Charge Delocalization in 1,3,5-Trithian Oxides Studied by *X*-Ray Induced Electron Spectroscopy

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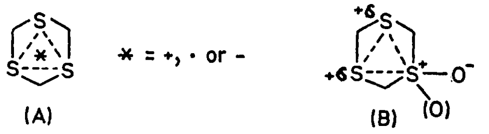
Summary The 2*s* and 2*p* core electron binding energies of the sulphur atoms in 1,3,5-trithian and a series of its oxides were measured by means of *X*-ray photoelectron spectroscopy and give evidence for charge delocalization between the sulphur atoms.

IN recent years there have been many examples in which the versatile carbanions derived from 1,3-dithians are strongly stabilized by introduction of the third sulphur atom.[1,2] More recently it was shown that the nucleophilic reactivity of the second and third sulphur atoms in 1,3,5-trithians is considerably lower than the first one.[2,3] These findings suggest the importance of electron delocalization between the three sulphur atoms in 1,3,5-trithian derivatives as in (A) which is a heterocyclic counterpart of the Winstein's trishomocyclopropenyl species.[4] We present here direct evidence for the presence of such interaction in a series of 1,3,5-trithian oxides as shown by the 2*s* and 2*p* core electron binding energy of the sulphur atoms.

All 1,3,5-trithian oxides were prepared and purified as described in the literature,[5] except the 1,1-dioxide which was obtained by permanganate oxidation of the corresponding 1-oxide as colourless prisms, m.p. 215°, analysed correctly for $C_3H_6O_2S_3$, n.m.r. ($CDCl_3$) δ 4·14 (s, $2CH_2$), 3·85 (s, CH_2). The 2*s* and 2*p* electron binding energies of the sulphur atoms were measured on a Varian IEE photoelectron spectrometer. The Mg-K_α fluorescence *X*-rays at a photon energy of 1253·6 eV irradiate a cylindrically mounted solid powder of the samples. Line positions are accurate to 0·1 eV. With resolution of the present spectrometer, separation of the $2p_{1/2}$ and $2p_{3/2}$ levels is not satis-



(A) (B)

factory; the $2p$ electron spectra of 1,3,5-trithian, the 1,3,5-trioxide, and the 1,1,3,3,5,5-hexoxide are only asymmetric and have a shoulder on the higher energy side of the peak.

TABLE

The 2s *and* 2p *electron binding energies* (eV) *of sulphur atoms in* 1,3,5-*trithian and its oxides*

1,3,5-Trithian	2s S	2s SO	2p S	2p SO	1,3,5-Trithian	2s S	2s SO_2	2p S	2p SO_2
—	227·5	—	163·5	—	—	227·5	—	163·5	—
1-Oxide	228·0	230·0	163·8	165·8	1,1-Dioxide	228·2	232·3	164·2	168·4
1,3,5-Trioxide	—	230·7	—	166·5	1,1,3,3,5,5-Hexoxide	—	233·5	—	169·5

A typical result is shown in the Figure by the $2p$ electron spectrum of the 1,1-dioxide, in which two peaks are observed at 164·2 and 168·4 eV in an intensity ratio of 2 to 1.

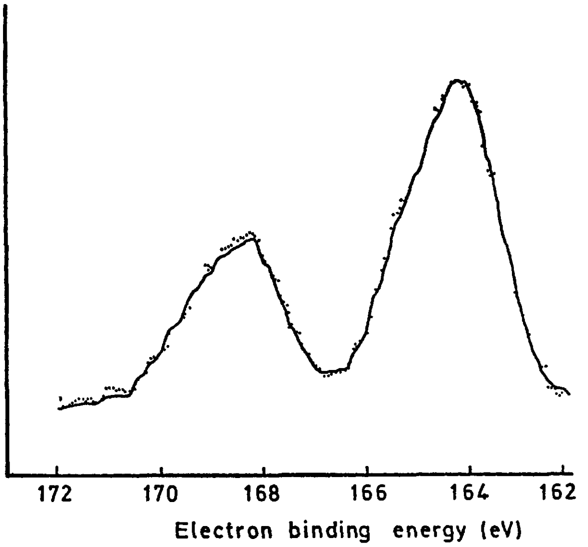


FIGURE. *The* 2p *photoelectron spectra of the sulphur atoms in* 1,3,5-*trithian* 1,1-*dioxide.*

The stronger peak should be assigned to two sulphide sulphur atoms and the weaker one to the sulphone sulphur atom. In the case of the 1-oxide, graphical separation of the overlapped signals due to the sulphide and sulphoxide sulphur atoms was made to give the numerical data summarized in the Table.

Based on the linear relationship between the $2p$ electron binding energy and the positive charge on the sulphur atom, which has been suggested empirically by Siegbahn and his co-workers and can be reasoned in terms of a simple free-ion model,[6] it is predicted that the sulphur atoms in the sulphoxide and sulphone groups listed in the Table have, on an average, net positive charge of 0·8 and 1·5, respectively. The electron binding energies of the SO sulphur in the 1-oxide and the SO_2 sulphur in the 1,1-dioxide are always lower than the corresponding values in the 1,3,5-trioxide and 1,1,3,3,5,5-hexoxide, respectively. The tendency is more pronounced in the case of SO_2. The electron binding energies of the sulphide sulphur in the 1-oxide and the 1,1-dioxide are, in contrast, always higher than that of 1,3,5-trithian itself.

We suggest as one of a number of possible mechanisms which might account for the above results the intramolecular charge transfer of the lone pair of electrons on the sulphide sulphur to the expanded vacant d-orbitals on the SO and SO_2 sulphur to effect partial neutralization of the positive charge on the latter by the sulphide sulphur atoms. The hypothesis may be regarded as a heterocyclic analogue of trishomocyclopropenyl cations[4] as shown in (B). Another extreme possibility of charge delocalization through the CH_2 bonds is less likely in view of development of only a small positive charge on the methylene carbon atoms as revealed by the carbon $1s$ electron binding energies and by the SCF–MO calculations.[7]

Referring again to the linear correlation in which the $2p$ electron binding energy increases *ca.* 5 eV per unit positive charge on a sulphur atom,[6] we can estimate that about a tenth (0·7/5) and two tenths (1·1/5) of a unit positive charge are transferred from the sulphoxide and sulphone sulphur atoms to the sulphide sulphur atoms, respectively.

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