Enthalpies of Formation of 1:1, 1:2, and 2:1 Adducts of Xenon Difluoride with Antimony, Niobium, and Tantalum Pentafluorides

By **John Burgess, Boris Frlec,**† and **John H. Holloway,*** Department of Chemistry, The University of Leicester, Leicester LE1 7RH

Standard enthalpies of formation of XeF_2,MF_5, $XeF_2,2MF_5$ (M = Sb, Ta, or Nb), and $2XeF_2,MF_5$ (M = Sb or Ta) have been estimated from their heats of alkaline hydrolyses. The ionicity order of these compounds (Sb > Ta > Nb) adduced from vibrational spectroscopy is confirmed by the thermochemical results.

THERE is considerable interest in the nature of adducts formed by combination of xenon difluoride and various pentafluorides. Both salt-like [1-3] and fluorine-bridged [4] formulations have been used to explain the bonding in these compounds, and it was suggested several years ago that there should be a gradation of ionic character in certain series of adducts.[5]

It has recently been shown [6] that it is possible to estimate the enthalpy of formation of $XeF_2,2SbF_5$, and the enthalpy for generation of this adduct from its components [equation (1)], from calorimetric measurements of enthalpies of hydrolysis of $XeF_2,2SbF_5$ and SbF_5 and the known enthalpy of formation of XeF_2.[7] In the present paper we report results of a similar study of two other adducts of formula $XeF_2,2MF_5$, and for the related adducts XeF_2,MF_5 and $2XeF_2,MF_5$ (M = Sb, Nb, or Ta). Chemical properties, such as the ease of formation of the adducts from their respective components and the thermal stability, are considered in relation to estimated enthalpy changes for equation (1) and its analogues.

$$XeF_2(c) + 2SbF_5(l) \longrightarrow XeF_2,2SbF_5(c) \qquad (1)$$

Although the xenon difluoride–metal pentafluoride adducts have some salt-like characteristics and their vibrational spectra are best interpreted on the basis of formulations such as $XeF^+MF_6^-$, $XeF^+M_2F_{11}^-$, and $Xe_2F_3^+MF_6^-$, there is also considerable covalent character in the molecules, and fluorine-bridged formulations also contribute significantly to the bonding.[2,5] Recently it has been demonstrated that the degree of ionic character in series of XeF_2,MF_5 adducts can be assessed from Raman and i.r. results.[8,9] In series involving SbF_5, TaF_5, and NbF_5 the fluorine-bridged interaction is increased in the order Sb < Ta < Nb.[9] These trends are compared with those from thermochemical results below.

EXPERIMENTAL

Adducts were prepared by melting stoicheiometric quantities of the component molecules together under an atmosphere of dry xenon or nitrogen as outlined previously.[9] The products were monitored for purity by Raman spectroscopy using a Coderg T800 spectrometer. Samples of the compounds were sealed under vacuum in previously dried Pyrex bulbs.

Thermochemistry.—The adducts XeF_2,MF_5 and $XeF_2,2MF_5$, and the pentafluorides MF_5, hydrolyse readily and fairly smoothly in 1M-NaOH or -KOH; hydrolysis of SbF_5 and its adducts is not complete in 0·1M-NaOH or -KOH within an experimentally convenient time. The adducts $2XeF_2,MF_5$ react rapidly and rather violently with 1M- or 0·1M-NaOH or -KOH. We were, therefore, only able to estimate limiting values of enthalpies of hydrolysis of this series of adducts. The antimony compounds in

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† On leave from the Jožef Stefan Institute, University of Ljubljana, Yugoslavia.

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alkaline solution form hexahydroxoantimonate(v) salts.[6] We used potassium hydroxide solutions since the salt $K[Sb(OH)_6]$, unlike $Na[Sb(OH)_6]$, is water soluble. Niobium and tantalum pentafluorides, and their various adducts with xenon difluoride, give mononuclear niobates and tantalates in strongly alkaline solutions. In fact the nature of the products does not have to be known; all that is essential is that the products of hydrolysis of XeF_2 and MF_5 separately, and of the XeF_2,nMF_5 adduct, are identical.

Enthalpies of hydrolysis (Table 1) were determined by measuring the change in temperature when a frangible bulb containing the appropriate compound was broken into potassium hydroxide solution contained in a thermostatted (298·2 K) Dewar vessel. Sample weights were normally within the range 0·1—0·3 g; the volume of solution used was 150 cm^3 in each case. Temperature changes on reaction were monitored by a thermistor incorporated in a Wheatstone-bridge circuit which included a Kipp–Zonen BD5 recorder. The apparatus was calibrated by dissipating a known amount of heat in the calorimeter from a constantan wire heater of known resistance. The performance of this calorimetric apparatus was checked periodically using reactions of known enthalpy change, either silver chloride precipitation[10] or tris(hydroxymethyl)methylamine neutralisation.[11]

TABLE 1

Enthalpies of hydrolysis (ΔH_h) of pentafluorides, MF_5, and of adducts, XeF_2,nMF_5, in aqueous alkali at 298·2 K

Compound	Alkali used	No. of hydrolyses	Mean ΔH_h / kJ mol^{-1}	S.e.m.[a] / kJ mol^{-1}
SbF_5(l)	1M-KOH	6	−511	4
TaF_5(c)	0·1M-KOH	4	−400	6
NbF_5(c)	0·1M-KOH	7	−407	1
XeF_2,SbF_5(c)	1M-KOH	11	−769	8
XeF_2,TaF_5(c)	0·1M-KOH	10	−711	3
XeF_2,NbF_5(c)	0·1M-KOH	6	−773	6
$XeF_2,2TaF_5$(c)	0·1M-KOH	7	−1 124	6
$XeF_2,2NbF_5$(c)	0·1M-KOH	15	−1 194	8
$2XeF_2,SbF_5$(c)	1M-KOH	9	−1 172[b]	
$2XeF_2,TaF_5$(c)	0·1M-KOH	7	−1 109[b]	

[a] Standard error of the quoted mean ΔH_h, from which confidence limits at any required level may be calculated by standard methods (see, for example, E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971, pp. 7—9).
[b] Limiting values for ΔH_h (see text).

RESULTS

The experimentally determined enthalpies of hydrolysis of the pentafluorides and of their various xenon difluoride adducts are summarised in Table 1. As we found it impossible to obtain directly a satisfactory value for the enthalpy of hydrolysis of xenon difluoride in alkaline solution,[6] we estimated the enthalpy change for reaction (2) from known enthalpies of formation of xenon difluoride,[7] hydroxide ion, and fluoride ion in aqueous solution, and water.[12] The enthalpy change thus calculated for equation (2) was −328 kJ mol^{-1}.

$$2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2 \quad (2)$$

From the results in Table 1 and the above value for the enthalpy of hydrolysis of xenon difluoride it is a straightforward matter to calculate enthalpies of formation of the XeF_2,nMF_5 adducts (Table 2). From these enthalpies of adduct formation from the component molecules, true enthalpies of formation (*i.e.* from the elements in their standard states) were derived (Table 3). In deriving the values listed in Table 3 the following published enthalpies of formation were used: $\Delta H_f^\ominus[XeF_2(c)] = -38{\cdot}9$;[7] $\Delta H_f^\ominus[SbF_5(l)] = -328$;* $\Delta H_f^\ominus[NbF_5(c)] = -433$;[13] and $\Delta H_f^\ominus[TaF_5(c)] = -455{\cdot}5$ kcal mol^{-1}.[14,†]

TABLE 2

Enthalpies of reaction (ΔH) of xenon difluoride with pentafluorides at 25 °C; all compounds in solid state except for liquid antimony pentafluoride

Product		XeF_2,MF_5	$XeF_2,2MF_5$	$2XeF_2,MF_5$
ΔH/kJ mol^{-1} for M =	Sb	−67	−59[a]	>+8
	Ta	−17	−4	>+50
	Nb	+38	+50	

[a] From ref. 6.

TABLE 3

Enthalpies of formation ($\Delta H_f^\ominus$) of the adducts XeF_2,nMF_5(c)

Product		XeF_2,MF_5	$XeF_2,2MF_5$
$\Delta H_f^\ominus$/kJ mol^{-1} for M =	Sb	−1 602	−2 950[a]
	Ta	−2 088	−3 979
	Nb	−1 937	−3 736

[a] From ref. 6.

DISCUSSION

Legitimate comparison of physical data of the 1 : 2, 1 : 1, and 2 : 1 series of XeF_2,MF_5 adducts (M = Sb, Ta, or Nb) is possible since *X*-ray powder photography and Raman and i.r. spectroscopy have shown that the adducts are structurally similar.[9] Indeed, *X*-ray powder photographs show that tantalum and niobium adducts of 1 : 2 and 1 : 1 composition are isostructural. In each of the three series the adduct with the greatest ionic character is the antimony-containing compound and fluorine bridging becomes increasingly significant when antimony is replaced first by tantalum and then niobium.[9] This is totally in accord with the accepted Lewis-acid strengths of the pentafluorides involved. As might be anticipated, the temperatures required for thermal

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* Mean value, from $\Delta H_f^\ominus[SbF_5(l)] = -330$ kcal mol^{-1} *via* Sb + BrF_3 (G. W. Richards and A. A. Woolf, *J. Fluorine Chem.*, 1971, **1**, 129; A. A. Woolf, personal communication) and $\Delta H_f^\ominus[SbF_5(l)] = -326$ kcal mol^{-1} *via* $SbCl_5$ and SbF_5 hydrolysis (ref. 6).

† 1 cal = 4·184 J.

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TABLE 4

Comparison of ionic character and thermal-decomposition temperature of the adducts and the temperature required for complete reaction of the components (XeF_2 and MF_5) with enthalpies of reaction (ΔH) of the components

Adduct	Degree of ionic character (on basis of Raman data) [a]	Observed decomposition temperature/K	Observed temperature (K) for complete reaction of components	ΔH/kJ mol^{-1}
$XeF_2,2SbF_5$	most ionic	>453 [a]	warm [b]	-59
$XeF_2,2TaF_5$	↓	329 slow; 351 rapid [c]	343—353 [d]	-4
$XeF_2,2NbF_5$	least ionic	*ca.* 315 [c]	*ca.* 323 [d]	$+50$
XeF_2,SbF_5	most ionic	>423 [d]	*ca.* 433 [e]	-67
XeF_2,TaF_5	↓	45 slow; 56 rapid [c]	343—353 [d]	-17
XeF_2,NbF_5	least ionic	*ca.* 303 [c]	*ca.* 323 [d,f]	$+38$
$2XeF_2,SbF_5$	more ionic	373 [d]	388 [d]	$>+8$
$2XeF_2,TaF_5$	less ionic	*ca.* 298 [d]	343 [d]	$>+50$
$2XeF_2,NbF_5$ [d,g]				

[a] R. D. Peacock, personal communication. [b] See A. J. Edwards, J. H. Holloway, and R. D. Peacock, *Proc. Chem. Soc.*, 1963, 275. [c] Ref. 5. [d] Ref. 9. [e] Complete solution is only obtained at *ca.* 433 K when stoicheiometric quantities are used. [f] When excess of XeF_2 is used it only dissolves at *ca.* 383 K. [g] Not obtained under the conditions used.

decomposition of the adducts also reflect the trend in ionic character of each of the series.[9] We also found that, with the exception of the reaction of xenon difluoride with excess of liquid antimony pentafluoride (which gives $XeF_2,2SbF_5$), the temperature necessary for complete reaction of the components in formation of the adducts decreases in the order Sb > Ta > Nb for each series.[9]

These three trends parallel values of the enthalpies of formation of the adducts from their two components (Table 4). Thus the values for $XeF_2,2SbF_5$ (-59 kJ mol^{-1}) and XeF_2,SbF_5 (-67 kJ mol^{-1}) are modestly negative and these two adducts have the greatest empirical thermal stability and are nearest to having the ionic formulations $XeF^+Sb_2F_{11}^-$ and $XeF^+SbF_6^-$. The analogous niobium adducts, on the other hand, are least ionic and decompose at temperatures little above room temperature.[5,9] In fact, decomposition of the adduct XeF_2,NbF_5 appears to be catalysed slightly by nickel or nickel difluoride and occurs quite rapidly in nickel containers at room temperature.[5] The trends in enthalpy of formation for the three series of adducts suggest that the value for $2XeF_2,NbF_5$ should be significantly positive (*i.e.* $>+50$ kJ mol^{-1}) and this is totally in keeping with our failure to prepare this adduct.[9]

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