

1

INTRODUCTION

Figure 1.1 summarizes the general pattern of the changes undergone by sulphur-containing compounds in nature and serves to stress the rather important role which living organisms play in the geochemistry of sulphur. This role is not coincidental but reflects the fact that sulphur-containing compounds participate in all living processes.

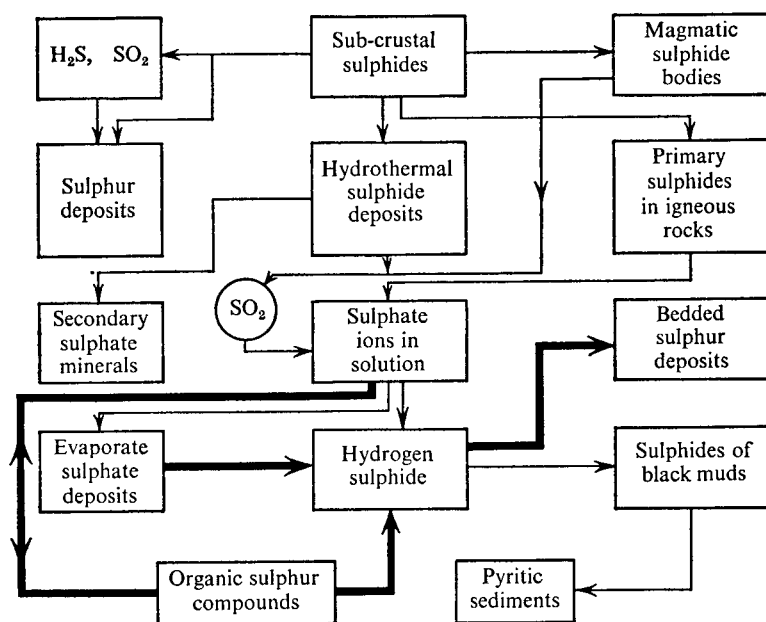


Fig. 1.1. The geochemical transformations of sulphur. Biological processes are outlined with thick lines. (Adapted from Day, 1963.)

Sulphur, as a constituent of amino acids such as cysteine and methionine and of cofactors such as biotin, thiamin, coenzyme A and lipoic acid, is essential for the structure and function of all living cells. The ultimate sources of this element are inorganic compounds of sulphur which, in the case of micro-organisms and plants, may be obtained directly from the

INTRODUCTION

environment and subsequently incorporated into organic forms. Animals, on the other hand, require preformed sulphur-containing amino acids and vitamins. In general, they obtain only small amounts of inorganic sulphur compounds from the environment and their requirements for such compounds are, for the most part, met by the oxidation of the sulphur-containing amino acids.

Aside from these general functions of sulphur, certain specialized groups of micro-organisms utilize either oxidative or reductive reactions on inorganic sulphur compounds in the energy-yielding processes of their metabolism.

The types of sulphur-containing compounds available to living organisms are many. In the hydrosphere they are mainly inorganic: in sea water, for instance, only sulphate is quantitatively important with a concentration of about 0.03 M. Fresh water is more variable in composition and, depending upon many factors—geological, physical and biological—may contain either oxidized or reduced forms of sulphur: that is, principally sulphate or sulphide. In the lithosphere the chemical composition is much more complex, again depending upon the interplay of many factors, and both sulphate-containing and sulphide-containing rocks are widespread. In soil, organic derivatives of sulphur are important and it may come as a surprise that sulphate esters can account for a considerable proportion of the sulphur in soil (Freney, 1967 *a*). A further source of sulphur which must not be forgotten is the atmosphere in which the main sulphur-containing compound is sulphur dioxide, except in areas where volcanic gases are important when large amounts of hydrogen sulphide may also be present. This sulphur dioxide may be utilized by higher plants either by its direct absorption through the leaves or indirectly after its uptake by, and interconversion in, the soil. The importance of this process must not be underestimated because it generally appears to be the case that the sulphur present in harvested crops exceeds the available sulphur of the soil in which they were grown so that the difference must come from the atmosphere.

The biological changes in the various compounds of sulphur are best summarized in the form of a sulphur cycle, fig. 1.2, which will be considered in rather more detail below: at present it can be summarized by saying that, in general, micro-organisms and plants utilize the inorganic sulphur-containing compounds of the soil (or water) to form the sulphur-containing amino acids and other organic compounds required for their existence. These complex organic compounds are then utilized by the

Cambridge University Press

978-0-521-14306-6 - The Biochemistry of Inorganic Compounds of Sulphur

A. B. Roy and P. A. Trudinger

Excerpt

[More information](#)

INTRODUCTION

higher animals. Simple inorganic compounds are reformed by degradative processes which occur, to some extent at least, in all organisms.

The importance of these interconversions cannot be too highly stressed because it is upon the production of 'reduced' sulphur that the higher animals depend for their nutrition. The only exception to this generalization is that ruminants, and probably also birds, can utilize inorganic compounds of sulphur through their symbiotic association with micro-organisms in their digestive tracts. Plants generally utilize inorganic compounds of sulphur but the fertility with respect to this element of any particular soil can be greatly modified by the activities of the micro-flora present therein.

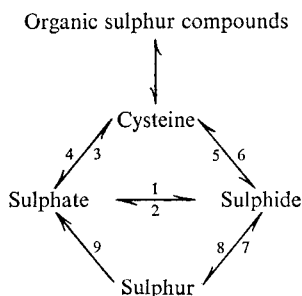


Fig 1.2

It must be stressed that the general picture of sulphur metabolism given in fig. 1.2 does not indicate the *pathways* of the various transformations in living organisms but only their end-points. Nevertheless, a convenient introduction to the general problem of the biochemistry of inorganic compounds of sulphur can be made through a brief consideration of the various changes enumerated in this figure.

1. *Reduction of sulphate to sulphide.* This transformation is carried out on an extensive scale only by certain micro-organisms, the dissimilatory sulphate-reducers (e.g. *Desulfovibrio* and *Desulfotomaculum*). On a small scale it is, of course, carried out by many micro-organisms and plants although not to any significant extent by higher animals.

2. *Oxidation of sulphide to sulphate.* Again on a small scale this is widespread, occurring even in mammals: on a large scale it is carried out by organisms such as thiobacilli and the photosynthetic sulphur bacteria.

3. *Incorporation of sulphate into amino acids.* This process is again quite widespread although it is absent, at least from a practical point of view, from mammals apart from ruminants.

INTRODUCTION

4. *Conversion of amino acids to sulphate.* This is the principal catabolic reaction undergone by the sulphur-containing amino acids and it probably occurs in all living organisms. In higher animals it is of unique importance because it is the main, if not the sole, source of inorganic compounds of sulphur.

5. *Conversion of amino acids to sulphide.* This reaction occurs in most micro-organisms. It can also occur in the higher animals but its extent and significance are not clear.

6. *Conversion of sulphide to amino acids.* This seems to be a quite ubiquitous process.

7. *Conversion of sulphur to sulphide.* This process can occur fairly readily by non-enzymatic reactions and so is probably of widespread, or potentially widespread, occurrence. Only in some bacteria and fungi does it normally occur to any extent and certainly the higher animals are unlikely ever to have to metabolize significant quantities of elemental sulphur.

8 and 9. *Oxidation of sulphide through sulphur to sulphate.* These transformations are characteristically bacterial in origin and they are of fundamental importance in organisms such as *Beggiatoa*, thiobacilli, and the photosynthetic sulphur bacteria.

In general terms, then, the subject matter of this book is concerned with the details of the above pathways and with their relation to other metabolic pathways in the organism. Some of these relationships are relatively clear, particularly in micro-organisms: for example, in certain photosynthetic bacteria sulphur compounds are accessory electron donors for the photosynthetic reaction while in certain chemoautotrophic organisms the oxidation of simple inorganic sulphur compounds is used to produce the energy required for synthetic processes. On the other hand, sulphate is used as an electron acceptor in the energy-yielding reactions carried out by the anaerobic dissimilatory sulphate-reducing bacteria. In micro-organisms generally and in plants the main role of sulphur metabolism seems to be the production of the sulphur-containing amino acids. Complications are caused, however, by the existence of a further metabolic cycle, the sulphate cycle represented in fig. 1.3, all the reactions of which are rather widely distributed in nature, occurring in micro-organisms, plants and animals. The enzymes involved in this cycle are rather specific and the details vary considerably from organism to organism but in general it can be said that it seems to reach its highest development (in the sense of the complexity of the enzyme systems) in the higher animals.

The relationship of this sulphate cycle to the general metabolic path-

Cambridge University Press

978-0-521-14306-6 - The Biochemistry of Inorganic Compounds of Sulphur

A. B. Roy and P. A. Trudinger

Excerpt

[More information](#)

INTRODUCTION

ways of the organism, particularly if it be a higher animal, is obscure, the more so as the synthesis of sulphate esters involves the intermediate formation of an 'activated sulphate', a process which requires the utilization of two molecules of ATP per molecule of sulphate. The energy so used is not, in general, recoverable by the fission of the sulphate-ester linkage and certainly not if the process is hydrolytic.

The transformations outlined in figs. 1.2 and 1.3 must be regarded as closely integrated parts of one complex metabolic pathway because activated forms of sulphate participate not only in the formation of sulphate esters but also in the interconversions of sulphate and sulphite.

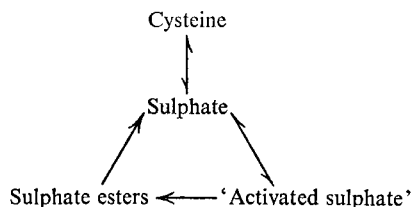


Fig. 1.3

Obviously much remains to be discovered about the function of sulphuric acid and its esters in biochemistry. It is difficult to avoid suggesting that our knowledge of this subject may only be at a stage not far removed from the understanding of the role of phosphoric acid and its esters prior to the work of Harden and Young in 1905. The true function of sulphate ions in biochemistry may have yet to be realized. One wonders what would be our present knowledge of the metabolic function of these ions if there had been available for their determination a method as simple and as sensitive as the colorimetric methods which have long been used for the determination of phosphate.

So far mention has been made only of the inorganic compounds of sulphur and of some simple organic derivatives thereof such as the sulphate esters. Living organisms, however, contain or can form many other organic compounds of sulphur, most of which contain C—S bonds: see, for example, the discussion by Freney (1967 *a*) of the types of sulphur compound found in soil. In general, such compounds will not be given detailed consideration in this book except for the special case of the thiosulphate esters, or Bunte salts, which contain the C—S bond but which are (or can be regarded as) sulphate esters of thiols. Other com-

Cambridge University Press

978-0-521-14306-6 - The Biochemistry of Inorganic Compounds of Sulphur

A. B. Roy and P. A. Trudinger

Excerpt

[More information](#)

INTRODUCTION

pounds containing C—S bonds will be considered only in so far as their metabolism is connected with the metabolism of inorganic compounds of sulphur. Examples of such substances are the many types of sulphonc acid found in nature: for instance, taurine with its important role in the metabolism of liver and its many other more or less well authenticated functions (see review by Jacobsen & Smith, 1968); isethionic acid with its possible role in regulating the excitability of tissues (Jacobsen & Smith, 1968) and 6-sulpho-D-quinovose, a constituent of the widely distributed plant sulpholipid (Benson, 1963). Many other types of compound containing C—S bonds could be mentioned including, for instance, ergothionine, lipoic acid, coenzyme A, thiamin, biotin and penicillin (the latter three being sulphur heterocycles) to name only a few, but the biochemistry of these compounds will not be considered here and information on them must be sought elsewhere (see Young & Maw, 1958; Kun, 1961). Compounds containing N—S bonds are rare in nature and only one type, the sulphamates, which can be regarded as atypical sulphate esters, will be considered briefly. Naturally occurring heterocycles containing N—S bonds do not appear to be known.

A considerable part of the interest in the biochemistry of sulphur and its inorganic compounds stems from the view that energy metabolism based on this element may have preceded, in an evolutionary sense, those based on oxygen. It is commonly held that the primordial conditions on the earth were highly reducing (Abelson, 1966; Cloud, 1968) and that sulphur existed largely in the form of sulphides: from this has developed the idea that primitive life may have been based on the photosynthetic oxidation of sulphides to sulphur and sulphate. Such primitive photosynthetic sulphur-oxidizers thus served as precursors of the modern photosynthetic sulphur bacteria as well as of dissimilatory sulphur reducers and the chemosynthetic sulphur oxidizers. Certainly there is evidence, based on the distribution of stable sulphur isotopes in nature, that dissimilatory sulphate reduction was occurring some 3.5×10^9 years ago which, in a geological sense, is soon after the emergence of life on the earth (about 4×10^9 years ago). Free oxygen, on the other hand, probably did not appear in the atmosphere until about $1-2 \times 10^9$ years ago and certainly only accumulated at a much later date, after the development of the photosynthetic activities of green plants. Presumably only after this time did the oxygen-requiring sulphur autotrophs develop. For a more detailed consideration of this topic the most interesting speculations of Peck (1966-7) should be consulted.

Cambridge University Press

978-0-521-14306-6 - The Biochemistry of Inorganic Compounds of Sulphur

A. B. Roy and P. A. Trudinger

Excerpt

[More information](#)

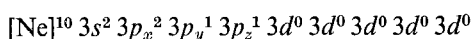
2

**THE CHEMISTRY OF SOME
SULPHUR COMPOUNDS**

In this chapter it is our intention to outline very briefly the structures and some properties of a number of sulphur compounds which are important in the metabolism of inorganic sulphur. The literature on sulphur chemistry is, of course, vast and for detailed treatments the reader is referred to standard texts such as those of Abegg, Auerbach & Koppel (1927), Mellor (1930), Gmelin (1960, 1963) and Durrant & Durrant (1962).

Our particular aims, in this chapter, are to highlight first those reactions which occur readily at physiological temperatures and pH values and thus may lead to secondary, non-specific events during metabolic experiments, and secondly some chemical reactions which may be models for enzymic reactions on sulphur compounds. Other reactions which are primarily of analytical interest are discussed in chapter 4.

Sulphur exhibits valencies of 2, 4 and 6 and oxidation states of -2 , 0, $+2$, $+4$ and $+6$, and its electronic structure in the ground state is depicted thus:



A characteristic feature of sulphur is its readiness to form the S—S bond and consequently to form long chains of sulphur atoms. Branched sulphur chains are apparently not formed (cf. Foss, 1950, 1960).

Pauling (1949) considered that the σ bond between two sulphur atoms is nearly pure p in character. Every sulphur atom then still possesses two free electron pairs, one of which, the s -pair, is spherically distributed around the nucleus. The remaining pair exist as $3p\pi$ electrons on the 90° axes and cause a barrier to rotation around the sulphur–sulphur bond which arises from Coulombic repulsion between unshared p -electrons on adjacent sulphur atoms.

This concept has been challenged by Schmidt (1963) who considers it inadequate to explain many experimental results on the nucleophilic degradation of sulphur–sulphur bonds. He suggests that the ‘free’ $p\pi$ electrons of a particular sulphur atom are not, in fact, free but are involved

Cambridge University Press

978-0-521-14306-6 - The Biochemistry of Inorganic Compounds of Sulphur

A. B. Roy and P. A. Trudinger

Excerpt

[More information](#)

THE CHEMISTRY OF SOME SULPHUR COMPOUNDS

in sulphur–sulphur bond formation by overlap with an available *d*-orbital of the bonding partner. The sulphur–sulphur bond would then have some *pd π* -bond character which may account for its stability (see also Foss, 1961 *a*) and possibly also its non-planarity (Krebs, 1957). Moffitt (1950) has shown that sulphur utilizes the 3*d* electron orbitals to attain the hexavalent state in compounds containing sulphur–oxygen bonds; these bonds therefore have some double bond character.

2.1 Structures of some inorganic compounds

2.1.1 Elemental sulphur

Elemental sulphur exists in a large number (about 30) of solid allotropes (Meyer, 1964) but only orthorhombic and colloidal sulphur will be considered here. The significance of the other allotropic forms with respect to metabolism is doubtful: indeed many of these forms are prepared and exist only under special conditions which are incompatible with biological activity.

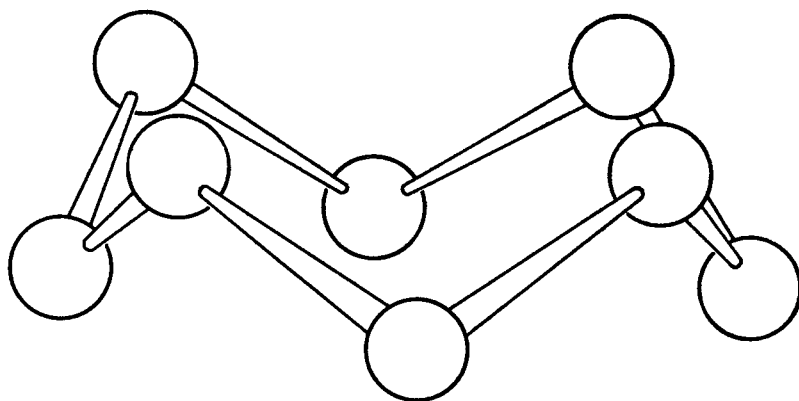


Fig. 2.1 The molecular structure of orthorhombic sulphur.

Orthorhombic sulphur (S_8) is the only thermodynamically stable form under normal temperatures and pressures: all other allotropes ultimately convert to it (Meyer, 1964). Its structure is that of a staggered eight membered ring (fig. 2.1; Warren & Burwell, 1935; Abrahams, 1955) with the following molecular constants (Donohue, 1961, 1965): average S–S bond length, 2.060 Å; average S–S–S bond angle, 108.0°; average S–S–S–S dihedral angle 99.3°. Orthorhombic sulphur is readily identified by means of its X-ray diffraction pattern (see index

Cambridge University Press

978-0-521-14306-6 - The Biochemistry of Inorganic Compounds of Sulphur

A. B. Roy and P. A. Trudinger

Excerpt

[More information](#)

STRUCTURES OF SOME INORGANIC COMPOUNDS

cards 8-247 and 8-248, powder diffraction file, American Society for testing and materials, Philadelphia, 1966).

Orthorhombic sulphur is essentially insoluble in water but dissolves in a number of organic solvents (table 2.1). Its solubility in some natural fats and oils may possibly be of biological significance (see, for example, Umbreit, Vogel & Vogler, 1942).

Colloidal sulphur exists in hydrophobic and hydrophilic forms according to the method of preparation (see Mellor, 1930). An early suggestion was that the hydrophilic form is stabilized by the presence of pentathionate in the micelles and Weitz, Gieles, Singer & Alt (1956) have shown that colloidal sulphur behaves, in many of its properties, as a polythionate containing 40–140 sulphur atoms.

TABLE 2.1 *Solubility of elemental sulphur (Linke, 1965)*

	Solubility (g sulphur/100 g solvent)		
	20°	100°	Other
CS ₂	41.8	92	.
CCl ₄	.	.	0.86 g/100 g sat. soln. at 25°
benzene	1.7	17.5	.
linseed oil	0.6(30°)	.	.
olive oil (S.G. 0.885)	4.3(30°)	.	.
lanoline (anhydrous)	0.38(45°)	.	.

2.1.2 Oxyacids of sulphur

Sulphur forms a large number of oxyacids although most of these are known only in solution; their ions, however, are well characterized. Sulphate, sulphite, thiosulphate, polythionates and possibly dithionate have been shown to be involved in various phases of the reductive and oxidative metabolism of sulphur. The occasional suggestions that other sulphuroxy ions such as dithionite and persulphates may also be metabolic intermediates await confirmation and these compounds will not be discussed further in this chapter. The hypothetical acids, sulphylic (sulphur dihydroxide, S(OH)₂), thiosulphurous (disulphur dihydroxide, S₂(OH)₂) and sulphenic (sulphur hydrate, SH₂O) whose structures are somewhat uncertain, have often been proposed as transient intermediates in hydrolytic reactions on inorganic sulphur compounds and may possibly be formally analogous to transient intermediates (free or bound) arising during metabolism of sulphur compounds.

Cambridge University Press

978-0-521-14306-6 - The Biochemistry of Inorganic Compounds of Sulphur

A. B. Roy and P. A. Trudinger

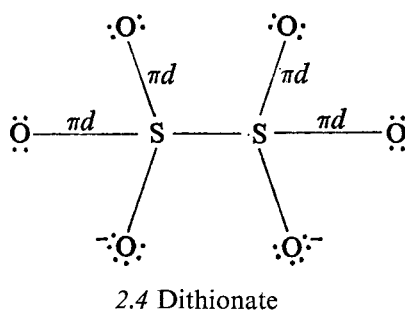
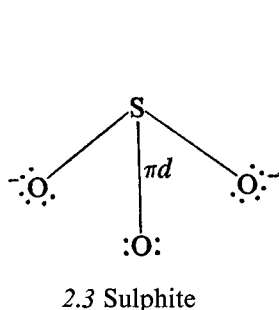
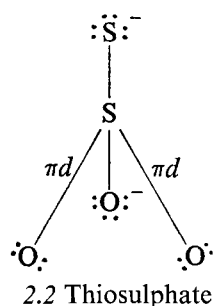
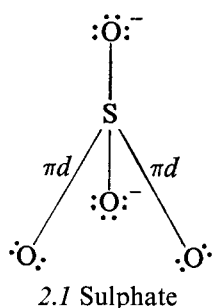
Excerpt

[More information](#)

THE CHEMISTRY OF SOME SULPHUR COMPOUNDS

Sulphate, thiosulphate, dithionate, sulphite

The structures of the sulphate, thiosulphate, sulphite and dithionate ions are shown in formulae 2.1 to 2.4



All are resonance structures in which the oxygen atoms are equivalent. The sulphate and thiosulphate groups are tetrahedral forms with the hexavalent sulphur at their centres as also are the two sulphonate groups of dithionate: sulphite is pyramidal.

Thiosulphate may be viewed as being derived from sulphate by substitution of an oxygen atom by sulphur. The non-equivalence of the two sulphur atoms in thiosulphate was elegantly demonstrated by Buch Andersen (1936) who synthesized thiosulphate from ^{35}S -labelled elemental sulphur and unlabelled sulphite (equation 2.1) and showed that the labelled product decomposed in the presence of hydrogen or silver ions to give the distribution of ^{35}S shown in equations 2.2 and 2.3.

