Oxidation of Bis(perfluoroethyl) Diselenide by Antimony Pentafluoride and by the Dioxygen(1+) Cation. Evidence for the Novel Cations $[\{Se(C_2F_5)\}_3]^+$ and $[\{Se(C_2F_5)\}_{4n}]^{2n+}$

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Bis(perfluoroethyl) diselenide is oxidized by both SbF_5 and $[O_2][Sb_2F_{11}]$ to give orange or wine-red products, under appropriate conditions. These products are formulated as the $[Sb_2F_{11}]^-$ salts of the cations $[\{Se(C_2F_5)\}_3]^+$ and $[\{Se(C_2F_5)\}_{4n}]^{2n+}$, where *n* is probably equal to 1.

ANTIMONY and arsenic pentafluorides behave both as moderate fluorinating agents and powerful fluoride-ion acceptors. This combination of properties has been employed[1] to prepare a number of salts of polyatomic cations of the Group 6 and 7 elements. Examples of such reactions are given in equations (1) and (2). Reactions involving SbF_5 are complicated by the formation

$$S_8 + 3AsF_5 \longrightarrow [S_8][AsF_6]_2 + AsF_3 \qquad (1)$$

$$2I_2 + 6SbF_5 \longrightarrow 2[I_2][Sb_2F_{11}] + SbF_3{\cdot}SbF_5 \qquad (2)$$

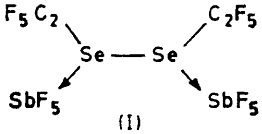
of the polymeric anions $[Sb_2F_{11}]^-$ and $[Sb_3F_{16}]^-$, and of complex compounds of the type xSbF$_3$·ySbF$_5$. However, the more electrophilic cations can only be isolated as salts of the very weakly basic, polymeric, fluoroantimonate anions,[2,3] *e.g.* $[Br_2][Sb_3F_{16}]$ and $[I_2][Sb_2F_{11}]$. Richardson and Bartlett[4] recently reported an elegant synthesis of $[AsF_6]^-$ and $[Sb_2F_{11}]^-$ salts of the $[C_6F_6]^+$ cation by oxidation of hexafluorobenzene with the corresponding salts of the dioxygen(1+) cation.

In the course of an investigation of the chemistry of bis(perfluoroethyl) diselenide,[5] we have found that it reacts with both SbF_5 and $[O_2][Sb_2F_{11}]$ to give orange and wine-red products. We present evidence for the formulation of these compounds as the $[Sb_2F_{11}]^-$ salts of the $[\{Se(C_2F_5)\}_3]^+$ and $[\{Se(C_2F_5)\}_{4n}]^{2n+}$ cations, respectively.

RESULTS AND DISCUSSION

Bis(perfluoroethyl) diselenide, hereinafter referred to as the diselenide, reacted with SbF_5 in the absence of solvent to give an orange material which reacted with more SbF_5 to yield an intense wine-red product. The i.r. spectra of both the coloured materials confirm that they contain C_2F_5 groups.[6] Hexafluoroethane was detected in small quantities over the red material, after standing for 11 d at room temperature. When the red material was heated to *ca.* 100 °C in a sealed tube, rapid decomposition occurred, with evolution of C_2F_6. The yellow residue was shown by Raman spectroscopy to contain the $[Se_4]^{2+}$ cation.[7] Attempts to sublime the red compound by more gentle warming under a dynamic vacuum resulted in a complex decomposition to C_2F_6 the diselenide, SbF_5, and a yellow residue.

A possible interpretation of the reaction sequence is formation of donor–acceptor complexes such as (I). Group 6 dialkyls are known to form similar complexes with boron halides.[8] Alternatively, a redox reaction could occur, giving fluoroantimonate salts of cations of the type $[\{Se(C_2F_5)\}_x]^{y+}$. This would be analogous to the oxidation of the Group 6 and 7 elements to give highly coloured polyatomic cations.[1]



(I)

The neat reaction is inhomogeneous, so a suitable solvent was needed to carry out quantitative studies. The coloured compounds are soluble in very weakly basic, polar, non-oxidizing solvents. They are completely immiscible with WF_6, in which both the diselenide and SbF_5 are very soluble. These observations are consistent with the coloured materials being ionic. Solutions in AsF_3 were generally stable for a few days. However, we could not obtain a pure dry product by removal of solvent, although red crystals were observed in the neat reaction mixture. Other solvents investigated (SO_2 and IF_5) gave solutions of much lower stability.

When the reaction between the diselenide and SbF_5 was carried out in AsF_3 solution, a white solid precipitated as the coloured species formed. This solid was isolated from several reactions and identified by elemental analysis and Raman spectroscopy as '$SbF_3{\cdot}SbF_5$ (A)' reported by Birchall *et al.*[9] The SbF_3–SbF_5 system is very complex, and phases having the compositions $6SbF_3{\cdot}5SbF_5$ and $2SbF_3{\cdot}SbF_5$ have also been identified.[10,11] Hewitt *et al.*[12] have recently shown that the

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[1] R. J. Gillespie and J. Passmore, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 49.

[2] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1971, 2318.

[3] C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. M. Sowa, *Canad. J. Chem.*, 1974, **52**, 2048.

[4] T. J. Richardson and N. Bartlett, *J.C.S. Chem. Comm.*, 1974, 427.

[5] C. D. Desjardins, C. Lau, and J. Passmore, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1037.

[6] N. Welcman and H. Regev, *J. Chem. Soc.*, 1965, 7511.

[7] R. J. Gillespie and G. P. Pez, *Inorg. Chem.*, 1969, **8**, 1229.

[8] J. W. George, *M.T.P. Internat. Rev. Sci.*, Inorganic Chemistry Series One, ed. H. J. Emeleus, Butterworths, London, 1972, vol. 2, p. 248 and refs. therein.

[9] T. Birchall, P. A. W. Dean, B. Della Valle, and R. J. Gillespie, *Canad. J. Chem.*, 1973, **51**, 667.

[10] A. J. Edwards and D. R. Slim, *J.C.S. Chem. Comm.*, 1974, 178.

[11] D. R. Slim, Ph.D. Thesis, University of Birmingham, 1974.

[12] A. J. Hewitt, J. H. Holloway, and B. Frlec, *J. Fluorine Chem.*, 1975, **5**, 169.

phase $6SbF_3{\cdot}5SbF_5$ corresponds to $SbF_3{\cdot}SbF_5$ (B), reported by Birchall *et al.*[9] We feel that $SbF_3{\cdot}SbF_5$ (A) is probably a genuine 1 : 1 complex. Its formation shows conclusively that a redox reaction occurs between the diselenide and SbF_5. We recovered $SbF_3{\cdot}SbF_5$ from the preparation of $[I_2][Sb_2F_{11}]$ under similar conditions, according to equation (2). The results of four different reactions are given in Table 1.

In two reactions [(*a*) and (*b*)] with a moderate excess, and one, (*c*), with a large excess of SbF_5, the weights of $SbF_3{\cdot}SbF_5$ (A) recovered are in excellent agreement with those predicted by equation (2). Reaction (*d*), which was carried out with a slight deficit of SbF_5, yielded a different white solid. Its Raman spectrum was different from $SbF_3{\cdot}SbF_5$ (A) or (B),[9] and from SbF_3.[13] When excess of SbF_5 was used the weights of blue solid recovered exceeded the predicted yields of $[I_2][Sb_2F_{11}]$; the discrepancies increased with the amount of excess of SbF_5, and are probably due to some $[I_2][Sb_3F_{16}]$ impurity. Although this compound is not known, the corresponding $[Br_2]^+$ and $[O_2]^+$ salts[2,11] are well characterized.

TABLE 1

Results of reactions of I_2 with SbF_5 in AsF_3

Reaction	Amount of I_2		Amount of SbF_5		Amount of AsF_3	Amount of $[I_2][Sb_2F_{11}]$		M.p.	Amount of $SbF_3{\cdot}SbF_5$	
	g	mmol	g	mmol	g	g [a]	g [b]	(θ_c/°C)	g [a]	g [b]
(*a*)	3.35	13.2	9.12	42.1	11.01	9.32	9.57 [c]	125—127	2.61	2.64
(*b*)	2.70	10.6	8.10	37.4	8.42	7.51	8.51 [d]		2.10	2.06
(*c*)	3.38	13.3	15.16	69.9	10.49	9.41	*e*		2.63	2.56
(*d*)	2.23	8.8	5.64	26.0	13.09	6.21	6.21 [d]	123—125	1.74	1.47 [f]

[a] Calculated on the basis of I_2, using equation (2). [b] Experimental. [c] After pumping to constant weight at 100 °C; weight after pumping at room temperature = 9.67 g. [d] After pumping to constant weight at room temperature. [e] Not determined. [f] Shown not to be $SbF_3{\cdot}SbF_5$ (see text).

In conclusion, '$SbF_3{\cdot}SbF_5$(A)' has very low solubility in AsF_3 under these conditions, and it can be used as a gravimetric measure of the extent of oxidation taking place in this type of reaction. Care is necessary in identifying $SbF_3{\cdot}SbF_5$ by Raman spectroscopy and elemental analysis, especially when SbF_5 is not in excess.

The Orange Cation.—The initial reaction between the diselenide and SbF_5, forming the orange material, was readily followed by titration in AsF_3 solution. The diselenide reduces the more highly oxidized, wine-red, cation back to the orange cation according to equilibrium (4). The end-point can be approached from either direction. The two visible indicators of equivalence are the disappearance of the immiscible layer of the diselenide over the AsF_3, and the formation of the deeper wine-red cation with excess of SbF_5.

The ratio diselenide : SbF_5 : $SbF_3{\cdot}SbF_5$ = 3 : 6 : 1 was established, showing that the reaction proceeds according to equation (3). The $[\{Se(C_2F_5)\}_3]^+$ salt cannot be

$$3[Se(C_2F_5)]_2 + 6SbF_5 \longrightarrow 2[\{Se(C_2F_5)\}_3][Sb_2F_{11}] + SbF_3{\cdot}SbF_5 \quad (3)$$

isolated, as it disproportionates on pumping, or on distilling out solvent, as equilibrium (4) is driven to the

$$2[\{Se(C_2F_5)\}_3]^+ \rightleftharpoons [Se(C_2F_5)]_2 + (2/n)[\{Se(C_2F_5)\}_{2n}]^{n+} \quad (4)$$

right. This disproportionation was not studied quantitatively, in the SbF_5 system, due to experimental difficulties, but it was investigated in the $[O_2]^+$ work, as described below.

The Wine-red Cation.—The end-point of the oxidation to the wine-red species could not be observed visually, due to the very intense colour. However, the extent of oxidation could still be determined from the weight of $SbF_3{\cdot}SbF_5$ produced in a reaction with excess of SbF_5. The results are consistent with equation (5). We cannot

$$2[Se(C_2F_5)]_2 + (2 + 2x)SbF_5 \longrightarrow (2/n)[\{Se(C_2F_5)\}_{2n}][Sb_xF_{5x+1}]_n + SbF_3{\cdot}SbF_5 \quad (5)$$

rule out cations such as $[\{Se(C_2F_5)\}_{9n}]^{4n+}$, but this seems to be very unlikely. We can certainly rule out $[\{Se(C_2F_5)\}_n]^{n+}$, isoelectronic[14a] with $[As(CF_3)]_n$, which would give 1.0 mole of $SbF_3{\cdot}SbF_5$ per mole of the diselenide.

Alternative Syntheses.—We investigated several potential alternative routes to these cations.

Arsenic pentafluoride. The diselenide reacted with AsF_5, only in the presence of AsF_3, to give an orange-red solution, stable only in the presence of excess of AsF_5. This decomposes rapidly on pumping. Apparently the cations described above are formed in this system, but the $[AsF_6]^-$ salts are extremely labile. This is consistent with the poorer ability of $[AsF_6]^-$ compared with $[Sb_2F_{11}]^-$ to stabilize electrophilic cations.

Displacement reactions. Several reactions of the type shown in equation (6), where X is a molecule of high

$$3[Se(C_2F_5)]_2 + 2X[Sb_2F_{11}] \longrightarrow 2X + 2[\{Se(C_2F_5)\}_3][Sb_2F_{11}] \quad (6)$$

ionization potential (O_2, NO, NO_2, or I_2), have been investigated. Neither $[NO]^+$ nor $[NO_2]^+$ salts reacted with the diselenide. The reaction with $[I_2][Sb_2F_{11}]$ gave $[Se(C_2F_5)I_2][Sb_2F_{11}]$, as described in ref. 14*b*. The diselenide reacted with $[O_2][Sb_2F_{11}]$ to give the desired products, but the reaction was difficult to control.

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[13] C. J. Adams and A. J. Down, *J. Chem. Soc. (A)*, 1971, 1534; L. E. Alexander and I. R. Beattie, *J.C.S. Dalton*, 1972, 1745; V. V. Fomichev, K. I. Petrov, and L. A. Sadokhina, *Russ. J. Inorg. Chem.*, 1972, **17**, 1348.

[14] (*a*) J. P. Crow and W. R. Cullen, *M.T.P. Internat. Rev. Sci.*, Inorganic Chemistry, Series One, ed. H. J. Emeleus, Butterworths, London, 1972, vol. 4, p. 385; (*b*) J. Passmore and P. Taylor, *J.C.S. Dalton*, 1976, 804.

Reaction of the diselenide with $[O_2][Sb_2F_{11}]$. This reaction is very vigorous, and only gives reasonable quantitative results under carefully controlled conditions. Above −45 °C, further oxidation, with evolution of C_2F_6, occurred very rapidly. Even at −50 or −63 °C, C_2F_6 evolution amounted to *ca.* 10% of the available fluorocarbon. At lower temperatures, reaction did not take place, due to the increased viscosity of the diselenide. Attempts to moderate the reaction using WF_6 diluant, as in the preparation of $[C_6F_6]^+$ salts,[4] were not successful.

Reaction with excess of the diselenide. Several reactions were carried out using excess of the diselenide with respect to reaction (6), $X = O_2$. Oxygen was evolved quantitatively, together with C_2F_6 (amounting to 5–10% of the available fluorocarbon). The product was a viscous orange liquid, similar in appearance to $[\{Se(C_2F_5)\}_3][Sb_2F_{11}]$ prepared from the diselenide and SbF_5. The weights of product, after distilling out excess of the diselenide, at −23 °C, were in good agreement with equation (6). More diselenide could be distilled out at room temperature, as the orange material disproportionated according to reaction (4). This reaction was complicated by further decomposition of the $[\{Se(C_2F_5)\}_{2n}]^{n+}$ salt. This second decomposition step is much slower than the first, and plots of weight of diselenide recovered against time showed a change of gradient at a point corresponding to completion of the first step. The weights of diselenide recovered at this point, corrected for the second decomposition process, agreed well with equation (5). This sequence of reactions thus lends support to our formulations of the coloured salts $[\{Se(C_2F_5)\}_3][Sb_2F_{11}]$ and $[\{Se(C_2F_5)\}_{2n}][Sb_2F_{11}]_n$.

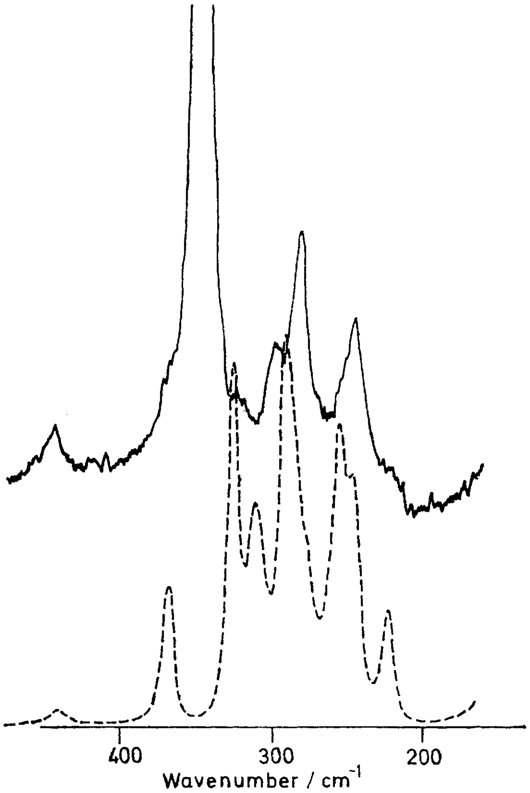
Reaction with excess of $[O_2][Sb_2F_{11}]$. This was carried out in order to investigate the direct displacement reaction (7). The results are consistent with an initial

$$[Se(C_2F_5)]_2 + [O_2][Sb_2F_{11}] \longrightarrow (1/n)[\{Se(C_2F_5)\}_{2n}][Sb_2F_{11}]_n \quad (7)$$

displacement, as in equation (7), followed by slow further oxidation according to (8).

$$(1/n)[\{Se(C_2F_5)\}_{2n}][Sb_2F_{11}]_n + 9[O_2][Sb_2F_{11}] \longrightarrow 9O_2 + 2C_2F_6 + 2[SeF_3][Sb_2F_{11}] + 16SbF_5 \quad (8)$$

Physical Measurements.—Infrared spectra of both cations show characteristic C_2F_5 and $[Sb_2F_{11}]^-$ peaks.[6,15] Raman spectra could only be obtained for the wine-red species of empirical formula $[\{Se(C_2F_5)\}_{2n}]^{n+}$; these are not of good quality because of the intense colour. Similar spectra were obtained under a wide variety of conditions using both 514.5 and 647.1 nm exciting lines. A typical spectrum is shown in the Figure. It is dominated by a very intense, polarized, peak at 347 cm^{-1}. The remainder of the spectrum is poorly resolved, but it broadly resembles that of the diselenide itself, which is also shown. Raman spectra of solutions of $[\{Se(C_2F_5)\}_3][Sb_2F_{11}]$ only showed peaks attributable to small concentrations of $[\{Se(C_2F_5)\}_{2n}]^{n+}$, presumably arising from equilibrium (4).



Raman spectra of the liquid diselenide (— — —) and a dilute solution of $[\{Se(C_2F_5)\}_{2n}]^{n+}$ (——), between 200 and 400 cm^{-1}

TABLE 2

Magnetic-susceptibility results

Sample	I/A	$10^5\Delta W^a$/g		
		obs.	calc.[b]	calc.[c]
(*a*)	1.5	−107	−121	6
(*a*)	1.9	−148	−167	8
(*a*)	2.2	−171	−200	10
(*b*)	1.5	−131	−116	53
(*b*)	1.9	−177	−159	69
(*b*)	2.2	−207	−191	82
(*c*)	1.5	−116	−112	
(*c*)	1.9	−158	−153	
(*c*)	2.2	−181	−183	

Sample	Composition/mmol		
	Diselenide	SbF_5	AsF_3
(*a*) (red)	0.5	4.9	6.4
(*b*) (red)	0.6	2.8	7.6
(*c*) (orange)	0.8	1.6	7.0

Compound	$10^6\chi$/c.g.s. units	
	Calc.[24]	Found
$[Se(C_2F_5)]_2$	−133	−134
AsF_3	−39.8	−38.6
SbF_5		−72

[a] Corrected for glass sample tube. [b] Based on diamagnetic susceptibilities only. [c] Based on paramagnetic $[\{Se(C_2F_5)\}_2]^+$, $\mu = 1.73$ B.M. (1 B.M. ≈ 9.27×10^{-24} A m^2).

Careful magnetic-susceptibility measurements (Table 2) showed that both $[\{Se(C_2F_5)\}_3]^+$ (as expected) and

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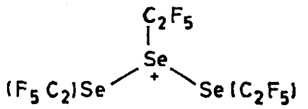
[15] C. Lau and J. Passmore, *J.C.S. Dalton*, 1973, 2528 and refs. therein.

$[\{Se(C_2F_5)\}_{2n}]^{n+}$ are diamagnetic in AsF_3 solution. The latter result indicates that $[\{Se(C_2F_5)\}_{2n}]^{n+}$ is polymeric and that n is even. We cannot rule out an equilibrium containing very small amounts of free monomer. This result is surprising, in view of the fact that $[Br_2]^+$ and $[I_2]^+$, with which $[\{Se(C_2F_5)\}_2]^+$ is formally analogous, are both monomeric at room temperature, in solution,[16,17] and the solid state.[2,3] However, solutions of $[I_2]^+$ turn from blue to red and become diamagnetic on cooling.[17]

We were unable to obtain ^{19}F n.m.r. spectra for these compounds.

Structures of the Cations.—(i) $[\{Se(C_2F_5)\}_3]^+$. We propose structure (II) for this cation, by analogy with the triatomic halogen cations,[1] $Se(C_2F_5)$ being electronically



(II)

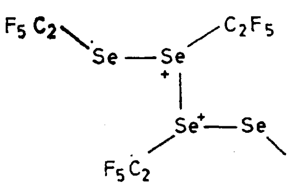
analogous to the bromine atom. The related cation $[(SMe)_3]^+$ has been proposed [18] to exist in equilibrium (9).

$$MeS_2Me + Me_2\overset{+}{S}SMe \rightleftharpoons SMe_2 + [(SMe)_3]^+ \qquad (9)$$

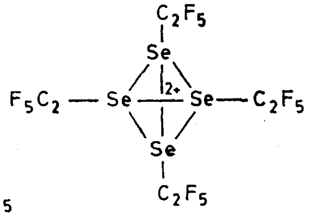
The salt $[(SMe)_3][SbCl_6]$ has been reported very recently.[19] Other cations of the type $[(SR)_3]^+$ have been suggested [20] as intermediates in some reactions of organic disulphides.

(ii) $[\{Se(C_2F_5)\}_{2n}]^{n+}$. This ion is diamagnetic; therefore, the empirical formula is restricted to even values of n. The simplicity of the Raman spectrum, and the high solubility of the salt in AsF_3, suggest that n is probably equal to 2. The arguments regarding bonding, which we present below, are equally applicable to a more highly polymerized cation.

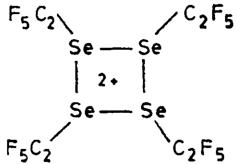
The very intense peak at 347 cm^{-1} in the Raman spectrum can be reasonably assigned to the symmetric stretching mode of the selenium framework of $[\{Se(C_2F_5)\}_4]^{2+}$. We cannot exclude the possibility that this peak is due to trace amounts of monomeric $[\{Se(C_2F_5)\}_2]^+$. However, the similarity of spectra obtained from both solid and solution samples, with different exciting lines, suggest that this is not the case. There are several possible structures for the cation. The classical structure, (III), has a selenium framework isoelectronic with Se_2Br_2, and should give rise to three Se–Se stretches in the Raman spectrum. We would expect all three to be close to the typical Se–Se single-bond stretching frequency[21] at *ca.* 290 cm^{-1}. It is difficult to reconcile the very high observed frequency with this structure. We have also considered the non-classical tetrahedral and square-planar arrangements, (IV) and (V). Assuming that only 4*s* and 4*p* orbitals are involved in bonding, these would have average Se–Se bond orders of 0.5 and 0.75, respectively. They, too, would therefore not be consistent with the very high Se–Se stretching frequency. The Se–Se stretching frequency of the neutral diselenide has not been established with certainty, but probably occurs at 289 cm^{-1}. The value of 347 cm^{-1} in the cation is therefore consistent with the bond order of 1.5 predicted for the free monomer, which is formally obtained by removal of a π^* electron from the Se–Se bond. A comparable increase in stretching frequency is observed[16] for $[Br_2]^+$ (360 cm^{-1}) over Br_2 (320 cm^{-1}). We envisage dimerization proceeding *via* pairing of the single π^* electrons in two $[\{Se(C_2F_5)\}_2]^+$ monomers, in either a side-on, (VIa), or an end-on configuration (VIb). This is similar to the bonding situation proposed[22] for NOF and O_2F_2. It should not result in any great change in the Se–Se bond order, and hence stretching frequency, relative to the free monomer. It is interesting to note that similar bonding may exist between the two $[S_3N_2]^+$ units in the $[S_6N_4]^{2+}$ cation found in the crystal structure[23] of $[S_6N_4][S_2ClO_6]_2$.



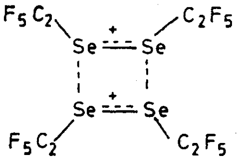
(III)



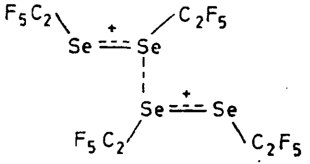
(IV)



(V)



(VIa)



(VIb)

EXPERIMENTAL

Except where otherwise stated, the apparatus and materials were the same as those described in ref. 14*b*.

Reaction of Iodine with SbF_5 *in* AsF_3.—These reactions,

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[16] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 1972, **11**, 586.

[17] R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, 1966, **5**, 1577; R. J. Gillespie, J. B. Milne, and M. J. Morton, *ibid.*, 1968, **7**, 2221.

[18] S. H. Smallcombe and M. C. Caserio, *J. Amer. Chem. Soc.*, 1971, **93**, 5826.

[19] G. Capozzi, O. DeLucchi, V. Lucchini, and G. Modena, *J.C.S. Chem. Comm.*, 1975, 248.

[20] C. G. Moore and M. Porter, *J. Chem. Soc.*, 1958, 2890; J. L. Kice and E. H. Morkved, *J. Amer. Chem. Soc.*, 1964, **86**, 2270; J. L. Kice and K. W. Bowers, *ibid.*, 1962, **84**, 2384.

[21] P. J. Hendra and P. J. D. Park, *J. Chem. Soc. (A)*, 1968, 908.

[22] R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, 1966, **88**, 2394.

[23] A. J. Banister, H. G. Clarke, I. Rayment, and H. M. M. Shearer, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 647.

and those between $[Se(C_2F_5)]_2$ and SbF_5 in AsF_3, were carried out in a one-piece glass apparatus, consisting of two arms linked by a tube incorporating a sintered-glass filter disc. One arm was fitted with a Teflon ' Rotaflo ' or Whitey 1KS4 valve. Details of different reactions are given in Table 1. Typically, iodine was loaded into one arm of the apparatus, which was then evacuated and AsF_3 and SbF_5 were condensed in, separately, at −196 °C. Reaction proceeded smoothly on warming up to room temperature, with shaking, giving an intense blue solution. After *ca.* 2 h, the solution was filtered through the sintered glass disc. The precipitated $SbF_3{\cdot}SbF_5$ was washed until free of blue colour, by cycling the AsF_3. The AsF_3 was then recovered, the reaction vessel pumped to constant weight, and the two solid products recovered and weighed in the Dri-Lab.

Reactions of $[Se(C_2F_5)]_2$ *with* SbF_5 *in* AsF_3.—(i) *Preparation of* $[\{Se(C_2F_5)\}_3]^+$. In a typical small-scale reaction, the diselenide (1.59 g, 4.0 mmol) and AsF_3 (4.33 g, 32.8 mmol) were condensed into a reaction vessel. A small amount of SbF_5 (0.39 g, 1.8 mmol) was added. On shaking at room temperature, an orange colour appeared in the AsF_3 layer, a white precipitate formed, and a lot of unchanged diselenide remained in a separate upper layer. More SbF_5 was added (total 1.66 g, 7.7 mmol), and after shaking it was evident that the reaction was close to the end-point; a little unchanged diselenide remained, but the AsF_3 solution had a red tinge. Addition of more SbF_5 (total 1.96 g, 9.0 mmol) resulted in uptake of the remaining free diselenide, and an intensification of the red colour. Filtration yielded 0.51 g (1.29 mmol) of $SbF_3{\cdot}SbF_5$. In a scaled-up reaction, the diselenide was titrated with SbF_5 (5.68 g, 26.2 mmol) in AsF_3 (7.95 g). The end-point lay between 5.17 and 5.42 g (13.05—13.7 mmol) of the diselenide. Filtration yielded 1.75 g (4.4 mmol) of $SbF_3{\cdot}SbF_5$, identified by elemental analysis (Table 4) and Raman spectroscopy as isomer (A).[9]

(ii) *Preparation of* $[\{Se(C_2F_5)\}_{2n}]^{n+}$. In a typical preliminary reaction, the diselenide (1.19 g, 3.0 mmol) was treated with excess of SbF_5 in AsF_3 solution. After standing for 3 h, filtration of the intense wine-red solution yielded $SbF_3{\cdot}SbF_5$ (0.51 g, 1.29 mmol). Removal of solvent, and pumping to constant weight, gave a paste-like wine-red product (2.60 g). The predicted yield of $[\{Se(C_2F_5)\}_{2n}]$-$[Sb_2F_{11}]_n$, based on the diselenide, is 2.55 g. In another, larger scale preparation, diselenide (10.8 mmol) and SbF_5 (11.89 g, 54.8 mmol) was used in AsF_3 (9.41 g, 71.3 mmol). Filtration yielded $SbF_3{\cdot}SbF_5$ (2.00 g, 5.1 mmol). The $SbF_3{\cdot}SbF_5$ recovered from several preparations was identified by elemental analysis (Table 3) and Raman spectroscopy as isomer (A).[9]

TABLE 3

Analytical results (%)

Compound	Sb	F	Se	I
SbF_3 (calc.)	68.1	31.9		
$SbF_3{\cdot}SbF_5$ (calc.)	61.55	38.45		
$SbF_3{\cdot}SbF_5$ [a]	61.3	38.15		0.55
$SbF_3{\cdot}SbF_5$ [b]	61.3	38.1	0.00	
$SbF_3{\cdot}SbF_5$ [c]	61.05	38.45	0.05	
$SbF_3{\cdot}SbF_5$ [c]	61.3	38.7	0.10	
$SbF_3{\cdot}SbF_5$ [c]	61.75	38.35	0.20	
Unknown [d]	68.45	31.45		0.00
$I_2Sb_2F_{11}$(calc.)	34.45	29.6		35.95
$I_2Sb_2F_4$ [e]	34.8	29.2		35.7

[a] From preparation (*c*) of $[I_2][Sb_2F_{11}]$. From preparation of $[\{Se(C_2F_5)\}_3][Sb_2F_{11}]$. [c] From three preparations of $[\{Se(C_2F_5)\}_{2n}][Sb_2F_{11}]_n$. [d] From preparation (*d*) of $[I_2][Sb_2F_{11}]$. [e] From preparation.

Magnetic-susceptibility Measurements.—Room-temperature magnetic susceptibilities were obtained by the Gouy method. Measurements were made at three different field strengths. The magnetic susceptibilities of the diselenide and AsF_3 were measured and agreed well with values derived from ref. 24. The susceptibility of SbF_5 was also measured. Samples of the coloured compounds were prepared *in situ*, in AsF_3 solution, in Pyrex sample tubes (6-mm outside diameter, 4-mm inside diameter). Weight changes observed at different field strengths were compared with values calculated from the susceptibilities of the reagents. No correction was made for $SbF_3{\cdot}SbF_5$: when it was allowed to settle, and the tube inverted and magnetic measurements retaken, no significant changes were observed. The results are given in Table 2; they show conclusively that both coloured species are diamagnetic in AsF_3 solution. As a further check on the wine-red compound, magnetic measurements were repeated after the samples had decomposed, and no significant changes were observed.

Characterization of $[O_2][Sb_2F_{11}]$.—This salt was prepared by the method of McKee and Bartlett [25] and was identified by Raman spectroscopy and *X*-ray powder photography. It was further characterized by its thermal decomposition [25] to $[O_2][SbF_6]$ (identified by its Raman spectrum) and SbF_5, and by two displacement reactions. Excess of Br_2 reacted with $[O_2][SbF_{11}]$ (1.94 mmol) liberating oxygen (1.92 mmol) and leaving a green-brown residue. This residue was not identified, but the reaction did not appear to be so clean as that [26] between Br_2 and $[O_2][AsF_6]$, which yields $[Br_3]$-$[AsF_6]$. The reaction between NO_2 and $[O_2][Sb_2F_{11}]$ was also investigated. Excess of NO_2 reacted with $[O_2][Sb_2F_{11}]$ (1.91 mmol), liberating oxygen quantitatively. The white residue was shown by Raman spectroscopy [27] to contain $[NO_2][SbF_6]$, rather than $[NO_2][Sb_2F_{11}]$. In addition, there is a Raman peak at 2 345 cm^{-1}, attributable [27] to the $[NO]^+$ cation. Evidently, the reaction is not a simple displacement, but also involves reaction of NO_2 with the $[Sb_2F_{11}]^-$ anion. Peacock and Wilson [28] studied the reactions of nitrogen oxides with SbF_5. They found that $[Sb_2F_{11}]^-$ salts are formed initially, but, after prolonged exposure to nitrogen oxides, $[SbF_6]^-$ salts predominate. The reaction with NO_2 is complex, and the products include $[NO]^+$ salts. These results are consistent with our observations of the NO_2–$[O_2][Sb_2F_{11}]$ system. Although these two displacement reactions were not straightforward they were useful in characterizing $[O_2][Sb_2F_{11}]$, in that oxygen was evolved quantitatively in each case.

Reactions of $[Se(C_2F_5)]_2$ *with* $[O_2][Sb_2F_{11}]$.—These reactions were carried out in 100-cm^3 round-bottomed flasks. The vessels were loaded with the $[O_2]^+$ salt in the Dri-Lab, then evacuated, and the diselenide was condensed above the $[O_2]^+$ salt at −196 °C. On slowly warming up to the appropriate slush-bath temperature, the diselenide was run on to, and reacted with, the $[O_2][Sb_2F_{11}]$. Oxygen and C_2F_6

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were measured separately as follows. The reaction vessel was frozen to −196 °C, and opened to the vacuum manifold, which was isolated from the pump and the volume of which was known. The pressure of oxygen was measured on a gauge. The manifold was then isolated from the vessel, the oxygen pumped away, and the procedure repeated until no pressure was observed. The sum of the pressure readings then gave the total pressure of gas in a known volume at room temperature, while keeping the reaction vessel cold. The procedure was repeated at −78 °C to measure the C_2F_6, which was also identified by its i.r. spectrum. The only impurities observed were trace amounts of CF_4 and SiF_4.

(i) *Reaction with excess of the diselenide.* The diselenide (3.52 g, 8.89 mmol) was allowed to react with $[O_2][Sb_2F_{11}]$ (1.588 g, 3.28 mmol) at −63 °C for 6 h, then allowed to warm up to room temperature over a period of 20 h. The gaseous products consisted of oxygen (3.46 mmol) and C_2F_6 (0.75 mmol). The residue was a mass of orange and wine-red material, together with a considerable amount of the diselenide. This was allowed to stand for 4 h, with shaking from time to time, after which the product was a viscous orange liquid, still topped by excess of the diselenide. The diselenide was distilled out at −23 °C, and amounted to 1.53 g (3.86 mmol), showing that 5.03 mmol had reacted compared with the 4.92 mmol required by reaction (7). More diselenide was distilled out at room temperature, and the weight recovered was plotted against time. As this proceeded, the colour of the residue changed from orange to intense wine-red. Some yellow material, probably an $[Se_4]^{2+}$ salt, was also present. A sharp inflection in the plot of the weight of diselenide against time was observed when 0.695 g (1.75 mmol) of the diselenide had been recovered. This indicated that reaction (4) had proceeded completely to the right. The diselenide continued to evolve slowly as the wine-red $[\{Se(C_2F_5)\}_{4n}]^{2n+}$ salt decomposed. The weight of diselenide recovered at the inflection point was rather greater than the 1.64 mmol expected for disproportionation of 3.28 mmol of $[\{Se(C_2F_5)\}_3][Sb_2F_{11}]$, and higher still if allowance is made for some decomposition in the initial reaction. We can relate this high value to some diselenide arising from decomposition of the red material before the disproportionation was complete. Similar results were obtained from several experiments. One reaction was carried out by adding small amounts of solid $[O_2][Sb_2F_{11}]$ to cooled liquid diselenide. We hoped that this would reduce C_2F_6 evolution, but no significant difference was found. We observed that the quality of the inflection in the plot of weight of diselenide against time improved considerably when the material was spread over as large a surface area as possible; this facilitated removal of the diselenide, and helped to drive equilibrium (4) to the right.

(ii) *Reaction with excess of* $[O_2][Sb_2F_{11}]$. In a typical reaction, $[O_2][Sb_2F_{11}]$ (2.32 g, 4.79 mmol) was treated with the diselenide (0.58 g, 1.47 mmol) at −50 °C. Reaction took place, quite vigorously at first, with appearance of the wine-red colour. Oxygen and C_2F_6 were monitored periodically, and the results are given in Table 4. In the first 30 min, *ca.* 1 mole of oxygen per mole of diselenide (1.52 mmol) was evolved, together with 0.28 mmol of C_2F_6. In the ensuing 6 h at −50 °C, further reaction occurred with generation of oxygen (2.00 mmol) and C_2F_6 (0.44 mmol). Virtually no further reaction was observed over the following 5 h, but, on warming to room temperature, reaction continued again until oxygen evolution was complete (4.77 mmol total from 4.79 mmol of salt). More C_2F_6 (0.43 mmol) was also produced.

TABLE 4

Evolution of O_2 and C_2F_6 in the reaction between the diselenide (0.58 g) and $[O_2][Sb_2F_{11}]$ (2.32 g) at −50 °C

t/min	Amount of O_2/mmol	Amount of C_2F_6/mmol
30	1.52	0.28
100	2.17	0.43
184	2.63	0.53
229	2.76	0.55
355	3.47	0.71
654	3.52	0.72

Another reaction was carried out between a small amount of the diselenide and a large excess (>10 : 1 mole ratio) of $[O_2][Sb_2F_{11}]$, initially at −40 °C and then at room temperature. The initial product was a viscous wine-red liquid, which continued to react, with gas evolution, until the colour was discharged. The product was a white paste, shown by Raman spectroscopy to contain $[SeF_3]^+$, $[O_2]^+$,[25] SbF_5,[29] and $[Sb_nF_{5n+1}]^-$.[30] We attribute peaks of medium and weak intensity at 788 and 763 cm^{-1} to ν_1 and ν_3, respectively, of $[SeF_3]^+$. These values are somewhat higher than those reported [31,32] for $[SeF_3][SbF_6]$, but correspond to frequencies we found for $[SeF_3][SbF_6]$ dissolved in excess of SbF_5. We thus have reasonable evidence that the initial reaction between the diselenide and $[O_2][Sb_2F_{11}]$ is a simple displacement, but the results are complicated by the strongly competing further oxidation reaction [equation (8)].

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