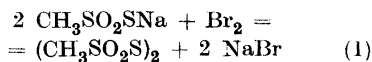


## Dimethanesulphonyl Disulphide

OLAV FOSS

*Universitetets Kjemiske Institutt,  
Blindern — Oslo, Norway*

Dimethanesulphonyl disulphide is the pseudohalogen corresponding to the pseudohalide, methanethiosulphonate. It is formed when sodium or potassium methanethiosulphonate, suspended in ether, reacts with bromine:



The compound separates from ether as colourless needles or plates, m. p. 61° C. It is insoluble in water, sparingly soluble in methanol and petroleum, and readily soluble in ether, benzene and chloroform. It was recovered unchanged from a 10 % solution in benzene after heating to 80° C for 5 minutes. A corresponding aromatic compound, dibenzenesulphonyl disulphide, undergoes rapid rearrangement if heated in glacial acetic acid<sup>1, 2</sup>.

Earlier<sup>3</sup>, the term 'thiosulphonatogen' was suggested for compounds of this type.

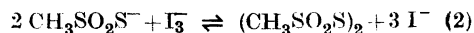
'Pro-xanthopterin' is not identical with pteroylglutamic acid or any of its photolytic products<sup>4</sup>.

Our thanks are due to Lederle Laboratories Division, American Cyanamid Co., New York, and to Kong Christian Xende Fond for financial support.

1. Koschura, W., and Hrubesch, A. *Z. physiol. Chem.* **238** (1939) 39.  
Koschura, W., Seipen, S. and Aldred, P. A. *Z. physiol. Chem.* **262** (1940) 158.
2. Kalekar, H. M., Klenow, H. *J. Biol. Chem.* **172** (1948) 349.
3. Schou, M. A. To be published.
4. Lowry, O. H., Bessey, O. A., and Crawford, E. J. *J. Biol. Chem.* **180** (1949) 389.

Received October 3, 1949.

Dimethanesulphonyl disulphide is the first aliphatic thiosulphonatogen to be prepared. Its pseudohalogen properties are displayed in the reversible equilibrium:



the equilibrium constant of which is the same as for the corresponding ethanethiosulphonate equilibrium<sup>4</sup>, viz., about unity, at room temperature.

In polythionic compounds there are, generally, two structural possibilities, viz., that of unbranched, zigzag sulphur chains, and that of branched, co-ordinated structures. The reactions (1) and (2) show that dimethanesulphonyl disulphide is built up from two methanethiosulphonate radicals. The unpaired electron of such a radical is situated on the thio sulphur atom of the radical, because of the lower electron affinity of sulphur as compared with oxygen, and therefore, the bond joining the two thiosulphonate groups of dimethanesulphonyl disulphide is between two divalent sulphur atoms. Thus, from chemical considerations, dimethanesulphonyl disulphide has an unbranched sulphur chain structure, like other thio pseudohalogens and disulphides.

*Experimental.* About 20 % excess, with respect to bromine, of finely powdered, dry sodium or potassium methanethiosulphonate was employed, and 10–15 ml of dry ether per g of thiosulphonate. The suspension was cooled in ice, and the bromine slowly added. On treatment of the solid particles with a glass rod the bromine colour vanished rapidly. The mixture was heated gently, and filtered with suction through a sintered glass filter. The residue on the filter was treated with warm ether, and the washings added to the filtrate. On partial evaporation and cooling the product separated as small needles or plates, m. p. 61° C (corr.). It is best recrystallized from ether.

## The Structure of Dimethanesulphonyl Disulphide

HARALD SØRUM AND OLAV FOSS

*Fysisk Institutt, Norges Tekniske Høgskole,  
Trondheim, Norway, and Universitetets  
Kjemiske Institutt, Blindern — Oslo, Norway*

In the present note, some preliminary results are reported of a crystal structure analysis of dimethanesulphonyl disulphide<sup>1</sup>. This compound is the analogue of potassium tetrathionate, for which lattice dimensions, space group and refractive indices are known<sup>2</sup>. No other data on tetrathionic compounds are reported in literature.

The crystals of dimethanesulphonyl disulphide are in most cases found as colourless, transparent needles or plates elongated in the *a*-axis direction. The most frequent faces of the monoclinic crystals are (010), (021), (001) and (011). The crystals seem to have good cleavage parallel to the planes (011) and (01 $\bar{1}$ ) with less good cleavage parallel to the (010) plane.

0.1029 g substance: 0.4325 g BaSO<sub>4</sub>.  
(CH<sub>3</sub>SO<sub>2</sub>S)<sub>2</sub> (222.3)

Calc. S 57.68. Found S 57.72.

Further experiments on aliphatic thio-sulphonates and disulphonyl disulphides, including measurements of their equilibria with iodide-iodine, will be described in a later article.

1. Otto, R., and Troeger, J. *Ber.* **24** (1891) 1125.
2. Troeger, J., and Hornung, V. *J. prakt. Chem.* [2] **60** (1899) 113.
3. Foss, O. *Acta Chem. Scand.* **1** (1947) 8.
4. Foss, O. *Acta Chem. Scand.* **1** (1947) 307.

Received October 30, 1949.

The dimensions of the unit cell were obtained from rotation and goniometer photographs:  $a = 5.52 \pm 0.02$  Å,  $b = 15.78 \pm 0.02$  Å,  $c = 10.05 \pm 0.02$  Å.  $\beta = 97.6^\circ$  and  $V = 866$  Å<sup>3</sup>. The values for the axial lengths correspond to axial ratios of  $a : b : c = 0.349 : 1 : 0.637$ . The density of the crystals is 1.71 g/cm<sup>3</sup> and the number of (CH<sub>3</sub>SO<sub>2</sub>S)<sub>2</sub> in the unit cell therefore 4. The following reflexions are absent in the X-ray photographs:  $0k0$  when  $k$  is odd,  $00l$  when  $l$  is odd, and  $h0l$  when  $l$  is odd. The  $b$ -axis is accordingly a twofold screw axis and the (010) plane is a glide plane of symmetry with translation  $c/2$ . Laue patterns indicate monoclinic holohedry and no other observations contradict this finding. The space group is therefore  $C_{2h}^5 - P_c^{21}$ .

The molecule could possibly have a plane, a centre or twofold axis of symmetry. The space group  $C_{2h}^5$  possesses only glide planes, screw axis and centres. The possibilities of molecular symmetry are therefore reduced to centre only. It has, however, proved impossible to account for the observed reflexion intensities if the centres of the molecules should be located to the symmetry centres of the space group. The molecules must consequently be placed in general positions, and can thus have no strict symmetry of its own. A general point repeats four times in the space group  $C_{2h}^5$ . All the molecules must therefore be crystallographically equivalent to each other, since there are only four molecules in the unit cell.

A preliminary analysis has shown that the molecule has an unbranched sulphur chain structure. The main direction of the sulphur chain is nearly parallel to the [011] or [01 $\bar{1}$ ] direction alternately. The approximate centres of the four molecules are located very closely to the positions:

$$x \frac{1}{8} \frac{1}{8}; x \frac{\bar{1}}{8} \frac{\bar{1}}{8} \text{ and } x \frac{7}{8} \frac{7}{8}; x \frac{\bar{7}}{8} \frac{\bar{7}}{8}$$