The Redox Chemistry of SbF_6^- Ion

Maja Ponikvar,*[a][‡] Joel F. Liebman,*[b][‡‡] and H. Donald B. Jenkins*[c][‡‡‡]

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Chemical analysis of Sb in coordination compounds requires quantitative reduction of Sb^V in the form of SbF_6^- (and its related fluoro-hydroxy species) to Sb^{III}. This process, although thermodynamically favoured, appears to be kinetically hindered. The experimentally observed stabilisation of SbF_6^- towards reduction, as happens when the associated metal counterion is complexed by XeF_2 (generally regarded as being an oxidizing agent), is also discussed.

Introduction

Various coordination compounds have been isolated from MF_q / PnF_5 / anhydrous HF systems (where M = metal in the oxidation state $q+$; PnF_5 = Lewis acid, Pn = P, As, Sb, Bi) because they are interesting as independent products in their own right and because new approaches to the syntheses of these compounds have been established. Such compounds can be further used as starting materials for the syntheses of coordination compounds with fluoro ligands, such as XeF_2 or AsF_3, coordinated to the metal centre. [1−5]

Estimation of the elemental composition of such compounds remains, despite the availability of numerous state-of-the-art, instrumental analytical techniques, still within the domain of classical analysis.[6] Diverse, classical analytical methods are available for the determination of the amounts of total Pn in different oxidation states, usually III or V. Usually, a prior reduction or oxidation of the element being determined has to be initially performed.[7] Problems associated with the determination of the total elemental composition of these compounds, including analytical methods for the determination of the amount of total respectively free fluoride (F_t^- and F_f^-) and the amounts of Pn, were resolved only recently.[8−10] Additional knowledge concerning the chemistry and properties of these compounds in aqueous media[11,12] was gained from the introduction and development of these analytical methods.

The aim of this paper is to explain the tendency shown towards reduction of coordination compounds of the type $M(SbF_6)_2$ (where M = Mg, Ca, Sr, Ba) in relation to their analogues having XeF_2 molecules coordinated in the form $M(SbF_6)_2 \cdot nXeF_2$ (n = 2−5), as is observed during the process of total chemical analysis employing these compounds. We also examine the thermodynamics of the redox chemistry of SbF_6^- and show that such chemistry may be subject to kinetic rather than thermodynamic barriers.

Results and Discussion

Prior to determination of antimony within coordination compounds containing SbF_6^-, the procedure followed is to quantitatively reduce the Sb^V in the SbF_6^- ion [and the hydrolytically derived Sb(V)-fluoro-hydroxo species] to Sb^{III}. Initially, reduction experiments were conducted according to the standard procedure for the conversion of Sb^V to Sb^{III}, as reported by Hillebrand and Lundell[13] using hydrazine and Na_2SO_3 in acidic (HCl) media. However, the results revealed that hydrazine was completely ineffective as a reductant for the transformation of Sb^V to Sb^{III} in all of the compounds studied, because no Sb^{III} was detected in the sample using redox titration methods once the process of reduction was completed. When the process of reduction of the compounds under study *was* repeated using Na_2SO_3 as a reductant, it was found that Na_2SO_3 was effective for reduction of Sb^V to Sb^{III} in $KSbF_6$ and also in $M(SbF_6)_2$ compounds (where M is Sr or Ba). We can conjecture that the ease of reduction could be related to the nature of the

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[a] Jožef Stefan Institute,
Jamova 39, 1000 Ljubljana, Slovenia
Fax: (internat.) + 386-1-423-21-25
E-mail: maja.ponikvar@ijs.si
[b] Department of Chemistry and Biochemistry, University of Maryland,
Baltimore County, Baltimore, MD 21250, USA
Fax: (internat.) + 1-410-455-2608
E-mail: jliebman@umbc.edu
[c] Department of Chemistry, University of Warwick,
Coventry CV4 7AL, West Midlands, UK
Fax: (internat.) + 44-2476-466747
E-mail: Don.Jenkins@warwick.ac.uk

[‡] For all correspondence about experimental measurements.

[‡‡] For all correspondence about the descriptive chemistry and qualitative relations.

[‡‡‡] For all correspondence about the thermochemistry.

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M−F bonding. The compounds having a more ionic M−F interaction, that is, $KSbF_6$ and $M(SbF_6)_2$ (where M = Sr, Ba) are reduced more readily than $NaSbF_6$ or than those having M = Mg, Ca with a more significant contribution of covalent fluorine-bridged structures. The M−F bond in $KSbF_6$ is more ionic than in $NaSbF_6$ because the charge−volume ratio of sodium is smaller [$V(Na^+) = 0.00394$ nm^3 [14]] than the charge−volume ratio of potassium [$V(K^+) = 0.00986$ nm^3 [14]]. So the Na−F bond is stronger than the K−F bond. As we descend the metal-cation group, the compounds should have an increased contribution to the ionic bond.

In addition, the analogous $M(SbF_6)_2$ compounds with an XeF_2 coordinated to the metal centre M were also examined with respect to their ease of reduction compared to those not having XeF_2 coordinated.

We further report that the reduction of Sb^V in the $M(SbF_6)_2$ compounds (M = Mg or Ca) using 50 mg of metallic Al powder in acid (HCl) media had to be initiated by a gentle heating of the suspension (at approximately 40−50 °C).[9] In contrast, for the compounds where XeF_2 was coordinated as a ligand to the metal centre M, more rigorous conditions were required in order to complete the reduction process: (1) heating to boiling whilst under reflux was required to initiate the reaction and (2) the procedure had to be repeated by one or two subsequent additions of 50 mg of metallic Al.

The tendency of the SbF_6^- ion towards reduction would be more easily rationalized were redox potentials of SbF_6^-/Sb^{III} or $Sb_2F_{11}^-/Sb^{III}$ couples or the other hexafluoropnictates(v) couples listed in the literature. Such is not the case. An alternative understanding of the thermochemistry of the redox chemistry of SbF_6^- and of the apparent resistance of SbF_6^- to reduction by XeF_2 complexation is therefore sought. The aim of the present work is to provide such a rationalisation.

The results of total chemical analysis of the compounds used in this work are presented in Table 1.

These results verify that the analyzed compounds were greater than 99% pure (although their stoichiometry was not always exact).

Conclusion

The Thermochemistry of the Redox Chemistry of SbF_6^-

The likely thermodynamics of three alternative reduction scenarios are considered below. Aqueous N_2H_4, an aqueous SO_3^{2-} salt and metallic Al powder were individually investigated as reducing agents for the purpose of the reduction of Sb^V in the SbF_6^- ion to Sb^{III}, with the assumption that their reaction products are N_2, aqueous SO_4^{2-} and aqueous Al^{III}, respectively. We consider the example of the K^+ salts in reactions (1) − (3), chosen because the relevant thermodynamic data can be estimated. To the extent that hexafluoroantimonate salts are strong electrolytes, the actual choice of counterion is irrelevant since the enthalpy and Gibbs energy of formation of the aqueous salt is the sum of the corresponding quantities for the component ions, in other words, the enthalpy of formation of aqueous K_2SO_3 is the sum of twice the aqueous enthalpies of formation of K^+, and that of SO_3^{2-}. Only enthalpies are discussed in the current study. The three redox reactions are:

$$\begin{aligned} &2\,KSbF_6(aq) + N_2H_4(aq) + 6\,H_2O(l) \rightarrow \\ &\qquad 2\,Sb(OH)_3(aq) + N_2(g) + 2\,KF(aq) + 10\,HF(aq) \end{aligned} \tag{1}$$

$$\begin{aligned} &2\,KSbF_6(aq) + K_2SO_3(aq) + 6\,H_2O(l) \rightarrow \\ &\qquad 2\,Sb(OH)_3(aq) + K_2SO_4(aq) + 2\,KF(aq) + 10\,HF(aq) \end{aligned} \tag{2}$$

$$\begin{aligned} &3\,KSbF_6(aq) + 2\,Al(s) + 3\,H_2O(l) \rightarrow \\ &\qquad 3\,Sb(OH)_3(aq) + 2\,AlF_3(aq) + 3\,KF(aq) + 6\,HF(aq) \end{aligned} \tag{3}$$

All of the desired enthalpy of formation data is available from the archival literature[15] except for that of the standard enthalpy of formation of the aqueous salt containing our anion of interest, that is, $\Delta_fH^0(KSbF_6, aq)$.

Recently, one of us reported a thermochemical study in which the gas-phase enthalpy of formation for SbF_6^-, $\Delta_fH^0(SbF_6^-, g)$, was derived.[16] Taking the standard enthalpy of formation for the solid $KSbF_6$ salt, $\Delta_fH^0(KSbF_6, s) = -2089 \pm 3$ kJ·mol^{-1} (the average value from the refer-

Table 1. The results of elemental chemical analyses of the coordination compounds with SbF_5

	Sb^V [%]				M^{II} [%]				F_t^- [%]				F_f^- [%]			
	Calcd.	Found	Diff.	RSD [%]	Calcd.	Found	Diff.	RSD [%]	Calcd.	Found	Diff.	RSD [%]	Calcd.	Found	Diff.	RSD [%]
$M(SbF_6)_2$ [9]																
$Mg(SbF_6)_2$	49.11	48.8	−0.3	0.20	4.90	4.9	0.0	0.00	45.99	44.4	−1.6	0.26	15.33	16.4	1.1	0.35
$Ca(SbF_6)_2$	47.60	48.3	0.7	0.12	7.83	5.8	−2.0	0.00	44.57	42.0	−2.6	0.14	14.86	11.9	−3.0	0.84
$Sr(SbF_6)_2$	43.55	44.3	0.8	0.00	15.67	13.1	−2.6	0.44	40.78	39.6	−1.2	0.00	13.59	14.8	1.2	0.39
$Ba(SbF_6)_2$	39.99	42.8	2.8	0.14	22.56	19.4	−3.2	0.52	37.45	37.5	0.1	0.27	12.45	19.0	6.6	0.00
$M(SbF_6)_2 \cdot nXeF_2$																
$Mg(SbF_6)_2 \cdot 2XeF_2$	29.18	29.4	0.2	0.20	2.91	2.8	−0.1	0.00	36.43	35.5	−0.9	0.23	18.22	18.5	0.3	0.00
$Ca(SbF_6)_2 \cdot 3.5XeF_2$	22.05	22.1	0.1	0.00	3.63	3.4	−0.2	0.00	32.70	32.5	−0.2	0.25	18.93	18.8	−0.1	0.00
$Sr(SbF_6)_2 \cdot 3XeF_2$	22.82	20.8	−2.0	0.28	8.21	5.4	−2.8	2.13	32.05	30.8	−1.3	0.16	17.81	18.0	0.2	0.00
$Ba(SbF_6)_2 \cdot 5XeF_2$	16.73	16.7	0.0	0.35	9.44	9.3	−0.1	−	28.78	28.7	−0.1	0.28	18.28	18.2	−0.1	0.32

ences[17,18] cited therein), in order to estimate $\Delta_f H^0$($KSbF_6$, aq), we then require the corresponding enthalpy of solution for the salt, $\Delta_{soln.}H^0$($KSbF_6$, s). From the data in ref.[15], although we can derive a value of $\Delta_{soln.}H^0(KPF_6, s) = 44\ kJ\cdot mol^{-1}$ for the valence isoelectronic KPF_6, in this source we find no additional data for any hexafluoropnictate salt or any other hexafluorometallate salt. The justification for the comparison made is that KPF_6 and $KSbF_6$ are both KEF_6 salts. Further support comes from the fact that a roughly "universal" value for $\Delta_{soln.}H^0$(KEO_4, s) of about 54 ± 10 $kJ\cdot mol^{-1}$ is found for a set of KEO_4 salts (where E = Cl, Br, I, Mn, Tc, Re) and yet another "universal" value of $\Delta_{soln.}H^0$(K_2EO_4, s) of about 11 ± 12 kJ/mol for K_2EO_4 salts (where E = S, Se, Cr, Mo, W), where it appears that changing the central metal, E, has a minimal effect on the thermochemical behaviour of these compounds when going into solution. Accordingly, we derive an enthalpy of formation of aqueous $KSbF_6$, $\Delta_f H^0$($KSbF_6$, aq), of about $-2045 \pm 3\ kJ\cdot mol^{-1}$ whereupon we find that ΔH for reaction (1) (as written) is exothermic by about 273 kJ, ΔH for reaction (2) by about 513 kJ and ΔH for reaction (3) by 2141 kJ. The uncertainties, although large, indicate that nonetheless these reactions remain unequivocally exothermic and since ΔS for all of them is likely to be positive, they are thermodynamically favoured. We can only conclude that the reduction reactions must be subject to a kinetic barrier. This confirms the long-held view that SbF_6^- is generally an "unreactive" ion.

Stabilization of SbF_6^- to Reduction by XeF_2 Complexation

From the experiments described above, we deduce that aqueous SbF_6^- is stabilized (i.e. more resistant to reduction) when the associated metal counterion is complexed by XeF_2. This is surprising. XeF_2 is generally regarded as being an oxidizing agent, although with the hitherto documented existence of highly stable, higher valence xenon-containing species in aqueous media [both Xe(VII) and Xe(VIII), $HXeO_4^-$ and various protonated forms of XeO_6^{4-}][19] XeF_2 can conceivably also serve as a reducing agent. However, for the counterions we employed for this SbF_6^- study no redox chemistry of any type was seen in the synthesis of the salts (no redox active metal was studied), and so none is expected here. So, why is there any effect at all on the ease of reduction of SbF_6^-? We showed earlier that AsF_6^-, a lighter valence isoelectronic analogue of SbF_6^-, is destabilized with regard to hydrolysis by multiply-charged cations.[12] The same destabilization mechanism may also apply to reduction processes. From elementary chemistry courses, we recall that these multiply-charged, aqueous cations should not be considered as M^{q+} but rather as $[M(H_2O)_n]^{q+}$. Although this is in the absence of XeF_2 as a ligand, we could postulate a similar $[M(H_2O)_w(XeF_2)_x]^{q+}$ ion where w and x are left intentionally unstated because of our admitted ignorance of the constitution of such complex ions in solution. It is clear that the complexing hydrogens are partially positive and so can assist in the decomposition of the anion much as the positive, bare metal cation might be expected to do. There is no reason to doubt that XeF_2 complexes the metal using one of its fluorine atoms whilst the other F atom faces the water molecules: these fluorines are partially negative and the 180° F−Xe−F angle precludes chelation using them both. As such, the metal cation is likely to have a neutral, if not partially negative, exterior and this will not assist in the hydrolytic decomposition of the anion. Indeed, that the exterior of the cationic metal is at least partially fluorinated, as is the anion, suggests they will avoid each other. Such avoidance is documented: Greenberg, Liebman and Van Vechten used similar logic as part of the theoretical interpretation of "the Perfluoroalkyl (R_f) effect" on the thermodynamic and kinetic stability of substituted highly strained organic molecules,[20] a phenomenon first enunciated in an experimental study made by Lemal and Dunlap.[21] Relatedly, where the negative charge on the anion is lessened, as with ion pairing that would arise with the smaller and less electropositive cations Na, Mg and Ca, reduction is also less likely.

Experimental Section

All reagents were of analytical grade and all solutions were prepared using double-distilled water.

Sample Preparation: Except $NaSbF_6$ (tech., Aldrich) and $KSbF_6$ (99%, Aldrich) that are not moisture sensitive, the analyzed coordination compounds are sensitive to traces of moisture. Therefore, the test samples for determination of each constituent were prepared by weighing in a dry box, with a precision of ± 0.05 mg into air and moisture tight Teflon containers. The containers were cooled in liquid nitrogen in order to moderate the subsequent reaction with water (20 mL) during suspension in a closed Erlenmeyer flask.[9]

Analyses: Both accurate and precise results of chemical analyses having an absolute error of less than 0.2−0.3% were obtained using classical analytical methods. A modified analytical technique, involving the use of a fluoride-ion-selective electrode enabled that us to achieve an absolute error of analysis of less than 0.3%, was applied to the determination of fluoride.

The amounts of antimony were determined after reductive decomposition of the acidic (HCl) sample by addition of metallic Al powder (50 mg).[9] If necessary, the sample was either gently heated to approximately 40−50 °C to initiate the reaction or further Al powder (50 mg) was added to the suspension whilst heating to boiling point under reflux to prevent losses of volatile SbF_3. The amount of Sb^{III} obtained was determined by potentiometric titration with $KBrO_3$ after dissolution of the antimony precipitate. The amount of F_t^- was determined after total reductive decomposition of the sample using Devarda alloy in alkaline (KOH) media.[8] The amounts of F_f^- were estimated in aqueous suspensions of the samples. The latter analyses were performed by direct potentiometry using a fluoride-ion-selective electrode.[8] The amounts of other metals (except alkaline metals) were determined using a corresponding complexometric titration with EDTA.[22]

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