

Tetrathiooxalate. Electrochemical Preparation and X-Ray Structure Determination of a Tetrathiooxalate

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Some years ago it was shown^{1,2} that earlier claims of the preparation of tetrathiooxalic acid^{3,4} by reduction of carbon disulfide (*1*) could not be substantiated. Later a number of groups have investigated the reduction of carbon disulfide⁵⁻¹⁴ electrochemically, by means of sodium amalgam, sodium in liquid ammonia or in hexamethylphosphoric triamide, potassium in DMF, or sodium naphthalenide in DMF. Similarly, carbon diselenide has been reduced.¹⁵

The reduction of *1* in aprotic medium followed by methylation yields^{1,2} 4,5-bis(methylthio)-1,3-dithiole-2-thione (*2*) together with dimethyl trithiocarbonate (*3*), tetrakis(methylthio) ethylene and some minor products. It has been shown¹⁴ by high-pressure liquid chromatography (HPLC) that tetrathiooxalate is formed during the electrochemical reduction in DMF, but the compound reacts slowly on standing in the mixture to trithiocarbonate dianion and other products.

Dimethyl tetrathiooxalate has been prepared^{16,17} from *2* through photochemical decarbonylation of 4,5-bis(methylthio)-1,3-dithiol-2-one and some of its chemical reactions have been described.¹⁸

The formation of *2* has been suggested¹ to proceed through a primary formation of tetrathiooxalate dianion (*4*) by dimerization of *1*⁻; an alternative mechanism has been proposed⁶ in which *2* is formed by reaction between carbon sulfide and trithiocarbonate dianion.

The former reaction route has been shown¹⁴ to be a major route to *2*, so there should be a chance of scavenging *4* in some way before it reacts further. An alkylating or acylating agent would produce compounds which would be expected to be further reducible under the employed conditions and thus not produce derivatives of *4*. A more promising possibility would be to work under conditions where *4* would form a slightly soluble salt; the tetrathiooxalate dianion would be expected to be difficultly reducible.

It has been reported^{10,12} that a yellow-brown precipitate has been obtained on electrochemical reduction of *1* in acetonitrile with tetraethylammonium bromide or perchlorate as supporting electrolyte; the precipitate has been suggested¹² from its elementary analysis, IR spectrum and chemical properties to be a bis(tetraethylammonium)hexathioperoxydicarbonate.

Electrochemical reduction of *1* in acetonitrile saturated with potassium iodide gave a brownish potassium salt in modest yield which was dissolved in water forming a red solution and precipitated with tetraphenylphosphonium chloride. Recrystallized from acetonitrile-diethyl ether it formed orange crystals (*4A*) which were analyzed as C₅₀H₄₄O₂P₂S₄(C₄₈H₄₀P₂, C₂S₄, 2 H₂O). The crystals were not suitable for X-ray structure analysis, but recrystallization from water produced needle-formed, orange crystals (*4B*) which according to the elementary analysis contained 6 mol of water of crystallization; the crystals were large enough for an X-ray examination. The elementary analysis suggested a tetrathiooxalate salt, but in order to establish the structure of *4B* an X-ray crystallographic analysis was made.

The crystals of *4B* are tetragonal, *P4*, with *a* = 13.026(3); *c* = 13.786(4) Å; *V* = 2339 Å³; *D*_x = 1.330 Mg/m³; $\mu_{\text{CuK}\alpha}$ = 2.86 mm⁻¹. The structure consists of an I-centred arrangement of the tetraphenylphosphonium ions in a cell with the *c*-axis halved. The anions and water molecules are placed in holes in this lattice as shown in Fig. 1. The tetrathiooxalate ion is placed across a twofold axis but is far from planar, the torsion angle being 79.5° (1.0), in contrast to the oxalates (*5*) which are usually planar¹⁹ or nearly so,²⁰ but analogous to the torsion angle in potassium dithiooxalate (76.5°).²¹

Table 1. Selected distances and angles. The mark ' denotes symmetry relation 2 - *x*, 1 - *y*, *z*.

Distance Å		Angle	Degrees
C—S1	1.713(9)	S1—C—S2	128.6(6)
C—S2	1.691(10)	S1—C—C'	114.7(8)
C—C'	1.461(19)	S2—C—C'	116.6(8)
S2—S2	3.068	C—P1—C	107.5 × 2
S1—S2'	3.530		110.5 × 4
S1—O3	3.339	C—P2—C	106.7 × 2
S2—O4	3.347		110.9 × 4
O1—O3	2.961	C—P3—C	107.7
O2—O4	2.905		110.8 × 4
P1—C	1.794		105.9
P2—C	1.796		
P3—C	1.793	Torsion angle	
	1.802	S1—C—C'—S2'	79.5(1.0)

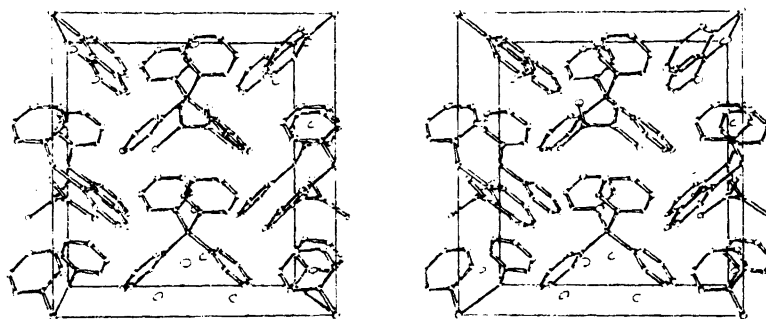


Fig. 1. Stereoscopic view of the structure of 4B. The *a*-axis is horizontal, *c* vertical in the projection. The unconnected atoms are water molecules.

The large torsion angle in 4B prevents close contacts between the sulfur atoms, but may also be enforced by the lattice. Indeed, the four water molecules in the similar hole *c*/2 away are arranged in almost the same way as the four sulfur atoms. The most important dimensions are given in Table 1. Unfortunately the accuracy is limited, and it is not possible to decide whether the two C—S bonds are equal, but they do show considerable double bond character. The C—C bond (1.46 Å) is apparently shorter than the bond in oxalate (1.56–1.58 Å);^{19,20} the C—C length in potassium dithiooxalate is 1.516.²¹

The π -electron systems in the two dithiocarboxyl groups of 4 are situated nearly as in allene and the length of the central C—C bond can be understood in this context. The difference between 4 and 5 with respect to torsion angle and C—C distance is probably connected with the much higher electronegativity of oxygen compared to that of sulfur.

Experimental. Preparation of ditetraphenylphosphonium tetrathiooxalate. Carbon disulfide (2 ml) was reduced at a mercury cathode at 0 °C in acetonitrile saturated with potassium iodide (~0.2 M) at –1.0 V vs. Ag/AgI (0.2 M). During the reduction was formed a brown precipitate which was washed with ether and dissolved in water. On addition of tetraphenylphosphonium chloride (2 g in 20 ml H₂O) a precipitate (0.7–1.5 g) was obtained; the yield varied for unknown reasons, in some cases a low water content in the acetonitrile (~0.1%) during electrolysis seemed preferable to (nominally) anhydrous acetonitrile. The precipitate was filtered, washed with cold acetonitrile, and recrystallized from acetonitrile–diethyl ether (4A) or water (4B). The crystals from A darkened at 130 °C, melted about 160 °C, solidified about 190 °C. Found: C 69.21; H 5.05; S 14.60. Calc. for C₅₀H₄₀P₂S₄·2 H₂O: C 69.26; H 5.11; S 14.79. IR spectrum (KBr, cm^{–1}): 3500–3300(w), 3040(w), 1580(w), 1478(m), 1437(s), 1105(s), 983(s), 968(sh), 925(w), 750(m), 720(s).

Table 2. Final coordinates and mean square vibration amplitudes for the tetrathiooxalate ion, the water molecules and the phosphorus atoms. The coordinates of the phenyl carbon atoms and the hydrogen atoms can be obtained from the author Rita Hazell. The expression for the temperature factor is $\exp[-2\pi^2(h^2a^{*2}u_{11} + \dots + 2klb^*c^*u_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i> ₁₁	<i>u</i> ₂₂	<i>u</i> ₃₃	<i>u</i> ₁₂	<i>u</i> ₁₃	<i>u</i> ₂₃
S1	0.9711(2)	0.3590(2)	0.4467(2)	0.070(2)	0.033(2)	0.039(2)	–0.007(2)	0.010(1)	0.005(1)
S2	1.1326(2)	0.4410(2)	0.3045(2)	0.039(2)	0.070(2)	0.039(2)	0.011(2)	0.008(1)	–0.005(2)
C0	1.0263(8)	0.4505(7)	0.3742(8)	0.068(7)	0.036(6)	0.040(5)	0.008(5)	–0.016(6)	–0.004(5)
O1	0.5422(11)	0.1386(11)	0.1875(9)	0.116(11)	0.080(8)	0.067(9)	–0.010(8)	0.017(6)	0.007(8)
O2	0.3688(11)	0.0402(13)	0.0619(8)	0.088(8)	0.143(11)	0.058(8)	0.021(8)	0.020(7)	0.004(8)
O3	0.5000	0.0000	0.3530(8)	0.066(10)	0.095(10)	0.049(10)	0.003(8)	0.000	0.000
O4	0.0000	0.5000	0.1042(8)	0.088(11)	0.091(9)	0.039(9)	0.003(8)	0.000	0.000
P1	0.0000	0.0000	0.0000	0.023	0.023	0.023	0.000	0.000	0.000
P2	0.0000	0.0000	0.5000	0.025	0.025	0.030	0.000	0.000	0.000
P3	0.5000	0.5000	–0.2520(5)	0.024	0.026	0.025	–0.001	0.000	0.000

685(s). Crystals from (B): C 63.95; H 5.57. Calc. for $C_{50}H_{40}P_2S_4 \cdot 6 H_2O$: C 63.94; H 5.58. The IR spectrum had, besides those described for (A), medium-strong bands at 3500–3300 and 1630 cm^{-1} . UV spectrum (96% ethanol, nm): λ_{max} : 222 (ϵ 10^5), 269 (ϵ 1.4×10^4), 277 (ϵ 1.7×10^4), 343 (broad, ϵ 1.6×10^4), 380 (shoulder, ϵ 7.4×10^3).

X-Ray technique. Symmetry and preliminary cell dimensions were obtained from films. A crystal of $0.1 \times 0.1 \times 0.5$ mm³ was used for the datacollection on a Packer FACS1 diffractometer with $CuK\alpha$ radiation. The cell was refined using 12 reflections centred at $\pm 2\theta$. Data for $h, k, l \geq 0$ out $\theta = 60^\circ$ were collected using a step-scan-technique giving 1824 independent reflections. Profile analysis by the Lehmann-Larsen method,²² Lorentz polarization and absorption corrections were applied.

The structure was solved by means of the MULTAN programme package²³ but not till it was applied to reflections with $l = 2n$ only. Reflections with $h + k + l/2 = 2n$ are 10 times stronger than the other reflections because of the special arrangement of the cations. Refinement by full matrix least squares was only stable when constraints were introduced:²⁴ The phenyl rings were constrained to be identical and with $mm2$ symmetry and each tetraphenylphosphonium ion was treated as a rigid body with extra libration around the P–C bonds giving a total of 138 refineable parameters. The final R-value was 0.062 for 1370 reflections with $I > 3\sigma(I)$.

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