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Thallium(I) and (III) Arene Sulphinates

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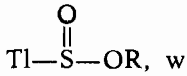
A number of thallium(I) and (III) derivatives of benzene-sulphinic acid and p–toluene sulphinic acid have been prepared. The infra-red spectra suggest O–sulphinate structures for the thallium(I) derivatives and S–sulphinate structures for the thallium(III) derivatives. The mass spectra are reported: the thallium(I) derivative fragments with loss of SO_2.

Introduction

Dimethylthallium methane sulphinate has been prepared by the reaction of sulphur dioxide with trimethylthallium, and postulated to have an O–sulphinate structure, with bridging SO_2Me groups.[1] A number of other diorganothallium(III) organo sulphinates have been prepared by reaction between the appropriate diorganothallium(III) halide and the silver salt of the sulphinic acid:[2] all the compounds were also postulated to have an O–sulphinate structure. This is rather surprising, since thallium(III) generally shows the properties of a 'class-b' metal,[3] and so would have been expected to give S–sulphinate complexes. We have therefore studied a wider range of sulphinate derivatives. Both thallium(I) p–toluene sulphinate and p–toluene sulphinato thallium(III) dichloride have been previously prepared.[4]

Results and Discussion

The thailium(I) arenesulphinates were prepared by mixing aqueous solutions of thallium(I) formate and the sodium salt of the sulphinic acid. The thallium(III) derivatives were prepared from thallium(III) chloride and the sodium salt of the acid in a 1:1 or 1:3 ratio in aqueous solution. Since the compounds were prepared under such mild conditions, a structure of the type  $Tl{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}OR$, with the organic group bonded to the oxygen, is very unlikely. There are then two possible monodentate modes of bonding, $TlOS(O)R$ and $TlS(O)_2R$, in addition to several bidentate and bridging types of attachment. Sulphinate complexes with S–sulphinate coordination have S–O stretching frequencies in the ranges c. 1250-1150 ($\nu_{asym}SO_2$) and c. 1100-1030 ($\nu_{sym}SO_2$), and O–sulphinate complexes in the region c. 1100-850 cm^{-1}. Values for bridging bidentate O–sulphinate groups are in the range c. 1030-900 cm^{-1}.[5]

Infra-red data for the compounds prepared are given in Table I. Assignment of the modes due to the SO_2 group follow from the assignments for iodobenzene[6] and dimethylsulphone.[7] The S–O stretching frequencies for thallium(I) benzene sulphinate are appreciably different from those of the sodium salt. Coordination of the benzene sulphinate anion through just one oxygen should shift $\nu_{asym}(SO_2)$ to higher and $\nu_{sym}(SO_2)$ to lower frequencies than in the free anion, as coordination removes the equivalence of the sulphur oxygen bonds. The observed spectrum is therefore consistent with O–sulphinate coordination, with the sulphinate bidentate or bridging.

Talbe I. (SO_2) bands in benzene sulphinates.

Compound	$\nu_{asym}SO_2$	$\nu_{sym}SO_2$	δ(SO_2)(bend) and ρ(SO_2)(rock)
$Na(C_6H_5SO_2)$	1041vs,br	992 976 } vs,br	586vs,br
$Tl(C_6H_5SO_2)$	1021vs	970vs	571 vs
$Tl(C_6H_5SO_2)Cl_2$	1230 1201 } m 1192	1067 1039 } m	583 m 570 s 535 m 525 m
$Tl(C_6H_5SO_2)_3$	1214s	1066 1048 } s	585 m 572 m
	1178 1142 } s	946vs	537 m 526 m

The data for the benzene sulphinato thallium(III) derivatives are considerably different. The data for benzene sulphinato thallium(III) dichloride agrees well with an S–sulphinate structure. The spectrum also shows bands at 398, 340, and 328 cm^{-1} not due to the benzene sulphinate group: the first of these is possibly associated with a Tl–S mode, and the latter two with Tl–Cl modes. If these latter two represent symmetric and antisymmetric Tl–Cl stretches, then the compound is probably monomeric in the solid state. A similar conclusion was reached for the struc-

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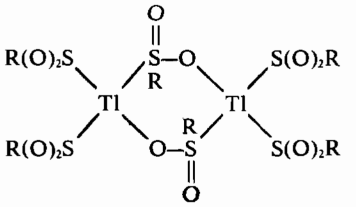
[1] A.G. Lee, *J. Chem. Soc.* (A), *1970*, 467.
[2] G.B. Deacon and V.N. Garg, *Inorg. Nucl. Chem. Let.*, *6*, 717 (1970).
[3] A.G. Lee, « The Chemistry of Thallium », Elsevier, 1971.
[4] H. Gilman and R.K. Abbott, *J. Amer. Chem. Soc.*, *71*, 659 (1949).
[5] G.B. Deacon and P.W. Felder, *Australian J. Chem.*, *22*, 549 (1969).
[6] D.H. Whiffen, *J. Chem. Soc.*, *1956*, 1350.
[7] W.R. Feairheller and J.E. Katon, *Spectrochim. Acta*, *20*, 1099 (1964).

ture of phenylthallium(III) dichloride.[8] The S–sulphinate group has been found to be only very weakly bridging for platinum(II) complexes.[9]

The spectrum of tris(benzenesulphinato)thallium(III) is more complex. Bands closely resembling those of $(C_6H_5SO_2)TlCl_2$ are present, but bands are also present at 1178 and 1142 and 946 cm^{-1}, and these can be assigned to the asymmetric and symmetric modes of a benzene sulphinate group in another environment. The spectra are most consistent with a bridging S–sulphinate group, the bridging being through the sulphur and one of the oxygens, rather than through the two oxygen atoms (structure 1):



(structure 1)

When bridging occurs through the two oxygen atoms, as in $Me_2TlOS(O)Me$, the spectrum shows two bands at 1000 and 965 cm^{-1} due to the bridging SO_2 group.[1] The only other compounds for which S–sulphinato bridging has been suggested are $[Pt_2(SO_2C_6H_4CH_3)_2(SnCl_3)_2(PEt_3)_2]$ and $[Pt_2Cl(SO_2C_6H_4CH_3)(SnCl_3)_2(PMe_2Ph)_2]$, and ν_{asym} and ν_{sym} in the former compound appear at 1180 and 941 cm^{-1}.[9]

The infra-red data for the thallium(I) and thallium(III) *p*–toluene sulphinates is somewhat more difficult to interpret, but again suggest an O–sulphinate structure for the thallium(I) derivative and a monomeric S–sulphinate structure for $(CH_3C_6H_4SO_2)TlCl_2$ and a bridged S–sulphinate structure for $(CH_3C_6H_4SO_2)_3Tl$.

N.m.r. spectra of both $(CH_3C_6H_4SO_2)TlCl_2$ and $(CH_3C_6H_4SO_2)_3Tl$ in $CDCl_3$ show single peaks at c. 7.60 τ, assignable to the CH_3 protons. The observation of a single peak is consistent with, but not confirmatory of, an S–sulphinate structure for these two compounds. The n.m.r. spectrum of thallium(I) *p*–toluene sulphinate, however, also shows only a single peak due to the CH_3 protons in both D_2O and $(^2H_6)$–dimethylsulphoxide as solvent: two peaks would have been expected for a monomeric, non-chelated, O–sulphinate. However, the CH_3 peak of the compound, in $(^2H_6)$–dimethylsulphoxide in particular, is broad (c. 5 Hz. at half height), consistent with an exchange process between a free sulphinate ion and the thallium(I) *p*–toluene sulphinate. Such an exchange would explain the single peak.

These results are consistent with the greater 'class-b' character of thallium(III) as compared to thallium(I).[3] Whereas the thallium(I) derivatives adopt O–sulphinate structures, the thallium(III) derivatives adopt S–sulphinate structures. The diorganothallium(III) group acts as a 'pseudo-thallium(I)' cation,[3] and thus forms O–sulphinates rather than S–sulphinates.

The monoisotropic mass spectrum (for ^{205}Tl) of thallium(I) *p*–toluene sulphinate is given in Table II.

Talbe II. Monoisotropic Mass Spectrum of $Tl(CH_3C_6H_4SO_2)$.

m/e	Species	Relative Abundance
360	$TlCH_3C_6H_4SO_2^+$	0.6
312	$TlCH_3C_6H_4O^+$	0.03
296	$TlCH_3C_6H_4^+$	10.0
269	$TlSO_2^+$	10.1
253	$TlSO^+$	1.6
221	TlO^+	1.8
205	Tl^+	100

Metastable Reactions	(Monoisotropic metastables ^{205}Tl)	
	Obsd.	Calc.
$TlCH_3C_6H_4^+ \rightarrow Tl^+ + CH_3C_6H_4$	142.0	142.0
$TlCH_3C_6H_4SO_2^+ \rightarrow TlCH_3C_6H_4^+ + SO_2$	243.3	243.3

Species assignments are shown with intensities normalized to the Tl^+ peak. Fragments containing one thallium atom give rise to characteristic doublets, at masses m and m+2, and of relative intensities approximately 3 and 7 respectively. No peaks were observed in the region above the parent ion. The observation of peaks due to $[TlSO_2]^+$, $[TlSO]^+$, and $[TlO]^+$, but not to $[TlS]^+$ is consistent with the postulated O–sulphinate structure. The appearance of a strong peak (and a metastable peak) due to the loss of SO_2 from the parent ion, is of interest. No such peak was observed in the mass spectrum of $Me_2TlOS(O)Me$,[1] and no such desulphination reactions have yet been confirmed for thallium. It has however, been noted that in the decomposition of $Me_2TlOS(O)C_5H_5$, SO_2 is lost, and that transient loss of SO_2 could explain the symmetrical collapse of the 2:2:1 pattern of the C_5H_5 protons in the n.m.r. spectrum of a solution of $Me_2TlOS(O)C_5H_5$ in liquid sulphur dioxide, on warming.[10]

The mass spectra of *p*–toluene sulphinato thallium(III)dichloride and tris(*p*–toluenesulphinato)thallium(III) are very similar. Only very weak peaks due to Tl^+ are observed, and no other thallium containing fragments appear in the spectrum. The strongest peak in the spectrum is at m/e = 155, and corresponds to $[CH_3C_6H_4SO_2]^+$. Fragments appear at m/e 139, 123, and 91 due to loss of O,S and SO_2 from this ion. A strong ion also appears at m/e 310, due to $[(CH_3C_5H_4SO_2)_2]^+$, and fragment ions due to loss of S, SO, and SO_2 followed by the loss of a second S or SO_2. Both thallium(III) compounds must therefore decompose at the source temperature (c. 130°).

Experimental Section

N.m.r. spectra were run on a Varian Associates HA 100 Spectrometer, operating at 100 Mc/sec for protons, fitted with the standard 5 mm. variable temperature probe. Spectra were scanned by use of the field-sweep mode, using TMS as lock. A frequency meter was used in determining chemical shifts from the standard. Mass spectra were run on an AEI MS9 instrument which was operated at 70 eV with an ionising current of 100 μA. The spectra were obtained with a direct insertion system: the source temperature was between 130 and 160°. I.r. spectra were recorded on a Perkin Elmer model 21 double beam spec-

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(8) A.G. Lee, *J. Organometallic Chem.*, *22*, 537 (1970).
(9) J. Chatt and D.M.P. Mingos, *J. Chem. Soc.* (A), *1969*, 1770.
(10) A.G. Lee, *J. Chem. Soc.* (A), *1970*, 2157.

Table III. Analysis of Compounds.

Compound	Calc. C	Calc. H	Obsd. C	Obsd. H
$TlC_7H_7SO_2$	23.7	1.9	23.5	1.8
$TlC_7H_7Cl_2SO_2$	19.5	1.6	18.8	1.4
$TlC_{21}H_{21}S_3O_6$	37.7	3.1	37.0	2.7
$TlC_6H_5SO_2$	20.8	1.4	20.6	1.3
$TlC_6H_5Cl_2SO_2$	17.3	1.2	16.6	1.0
$TlC_{18}H_{15}S_3O_6$	34.4	2.4	33.7	2.0

trometer and on a Perkin Elmer 457 spectrometer, using nujol and hexachlorobutadiene mulls between CsBr plates.

The thallium(I) derivatives (see Table III) were prepared by mixing aqueous solutions of thallium(I) formate and the sodium salt of the sulphinic acid in 1:1 ratio. The thallium(I) salt precipitated out, was recrystallized from water, and dried in vacuo. The thallium(III) salts were prepared similarly from thallium(III) chloride (from a suspension of thallium(I) chloride in water with chlorine) and the sodium salt in 1:1 or 1:3 ratio. These derivatives were somewhat light sensitive, and were slowly hydrolyzed in moist air. For the *p*–toluene sulphinates, ν_{asym}, ν_{sym} and $\delta(SO_2)$ are as follows: $(CH_3C_6H_4SO_2)Tl$, 1019 vs, 940 vs, 572 vs: $(CH_3C_6H_4SO_2)TlCl_2$, 1192 vs, 1068 m, 1056 m, 578 vs, 536 vs: $(CH_3C_6H_4SO_2)_3Tl$, 1215 sh, 1210 m, 1200 sh, 1194 m, 1100 m, 1069 w, 1054 m, 1018 m, 579 vs, 555 m, 538 vs.

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