The Preparation and Characterisation by Raman Spectroscopy of $AsBr_4^+AsF_6^-$ containing the Tetrabromoarsenic(V) Cation

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The thermodynamically unstable $AsBr_4^+AsF_6^-$ was prepared by the reaction of $AsBr_3$, Br_2, and AsF_5 at low temperatures, and characterised by Raman spectroscopy.

There is a definite tendency[1] for the non-metals of the fourth row, As, Se, and Br, to be unstable in their maximum oxidation state. For example, although phosphorus and antimony pentachlorides are stable compounds,[2] the recently prepared arsenic pentachloride[3] is only stable at low temperatures. Salts containing $AsCl_4^+$ are, however, known, for example in $AsCl_4^+AsF_6^-$[4,5] which is readily prepared by the reaction of AsF_3 and Cl_2 at room temperature. We have shown that reaction of arsenic pentafluoride with stoicheiometric amounts of selenium and iodine, and sulphur and bromine leads to the quantitative preparation of $SeI_3^+AsF_6^-$[6,7] and $SBr_3^+AsF_6^-$,[6,8] formally containing derivatives of the unknown SeI_4 and SBr_4. We estimated[6] that these reactions were both thermodynamically allowed on the basis of a simple Born–Haber cycle. Using a similar approach (Scheme 1) we showed that the analogous reaction [equation (1)] leading to $AsBr_4^+AsF_6^-$ is also thermodynamically favourable.

$$3AsF_5 + 2AsBr_3 + Br_2 \rightarrow 2AsBr_4^+AsF_6^- + AsF_3 \quad (1)$$

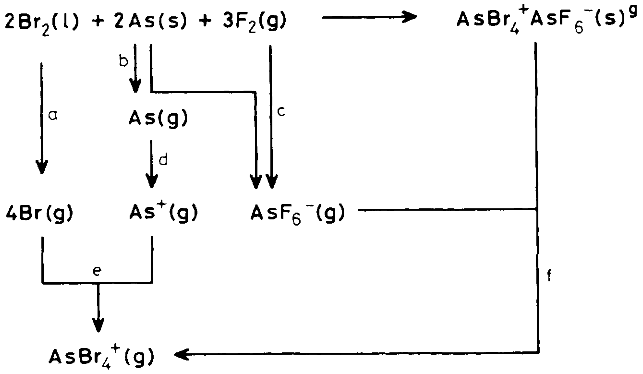
Subsequently we identified $AsBr_4^+AsF_6^-$ from its Raman spectrum (Table 1). Although $AsBr_4^+AsF_6^-$ has sufficient stability to be isolated for a short time as a pure white compound at −5 °C, it readily decomposes to the thermodynamically more stable products, AsF_3 and Br_2. Thus we have prepared and characterised a salt of $AsBr_4^+$, formally a derivative of the unknown arsenic pentabromide. Some compounds containing the As(V)–Br bond, have, however, been reported, *e.g.* in $AsPh_3Br_2$[2], and in AsF_5Br^-.[9]

In a typical reaction, AsF_5 (7.05 mmol) was condensed at −196 °C onto a mixture of Br_2 (2.35 mmol) and $AsBr_3$ (4.70 mmol) that had been previously held at room temperature in a 10 mm glass tube incorporating a Teflon-in-glass rotoflow valve and an attached 5 cm thin-walled 5 mm n.m.r. tube (for Raman spectroscopy). The reaction mixture was warmed to −5 °C until a clear solution formed (1 min) and then recooled

Table 1. Raman spectrum of $AsBr_4^+AsF_6^-$,[a] $AsCl_4^+AsF_6^-$,[a,4,5] and $GeBr_4$.[b]

$AsBr_4^+AsF_6^-$	$GeBr_4$	$AsCl_4^+AsF_6^-$	Assignment
88(94)	75	156	ν_2
115(74)	111	187	MX_4 ν_4
244(100)	236	422	ν^1
349(28)	332	500	ν_3
370(7)		371	ν_5
568(5)		570	AsF_6^- ν_2
671(17)		680	ν_1
702(1)			

[a] Spex Ramalab, Spectra Physics 2W argon-ion laser, 5145 Å exciting line, green laser, slit width 4 cm^{-1}, −196 °C. ν in cm^{-1} (relative intensity). [b] Refs. 10, 11.



Scheme 1. Energy cycle for the formation of $AsBr_4^+AsF_6^-$.
a; Atomisation energy = 26.8 kcal/mol.[13]
b; Atomisation energy = 72.4 kcal/mol.[13]
c; $\Delta H_f^\ominus(AsF_6^-,g) = -471.4$ kcal/mol.[12,13,16]
d; First ionisation potential = 226.2 kcal/mol.[17]
e; As^+–Br bond energy in $AsBr_4^+$, estimated as As–Br bond energy in $AsBr_3$[13] + 5% (calibrated on $2AsF_3 + 2Cl_2 \rightarrow AsCl_4^+AsF_6^-$ with $\Delta H = -25$ kcal/mol; thus giving As^+–Cl bond energy in $AsCl_4^+$: −77.6 kcal/mol, 5% greater than in $AsCl_3$). This gives As^+–Br: −64.1 kcal/mol in $AsBr_4^+$.
f; Crystal lattice energy [U_L/(kcal/mol)] calculated from the molecular volume (V_m/Å^3) using the linear relationship: $U_L = 556.3(V_m)^{-0.33} + 26.3$;[16,17] $V_m(AsBr_4^+)$ was taken to be equal to $V(GeBr_4) = 178$ Å^3;[18] $V_m(AsF_6^-) = 105$ Å^3.[14] This gives $U_L(AsBr_4^+AsF_6^-) = -111$ kcal/mol.
g; $\Delta H_f^\ominus$, $AsBr_4^+AsF_6^-(s) = -433$ kcal/mol; thus the heats of reaction for equation (1): $\Delta H_1 = -57$ kcal/mol; for equation (2): $\Delta H_2 = -23$ kcal/mol [$\Delta H_f^\ominus$, AsF_5 (g) = −295.6 kcal/mol;[12] $\Delta H_f^\ominus$, $AsBr_3(s) = -47.1$ kcal/mol;[2] $\Delta EH_f^\ominus$, $AsF_3(l) = -228.8$ kcal/mol[13]].

to −196 °C. A white solid formed after this process had been repeated more than 10 times. Volatile products (AsF_3) were removed under dynamic vacuum at −5 °C for 10 min, leaving a white solid, the Raman spectrum of which showed $AsBr_4^+$ to be present (see Table 1). The part of the spectrum assigned to $AsBr_4^+$ consists of four bands which are very similar in intensity and relative position to those observed for $AsCl_4^+$[4,5] and (the isoelectronic) $GeBr_4$,[10,11] and is consistent with its possessing T_d geometry.

$AsBr_4^+AsF_6^-$ is indefinitely stable at −196 °C. It decomposes slowly at −78 °C, and rapidly at room temperature according to equation (2) (established by i.r. and Raman)

$$AsBr_4^+AsF_6^-(s) \rightarrow 2AsF_3(l) + 2Br_2(l) \qquad (2)$$

The synthesis and decomposition of $AsBr_4^+AsF_6^-$ may be discussed in terms of a simple thermodynamic model. The heat of formation of $AsBr_4^+AsF_6^-$ was estimated from Scheme 1 to be −433 kcal/mol,† and it follows that the enthalpy changes of reactions (1) and (2) are −57 kcal/mol and −23 kcal/mol respectively. Both the formation and decomposition of $AsBr_4^+AsF_6^-$ are therefore seen to be thermodynamically allowed. The rapid decomposition of $AsBr_4^+AsF_6^-$ at room temperature contrasts with the stability of other cations containing elements from groups 15, 16, and 17. Some of these are thermodynamically stable (*e.g.* $AsCl_4^+AsF_6^-$[4,5] and $O_2^+AsF_6^-$[14,15]). Others are only likely to be kinetically stable under ambient conditions. This kinetic stability may arise from the higher stability of neutral intermediates, including AsF_5 which may not be reduced, or at least not rapidly reduced, in the decomposition. This is not the case for the kinetically unstable $AsBr_4^+AsF_6^-$.

We have estimated from a simple Born–Haber cycle that $AsBr_4^+AlBr_4^-$ would be much more chemically stable with respect to decomposition that $AsBr_4^+AsF_6^-$. Consistently $AsBr_4^+AlBr_4^-$ exists in equilibrium with its dissociation products $AsBr_3$, $AlBr_3$, and Br_2 at room temperature (Raman evidence).

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References

1 J. E., Huheey, 'Inorganic Chemistry,' 3rd edn., Harper, Cambridge, 1983, p. 841; see also ref. 18, p. 644.
2 J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, 'Comprehensive Inorganic Chemistry,' Pergamon Press, Oxford, vol. 2, 1973.
3 K. Seppelt, *Angew Chem., Int. Ed. Engl.*, 1976, **15**, 377.
4 A. Müller and A. Fadini, *Z. Anorg. Allg. Chem.*, 1967, **349**, 164.
5 J. Weidlein and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1965, **337**, 113.
6 J. P. Johnson, M. P. Murchie, J. Passmore, M. Tajik, P. S. White, and C.-M. Wong, *Can. J. Chem.*, 1987, **65**, 2744.
7 J. Passmore and P. Taylor, *J. Chem. Soc., Dalton Trans.*, 1976, 804.
8 J. Passmore, E. K. Richardson, and P. Taylor, *Inorg. Chem.*, 1978, **16**, 1681.
9 M. F. A. Dove, J. C. P. Sanders, E. L. Jones, and M. J. Parkin, *J. Chem. Soc., Chem. Commun.*, 1984, 1578; L. Kolditz and H. P. Krause, *Z. Chem.*, 1967, **7**, 157.
10 R. J. H. Clark and D. M. Rippon, *Chem. Commun.*, 1971, 1295.
11 R. J. H. Clark and P. D. Mitchell, *J. Chem. Soc., Faraday Trans. 2*, 1975, **51**, 515.
12 I. Barin, O. Knackle, and O. Kubauchewski, 'Thermodynamic Properties of Inorganic Substances,' Springer-Verlag, New York, 1977, supplement.
13 D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' Cambridge University Press, Cambridge, 2nd edn., 1982, appendix.
14 N. Burford, J. Passmore, and J. C. P. Sanders, 'Molecular Structure and Bonding,' 8, From Atoms to Polymers: Isoelectronic Analogies, eds. J. F. Liebman and A. Greensberg, VCH, and refs therein, in the press.
15 J. Shamir and J. Binenboym, *Inorg. Chim. Acta*, 1968, **2**, 37.
16 T. E. Mallouk, G. L. Rosenthal, G. Müller, R. Brusasco, and N. Bartlett, *Inorg. Chem.*, 1984, **23**, 3167.
17 T. J. Richardson, F. L. Tarzella, and N. Bartlett, *J. Am. Chem. Soc.*, 1986, **108**, 4937.
18 N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements,' Pergamon Press, Oxford, 1984.

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† 1 kcal/mol = 4.184 kJ/mol.