

The Reaction of 1,4-Oxathiane with Hydrohalic Acids

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As part of our studies of the coordination of sulphur donor ligands to rhenium (1) we attempted the reaction of 1,4-oxathiane with $K_2 ReCl_6$ and $K_2 ReBr_6$ in concentrated hydrochloric and hydrobromic acids, respectively. The salts isolated from these reactions had far infrared, Raman spectra (Table 1) and visible and ultra-violet spectra (Table 2) similar to the starting materials indicating that the unsubstituted ReX_6^{2-} moiety was present. Similar reactions starting with osmium (IV), tin (IV), and tellurium (IV) salts gave products containing the MX_6^{2-} ions (Table 1), whereas cobalt (II), manganese (II) and copper (II) chlorides under the same conditions gave the MCl_4^{2-} salts.

To establish the nature of the cation, 1,4-oxathiane was reacted with concentrated hydrobromic or hydrochloric acid. The simple bromo and chloro salts were isolated and a full elemental analysis established their composition as $C_{12}H_{24}Br_2O_2S_3$ and $C_{12}H_{24}Cl_2O_2S_3$. Gravimetric silver halide analysis of the aqueous solutions showed that all the halogen was ionic. The 1H n.m.r. spectrum of the bromo salt consisted of a complex multiplet between 5.5 and 7.0 τ indicating the presence of only methylene protons. The infrared spectra of all the salts (Table 3) showed ring stretching modes characteristic of cyclic C-O-C and C-S-C groups (1,2), indicating that the 1,4-oxathiane ring was still present.

A probable reaction sequence for 1,4-oxathiane with hydrohalic acids is initially the acid catalyzed ether cleavage (3) (Equation 1). Subsequent reaction with the hydrohalic acid (4) gives β -bromoethyl sulphide (Equation 2). This dibromide reacts with more 1,4-oxathiane to give β -(1,4-oxathian-4-ium)ethyl sulphide dibromide (Equation 3). The bromide in the bromo salt was readily replaced by perchlorate, tetraphenylborate and hexabromorhenate (IV).

The *asym* and *sym* (C-O-C) bands of the salts (Table 3) are similar to those in free 1,4-oxathiane, whereas *asym* and *sym* (C-S-C) bands are lowered some 30-40 cm^{-1} in keeping with the formulated structure of the cation with oxathianes bonded through sulphur.

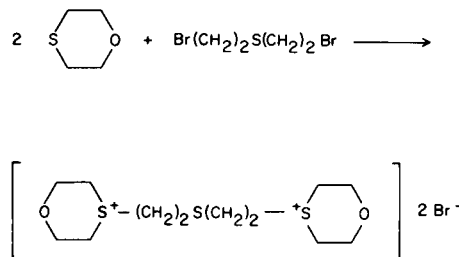
Equation 1.



Equation 2.



Equation 3.



EXPERIMENTAL

1,4-oxathiane was a commercial sample (Aldrich Chemical Co.). Visible and ultra-violet spectra were carried out in distilled *N,N*-dimethylformamide on a Unicam SP. 800 spectrophotometer.

Infrared spectra were recorded as Nujol mulls on a Perkin Elmer 457 (4,000-250 cm^{-1}) spectrophotometer. Raman spectra were recorded on the solid samples on a Cary 81 laser raman spectrometer with He-Ne source (5). 1H n.m.r. spectra were recorded in deuterium oxide on a Perkin-Elmer R.10 spectrophotometer using sodium 3-(trimethylsilyl)propane sulphonate as internal standard. Micro analyses were carried out by Dr. F. and E. Pascher, Microanalytical Laboratory, Bonn, Germany.

β -(1,4-oxathian-4-ium)ethyl sulphide dibromide $[C_{12}H_{24}O_2S_3]Br_2$.

1,4-oxathiane (5.0 ml.) and concentrated hydrobromic acid (S.G., 1.47, 20 ml.) were heated under reflux for 1 hour. The solution was cooled and then the product was precipitated on the

TABLE I

Metal-halogen Infrared and Raman Frequencies (cm^{-1}) (a)

Compound	ν_1	ν_2	ν_3	ν_5
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{ReCl}_6]$	341	284	335, 295	162
$\text{ReCl}_6^{2-}(\text{b})$	346	275	331.5, 319	159
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{ReBr}_6]$	210	183	—	109
$\text{ReBr}_6^{2-}(\text{b})$	213	174	—	104
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{SnCl}_6]$	309, 306	244, 240 223	332, 295	157
$\text{SnCl}_6^{2-}(\text{b})$	311	229	313	158
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{SnBr}_6]$	186	148	—	110
$\text{SnBr}_6^{2-}(\text{b})$	185	138	—	95
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{TeCl}_6]$	289	254	332, 260	—
$\text{TeCl}_6^{2-}(\text{c})$	287	247	260	—

(a) ν_4 was beyond the range of our instrument. (b) D. M. Adams, "Metal-ligand and Related Vibrations" Arnold, London, 1967. (c) P. J. Hendra and Z. Jovic, *J. Chem. Soc.*, (a), 1968, 600.

TABLE II

Visible and Ultraviolet Absorption Frequencies (cm^{-1})

$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{ReBr}_6]$	26200 (sh),	28400,	30800,	32900 (sh)
K_2ReBr_6	26200 (sh),	28400,	30800,	32900 (sh)
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{ReCl}_6]$	31400 (sh),	33900 (sh),	35500,	38800 (sh)
K_2ReCl_6	31400(sh),	33800 (sh),	35500,	38900 (sh)

TABLE III

1,4-Oxathiane Infrared Frequencies (cm^{-1})

Compound	C-O-C stretch	C-S-C stretch
1,4-oxathiane	1105 vs 834 vs	693 w 664 m
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3]\text{Br}_2$	1098 vs 830 s 1107 vs 839 s	642 vw 610 w
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{ReCl}_6]$	1100 vs 828 vs	668 w 623 w
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{ReBr}_6]$	1098 vs 823 vs	—
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{SnCl}_6]$	1100 vs 824 vs	665 w 621 w
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{SnBr}_6]$	1103 vs 828 vs	663 w
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{TeCl}_6]$	1098 vs 823 vs	660 vw 618 w
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{TeBr}_6]$	1100 vs 824 vs	665 vw 615 w
$[\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}_3][\text{OsBr}_6]$	1103 vs 829 vs	663 w

addition of ethanol (150 ml.) and ethyl ether (50 ml.) yielding 4.50 g. Recrystallization from aqueous ethanol gave colourless crystals, m.p. 168-170°.

Anal. Calcd. for $C_{12}H_{24}Br_2O_2S_3$: C, 31.6; H, 5.3; Br, 35.0; O, 7.0; S, 21.1. Found: C, 31.9; H, 5.4; Br, 34.75; O, 7.05; S, 20.9.

β -(1,4-oxathian-4-ium)ethyl sulphide ditetraphenylborate [$C_{12}H_{24}O_2S_3$][BPh₄]₂.

A solution of the corresponding bromide prepared above (0.20 g.) in water (10 ml.) was added to a solution of sodium tetraphenylborate (0.40 g.) in water (10 ml.). The precipitate was allowed to stand one day, collected and dried giving a colourless solid, m.p. 170-175°.

Anal. Calcd. for $C_{60}H_{64}B_2O_2S_3$: C, 77.05; H, 6.9; O, 3.4; S, 10.3. Found: C, 76.85; H, 7.1; O, 2.95; S, 10.0.

β -(1,4-oxathian-4-ium)ethyl sulphide diperchlorate [$C_{12}H_{24}O_2S_3$][ClO₄]₂.

A solution of the corresponding bromide described above (0.60 g.) in a minimum of water was added to a saturated aqueous solution of sodium perchlorate (1.20 g.). The precipitate was recrystallized from water as colourless crystals, m.p. 132-133° (0.38 g.).

Anal. Calcd. for $C_{12}H_{24}Cl_2O_{10}S_3$: C, 29.1; H, 4.9; O, 32.3; Cl, 14.3; S, 19.4. Found: C, 28.9; H, 4.9; O, 31.7; Cl, 14.7; S, 19.9.

β -(1,4-oxathian-4-ium)ethyl sulphide dichloride [$C_{12}H_{24}O_2S_3$]₂Cl₂.

1,4-Oxathiane (5.0 ml.) and concentrated hydrochloric acid (20 ml.) were heated under reflux for 40 hours. The solution was cooled and a colourless oil separated on addition of ethanol (50 ml.) and ethyl ether (100 ml.). The oil crystallized from a solution in ethanol containing 1,4-oxathiane (1 ml.). Recrystallization from ethanol gave colourless crystals, m.p. 158-161° (0.20 g.).

Anal. Calcd. for $C_{12}H_{24}Cl_2O_2S_3$: C, 39.2; H, 6.6; Cl, 19.3. Found: C, 39.45; H, 6.6; Cl, 18.8.

β -(1,4-oxathian-4-ium)ethyl sulphide hexabromorhenate IV [$C_{12}H_{24}O_2S_3$][ReBr₆].

A solution of the corresponding bromide described above (0.20 g.) in water (10 ml.) was added to a solution of dipotassium hexabromorhenate IV (0.30 g.) in dilute hydrobromic acid to give yellow crystals (0.35 g.). The x-ray powder pattern of this material was identical with that of a sample prepared by the method described below.

Anal. Calcd. for $C_{12}H_{24}Br_6O_2ReS_3$: C, 15.0; H, 2.5; Br, 49.9; Found: C, 15.3; H, 2.6; Br, 50.5.

β -(1,4-oxathian-4-ium)ethyl sulphide hexachlororhenate IV [$C_{12}H_{24}O_2S_3$][ReCl₆].

A solution of dipotassium hexachlororhenate IV (0.5 g.) in concentrated hydrochloric acid (40 ml.) was boiled under reflux with 1,4-oxathiane (5 ml.) for 1 hour. The product separated as pale green crystals, m.p. 200-215° (dec.) (0.80 g.), and was washed with ethyl ether.

Anal. Calcd. for $C_{12}H_{24}Cl_6O_2ReS_3$: C, 20.7; H, 3.5; O, 4.6; S, 13.8. Found: C, 20.95; H, 3.45; O, 4.9; S, 14.2.

The hexachlorostannate IV and hexachlorotellurate IV salts were prepared in a similar manner from the tetrachlorides, as colourless crystals, m.p. 250-265° (dec.) and yellow solid, m.p. 170-174°, respectively.

Anal. Calcd. for $C_{12}H_{24}Cl_6O_2S_3Sn$: C, 22.95; H, 3.85. Found: C, 23.35; H, 3.65. *Anal.* Calcd. for $C_{12}H_{24}Cl_6O_2S_3Te$: C, 22.6; H, 3.8. Found: C, 22.6; H, 3.75.

The hexabromometallate IV salts were prepared in a similar manner to the chloro salts using hydrobromic acid (S.G. 1.47) and dipotassium hexabromorhenate IV, tin tetrabromide, tellurium dioxide and osmium tetroxide to give the rhenium, tin, tellurium and osmium salts as yellow crystals m.p. 180-190° (dec.), yellow crystals, m.p. 190-200° (dec.), orange solid m.p. 195-203° (dec.) and brown solid, respectively.

Anal. Calcd. for $C_{12}H_{24}Br_6O_2ReS_3$: C, 15.0; H, 2.5; S, 10.0. Found: C, 15.4; H, 2.6; S, 10.1. *Anal.* Calcd. for $C_{12}H_{24}Br_6O_2S_3Sn$: C, 16.1; H, 2.7; Br, 53.6. Found: C, 16.0; H, 2.55; Br, 54.1. *Anal.* Calcd. for $C_{12}H_{24}Br_6O_2S_3Te$: C, 16.0; H, 2.7. Found: C, 16.5; H, 2.85. *Anal.* Calcd. for $C_{12}H_{24}Br_6O_2OsS_3$: C, 14.9; H, 2.5. Found: C, 15.35; H, 2.5.

β -(1,4-oxathian-4-ium)ethyl sulphide tetrachlorocuprate II [$C_{12}H_{24}O_2S_3$][CuCl₄].

A solution of copper (II) chloride (2.0 g.) in concentrated hydrochloric acid (50 ml.) was boiled under reflux with 1,4-oxathiane (8.0 ml.) for 1 hour. The solution was cooled and on addition of ethanol (100 ml.) and ethyl ether (300 ml.) the product precipitated as yellow crystals (0.51 g.), m.p. 112-114° (dec.).

Anal. Calcd. for $C_{12}H_{24}Cl_4CuO_2S_3$: C, 28.7; H, 4.8; Cl, 28.25. Found: C, 28.4; H, 4.8; Cl, 28.7.

The tetrachlorocobaltate II and tetrachloromanganate II salts were prepared in a similar manner to the tetrachlorocuprate II salt as blue solid, m.p. 142-147°, and pale green crystals, m.p. 138-141°, respectively.

Anal. Calcd. for $C_{12}H_{24}Cl_4CoO_2S_3$: C, 29.0; H, 4.85; O, 6.45; S, 19.35. Found: C, 29.2; H, 4.75; O, 6.6; S, 19.1. *Anal.* Calcd. for $C_{12}H_{24}Cl_4MnO_2S_3$: C, 29.2; H, 4.9; Cl, 28.75; O, 6.5; S, 19.5. Found: C, 29.35; H, 5.2; Cl, 29.2; O, 6.75; S, 19.25.

REFERENCES

- (1) E. A. Allen, N. P. Johnson, D. T. Rosevear and W. Wilkinson, *J. Chem. Soc.*, (A), 788, (1969).
- (2) F. E. Malherbe and H. J. Bernstein, *J. Am. Chem. Soc.*, **74**, 4408 (1952).
- (3) E. Staude and F. Patat, *The Chemistry of the Ether Linkage*, Ed., S. Patal, *Interscience Publishers*, London 1967, p. 22. E. Cerkovnikov and P. Stern, *Archiv. Chem.*, **18**, 12 (1946).
- (4) L. N. Woodward, *J. Chem. Soc.*, 35, (1948).
- (5) Our thanks are due to Professor I. R. Beattie of Southampton University for use of the Raman instrument.

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