The Adduct of Tin(IV) Chloride with Dinitrogen Tetroxide

By C. C. Addison and W. B. Simpson

Experimental conditions are described which enable the adduct SnCl₄, N₂O₄ to be obtained in precisely 1:1 stoicheiometry. The unusual stability is explained by its formulation as the ionic compound NO+[SnCl₄(NO₃)]⁻. The nitrate ligand is probably bidentate, so the tin atom has 6-co-ordination. This formulation is supported by the infrared spectrum, and by the hydrolysis products in water and sodium hydroxide solution. On thermal decomposition at 170°, a sublimate of composition SnCl₄,2NOCl is obtained.

Some metal chlorides (e.g., ZnCl₂,¹ TiCl₄²) undergo conversion into the anhydrous nitrates in liquid dinitrogen tetroxide; where solvolysis does not occur (e.g., with FeCl₃,³ CrCl₃), the metal chlorides involved are generally quite unreactive, and adducts with the tetroxide are seldom observed. Tin(IV) chloride is exceptional in that it does not undergo solvolysis in dinitrogen tetroxide at room temperature, but nevertheless forms a fairly stable adduct. In the adducts of dinitrogen tetroxide with metal nitrates, stability is associated with the formation of a nitrosonium salt of a nitrato-complex anion {e.g., the adduct with iron(III) nitrate is a salt, $(NO^+)[Fe(NO_3)_4]^-$, rather than a lattice compound, $\mathrm{Fe}(\mathrm{NO}_3)_3, \mathrm{N_2O_4}{}^3\}.~$ The present Paper reports some experiments which indicate that the formation of a tin(IV) chloride adduct can be accounted for in a similar way.

The adduct has been reported as having the composition $SnCl_4, 0.5N_2O_4, 4$ SnCl₄,1.5N₂O₄,⁵ and $SnCl_4, 1.25N_2O_4$; ⁵ we have therefore also attempted to define the stoicheiometry more precisely.

EXPERIMENTAL

The variations in the stoicheiometry of the adduct with conditions of formation are summarised in the Table. The heat of adduct-formation gives the impression of a violent reaction when the reagents are mixed at room temperature, but adduct-formation is smooth at -10° . In no case was a value of x greater than 1.0 obtained. When excess reagents were removed under a vacuum, the vacuum was applied only for as long as was necessary to obtain a dry product, but it is clear that the adduct loses dinitrogen tetroxide when isolated in a vacuum. The fact that the same adduct is obtained when ethyl acetate or methyl cyanide is used as solvent is of particular interest, since

these solvents often enhance the reactivity of the tetroxide and bring about solvolysis of halides under conditions in which the tetroxide alone is not reactive.³

Variations in $SnCl_4$: N_2O_4 st	oicheiometry
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	Excess of	
Conditions	reagent or solvent removal	Value of x in SnCl. $xN_{2}O_{2}$
Pure liquids mixed at 20°	Vacuum	Very variable
Pure liquids mixed at -10	° Vacuum (20°) Vacuum (35°)	$0.82 - 0.89 \\ 0.75$
Pure liquids mixed at -10	° Stream of dry N ₂ (20°)	1.0
Reagents dissolved in ethy acetate, methyl cyanide or light petroleum	d Vacuum e,	0.84-0.91

Under the best conditions, the product was filtered off using a sintered glass plate, and an intermittent and gentle stream of dry nitrogen passed through the product at room temperature until the atmosphere above the solid was no longer brown. [Analysis of three samples prepared in this way gave: Sn, 34.1, 33.8, 34.2; N, 7.7, 7.6, 7.8; Cl, 40.5, 40.1, 40.4. SnCl₄, N₂O₄ requires Sn, 33.7; N, 7.9; Cl, 40.0%.] In preparing the adduct, it was not necessary to use measured quantities of the reagents, since appreciable variation in the relative amounts used had no influence on the 1:1 stoicheiometry of the product.

RESULTS AND DISCUSSION

The adduct SnCl₄,N₂O₄ is a pale yellow, extremely hygroscopic powder. It is very soluble in water to give a clear, colourless solution; the green aqueous solution reported by Partington and Whynnes⁶ is presumably due to the excess dinitrogen tetroxide in their product. The adduct is also soluble in alcohol, slightly soluble in ethyl acetate and methyl cyanide, but insoluble in nonpolar organic solvents. The infrared spectrum, obtained

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using Nujol and Halocarbon oil mulls with protected windows, gave bands (cm.⁻¹) as follows: 2216m (NO⁺), 1580vs,br (ν_1), 1254vs,br (ν_4), 1000s (ν_2), 788m and 760m (ν_3), 712w and 694w (ν_5 and ν_6). The assignments are made on the basis of a bidentate nitrate group.⁷ No bands attributable to dinitrogen tetroxide were observed, and the spectrum is consistent with the formulation of the adduct as $NO^{+}[SnCl_{4}(NO_{3})]^{-}$. The highest nitrate band (1580 cm.⁻¹) is at a much higher frequency than that associated with a unidentate nitrate group, but approaches v_1 in the Sn(NO₃)₄ molecule (1630 cm.⁻¹), in which the nitrate groups are known to be bidentate.^{7,8} Since v_1 represents the terminal N=O stretch, its frequency is reduced as the electron-withdrawing power of the metal atom is reduced, and the four chlorine atoms present in the anion $[SnCl_4(NO_3)]^-$ may be responsible for the shift in v_1 when compared with tin(IV) nitrate. Assuming bidentate nitrate configuration, the tin atom in the complex anion is then 6-co-ordinate.

Adducts which are prepared with less dinitrogen tetroxide than is required by 1:1 stoicheiometry do not react further with the tetroxide, and this is also attributed to the presence of complex anions. Each of the tetroxide-deficient adducts referred to in the Table was shaken with a large excess of liquid dinitrogen tetroxide, which was then removed under conditions (*i.e.*, in a stream of nitrogen) which would yield the 1:1 compound if this had been formed. In each case, however, the composition was unchanged by treatment with excess of tetroxide. If the excess of tin(IV) chloride in these compounds enters the anion to form a binuclear complex, e.g., $[Sn_2Cl_8(NO_3)]^-$, it is protected from further association with additional tetroxide.

Ultraviolet Spectra.-The spectra of the clear solutions obtained by dissolving the 1:1 adduct in 2M-sodium hydroxide solution and in water showed two peaks at 302 and $354 \text{ m}\mu$, characteristic of nitrate and nitrite ions, In the absence of other interfering respectively. absorption in this region, these peaks may be used as an approximate measure of the concentration of free nitrate and nitrite ions produced by hydrolysis. In the alkaline solution, ε values on the fresh solution were 3.75 and 8.4, corresponding to 0.53 g.-ions of NO₃⁻ and 0.40 g.-ions of NO_2^{-} . These values may vary a little in different experiments, but the total nitrogen remains approximately 1 g.-atom per mole, whereas hydrolysis of a lattice compound $(SnCl_4 + N_2O_4)$ would have produced 2 g.-atoms of nitrogen in the form of equal quantities of nitrate and nitrite. Analysis of the solution by the Kjeldahl method showed that 2 g.-atoms of nitrogen per gram mole of the adduct were, in fact, present in solution. The solution process is readily explained on the basis of the initial reaction

 $NaOH + NO[SnCl_4(NO_3)] \longrightarrow Na[SnCl_4(NO_3)] + HNO_2$

whereby the only nitrogen detected in the ultraviolet spectrum is that originally present as NO⁺ ions in the adduct. The co-ordinated nitrate does not absorb at $302 \text{ m}\mu$, and the complex ion will hydrolyse only slowly in alkaline solution. The reaction $NO^+ + OH^- \longrightarrow$ HNO_2 is seldom achieved in the presence of air without some oxidation to nitric acid; in this case the reaction of the adduct with the aqueous solution is vigorous, and we regard the free nitrate present in solution as having been formed by oxidation of nitrite during the solution process.

In the spectrum measured using a fresh solution in water, ε values were 10.7 (302 m μ) and 3.2 (354 m μ), corresponding to 1.50 g.-ions of NO₃⁻ and 0.15 g.-ions of NO₂⁻. This solution is also strongly acid, and the more rapid hydrolysis of the complex leads to release of coordinated nitrate groups. Again, hydrolysis of the NO⁺ ions will give rise to nitrous acid molecules in an acid solution, and the decomposition of nitrous acid to insoluble nitrogen oxides (e.g., nitric oxide) probably accounts for much of the difference between the 1.65 g.-ions of NO_3^- and NO_2^- in solution, and the 2.0 g.-ions which ideal hydrolysis would produce.

The ultraviolet spectrum of solutions of the adduct in ethyl alcohol showed only one absorption band, at 273 mµ ($\epsilon = 5.0$).

Thermal Decomposition.— When the dinitrogen tetroxide adduct was heated to 170° under a vacuum, a sublimate of the compound SnCl₄,2NOCl was obtained on a cold finger at 20°. The thermal decomposition is represented by

 $2SnCl_4$, $N_2O_4 \longrightarrow SnCl_4$, $2NOCI + SnO_2 + 2NO_2 + Cl_2$

Tin(IV) oxide was the only involatile product, and nitrogen dioxide and chlorine were identified in the evolved gases. The nitrosyl chloride adduct is well known,⁹ and its physical properties 10,11 show it to be a nitrosonium compound, $(NO^+)_2[SnCl_6]^{2-}$. It is of interest that the thermal decomposition of a 1:1 dinitrogen tetroxide adduct yields a 1:2 nitrosyl chloride adduct, thereby retaining 6-co-ordination of tin in the complex anion.

Although precise 1:2 stoicheiometry can be obtained by direct reaction of tin(IV) chloride and nitrosyl chloride, the sublimate obtained from the above decomposition has been described both as SnCl₄,2NOCl¹² and 3SnCl₄,4NOCl.^{4,13} We have therefore carried out this thermal decomposition several times, maintaining the same experimental conditions, and find that the value of x in $SnCl_4$, xNOCl varies between 1.7 and 2.1. The 1:2 adduct is therefore the main component of the sublimate, but other closely related adducts are also formed under these conditions.

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