H}_2\text{O}$  (2.85 V),  $\text{F}_2/2\text{F}^-$  (2.87 V) and  $\text{F}_2, 2\text{H}^+/2\text{HF}(\text{aq})$  (3.06) — see also  $\text{O}(\text{g})$ ,  $2\text{H}^+/\text{H}_2\text{O}$  (2.42 V),  $\text{OH}, \text{H}^+/\text{H}_2\text{O}$  (2.8 V).

<sup>194</sup> G. J. LEIGH (ed.), *Nomenclature of Inorganic Chemistry* (The IUPAC 'Red Book'), Blackwell Scientific Publications, Oxford, 1990, pp. 268, 269.

<sup>195</sup> J. FLANAGAN, W. P. GRIFFITH and A. C. SKAPSKI, *J. Chem. Soc., Chem. Commun.*, 1574–5 (1984).

### Thiosulfuric acid, H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

Attempts to prepare thiosulfuric acid by acidification of stable thiosulfates are invariably thwarted by the ready decomposition of the free acid in the presence of water. The reaction is extremely complex and depends on the conditions used, being dominated by numerous redox interconversions amongst the products: these can include sulfur (partly as *cyclo-S*<sub>6</sub>), SO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>S<sub>n</sub>, H<sub>2</sub>SO<sub>4</sub> and various polythionates. In the absence of water, however, these reactions are avoided and the parent acid is more stable: it decomposes quantitatively below 0° according to the reaction H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> → H<sub>2</sub>S + SO<sub>3</sub> (cf. the analogous decomposition of H<sub>2</sub>SO<sub>4</sub> to H<sub>2</sub>O and SO<sub>3</sub> above its bp ~300°). Successful anhydrous syntheses have been devised by M. Schmidt and his group (1959–61), e.g.:

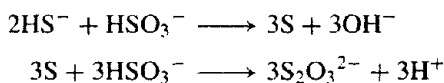


Combination of stoichiometric amounts of H<sub>2</sub>S and SO<sub>3</sub> at low temperature yields the white crystalline adduct H<sub>2</sub>S.SO<sub>3</sub> which is isomeric with thiosulfuric acid.

In contrast to the free acid, stable thiosulfate salts can readily be prepared by reaction of H<sub>2</sub>S on aqueous solutions of sulfites:

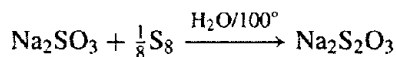


The reaction appears to proceed first by the formation of elemental sulfur which then equilibrates with more HSO<sub>3</sub><sup>-</sup> to form the product.<sup>(196)</sup>

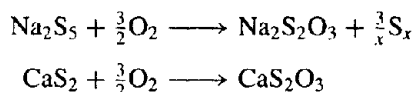


<sup>196</sup> G. W. HEUNISH, *Inorg. Chem.* **16**, 1411–13 (1979) and references therein.

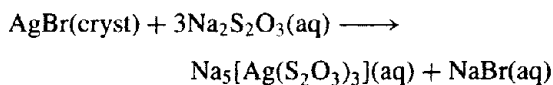
Consistent with this, experiments using HS<sup>-</sup> labelled with radioactive <sup>35</sup>S (p. 661) show that acid hydrolysis of the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> produces elemental sulfur in which two-thirds of the <sup>35</sup>S activity is concentrated. Thiosulfates can also be made by boiling aqueous solutions of metal sulfites (or hydrogen sulfites) with elemental sulfur according to the stoichiometry



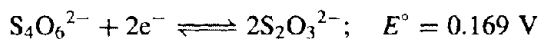
Aerial oxidation of polysulfides offers an alternative industrial route:



The thiosulfate ion closely resembles the SO<sub>4</sub><sup>2-</sup> ion in structure and can act as monodentate η<sup>1</sup>-S ligand, a monhapto bidentate bridging ligand (μ,η<sup>1</sup>-S), or a dihapto chelating η<sup>2</sup>-S,O ligand as illustrated in Fig. 15.30.<sup>(197)</sup> Hydrated sodium thiosulfate Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O (“hypo”) forms large, colourless, transparent crystals, mp 48.5°; it is readily soluble in water and is used as a “fixer” in photography to dissolve unreacted AgBr from the emulsion by complexation:



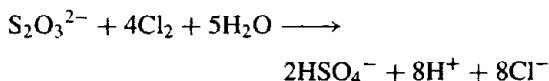
The thiosulfate ion is a moderately strong reducing agent as indicated by the couple



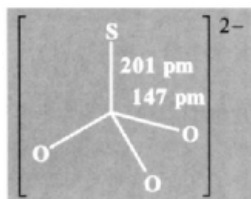
Thus the quantitative oxidation of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> by I<sub>2</sub> to form tetrathionate and iodide is the basis for the iodometric titrations in volumetric analysis



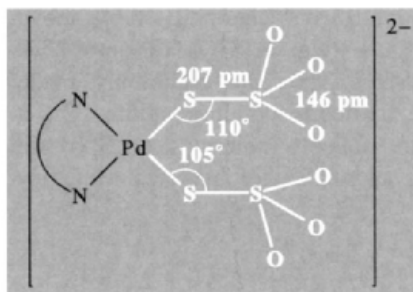
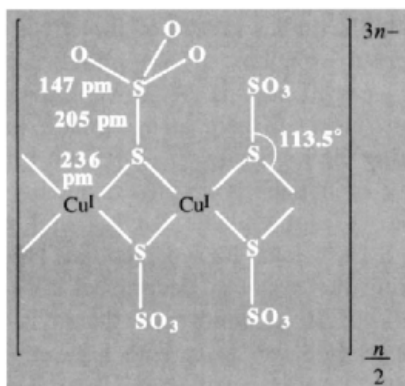
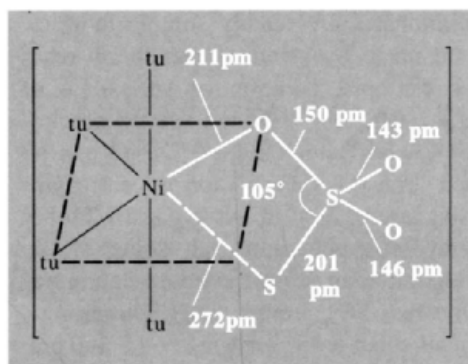
Stronger oxidizing agents take the reaction through to sulfate, e.g.:



<sup>197</sup> See p. 723 of ref. 103 for detailed references.



(a) Uncoordinated

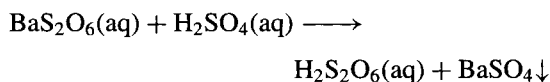
(b) Monodentate ( $\eta^1-S$ ): the  $S^{VI}$  atoms are not coplanar with the  $\{PdN_2S_2\}$  group(c) Monohapto bidentate bridging ( $\mu, \eta^1-S$ )(d) Dihapto bidentate chelating ( $\eta^2-S,O$ )

**Figure 15.30** Structure of the thiosulfate ion and its various modes of coordination: (a) uncoordinated  $S_2O_3^{2-}$ ; (b) monodentate ( $\eta^1-S$ ) in the anion of the orange complex  $[Pd^{II}(en)_2][Pd^{II}(en)(S_2O_3)_2]$ ; (c) monohapto bidentate bridging ( $\mu, \eta^1-S$ ) in the polymeric anion of the pale-violet mixed valence copper complex  $Na_4[Cu^I(NH_3)_4][Cu^I(S_2O_3)_2]_2$ ; and (d) dihapto chelating ( $\eta^2-S,O$ ) in the thiourea nickel complex  $[Ni(S_2O_3)(tu)_4] \cdot H_2O$ .

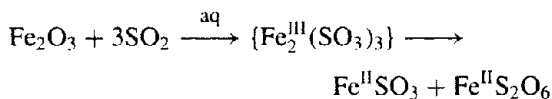
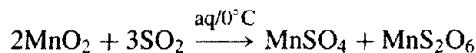
This reaction is the basis for the use of thiosulfates as “antichlorine” in the bleaching industry where they are used to destroy any excess of  $Cl_2$  in the fibres. Bromine, being intermediate between iodine and chlorine, can cause  $S_2O_3^{2-}$  to act either as a 1-electron or an 8-electron reducer according to conditions. For example, in an amusing and instructive experiment, if concentrated aqueous solutions of  $S_2O_3^{2-}$  and  $Br_2$  are titrated, and the titration is then repeated after having diluted both the  $S_2O_3^{2-}$  and  $Br_2$  solutions 100-fold, then the titre will be found to have increased by a factor of exactly 8.

### Dithionic acid, $H_2S_2O_6$

In dithionic acid and dithionates,  $S_2O_6^{2-}$ , the oxidation state of the 2 S atoms has been reduced from VI to V by the formation of an S–S bond (Table 15.18, p. 705). The free acid has not been obtained pure, but quite concentrated aqueous solutions can be prepared by treatment of the barium salt with the stoichiometric amount of  $H_2SO_4$ :



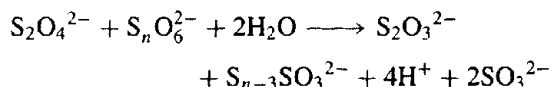
Crystalline dithionates are thermally stable above room temperature (e.g.  $\text{K}_2\text{S}_2\text{O}_6$  decomp  $258^\circ$  to  $\text{K}_2\text{SO}_4 + \text{SO}_2$ ). They are commonly made by oxidizing the corresponding sulfite. On a technical scale aqueous solutions of  $\text{SO}_2$  are oxidized by a suspension of hydrated  $\text{MnO}_2$  or  $\text{Fe}_2\text{O}_3$ :



All the dithionates are readily soluble in water and can be made by standard metathesis reactions. For example, addition of an excess of  $\text{Ba}^{\text{II}}$  ions to the  $\text{Mn}^{\text{II}}$  solution above precipitates  $\text{BaSO}_4$ , after which  $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  can be crystallized. The  $[\text{O}_3\text{SSO}_3]^{2-}$  ion is centrosymmetric (staggered)  $D_{3d}$  in  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  but in the anhydrous potassium salt some of the  $\text{S}_2\text{O}_6^{2-}$  ions have an almost eclipsed configuration for the two  $\text{SO}_3$  groups ( $D_{3h}$ ). Dimensions are unremarkable: S-S 215 pm, S-O 143 pm, and angle S-S-O  $103^\circ$ . In a curious reaction between dibenzenechromium(0) and dry, oxygen-free  $\text{SO}_2$  in toluene, a red precipitate is formed which subsequently turns black. The unexpected product is  $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]_2[\text{S}_4\text{O}_{10}]$ , which contains the dianion  $[\text{S}_4\text{O}_{10}]^{2-}$  formed by coordination of two  $\text{SO}_2$  molecules to a dithionate ion,  $[\text{O}_2\text{S} \rightarrow \text{OS}(\text{O})_2 - \text{S}(\text{O})_2\text{O} \leftarrow \text{SO}_2]^{2-}$  with S-S 221.8 pm, S-O 243.3 pm and angle S-O-S  $129.3^\circ$ .<sup>(198)</sup>

Dithionates are relatively stable towards oxidation in solution though strong oxidants such as the halogens, dichromate and permanganate oxidize them to sulfate. Powerful reductants (e.g.  $\text{Na}/\text{Hg}$ ) reduce dithionates to sulfites and dithionites ( $\text{S}_2\text{O}_4^{2-}$ ). In neutral and slightly acidic aqueous solutions dithionite itself decomposes by pH-dependent routes to thiosulfite ( $\text{S}_2\text{O}_3^{2-}$ ), sulfite ( $\text{SO}_3^{2-}$ ), sulfide ( $\text{S}^{2-}$ ), etc. These, and the products of the

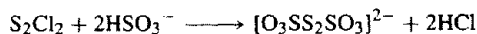
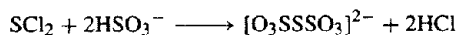
reactions of dithionites with polythionates ( $\text{S}_n\text{O}_6^{2-}$ ,  $n = 3-5$ ) have been studied by ion-pair chromatography:<sup>(199)</sup>



### Polythionic acids, $\text{H}_2\text{S}_n\text{O}_6$

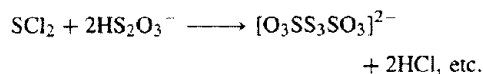
The numerous acids and salts in this group have a venerable history and the chemistry of systems in which they occur goes back to John Dalton's studies (1808) of the effect of  $\text{H}_2\text{S}$  on aqueous solutions of  $\text{SO}_2$ . Such solutions are now named after H. W. F. Wackenroder (1846) who subjected them to systematic study. Work during the following 60-80 y indicated the presence of numerous species including, in particular, the tetrathionate  $\text{S}_4\text{O}_6^{2-}$  and pentathionate  $\text{S}_5\text{O}_6^{2-}$  ions. New perceptions have emerged during the past few decades as a result of the work of H. Schmidt and others in Germany: just as  $\text{H}_2\text{S}$  can react with  $\text{SO}_3$  or  $\text{HSO}_3\text{Cl}$  to yield thiosulfuric acid,  $\text{H}_2\text{S}_2\text{O}_3$  (p. 714), so reaction with  $\text{H}_2\text{S}_2$  yields "disulfane monosulfonic acid",  $\text{HS}_2\text{SO}_3\text{H}$ ; likewise polysulfanes  $\text{H}_2\text{S}_n$  ( $n = 2-6$ ) yield  $\text{HS}_n\text{SO}_3\text{H}$ . Reaction at both ends of the polysulfane chain would yield "polysulfane disulfonic acids"  $\text{HO}_3\text{SS}_n\text{SO}_3\text{H}$  which are more commonly called polythionic acids ( $\text{H}_2\text{S}_{n+2}\text{O}_6$ ). Many synthetic routes are available, though mechanistic details are frequently obscure because of the numerous simultaneous and competing redox, catenation and disproportionation reactions that occur. Typical examples include:

- Interaction of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in Wackenroder's solution (see above).
- Reaction of chlorosulfanes with  $\text{HSO}_3^-$  or  $\text{HS}_2\text{O}_3^-$ , e.g.:



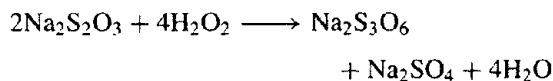
<sup>198</sup> C. ELSCHENBROICH, R. GONDRUM and W. MASSA, *Angew. Chem. Int. Edn. Engl.* **24**, 967-8 (1985).

<sup>199</sup> V. MUNCHOW and R. STEUDEL, *Z. anorg. allg. Chem.* **620**, 121-6 (1994).



- (c) Oxidation of thiosulfates with mild oxidants (p. 714) such as  $\text{I}_2$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{H}_2\text{O}_2$ .
- (d) Specific syntheses as noted below.

Sodium trithionate,  $\text{Na}_2\text{S}_3\text{O}_6$ , can be made by oxidizing sodium thiosulfate with cooled hydrogen peroxide solution



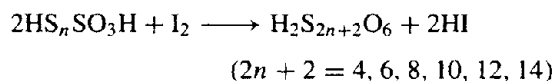
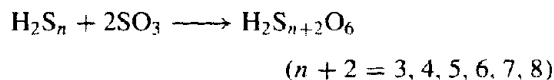
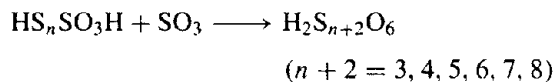
The potassium (but not the sodium) salt is obtained by the obscure reaction of  $\text{SO}_2$  on aqueous thiosulfate. Aqueous solutions of the acid  $\text{H}_2\text{S}_3\text{O}_6$  can then be obtained from  $\text{K}_2\text{S}_3\text{O}_6$  by treatment with tartaric acid or perchloric acid.

Sodium (and potassium) tetrathionate,  $\text{M}_2\text{S}_4\text{O}_6$ , can be made by oxidation of thiosulfate by  $\text{I}_2$  (p. 714) and the free acid liberated (in aqueous solution) by addition of the stoichiometric amount of tartaric acid.

Potassium pentathionate,  $\text{K}_2\text{S}_5\text{O}_6$ , can be made by adding potassium acetate to Wackenroder's solution and solutions of the free acid  $\text{H}_2\text{S}_5\text{O}_6$  can then be obtained by subsequent addition of tartaric acid.

Potassium hexathionate,  $\text{K}_2\text{S}_6\text{O}_6$ , is best synthesized by the action of  $\text{KNO}_2$  on  $\text{K}_2\text{S}_2\text{O}_3$  in conc  $\text{HCl}$  at low temperatures, though the ion is also a constituent of Wackenroder's solution.

Anhydrous polythionic acids can be made in ether solution by three general routes:



The structure of the trithionate ion (in  $\text{K}_2\text{S}_3\text{O}_6$ ) is shown in Fig. 15.31a and calls for little

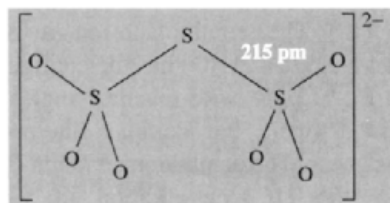
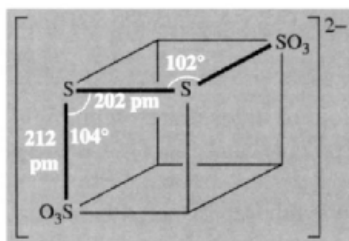
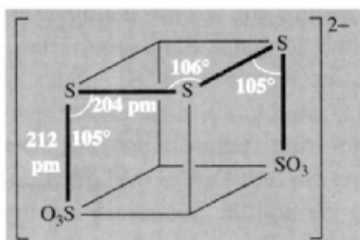
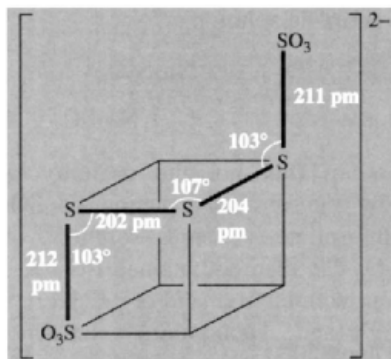
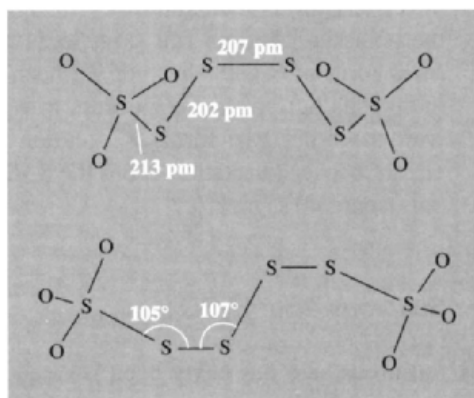
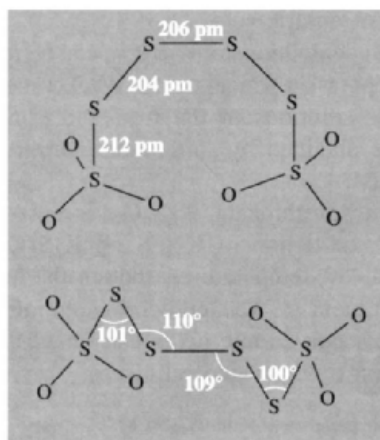
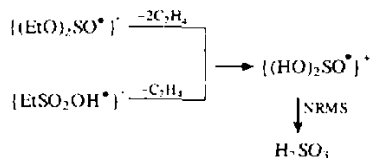
comment (cf. the disulfate ion  $\text{O}_3\text{SOSO}_3^{2-}$ , p. 712). The tetrathionate ion (in  $\text{BaS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ ) has the configuration shown in Fig. 15.31b with dihedral angles close to  $90^\circ$  and a small, but definite, alternation in S-S distances. The pentathionate ion in  $\text{BaS}_5\text{O}_6 \cdot 2\text{H}_2\text{O}$  has the *cis* configuration in which the  $\text{S}_5$  unit can be regarded as part of an  $\text{S}_8$  ring (p. 655) from which 3 adjacent S atoms have been removed (Fig. 15.31c). By contrast, in the potassium salt  $\text{K}_2\text{S}_5\text{O}_6 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  the pentathionate ion adopts the *trans* configuration in which the two terminal  $\text{SO}_3$  groups are on opposite sides of the central  $\text{S}_3$  plane (Fig. 15.31d). These structural differences persist in the seleno- and telluro-analogues  $\text{O}_3\text{SSeSSO}_3^{2-}$  and  $\text{O}_3\text{SSTeSSO}_3^{2-}$ , the dihydrated Ba salts being *cis* and the potassium hemihydrates being *trans*.<sup>(200)</sup> There are three possible rotameric forms of the hexathionate ion  $\text{S}_6\text{O}_6^{2-}$ : the extended *trans-trans* form analogous to spiral chains of fibrous sulfur (p. 660) occurs in the *trans*- $[\text{Co}^{\text{III}}(\text{en})_2\text{Cl}_2]^+$  salt (Fig. 15.31e), whereas the *cis-cis* form (analogous to *cyclo-S}\_8*) occurs in the potassium barium salt (Fig. 15.31f); the *cis-trans* form of  $\text{S}_6\text{O}_6^{2-}$  has not yet been observed in crystals but presumably occurs in equilibrium with the other two forms in solution since the energy barrier to rotation about the S-S bonds is only some  $40 \text{ kJ mol}^{-1}$ .

### Sulfurous acid, $\text{H}_2\text{SO}_3$

Sulfurous acid has never been isolated as a pure compound, although it has recently been detected in the gas phase by neutralization reionization mass spectrometry (NRMS) following the facile dissociative ionization (70 eV) of either diethyl sulfite or ethanesulfonic acid.<sup>(201)</sup>

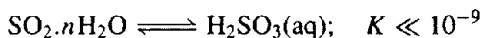
<sup>200</sup> O. FOSS, *IUPAC Additional Publication* (24th International Congress, Hamburg, 1973), Vol. 4, *Compounds of Non-Metals*, pp. 103-13. Butterworths, London, 1974, and references therein.

<sup>201</sup> D. SULZLE, M. VERHOEVEN, J. K. TERLOUW and H. SCHWARZ, *Angew. Chem. Int. Edn. Engl.* **27**, 1533-4 (1988).

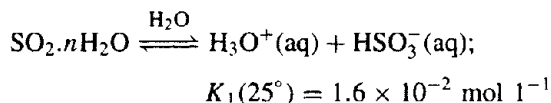
(a)  $S_3O_6^{2-}$ (b)  $S_4O_6^{2-}$ (c) *cis*- $S_5O_6^{2-}$ (d) *trans*- $S_5O_6^{2-}$ (e) *trans-trans*- $S_6O_6^{2-}$  (above: normal to the twofold axis; below: along this axis)(f) *cis-cis*- $S_6O_6^{2-}$  (above: normal to the twofold axis; below: along this axis)**Figure 15.31** Structures of some polythionate ions.<sup>(200)</sup>

The experimental finding was substantiated by high-level *ab initio* calculations. The unionized acid exists in only minute concentrations (if at all) in aqueous solutions of  $\text{SO}_2$ . However, its salts, the sulfites, are quite stable and many are known

in crystalline form; a second series of salts, the hydrogen sulfites  $\text{HSO}_3^-$ , are known in solution. Spectroscopic studies of aqueous solutions of  $\text{SO}_2$  suggest that the predominant species are various hydrates,  $\text{SO}_2 \cdot n\text{H}_2\text{O}$ ; depending on the concentration, temperature and pH, the ions present are  $\text{H}_3\text{O}^+$ ,  $\text{HSO}_3^-$  and  $\text{S}_2\text{O}_5^{2-}$  together with traces of  $\text{SO}_3^{2-}$ . The undissociated acid  $\text{OS}(\text{OH})_2$  has not been detected:



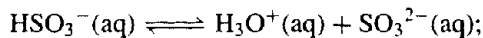
The first acid dissociation constant of "sulfurous acid" in aqueous solution is therefore defined as:



where

$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{HSO}_3^-]}{[\text{total dissolved SO}_2] - [\text{HSO}_3^-] - [\text{SO}_3^{2-}]}$$

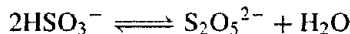
The second dissociation constant is given by the equation



$$K_2(25^\circ) = 1.0 \times 10^{-7} \text{ mol l}^{-1}$$

$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]}$$

Most sulfites (except those of the alkali metals and ammonium) are rather insoluble; as indicated above such solutions contain the  $\text{HSO}_3^-$  ion predominantly, but attempts to isolate  $\text{M}^+\text{HSO}_3$  tend to produce disulfites (p. 720) by "dehydration":

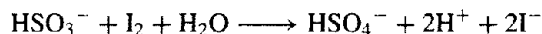


Only with large cations such as Rb, Cs and  $\text{NR}_4$  (R = Et, Bu<sup>n</sup>, *n*-pentyl) has it proved possible to isolate the solid sulfites  $\text{MHSO}_3$ .<sup>(202)</sup>

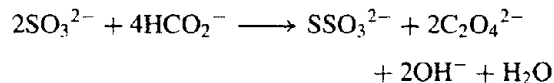
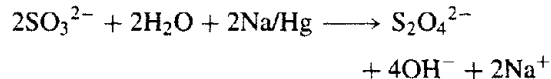
The sulfite ion  $\text{SO}_3^{2-}$  is pyramidal with  $C_{3v}$  symmetry: angle O-S-O 106°, S-O 151 pm. The hydrogen sulfite ion also appears to have  $C_{3v}$  symmetry both in the solid state and in solution, i.e. protonation occurs at S rather than

O to give  $\text{H-SO}_3^-$  rather than  $\text{HO-SO}_2^-$  ( $C_s$  symmetry). However, recent <sup>17</sup>O nmr studies appear to provide evidence for the existence in solution of a dynamic equilibrium between the two isomers:  $\text{H-SO}_3^- \rightleftharpoons \text{HO-SO}_2^-$ .<sup>(203)</sup> The sulfite ion also coordinates through S in transition-metal complexes, e.g.  $[\text{Pd}(\text{NH}_3)_3(\eta^1\text{-SO}_3)]$ , *cis*- and *trans*- $[\text{Pt}(\text{NH}_3)_2(\eta^1\text{-SO}_3)_2]^{2-}$ . The structure of hydrogen-sulfito complex *trans*- $[\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{SO}_3\text{H})_2]$  is also S-bonded, implying a 1,2 proton shift to give  $\text{M}[\text{SO}_2(\text{OH})]$ .<sup>(204)</sup>

Sulfites and hydrogen sulfites are moderately strong reducing agents (p. 706) and, depending on conditions, are oxidized either to dithionate or sulfate. The reaction with iodine is quantitative and is used in volumetric analysis:



Conversely, sulfites can act as oxidants in the presence of strong reducing agents; e.g. sodium amalgam yields dithionite, and formates (in being oxidized to oxalates) yield thiosulfate:



Thiosulfates also result from reduction of  $\text{SO}_3^{2-}$  or  $\text{HSO}_3^-$  with elemental sulfur (p. 714), whereas reduction with  $\text{H}_2\text{S}$  in Wackenroder's solution (pp. 716-7) yields polythionates. It is also notable that the sulfite ion is involved in the 6-electron sulfite reductase reaction:  $\text{SO}_3^{2-} + 6\text{H}^+ + 6\text{e}^- \longrightarrow \text{S}^{2-} + 3\text{H}_2\text{O}$ ;  $E^\circ = 0.380 \text{ V}$ . Indeed, there are only three such  $6\text{e}^-$  reductions known in the whole of biology, the other two being nitrite reductase ( $\text{NO}_2^- + 7\text{H}^+ + 6\text{e}^- \longrightarrow \text{NH}_3 + 2\text{H}_2\text{O}$ ) and nitrogenase ( $\text{N}_2 + 6\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{NH}_3$ ).

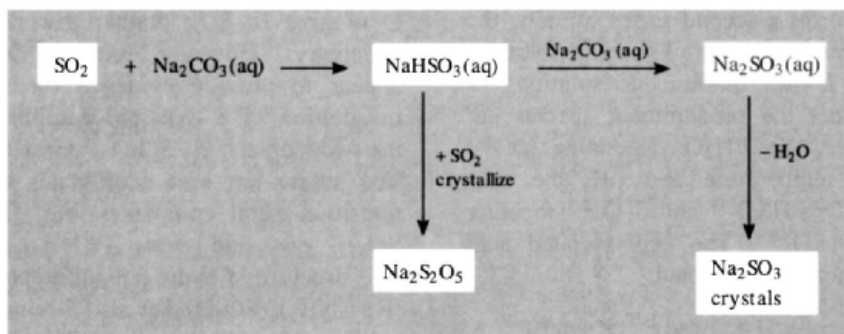
On a technical scale, solutions of sodium hydrogen sulfite are prepared by passing  $\text{SO}_2$

<sup>203</sup> D. A. HORNER and R. E. CONNICK, *Inorg. Chem.* **25**, 2414-7 (1986).

<sup>204</sup> D. K. BREITINGER and R. BREITER, *Z. Naturforsch.* **45b**, 1651-6 (1990).

<sup>202</sup> R. MAYLOR, J. B. GILL and D. C. GOODALL, *J. Chem. Soc., Dalton Trans.*, 2001-3 (1972) and references therein.





into aqueous  $\text{Na}_2\text{CO}_3$ . As shown in the Scheme above, addition of a further equivalent of  $\text{Na}_2\text{CO}_3$  allows the normal sulfite to be crystallized, whereas addition of more  $\text{SO}_2$  yields the disulfite (see the next subsection below).

Crystallization of  $\text{Na}_2\text{SO}_3$  above  $37^\circ$  gives the anhydrous salt; below this temperature  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  is obtained. World production of the anhydrous salt exceeds 1 million tonnes pa; most is used in the paper pulp industry, but other applications are as an  $\text{O}_2$  scavenger in boiler-water treatment, and as a reducing agent in photography. Similarly,  $\text{K}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$  is obtained by passing  $\text{SO}_2$  into aqueous  $\text{KOH}$  until samples of the solution are neutral to phenolphthalein. For a compilation of critically evaluated solubility data, see ref. 205

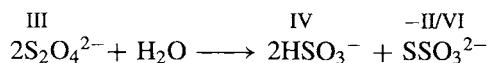
### Disulfurous acid, $\text{H}_2\text{S}_2\text{O}_5$

Like "sulfurous acid", disulfurous acid is unknown either in the free state or in solution. However, as indicated in the preceding section, its salts, are readily obtained from concentrated solutions of hydrogen sulfite:  $2\text{HSO}_3^- \rightleftharpoons \text{S}_2\text{O}_5^{2-} + \text{H}_2\text{O}$ . Unlike disulfates (p. 712), diphosphates (p. 522), etc., disulfites condense by forming an S-S bond. As indicated in Fig. 15.32a this S-S bond is rather long, but the S-O distances are unexceptional.

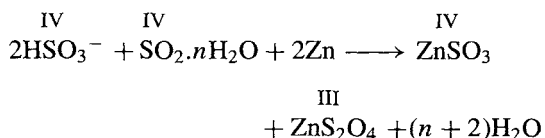
Acidification of solutions of disulfites regenerates  $\text{HSO}_3^-$  and  $\text{SO}_2$  again, and the solution chemistry of  $\text{S}_2\text{O}_5^{2-}$  is essentially that of the normal sulfites and hydrogen sulfites, despite the formal presence of  $\text{S}^{\text{V}}$  and  $\text{S}^{\text{III}}$  (rather than  $\text{S}^{\text{IV}}$ ) in the solid state.

### Dithionous acid, $\text{H}_2\text{S}_2\text{O}_4$

Dithionites,  $\text{S}_2\text{O}_4^{2-}$  are quite stable when anhydrous, but in the presence of water they disproportionate (slowly at  $\text{pH} \geq 7$ , rapidly in acid solution):

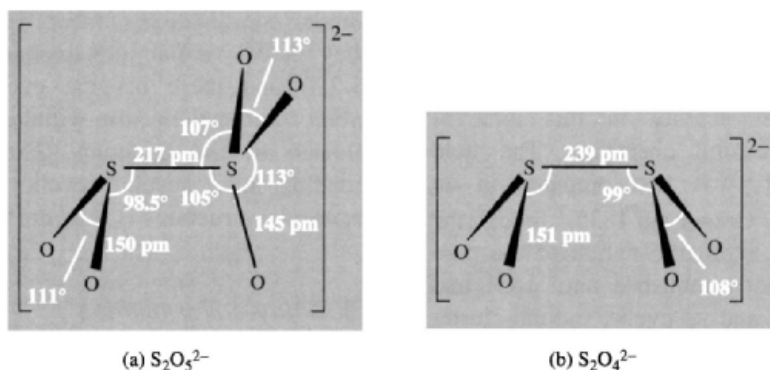


The parent acid has no independent existence and has not been detected in aqueous solution either. Sodium dithionite is widely used as an industrial reducing agent and can be prepared by reduction of sulfite using Zn dust, Na/Hg or electrolytically, e.g.:



The dihydrate  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  can be precipitated by "salting out" with  $\text{NaCl}$ . Air and oxygen must be excluded at all stages in the process to avoid reoxidation. The dithionite ion can also be produced *in situ* on an industrial scale by reaction

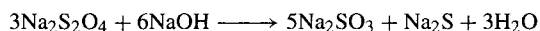
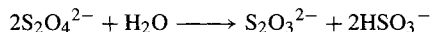
<sup>205</sup> M. R. MASSON, H. D. LUTZ and B. ENGELEN (eds.) *Sulfites, Selenites and Tellurites*, Pergamon Press, Oxford, 1986, 474 pp.



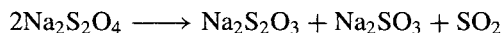
**Figure 15.32** Structure of (a) the disulfite ion  $\text{S}_2\text{O}_5^{2-}$  in  $(\text{NH}_4)_2\text{S}_2\text{O}_5$ , and (b) the dithionite ion  $\text{S}_2\text{O}_4^{2-}$  in  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

between  $\text{NaHSO}_3$  and  $\text{NaBH}_4$  (p. 167). Its main use is as a reducing agent in dyeing, bleaching of paper pulp, straw, clay, soaps, etc., and in chemical reductions (see below). Current worldwide demand is about 300 000 tonnes per annum.

The dithionite ion has a remarkable eclipsed structure of approximate  $C_{2v}$  symmetry (Fig. 15.32b). The extraordinarily long S–S distance (239 pm) and the almost parallel  $\text{SO}_2$  planes (dihedral angle  $30^\circ$ ) are other unusual features. Electron-spin-resonance studies have shown the presence of the  $\text{SO}_2^{\cdot -}$  radical ion in solution ( $\sim 300$  ppm), suggesting the establishment of a monomer-dimer equilibrium  $\text{S}_2\text{O}_4^{2-} \rightleftharpoons 2\text{SO}_2^{\cdot -}$ . Consistent with this, air-oxidation of alkaline dithionite solutions at  $30$ – $60^\circ$  are of order one-half with respect to  $[\text{S}_2\text{O}_4^{2-}]$ . Acid hydrolysis (second order with respect to  $[\text{S}_2\text{O}_4^{2-}]$ ) yields thiosulfate and hydrogen sulfite, whereas alkaline hydrolysis produces sulfite and sulfide:



Hydrated dithionites can be dehydrated by gentle warming, but the anhydrous salts themselves decompose on further heating. For example,  $\text{Na}_2\text{S}_2\text{O}_4$  decomposes rapidly at  $150^\circ$  and violently at  $190^\circ$ :



Dithionites are strong reducing agents and will reduce dissolved  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{I}_2$ ,  $\text{IO}_3^-$  and  $\text{MnO}_4^-$ .

Likewise  $\text{Cr}^{\text{VI}}$  is reduced to  $\text{Cr}^{\text{III}}$  and  $\text{TiO}^{2+}$  to  $\text{Ti}^{\text{III}}$ . Heavy metal ions such as  $\text{Cu}^{\text{I}}$ ,  $\text{Ag}^{\text{I}}$ ,  $\text{Pb}^{\text{II}}$ ,  $\text{Sb}^{\text{III}}$  and  $\text{Bi}^{\text{III}}$  are reduced to the metal. Many of these reactions are useful in water-treatment and pollution control.

### 15.2.7 Sulfur–nitrogen compounds<sup>(206–210)</sup>

The study of S–N compounds is one of the most active areas of current inorganic research: many novel cyclic and acyclic compounds are being prepared which have unusual structures and which pose considerable problems in terms of simple bonding theory. The discovery in 1975 that the polymer  $(\text{SN})_x$  is a metal whose conductivity *increases* with decrease in

<sup>206</sup> M. BECKE-GOEHRING and E. FLUCK, Chap. 3 in C. B. COLBURN (ed.), *Developments in Inorganic Nitrogen Chemistry*, Vol. 1, pp. 150–240, Elsevier, Amsterdam, 1966.

<sup>207</sup> I. HAJDUC, *The Chemistry of Inorganic Ring Systems*, Part 2, (sulfur–nitrogen heterocycles), pp. 909–83, Wiley, London, 1970.

<sup>208</sup> H. G. HEAL, *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*, Academic Press, London, 1981, 288 pp.

<sup>209</sup> H. W. ROESKY, *Adv. Inorg. Chem. Radiochem.* **22**, 239–301 (1979).

<sup>210</sup> *Gmelin Handbook of Inorganic Chemistry*, Sulfur–Nitrogen Compounds: Part 1, 288 pp (1977); Part 2, 333 pp (1985); Part 3, 325 pp (1987); Part 4, 272 pp (1987); Part 5, 276 pp (1990), Springer Verlag, Berlin.