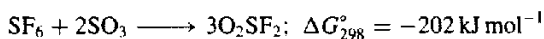


All these compounds have (distorted) tetrahedral molecules, those of formula O_2SX_2 having C_{2v} symmetry and the others C_s . Dimensions are in Table 15.15: the remarkably short O–S and S–F distances in O_2SF_2 should be noted (cf. above). Indeed, the implied strength of bonding in this molecule is reflected by the fact that it can be made by reacting the normally extremely inert compound SF_6 (p. 687) with the fluoro-acceptor SO_3 :



A 20% conversion can be effected by heating the two compounds at 250° for 24 h.

15.2.5 Oxides of sulfur

At least thirteen proven oxides of sulfur are known to exist⁽¹⁶³⁾ though this profusion should not obscure the fact that SO_2 and SO_3 remain by far the most stable and unquestionably the most important economically. The six homocyclic polysulfur monoxides S_nO ($5 < n < 10$) are made by oxidizing the appropriate *cyclo-S_n* (p. 656) with trifluoroperoxoacetic acid, $CF_3C(O)OOH$, at -30° . The dioxides S_7O_2 and S_6O_2 are also known. In addition there are the thermally unstable acyclic oxides S_2O , S_2O_2 , SO and the fugitive species SOO and SO_4 . Several other compounds were described in the older literature (pre-1950s) but these reports are now known to be in error. For example, the blue substance of composition “ S_2O_3 ” prepared from liquid SO_3 and sulfur now appears to be a mixture of salts of the cations S_4^{2+} and S_8^{2+} (p. 664) with polysulfate anions. Likewise a “sulfur monoxide” prepared by P. W. Schenk in 1933 was shown by D. J. Meschi and R. J. Meyers in 1956 to be a mixture of S_2O and SO_2 . The well-established lower oxides of S will be briefly reviewed before SO_2 and SO_3 are discussed in more detail.

Lower oxides⁽¹⁶³⁾

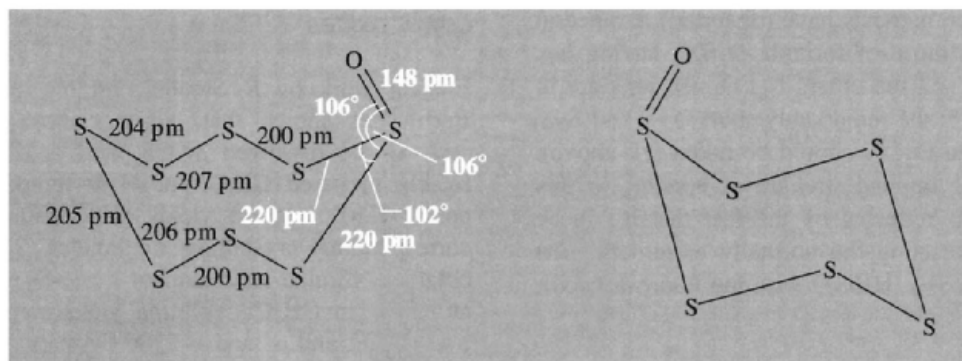
Elegant work by R. Steudel and his group in Berlin has shown that, when *cyclo-S₁₀*, *-S₉*, and *-S₈* are dissolved in CS_2 and oxidized by freshly prepared $CF_3C(O)O_2H$ at temperatures below -10° , modest yields (10–20%) of the corresponding crystalline monoxides S_nO are obtained. Similar oxidation of *cyclo-S₇*, and α - and β - S_6 in CH_2Cl_2 solution yields crystalline S_7O , S_7O_2 , and α - and β - S_6O . Crystals of S_6O_2 and S_5O ($d > -50^\circ$) have not yet been isolated but the compounds have been made in solution by the same technique. S_8O had previously been made (1972) by the reaction of $OSCl_2$ and H_2S_7 in CS_2 at -40° : it is one of the most stable compounds in the series and melts (with decomposition) at 78° . All the compounds are orange or dark yellow and decompose with liberation of SO_2 and sulfur when warmed to room temperature or slightly above. Structures are in Fig. 15.24. It will be noted that S_7O is isoelectronic and isostructural with $[S_7I]^+$ (p. 692). This invites the question as to whether S_7S can be prepared as a new structural isomer of *cyclo-S₈*.

S_8O reacts with $SbCl_5$ in CS_2 over a period of 9 days at -50° to give a 71% yield of the unstable orange adduct $S_8O \cdot SbCl_5$ ⁽¹⁶⁴⁾ its structure and dimensions are in Fig. 15.25a. It will be noted that the S_8O unit differs from molecular S_8O in having an equatorially bonded O atom and significantly different S–O and S–S interatomic distances. The X-ray crystal structure was determined at $-100^\circ C$ as the adduct decomposes within 5 min at 25° to give $OSCl_2$, $SbCl_3$ and S_8 . When a similar reaction was attempted with β - S_6O , the novel dimer $S_{12}O_2 \cdot 2SbCl_5 \cdot 3CS_2$ was obtained as orange crystals in 10% yield after 1 week at -50° ⁽¹⁶⁵⁾ (Fig. 15.25b). Formation of the centrosymmetric $S_{12}O_2$ molecule, which is still unknown in the uncoordinated state, can be

¹⁶⁴ R. STEUDEL, T. SANDOW and J. STEIDEL, *J. Chem. Soc., Chem. Commun.*, 180–1 (1980).

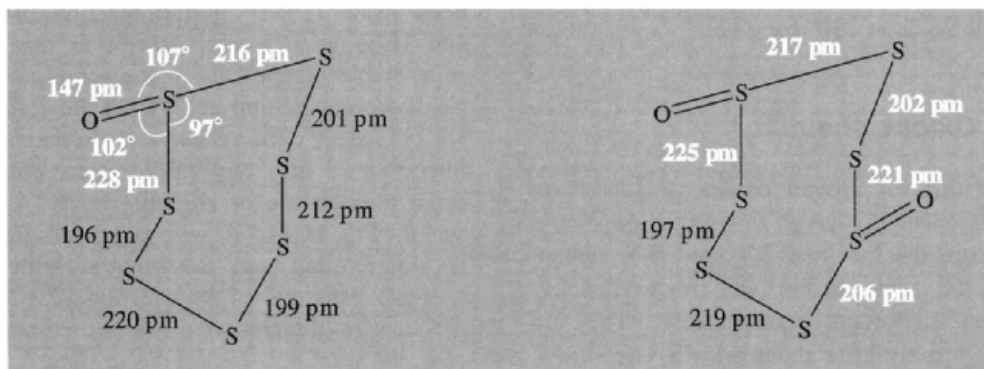
¹⁶⁵ R. STEUDEL, J. STEIDEL and J. PICKARDT, *Angew. Chem. Int. Edn. Engl.* **19**, 325–6 (1980).

¹⁶³ *Gmelin Handbuch der Anorganischen Chemie*, 8th edn., Schwefel Oxide, Ergänzungsband 3, 1980, 344 pp.



S_8O : orange-yellow crystals,
mp 78° (decomp)

α - S_6O : orange-yellow crystals, mp 39° (d)
 β - S_6O : dark orange, mp 34° (d)



S_7O : orange crystals, mp 55° (d)

S_7O_2 : dark orange crystals,
decomp $>$ room temp

Figure 15.24 Structures of S_8O , S_7O , S_7O_2 and S_6O ; in each case the O atom adopts an axial conformation. For S_8O there is an alternation of S–S distances, the longest being adjacent to the exocyclic O atoms; S–S–S angles are in the range 102 – 108° and dihedral angles (p. 654) vary from 95° to 112° (+ and –). For S_7O there is again an alternation in S–S distances; ring angles are in the range 97 – 106° the smallest angle again being at the S atom carrying the pendant O. The structure of S_7O_2 was deduced from its Raman spectrum, the interatomic distances (d/pm) being computed from the relation $\log(d/\text{pm}) = 2.881 - 0.213 \log(\nu/\text{cm}^{-1})$. The two modifications α - and β - S_6O have the same Raman spectrum in solution.

explained in terms of a dipolar addition reaction (Fig. 15.25c). Its conformation differs drastically from the D_{3d} symmetry of the parent *cyclo*- S_{12} (p. 658).

The fugitive species SO was first identified by its ultraviolet spectrum in 1929 but it is thermodynamically unstable and decomposes completely in the gas phase in less than 1 s. It is formed by reduction of SO_2 with sulfur vapour in a glow discharge and its spectroscopic properties

have excited interest because of its relation to O_2 ($^3\Sigma^-$ ground state, p. 605). Molecular properties include internuclear distance 148.1 pm, dipole moment 1.55 D, equilibrium bond energy D_e 524 kJ mol^{-1} . The use of transition-metal complexes to trap SO has received considerable attention.⁽¹⁶⁶⁾ It can bond in several modes including

¹⁶⁶ W. A. SCHENK, *Angew. Chem. Int. Edn. Engl.* **26**, 98–109 (1987).

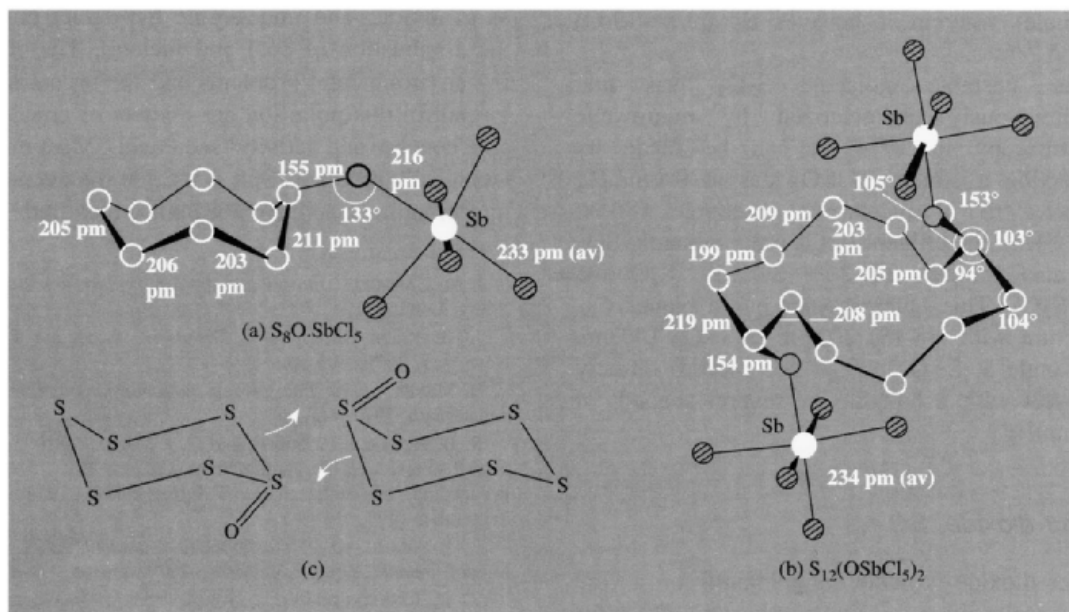


Figure 15.25 Molecular structure and dimensions of (a) the adduct $S_8O \cdot SbCl_5$ at -100° , and (b) the dimeric unit $Sb_{12}O_2 \cdot 2SbCl_5$ in $Sb_{12}O_2 \cdot 2SbCl_5 \cdot 3CS_2$ at $-115^\circ C$. (c) Possible dipolar addition of $2S_8O$ to form $S_{12}O_2$.

4-centre-2 electron ($4c-2e$) as in $[Fe_3(CO)_9S(\mu_3-SO)]$,⁽¹⁶⁷⁾ $2c-2e$ as in $[IrCl(SO)(PR_3)_2]$,⁽¹⁶⁸⁾ and also $3c-4e$ and $3c-2e$ in several dinuclear transition-metal complexes.^(169,170) A novel and unprecedented route to this last class of $\mu-SO$ complexes involves the direct oxidative addition of $OSCl_2$ to the Ni^0 complex $[Ni(cod)_2]$ in the presence of $dppm$ ($cod = \text{cycloocta-1,5-diene}$, $dppm = Ph_2PCH_2PPh_2$) to form the purple crystalline dinickel A-frame complex, $[Ni_2(\mu-SO)(dppm)_2Cl_2]$.⁽¹⁷¹⁾ X-ray analysis reveals two slightly differing geometries, with SO

144 and 145.9 pm, respectively (both shorter than in the free molecule, 148.1 pm), and with the SO ligand being tilted with respect to the $Ni \cdots Ni$ vector.

S_2O is also an unstable species but survives for several days in the gas phase at $<1 \text{ mmHg}$ pressure. It is formed by decomposition of SO (above) and by numerous other reactions between S - and O -containing species but cannot be isolated as a pure compound. Typical recipes include: (a) passing a stream of $OSCl_2$ at $0.1-0.5 \text{ mmHg}$ over heated Ag_2S at 160° , (b) burning S_8 in a stream of O_2 at $\sim 8 \text{ mmHg}$ pressure, and (c) passing SO_2 at 120° and $<1 \text{ mmHg}$ through a high-voltage discharge ($\sim 5 \text{ kV}$). Spectroscopic studies in the gas phase have shown it to be a nonlinear molecule (like O_3 and SO_2) with angle $S-S-O$ 118° and the interatomic distances $S-S$ 188, $S-O$ 146 pm. S_2O readily decomposes at room temperature to SO_2 and sulfur. As with SO , the fugitive S_2O species can be trapped with transition-metal complexes (of Mn and Ir , for

¹⁶⁷ L. MARKÓ, B. MARKÓ-MONOSTORY, T. MADACH and H. VAHRENKAMP, *Angew. Chem. Int. Edn. Engl.* **19**, 226-7 (1980).

¹⁶⁸ W. A. SCHENK, J. LEISSNER and C. BURSCHKA, *Angew. Chem. Int. Edn. Engl.* **23**, 806-7 (1984).

¹⁶⁹ I.-P. LORENZ, J. MESSELHAUSER, W. HILLER and K. HAUG, *Angew. Chem. Int. Edn. Engl.* **3**, 24-5 (1985).

¹⁷⁰ G. BESENEI, C. L. LEE, J. GULINSKI, S. J. RETTIG, B. R. JAMES, D. A. NELSON and M. A. LILGA, *Inorg. Chem.* **26**, 3622-8 (1987).

¹⁷¹ J. K. GONG, P. E. FANWICK and C. P. KUBIAK, *J. Chem. Soc., Chem. Commun.*, 1190-1 (1990).

example) wherein it behaves as an η^2 -SS(O) ligand.⁽¹⁷²⁾

The unstable molecule S_2O_2 was first unambiguously characterized by microwave spectroscopy in 1974. It can be made by subjecting a stream of SO_2 gas at 0.1 mmHg pressure to a microwave discharge (80 W, 2.45 GHz): the effluent gas is predominantly SO_2 but also contains 20–30% SO , 5% S_2O and 5% S_2O_2 . This latter species has a planar C_{2v} structure with $r(S-S)$ 202 pm, $r(S-O)$ 146 pm, and angle $S-S-O$ 113° ; it decomposes directly into SO with a half-life of several seconds at 0.1 mmHg.

Sulfur dioxide, SO_2

Sulfur dioxide is made commercially on a very large scale either by the combustion of sulfur or H_2S or by roasting sulfide ores (particularly pyrite, FeS_2) in air (p. 651). It is also produced

¹⁷² G. A. UROVE and M. E. WELKER, *Organometallics* **7**, 1013–4 (1988).

as a noxious and undesirable byproduct during the combustion of coal and fuel oil. The ensuing environmental problems and the urgent need to control this pollution are matters of considerable concern and activity (see Panel). Most of the technically produced SO_2 is used in the manufacture of sulfuric acid (p. 708) but it also finds use

¹⁷³ I. M. CAMPBELL, *Energy and the Atmosphere*, pp. 202–9, Wiley, London, 1977.

¹⁷⁴ J. HEICKLEN, *Atmospheric Chemistry*, Academic Press, New York, 1976, 406 pp.

¹⁷⁵ B. MEYER, *Sulfur, Energy, and the Environment*, Elsevier, Amsterdam, 1977, 448 pp.

¹⁷⁶ R. B. HUSAR, J. P. LODGE, and D. J. MOORE (eds.), *Sulfur in the Atmosphere*, Pergamon Press, Oxford, 1978, 816 pp. Proceedings of the International Symposium at Dubrovnik, September 1977.

¹⁷⁷ J. O. NRIAGU (ed.), *Sulfur in the Environment. Part 2. Ecological Impacts*, Wiley, Chichester, 1979, 494 pp.

¹⁷⁸ R. W. JOHNSON and G. E. GORDON (eds.), *The Chemistry of Acid Rain*, ACS Symposium **349**, 337 pp. (1987). See also M. Freemantle, *Chem. and Eng. News*, pp. 10–17, May 1, 1995.

¹⁷⁹ D. J. LITTLER (ed.), *Acid Rain*, CEGB Research, Special Issue No. 20, 64 pp. (1987), published by the Central Electricity Generating Board, Southampton SO4 4ZB. See also W. D. Halstead, *CEGB Research* **22**, 3–11 (1988).

Atmospheric SO_2 and Environmental Pollution^(173–179)

The pollution of air by smoke and sulfurous fumes is no new problem[†] but the quickening pace of industrial development during the nineteenth century, and the growing concern for both personal health and protection of the environment generally since the 1950s, has given added impetus to measures required to eliminate or at least minimize the hazard.

As indicated on p. 647, there are vast amounts of volatile sulfur compounds in the environment as a result of natural processes. Geothermal activity (especially volcanic) releases large amounts of SO_2 together with smaller quantities of H_2S , SO_3 , elemental S and particulate sulfates. From a global viewpoint, however, this accounts for less than 1% of the naturally formed volatile S compounds (Fig. A). By far the most important source is the biological reduction of S compounds which occurs most readily in the presence of organic matter and under oxygen-deficient conditions. Much of this is released as H_2S but other compounds such as Me_2S are probably also implicated. The final natural source of atmospheric S compounds is sea-spray (sulfate is the second most abundant anion in sea-water being about one-seventh the concentration of chloride). Though much sulfur is transported as sulfate by wind-driven sea spray and by river run off, its environmental impact is not severe.

[†]One of the earliest tracts on the matter was John Evelyn's *Fumifugium, or the Inconvenience of the Aer and Smoake of London Dissipated* which he submitted (with little effect) to Charles II in 1661. Evelyn, a noted diarist and a founder Fellow of the Royal Society, outlined the problem as follows: "For when in all other places the Aer is most Serene and Pure, it is here [in London] Ecclipsed with such a Cloud of Sulphure, as the Sun itself, which gives day to all the World besides, is hardly able to penetrate and impart it here; and the weary Traveller, at many Miles distance, sooner smells than sees the City to which he repairs. This is that pernicious Smoake which sullies all her Glory, superinducing a sooty Crust or Fur upon all that it lights, spoyling the moveables, tarnishing the Plate, Gildings, and Furniture, and corroding the very Iron-bars and hardest Stones with these piercing and acrimonious Spirits which accompany its Sulphure; and executing more in one year than exposed to the pure Aer of the Country it could effect in some hundreds."

Panel continues

Much more serious is the effect of volatile S compounds (mainly SO_2) released into the atmosphere as a result of man's domestic and industrial activities. This has been estimated to be some 200 million tonnes pa, and is comparable in amount to all the sulfur released by natural processes ($\sim 310 \times 10^6$ tonnes pa). Unfortunately, by the very nature of its origin, this SO_2 is released in the heart of densely populated areas and does great damage to the respiratory organs of man and animals, to buildings, and perhaps most seriously to plants, lake-waters and aquatic life as a result of "acid rain". Dispersal by means of high chimney stacks is inadequate since this merely transfers the problem to neighbouring regions. For example, only one-tenth of the serious $\text{SO}_2/\text{H}_2\text{SO}_4$ pollution of lakes and streams in Sweden is as a result of atmospheric SO_2 emissions in Sweden itself; one-tenth is due to emissions from the UK, and the remaining four-fifths is from industrial regions in northern Europe.

In Europe and the USA (and presumably elsewhere) the major source of SO_2 pollution is in coal-based power generation; this, together with other coal consumption and coking operations accounts for some 60% of the emissions. A further 25% arises from oil-refinery operations, oil-fired power generation, and other oil consumption. Copper-smelting (together with much smaller amounts from zinc and lead ore processing) accounts for some 12% of the annual release of SO_2 . The sulfuric acid manufacturing industry, which is the only one designed actually to make SO_2 on a large scale, only contributes <2% to the total, probably because of the efficient design of the process.

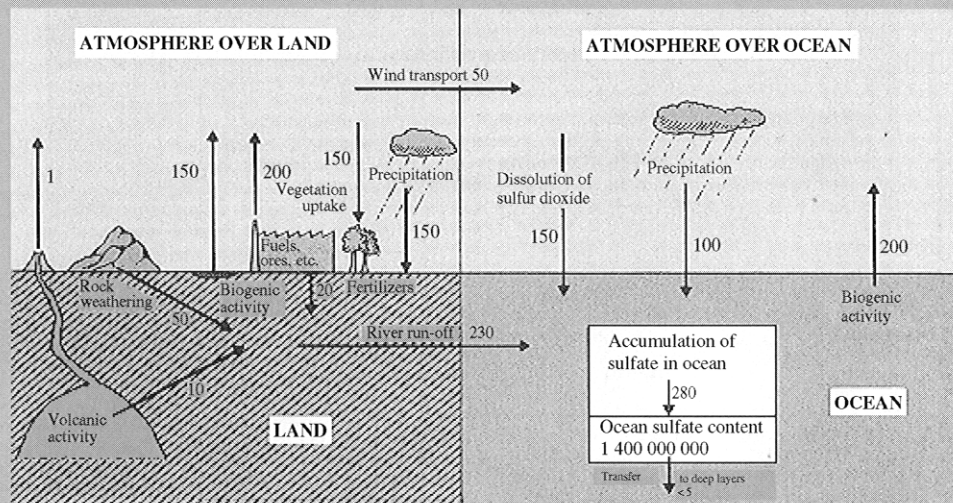
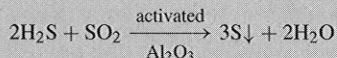


Figure A The sulfur budget for the land-atmosphere-ocean system. Annual turnover rates are indicated in units of 10^6 tonnes (as estimated for 1977).⁽¹⁷³⁾

Ultimately, pollution can only be avoided by complete removal of SO_2 from the effluent gases, but this council of perfection is both technologically and economically unattainable. Many processes are available to reduce the SO_2 concentration to very low figures, but the vast scale of power generation and domestic heating by coal and oil still results in substantial emission. SO_2 can be removed by scrubbing with a slurry of "milk of lime", $\text{Ca}(\text{OH})_2$. Alternatively, partial reduction to H_2S using natural gas (CH_4), naphtha or coal, followed by catalytic conversion to elemental sulfur by the Claus process can be used:



The detection of SO_2 in the atmosphere has become a refined analytical procedure. Several techniques are available such as (a) absorption in aqueous H_2O_2 and titration (or conductimetric determination) of the resulting H_2SO_4 ($\text{H}_2\text{O}_2 + \text{SO}_2 \longrightarrow \text{H}_2\text{SO}_4$); and (b) reaction with $\text{Na}_2[\text{HgCl}_4]$ or $\text{K}_2[\text{HgCl}_4]$:



The resulting disulfite-mercurate is determined colorimetrically after addition of acidic pararosaniline and formaldehyde (P. W. West and G. C. Gaeke, 1956). Other methods are (c) flame-photometric monitoring of the gas stream using a reducing H_2 /air flame and emission of S_2 at 394 nm sensitive down to 1 part in 10^9 by volume and (d) pulsed fluorescent analyser using radiation in the region of 214 nm; this is specific for SO_2 and response is linear over wide ranges down to 1 in 10^9 . Commercial instruments are available.

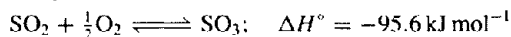
Table 15.16 Some molecular and physical properties of SO₂

Property	Value	Property	Value
MP/°C	-75.5	Electrical conductivity κ /ohm ⁻¹ cm ⁻¹	<10 ⁻⁸
BP/°C	-10.0	Dielectric constant ϵ (0°)	15.4
Critical temperature/°C	157.5	Dipole moment μ /D	1.62
Critical pressure/atm	77.7	Angle O-S-O	119°
Density(-10°)/g cm ⁻³	1.46	Distance r (S-O)/pm	143.1
Viscosity η (0°)/centipoise	0.403	ΔH_f° (g)/kJ mol ⁻¹	-296.9

as a bleach, disinfectant (Homer, p. 645), food preservative, refrigerant and nonaqueous solvent. Other chemical uses are in the preparation of sulfites and dithionites (p. 716) and, with Cl₂, in the derivatization of hydrocarbons via sulfochlorination reactions. There is also much current interest in its properties as a multimode ligand (p. 701).

SO₂ is a colourless, toxic gas with a choking odour. Maximum permitted atmospheric concentration for humans is 5 ppm but many green plants suffer severe distress in concentrations as low as 1–2 ppm. SO₂ neither burns in air nor supports combustion. Some molecular and physical properties of the compound are in Table 15.16. Comparison of these properties with those of ozone (p. 607) is instructive. Note also that the S–O distance of 143.1 pm in SO₂ is less than that in unstable SO (148.1 pm) whereas the O–O distance of 127.8 pm in O₃ is greater than that in stable O₂ (120.7 pm). Furthermore the mean bond energy in SO₂ is 548 kJ mol⁻¹ which is greater than that for SO (524 kJ mol⁻¹) whereas the mean bond energy in O₃ is 297 kJ mol⁻¹ which is less than the value for O₂ (490 kJ mol⁻¹). This has been taken to imply an S–O bond order of at least 2 in SO₂, compared with only 1.5 for O–O in O₃ (p. 607).

By far the most important chemical reaction of SO₂ is its further oxidation to SO₃ according to the equilibrium:



The equilibrium constant, $K_p = p(\text{SO}_3)/[p(\text{SO}_2) \cdot p^{1/2}(\text{O}_2)]$, decreases rapidly with increasing temperature; for example: $\log K_p = 3.49$ at 800°C and -0.52 at 1100°C. Thus for maximum oxidation during the manufacture of H₂SO₄ it is necessary to work at lower temperatures and to increase the rate of reaction by use of catalysts.

Typical conditions would be to pass a mixture of SO₂ and air over Pt gauze or more commonly a V₂O₅/K₂O contact catalyst supported on Kieselguhr or zeolite.

Gaseous SO₂ is readily soluble in water (3927 cm³ SO₂ in 100 g H₂O at 20°). Numerous species are present in this aqueous solution of "sulfurous acid" (p. 717). At 0° a cubic clathrate hydrate also forms with a composition ~SO₂·6H₂O; its dissociation pressure reaches 1 atm at 7.1°. The ideal composition would be SO₂·5 $\frac{3}{4}$ H₂O (p. 627).

In addition to the role of gaseous SO₂ in the manufacture of H₂SO₄, pure (liquid) SO₂ is manufactured on a large scale for the uses mentioned above. Typical production levels (in 1985) were 162 000 tonnes in USA and 65 000 tonnes in (West) Germany. About half of this is used in the manufacture of S-containing chemicals such as sulfites, hydrogen sulfites, thiosulfates, dithionites, salts of hydroxalkane-sulfinic acids and alkane sulfonates. It is also used in cellulose manufacture, in the chemical dressing of Mn-ores, in the removal of S-containing impurities from mineral oils, for food disinfection and preservation, and for treatment of water.

Liquid SO₂ has been much studied as a nonaqueous solvent.⁽¹⁸⁰⁾ Some of the early work (particularly on the physical properties of the solutions) is now known to be in error but

¹⁸⁰T. C. WADDINGTON, Liquid sulfur dioxide, Chap. 6 in T. C. WADDINGTON (ed.), *Nonaqueous Solvent Systems*, pp. 253–84, Academic Press, London, 1965. W. KARCHER and H. HECHT, *Chemie in Flüssigem Schwefeldioxid*, Vol. 3, Part 2, of G. JANDER, H. SPAUNDAU and C. C. ADDISON, *Chemistry in Nonaqueous Ionizing Solvents*, pp. 79–193, Pergamon Press, Oxford, 1967. See also D. F. BUROW, Liquid sulfur dioxide, in J. J. LAGOWSKI (ed.), *Nonaqueous Solvents*, Vol. 3, pp. 138–85, Academic Press, New York, 1970.

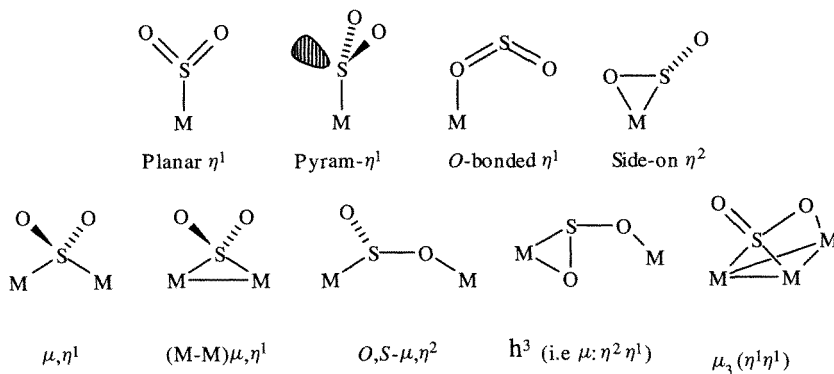
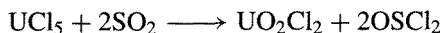
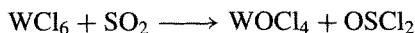
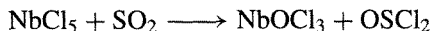


Figure 15.26 Various bonding modes of SO_2 as a ligand.

the solvent is especially useful for carrying out a range of inorganic reactions. It is also an excellent solvent for proton nmr studies. In general, covalent compounds are very soluble: e.g. Br_2 , ICl , OSX_2 , BCl_3 , CS_2 , PCl_3 , OPCl_3 and AsCl_3 are completely miscible, and most organic amines, ethers, esters, alcohols, mercaptans and acids are readily soluble. Many uni-univalent salts are moderately soluble, and those with ions such as the tetramethylammonium halides and the alkali metal iodides are freely so. The low dielectric constant of liquid SO_2 leads to extensive ion-pair and ion-triplet formation but the solutions have limiting molar conductances in the range $190\text{--}250 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at 0° . Solvate formation is exemplified by compounds such as $\text{SnBr}_4 \cdot \text{SO}_2$ and $2\text{TiCl}_4 \cdot \text{SO}_2$ (see below for SO_2 as a ligand). Solvolysis reactions are also documented, e.g.:



Several other reaction types have also appeared in the literature but are sometimes purely formal schemes dating from the time when the solvent was (incorrectly) thought to undergo self-ionic dissociation into SO^{2+} and SO_3^{2-} or SO^{2+} and $\text{S}_2\text{O}_5^{2-}$. More recently it has been shown that, whereas neither SO_2 nor OSMe_2 (dmsO) react with first-row transition metals, the mixed solvent smoothly effects

dissolution of the metals with simultaneous oxidation of S^{IV} to S^{VI} , thereby enabling the production of crystalline solvated metal disulfates ($\text{S}_2\text{O}_7^{2-}$) in high yield.⁽¹⁸¹⁾ Examples are: colourless $[\text{Ti}^{\text{IV}}(\text{OSMe}_2)_6][\text{S}_2\text{O}_7]_2$, green $[\text{V}^{\text{III}}(\text{OSMe}_2)_6][\text{S}_2\text{O}_7]_3$ and the salts $[\text{M}^{\text{II}}(\text{OSMe}_2)_6][\text{S}_2\text{O}_7]$, where $\text{M} = \text{Mn}$ (yellow), Fe (pale green), Co (pale pink), Ni (green), Cu (pale blue), Zn (white) and Cd (white). This is by far the most convenient way to prepare pure disulfates. Dissolution of metals in SO_2 mixed with other solvents such as dmf, dma, or hmpa also occurs, but in these cases there is no oxidation of the S^{IV} , and the product is usually the metal dithionite, $\text{M}^{\text{II}}[\text{S}_2\text{O}_4]$.

Sulfur dioxide as a ligand

The coordination chemistry of SO_2 has been extensively studied during the past two decades and at least 9 different bonding modes have been established.⁽¹⁶⁶⁾ These are illustrated schematically in Fig. 15.26 and typical examples are given in Table 15.17.^(166,182) It is clear that nearly all the transition-metal complexes involve the metals in oxidation state zero or +1. Moreover, SO_2 in the pyramidal η^1 -clusters tends to be reversibly bound (being eliminated when

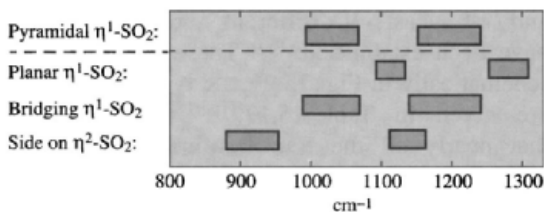
¹⁸¹ W. D. HARRISON, J. B. GILL and D. C. GOODALL, *J. Chem. Soc., Dalton Trans.*, 847–50 (1979). See also *ibid.*, 2995–7 (1987); 728–9 (1988).

Table 15.17 Example of structurally characterized complexes containing SO₂

Planar η^1	Pyramidal η^1	O-bonded η^1	Side-on η^2
[Mn(C ₅ H ₅)(CO) ₂ (SO ₂)]	[RhCl(CO)(PPh ₃) ₂ (SO ₂)]	[SbF ₅ (OSO)]	[Mo(CO) ₂ (PMe ₃) ₂ (η^2 -SO ₂)]
[RuCl(NH ₃) ₄ (SO ₂)Cl]	[[RhCl(PPh ₃) ₂ (SO ₂) ₂]	[[Mg(OSO) ₂ (AsF ₆) ₂] _n]	[Mo(CO) ₂ (bpy)(η^2 -SO ₂)]
[Os(CO)ClH(PCy ₃) ₂ (SO ₂)]	[IrCl(CO)(PPh ₃) ₂ (SO ₂)]	[[Ti(η^6 -C ₆ H ₆)Cl ₄ (OSO)] ₂]	[Mo(η^2 -S ₂ CNEt ₂) ₃ (η^2 -SO ₂)]
[Co(NO)(PPh ₃) ₂ (SO ₂)]	[Ir(SPh)(CO)- (PPh ₃) ₂ (SO ₂)]	[Mn(OPPh ₃) ₄ (OSO) ₂] ₂	[RuCl(η^2 -S ₂ CNEt ₂) ₃ (η^2 -SO ₂)]
[Rh(C ₅ H ₅)(C ₂ H ₄)(SO ₂)]			[Rh(NO)(η^2 -S ₂ CNEt ₂) ₃ - (η^2 -SO ₂)]
[Ni(PPh ₃) ₃ (SO ₂)]	[Pt(PPh ₃) ₃ (SO ₂)]		
[Ni(PPh ₃) ₂ (SO ₂) ₂]	[Pt(PPh ₃) ₂ (SO ₂) ₂]		
Bridging η^1	M-M bridging η^1	Others	
[[Fe(C ₅ H ₅)(CO) ₂] ₂ (μ -SO ₂)]	[Fe ₂ (CO) ₈ (μ -SO ₂)]	<i>O,S</i> - μ - η^2 : [Rh ₂ (PPh ₃) ₄ (μ -Cl)- (μ -OSO) ₂] ₂ (SO ₄)	
[[Co(η^5 -C ₅ H ₅)(μ -PR ₂) ₂] ₂ (μ SO ₂)]	[Fe ₂ (C ₅ H ₅) ₂ (CO) ₃ (μ -SO ₂)]	η^3 (μ : η^2 η^1): [[Mo(CO) ₂ (PPh ₃)- (py)(μ η^3 -SO ₂) ₂] ₂ .2CH ₂ Cl ₂	
[[IrH(CO) ₂ (PPh ₃) ₂] ₂ (μ -SO ₂)]	[Pd ₂ Cl ₂ (dpm) ₂ (μ -SO ₂)]	μ_3 (η^1 η^1): [Rh ₄ (μ -CO) ₄ (μ_3 - SO ₂)[P(OPh) ₃] ₄]. $\frac{1}{2}$ C ₆ H ₆	
[[IrI(CO)(PPh ₃) ₂] ₂ (μ -SO ₂)]	[Pd ₃ (CNBu ^t) ₅ (μ -SO ₂) ₂]	[Pd ₅ (PMe ₃) ₅ (μ_2 -SO ₂) ₂ - (μ_3 -SO ₂) ₂]	
	[Pt ₃ (PPh ₃) ₃ (μ -SO ₂) ₃]		
	[Pt(PPh ₃) ₃ (μ , η^1 -Ph)(μ - PPh ₂)(μ -SO ₂)]		

the complex is heated to <200° and recombining when the system is cooled to room temperature) whereas this tends not to be the case for the other bonding modes. Facile oxidation of the SO₂ by molecular O₂ to give coordinated sulfato complexes (SO₄²⁻) is also a characteristic of pyramidal η^1 -SO₂ which is not shared by the other types.

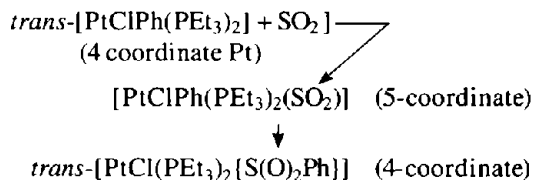
In the absence of X-ray crystallographic data vibrational spectroscopy can sometimes provide information concerning the mode of ligation, the position of the two ν (SO) stretching modes in particular often providing a useful but not always reliable diagnostic.⁽¹⁸²⁾



With such structural diversity it is perhaps not surprising that no certain method has been devised for theoretically predicting the mode of bonding to be expected in specific cases, although

plausible *post hoc* rationalization of the observed structure is sometimes possible.

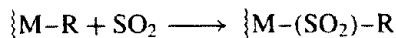
Sometimes coordination of SO₂ to an organometallic complex is followed by intramolecular insertion of SO₂ into the M-C σ bond, e.g.



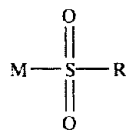
Intermolecular insertion of SO₂ can also occur (without prior formation of an isolable complex) and the general reaction can be represented by the equation:⁽¹⁸³⁾

¹⁸² G. J. KUBAS, *Inorg. Chem.* **18**, 182-8 (1979) and references therein. R. R. RYAN, G. J. KUBAS, D. C. MOODY and P. G. ELLER, *Structure and Bonding*, **46**, 47-100 (1981). More recent work can be found in the following references: J. SIELER *et al.* *Z. anorg. allg. Chem.* **549**, 171-6 (1987); E. WENSCHUH *et al.*, *Z. anorg. allg. Chem.* **600**, 55-60 (1991) and **603**, 21-4 (1991); E. SOLARI, C. FLORIANI and K. SCHENK, *J. Chem. Soc., Chem. Commun.*, 963-4 (1990); D. M. P. MINGOS *et al.* *J. Chem. Soc., Chem. Commun.*, 1048-9 (1988); *J. Chem. Soc., Dalton Trans.*, 1535-41 (1986); 1509-22 (1988); 261-8 (1992).

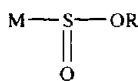
¹⁸³ A. WOJCIK, *Adv. Organomet. Chem.* **12**, 31-81 (1974).



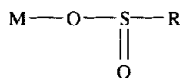
where $\{M$ represents a metal atom and its pendant ligands and R is an alkyl, aryl or related σ -bonded carbon group. The reaction is more flexible (though less important industrially) than the analogous carbonylation reaction of CO (p. 306) and can, in principle, lead to four different types of product:



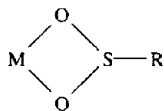
S-sulfinate



O-alkyl-S-sulfoxylate



O-sulfinate



O-O'-sulfinate

Examples of all except possibly the second mode are known.

Sulfur trioxide

SO_3 is made on a huge scale by the catalytic oxidation of SO_2 (p. 700): it is not usually isolated but is immediately converted to H_2SO_4 (p. 708). It can also be obtained by the thermolysis of sulfates though rather high temperatures are required. SO_3 is available commercially as a liquid: such samples contain small amounts (0.03–1.5%) of additives to inhibit polymerization. Typical additives are simple compounds of boron (e.g. B_2O_3 , $B(OH)_3$, HBO_2 , BX_3 , MBF_4 , $Na_2B_4O_7$), silica, siloxanes, $SOCl_2$, sulfonic acids, etc. The detailed mode of action of these additives remains obscure. SO_3 is also readily available as fuming sulfuric acid (or oleum) which is a solution of 25–65% SO_3 in H_2SO_4 (p. 707). Because of its extremely aggressive reaction with most materials, pure anhydrous SO_3 is difficult to handle although it is made in the USA (for example) on a

scale approaching 90 000 tonnes per annum. It can be obtained on a laboratory scale by the double distillation of oleum in an evacuated all-glass apparatus; a small amount of $KMnO_4$ is sometimes used to oxidize any traces of SO_2 .

In the gas phase, monomeric SO_3 has a planar (D_{3h}) structure with S–O 142 pm. This species is in equilibrium with the cyclic trimer S_3O_9 in both the gaseous and liquid phases: $K_p \approx 1 \text{ atm}^{-2}$ at 25° , $\Delta H^\circ \approx 125 \text{ kJ (mole } S_3O_9)^{-1}$. Bulk properties therefore often refer to this equilibrium mixture, e.g. bp 44.6°C , $d(25^\circ)$ 1.903 g cm^{-3} , $\eta(25^\circ)$ 1.820 centipoise. Below the mp (16.86°), colourless crystals of ice-like orthorhombic γ - SO_3 separate and structural studies reveal that the only species present is the trimer S_3O_9 (Fig. 15.27). Traces of water (10^{-3} mole%) lead to the rapid formation of glistening, white, needle-like crystals of β - SO_3 which is actually a mixture of fibrous, polymeric polysulfuric acids $HO(SO_2O)_xH$, where x is very large ($\approx 10^3$). The helical chain structure of β - SO_3 is shown in Fig. 15.27 (cf. polyphosphates, p. 528). A third and still more stable form, α - SO_3 , also requires traces of moisture or other polymerizing agent for its formation but involves some cross-linking between the chains to give a complex layer structure (mp 62°). The standard enthalpies of formation ($\Delta H_f^\circ/\text{kJ mol}^{-1}$) of the various forms of SO_3 at 25°C are: gas -395.2 , liquid -437.9 , γ -crystals -447.4 , β -crystals -449.6 , α -solid -462.4 .

SO_3 reacts vigorously and extremely exothermically with water to give H_2SO_4 . Substoichiometric amounts yield oleums and mixtures of various polysulfuric acids (p. 712). Hydrogen halides give the corresponding halogenosulfuric acids HSO_3X . SO_3 extracts the elements of H_2O from carbohydrates and other organic matter leaving a carbonaceous char. It acts as a strong Lewis acid towards a wide variety of inorganic and organic ligands to give adducts: e.g. oxides give SO_4^{2-} , Ph_3P gives $Ph_3P \cdot SO_3$ (with a rather long P–S bond, 217.6 pm)⁽¹⁸⁴⁾

¹⁸⁴ R. L. BEDDOES and O. S. MILLS, *J. Chem. Research* (M) 2772–89 (1981); (S) 233 (1981); see also *J. Chem. Soc., Chem. Commun.*, 789–90 (1981).

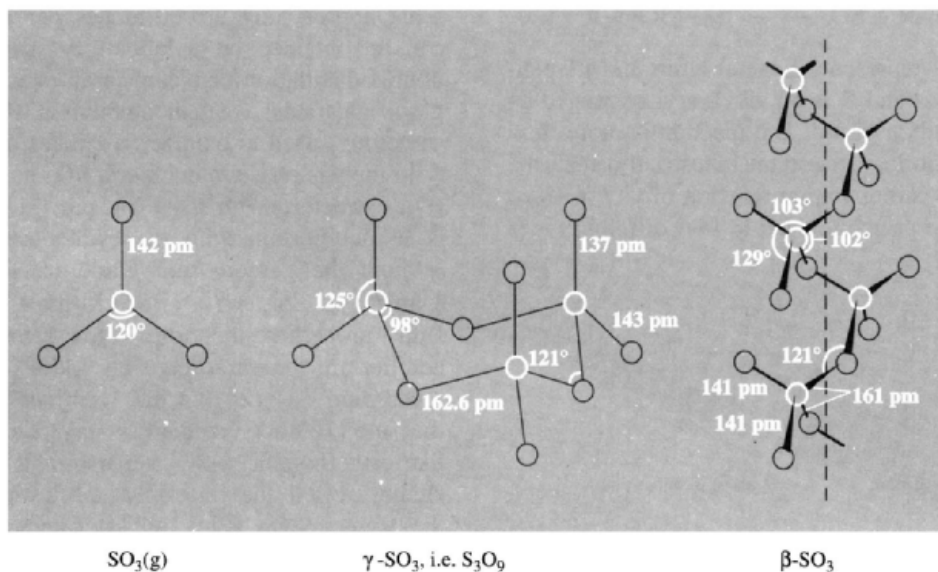
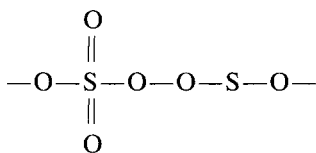


Figure 15.27 Structure of the monomeric, trimeric and chain-polymeric forms of sulfur trioxide.

Ph_3AsO gives $\text{Ph}_3\text{AsO}\cdot\text{SO}_3$ etc. Frequently further reaction ensues: thus, under various conditions reaction with NH_3 yields $\text{H}_2\text{NSO}_3\text{H}$, $\text{HN}(\text{SO}_3\text{H})_2$, $\text{HN}(\text{SO}_3\text{NH}_4)_2$, $\text{NH}_4\text{N}(\text{SO}_3\text{NH}_4)_2$, etc. SO_3 can also act as a ligand towards strong electron-pair acceptors such as AsF_3 , SbF_3 and SbCl_3 . It is reduced to SO_2 by activated charcoal or by metal sulfides. The reaction with metal oxides (particularly Fe_3O_4) to give sulfates is used industrially to rid stack-gases of unwanted byproduct SO_3 .

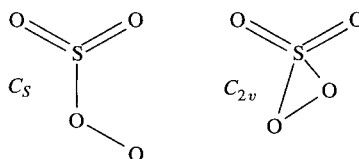
Higher oxides

The reaction of gaseous SO_2 or SO_3 with O_2 in a silent electric discharge gives colourless polymeric condensates of composition SO_{3+x} ($0 < x < 1$). These materials are derived from $\beta\text{-SO}_3$ by random substitution of oxo-bridges by peroxy-bridges:



Hydrolysis of the polymers yields H_2SO_4 and H_2SO_5 (p. 712), with H_2O_2 and O_2 as secondary products.

Monomeric neutral SO_4 can be obtained by reaction of SO_3 and atomic oxygen; photolysis of SO_3 /ozone mixtures also yields monomeric SO_4 , which can be isolated by inert-gas matrix techniques at low temperatures (15–78 K). Vibration spectroscopy indicates either an open peroxy C_s structure or a closed peroxy C_{2v} structure, the former being preferred by the most recent study, on the basis of agreement between observed and calculated frequencies and reasonable values for the force constants:⁽¹⁸⁵⁾



The compound decomposes spontaneously below room temperature.

¹⁸⁵ P. LA BONVILLE, R. KUGEL, and J. R. FERRARO, *J. Chem. Phys.* **67**, 1477–81 (1977).

Table 15.18 Oxoacids of sulfur

Formula	Name	Ox. states	Schematic structure*	Salt
H ₂ SO ₄	sulfuric	VI		sulfate, SO ₄ ²⁻ H-sulfate, HOSO ₃ ⁻
H ₂ S ₂ O ₇	disulfuric	VI		disulfate, O ₃ SOSO ₃ ²⁻
H ₂ S ₂ O ₃	thiosulfuric	IV, 0, (or VI, -II)		thiosulfate, SSO ₃ ²⁻
H ₂ SO ₅	peroxomonosulfuric	VI		peroxomonosulfate, OOSO ₃ ²⁻
H ₂ S ₂ O ₈	peroxodisulfuric	VI		peroxodisulfate, O ₃ SOOSO ₃ ²⁻
H ₂ S ₂ O ₆	dithionic*	V		dithionate, O ₃ SSO ₃ ²⁻
H ₂ S _{n+2} O ₆	polythionic	V, 0		polythionate, O ₃ S(S) _n SO ₃ ²⁻
H ₂ SO ₃	sulfurous*	IV		sulfite, SO ₃ ²⁻ H-sulfite, HOSO ₂ ⁻
H ₂ S ₂ O ₅	disulfurous*	V, III		disulfite, O ₃ SSO ₂ ²⁻
H ₂ S ₂ O ₄	dithionous*	III		dithionite, O ₂ SSO ₂ ²⁻

*Acids marked with an asterisk do not exist in the free state but are known as salts.