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Sulphur–Nitrogen Compounds, Part 3[a]. Reaction of Heavy-metal Cations with Nitroso-disulphonate, Hydroxylamine-*N*,*N*-disulphonate, and Similar Anions

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Silver(I) ions are reduced to the metal by both $ON(SO_3)_2^{-2}$ and $HON(SO_3)_2^{-2}$, but react with $HN(SO_3K)_2$ and $K_3NS_2O_6$ to yield $Ag_3NS_2O_6$ and $Ag_2KNS_2O_6$ respectively. Lead(II) and mercury(II), but not mercury(I), react with both $ON(SO_3)_2^{-2}$ and $HON(SO_3)_2^{-2}$ to yield MSO_4 (M = Pb, Hg) and mixtures of SO_4^{-2} and SO_3^{-2}. Stoichiometries are established, and possible mechanisms discussed, for some of these decompositions.

Introduction

As part of a study of sulphonylhydroxylamines [1, 2], we have sought routes to neutral, soluble analogues of Fremy's radical–dianion, nitrosyl disulphonate, $ON(SO_3)_2^{-2}$ [3], of type $ON(SO_2OR)$ (R = alkyl, aryl, etc.). One possible route to such species is the reaction of molecular halides with the heavy metal derivatives both of $ON(SO_3)_2^{-2}$ and of hydroxylamine-*N*,*N*-disulphonate $HON(SO_3)_2^{-2}$, oxidation of species $HON(SO_2OR)_2$ being expected to yield $ON(SO_2OR)_2$. In this paper we report the results of an investigation of the reactions of the heavy metal ions Ag^+, Hg^{+2}, Hg_2^{+2}, Tl^+ and Pb^{+2} with the anions $ON(SO_3)_2^{-2}$ and $HON(SO_3)_2^{-2}$, and also with the closely analogous anions imidodisulphonate, $HN(SO_3)_2^{-2}$, nitrilotrisulphonate $N(SO_3)_3^{-3}$, hydroxylamine-*N*,*O*-disulphonate $[(O_3S)ONH(SO_3)]^{-2}$ and hydroxylamine-*N*,*N*,*O*-trisulphonate $[(O_3S)ON(SO_3)_2]^{-3}$.

Salts with the metals of Groups I and II have been described for the anions $ON(SO_3)_2^{-2}$ [3, 4], $HON(SO_3)_2^{-2}$ [5, 6], $HN(SO_3)_2^{-2}$ [5, 7, 8], $N(SO_3)_3^{-3}$ [3, 9], and $[(O_3S)ON(SO_3)_2]^{-2}$ [3, 10], but no heavy metal derivatives have been reported for these anions except $HN(SO_3)_2^{-2}$ [5] of which a number of silver(I), lead(II) and mercury(II) derivatives have been described, and $HON(SO)_2^{2-}$ of which some lead(II) derivatives have been reported [6]: all of these materials are of complex stoichiometry and unknown constitution. Of the $HN(SO_3)_2^{-2}$ derivatives, those of silver include $Ag_3NS_2O_6$ [5, 7] and $Ag_2NaS_2O_6$ [5]; amongst the lead derivatives, no binary species such as $Pb_3(NS_2O_6)_2$ or $HN(SO_3)_2Pb$ appear to exist [5] but only hydroxolead species such as $(HOPb)_3NS_2O_6$ and $[(HOPb)_3NS_2O_6]\cdot Pb(OH)_2$ [5]. Similarly no binary mercury(II) derivatives appear to have been described, but a large number of mixed derivatives, such as $Hg[N(SO_3K)_2]_2$ exist [5, 7], together with a number of oxomercury species of bewildering composition, such as $HNS_2O_6\cdot Hg_3O_2$ [5] and $(NS_2O_6)_2Hg_5O_2$ [7]. No binary heavy-metal derivatives of the $HON(SO_3)_2^{-2}$ ion appear to exist [6]; only hydroxolead species, such as $(HOPb)_3(ONS_2O_6)$ and $(HOPb)_2(HONS_2O_6)$ have been described: these form part of a series of materials [6] in which the Pb:N ratio varies from 3:1 to 2:3. The reported members of this series may be distinct compounds, or mixtures, or may be phases of apparently stoichiometric composition.

Experimental

Standard methods were employed for the preparation of $ON(SO_3K)_2$ [4], $HON(SO_3K)_2$ [11], $HN(SO_3K)_2$ [11], $N(SO_3K)_3$ [11], $(KO_3S)ONH(SO_3K)$ [11] and $(KO_3S)ON(SO_3K)_2$ [11]. Nitrates of Ag(I), Hg(II), Hg(I), Tl(I) and Pb(II) were AnalaR where available and all were used as supplied. $KN(SO_3K)_2$ was prepared by reaction of $HN(SO_3K)_2$ with aqueous KOH.

Analysis

Metals were determined using a Perkin–Elmer model 360 Atomic Absorption Spectrophotometer; $ON(SO_3)_2^{-2}$ was determined iodimetrically, and SO_3^{-2} and SO_4^{-2} were determined gravimetrically. Hydrogen and nitrogen analyses were by the microanalytical laboratory of this Department.

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[a] Part 2, ref [2].

Reactions of $ON(SO_3K)_2$

With Ag^+

Solutions of $ON(SO_3K)_2$ (23.95 mmol) and $AgNO_3$ (11.97 mmol) were mixed: the mixture became colourless after 1.5 h, and after 2 d a grey precipitate (1.2903 g: 11.96 mmol: 100%) was formed (Found: Ag, 98.2%). The filtrate contained sulphate(VI) (45.2 mmol: 94.4%).

With Hg^{+2}

Solutions of $ON(SO_3K)_2$ (23.95 mmol) and $Hg(NO_3)_2$ (11.98 mmol) were mixed: the mixture became colourless within 1 h. A white precipitate (3.09 g) was formed (Found: Hg, 67.9; S, 11.2; N, 0.0%; HgO_4S requires: Hg, 67.6, S, 10.8%). The filtrate contained SO_4^{-2} (28.7 mmol) and SO_3^{-2} (5.4 mmol), mol ratio $SO_4^{-2} : SO_3^{-2} = 5.31:1$.

With Pb^{+2}

Solutions of $ON(SO_3K)_2$ (23.95 mmol) and $Pb(NO_3)_2$ (11.97 mmol) were mixed: the mixture became colourless within 1 h. A white precipitate (3.461 g) was formed (Found: Pb, 65.2; S, 10.2; N, 0.0%; O_4PbS requires: Pb, 68.3; S, 10.6%). The filtrate contained SO_4^{-2} (27.2 mmol) and SO_3^{-2} (5.82 mmol), mol ratio $SO_4^{-2} : SO_3^{-2} = 4.68:1$.

With Tl^+

Mixtures of $ON(SO_3K)_2$ and $TlNO_3$ in molar ratio 1:1, 2:1, 3:1 and 4:1 all became colourless within 12 h, but no insoluble products resulted.

Reactions of $HON(SO_3K)_2$

With Ag^+

Solutions of $HON(SO_3K)_2$ (10.09 mmol) and $AgNO_3$ (10.09 mmol) were mixed, and kept in the absence of light for a week, during which time gases were evolved. A dark precipitate (1.0073 g: 9.33 mmol: 92.5%) was produced (Found: Ag, 98.2; S, 0.0%). The filtrate contained sulphate(VI) (19.0 mmol, 94.2%).

With Hg^{+2}

Solutions of $HON(SO_3K)_2$ (1.00 mmol) and $Hg(NO_3)_2$ (2.00 mmol) were mixed together at pH 6.8 (phosphate buffer). A white precipitate (0.3815 g) was formed (Found: Hg, 67.9; S, 11.2; N, 0.0%; HgO_4S requires: Hg, 67.6; S, 10.8%). The filtrate contained mercury(II), (1.40 mmol), SO_4^{-2} (0.50 mmol) and SO_3^{-2} (0.50 mmol).

With Pb^{+2}

Solutions of $HON(SO_3K)_2$ (9.71 mmol) and $Pb(NO_3)_2$ (9.71 mmol) were mixed together and after stirring during 24 h afforded a white solid (2.834 g: 9.35 mmol: 96.3%) (Found: Pb, 68.8; S, 11.1; N, 0.0%; O_4PbS requires: Pb, 68.3; S, 10.6%). The filtrate contained SO_4^{-2} (5.63 mmol) and SO_3^{-2} (4.02 mmol).

With Hg_2^{+2} and Tl^+

No reaction was observed between $HON(SO_3)_2^{-2}$ and either Hg_2^{+2} or Tl^+.

Reactions of $HN(SO_3K)_2$

With Ag^+

Although no reaction was observed between equimolar solutions of $HN(SO_3K)_2$ and $AgNO_3$ during 3 weeks, when the molar ratio $HN(SO_3K)_2 : AgNO_3$ was 1:3, yields of up to 68% of $Ag_3NS_2O_6$ were obtained (Found: Ag, 64.6; N, 2.6; S, 13.3%. $Ag_3NO_6S_2$ requires: Ag, 65.1; N, 2.8; S, 12.9%).

With Pb^{+2}

Addition of a solution of lead(II) acetate or nitrate (0.01 mol) to a stirred solution of $HN(SO_3K)_2$ (0.04 mol) yielded a white flocculent precipitate of $(HOPb)N[SO_3(PbOH)]_2$ (Found: H, 0.3; N, 1.4. Pb, 74.7; S, 7.2%. $H_3NO_9Pb_3S_2$ requires: H, 0.4; N, 1.6; Pb, 73.4; S, 7.6%).

With Hg^{+2}, Hg_2^{+2}, and Tl^+

No reactions were observed between $HN(SO_3K)_2$ and Hg^{+2}, Hg_2^{+2}, and Tl^+.

Reaction of $KN(SO_3K)_2$ with Silver Nitrate

An aqueous solution of $KN(SO_3K)_2$ (0.60 g: 2.06 mmol) was slowly stirred into a solution of $AgNO_3$ (0.74 g: 4.10 mmol). A pale sand-coloured precipitate of $Ag_2KNS_2O_6$ was formed. Found: Ag, 49.7; K. 9.1; N, 3.3; S, 14.6%. $Ag_2KNO_6S_2$ requires: Ag, 50.3; K. 9.1; N, 3.3; S, 14.9%.

Reactions of $N(SO_3K)_3$

No reactions were observed between $N(SO_3K)_3$ and $AgNO_3$, $Hg(NO_3)_2$, $Hg_2(NO_3)_2$, or $TlNO_3$. When solutions of $N(SO_3K)_3$ (8.08 mmol) and $Pb(NO_3)_2$ (7.97 mmol) were mixed, an immediate white precipitate (7.83 mmol, 98.2%) of $PbSO_4$ was formed. Found: Pb, 68.5; S, 10.8%. O_4PbS requires: Pb, 68.3; S, 10.6%.

Reactions of $(KO_3S)ONH(SO_3K)$ and $(KO_3S)ON(SO_3K)_2$

No reactions were observed between either of these salts, and any of the metal ions Ag^+, Hg^{+2}, Hg_2^{+2}, Tl^+ and Pb^{+2}.

Reactions with Molecular Halides

No reaction was observed in, and the starting materials were recovered unchanged from, the following systems:

(a)	$PhCH_2Br$	$+ ON(SO_3K)_2$	in CH_3CN (reflux, 3 h)
(b)	$PhCH_2Br$	$+ HON(SO_3K)_2$	in CH_3CN (reflux, 2 h)
(c)	EtI	$+ Ag_2KNS_2O_6$	in C_6H_6 (R.T., 48 h)
(d)	EtI	$+ Ag_3NS_2O_6$	in C_6H_6 (R.T., 48 h)
(e)	$C_8H_{17}Br$	$+ Ag_3NS_2O_6$	in C_6H_6 (reflux, 48 h)
(f)	Me_3SiCl	$+ HON(SO_3K)_2$	in CH_3CN or $(CH_3)_2SO$ (R.T., 48 h)
(g)	Me_3SiCl	$+ HN(SO_3K)_2$	in CH_3CN or $(CH_3)_2SO$ (R.T., 48 h)

Results and Discussion

With silver nitrate, the $HON(SO_3)_2^{-2}$ ion is converted quantitatively to sulphate(VI) with concurrent reduction of Ag(I) to metallic silver, equation (1):

$$Ag^+ + HON(SO_3)_2^{-2} + 4H_2O \rightarrow Ag + 2SO_4^{-2} + \tfrac{1}{2}N_2 + 3H_3O^+ \quad (1)$$

By contrast, both Pb(II) and Hg(II) nitrates yield precipitate of MSO_4 (M = Pb, Hg), leaving equimolar sulphate(VI) and sulphate(IV) in solution, equation (2):

$$2M^{+2} + 2HON(SO_3)_2^{-2} + 5H_2O \rightarrow 2MSO_4 + SO_4^{-2} + SO_3^{-2} + N_2 + 4H_3O^+ \quad (2)$$

This reaction of lead(II) nitrate should be contrasted with that of basic lead(II) acetate, $Pb(OCOCH_3)_2 \cdot nPb(OH)_2$, which yields the hydroxolead(II) hydroxylamine disulphonate $(HOPb)_3(ONS_2O_6)$ [6]. Neither of Hg_2^{+2} and Tl^+ appears to react (at least when as the nitrate) with the $HON(SO_3)_2^{-2}$ ion.

Silver ions react with the $ON(SO_3)_2^{-2}$ radical–ion in a reaction of stoichiometry $1Ag{:}2ON(SO_3)_2^{-2}$, to yield metallic silver and sulphate(VI), equation (3):

$$2Ag^+ + 4ON(SO_3)_2^{-2} + 15H_2O \rightarrow 2Ag + 8SO_4^{-2} + 10H_3O^+ + N_2O + N_2 \quad (3)$$

it is possible that the reaction proceeds *via* the $HON(SO_3)_2^{-2}$ ion, equation (4) [12]:

$$4ON(SO_3)_2^{-2} + 7H_2O \rightarrow 2HON(SO_3)_2^{-2} + 4SO_4^{-2} + N_2 + 4H_3O^+ \quad (4)$$

this ion then would react further according to equation (1). However it should be noted that reaction (3) is complete within 1.5 hours, although the uncatalysed decomposition of $ON(SO_3)_2^{-2}$, equation (4) is slow, taking *ca.* 500 h for completion at pH 8.

Fast decomposition of $ON(SO_3)_2^{-2}$ also occurs in the presence of Pb^{+2} and Hg^{+2}, to yield MSO_4 (M = Pb, Hg) together with sulphate(VI) and sulphate(IV) in a molar ratio of 5:1, equation (5):

$$4ON(SO_3)_2^{-2} + 2M^{+2} + 12H_2O \rightarrow 2MSO_4 + 5SO_4^{-2} + SO_3^{-2} + N_2 + N_2O + 8H_3O^+ \quad (5)$$

Equation (5) can be regarded as the sum of equations (2) and (4), just as for Ag(I), equation (3) could be regarded as the sum of equations (1) and (4). The rate of decomposition of $ON(SO_3)_2^{-2}$ is found to depend on the metal ion present, thus:

$$Pb^{+2} \sim Hg^{+2} > Ag^+ > Tl^+ \gg K^+ \sim Cd^{+2}$$

The rate of decomposition of $ON(SO_3)_2^{-2}$ has been found [12] to be pH dependent, being least at pH 8, and to be catalysed also by nitrate(III) and chloride [4, 12], but these are both absent from the systems in this study. The production of a water-insoluble product is not a necessary requirement for a fast rate of decomposition, but it is perhaps significant that each of the metals found here to promote fast decomposition of $ON(SO_3)_2^{-2}$ has at least two oxidation states accessible (albeit only transiently in some instances) in aqueous solution, so that one- or two-electron redox reactions involving the metal are possible; by contrast, with cadmium which has but a single oxidation state accessible in aqueous solution, the rate of decomposition of $ON(SO_3)_2^{-2}$ is essentially unchanged from that of the pure potassium salt, and no insoluble product results. The hypothesis that at least two accessible oxidation states of the cation are necessary for fast decomposition rationalises adequately the observation that derivatives of $ON(SO_3)_2^{-2}$ have hitherto been described only of Group I and Group II metals, and further, suggests that other simple stable derivatives will be accessible only of metal ions such as Sc^{+3}, Y^{+3}, La^{+3}, Zn^{+2}, and Cd^{+2}.

Silver ions react, in the presence of potassium ions, with both $HN(SO_3)_2^{-2}$ and $N(SO_3)_2^{-3}$, although not with $N(SO_3)_3^{-3}$ to yield respectively $Ag_3NS_2O_6$ and $Ag_2KNS_2O_6$: the constitutions of these compounds are probably complex. A similar precipitation without decomposition results from the reaction of lead(II) nitrate with $HN(SO_3)_2^{-2}$ to yield the previously described [6] hydroxolead species $(HOPb)_3(NS_2O_6)$: that lead nitrate produces an hydroxo compound with $HN(SO_3)_2^{-2}$ is surprising since with $HON(SO_3)_2^{-2}$ the basic acetate was required for the production of $(HOPb)_3(ONS_2O_6)$ [6], the nitrate yielding only $PbSO_4$.

The only reaction observed for $N(SO_3)_3^{-3}$ was that with Pb^{+2} ions, in which $PbSO_4$ is formed quantitatively. In contrast to the reactivity of hydroxylamine-*N,N*-disulphonate, $HON(SO_3)_2^{-2}$, its isomer, the *N,O*-disulphonate, $[(O_3S)ONH(SO_3)]^{-2}$ reacts with none of the metal ions studied here; similarly the *N,N,O*-trisulphonate $[(O_3S)ON(SO_3)_2]^{-3}$ shows no reaction with these metal ions.

The salt $HON(SO_3K)_2$ was found to react neither with $PhCH_2Br$ nor with Me_3SiCl: similarly no reaction was found between $ON(SO_3K)_2$ and $PhCH_2Br$, or between Me_3SiCl and $HN(SO_3K)_2$. It was the failure of the potassium salts to react with molecular halides which led us to attempt the preparation of heavy-metal derivatives: however these were prepared only from the anion $HN(SO_3)_2^{-2}$; neither $Ag_3NS_2O_6$ nor $Ag_2KNS_2O_6$ was found to react with haloalkanes even during 48 hours reflux.

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