# Thermochemistry of Alkali Metal Hexafluoromolybdates(V) and Hexafluorotungstates(V)

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From measurements of the respective heats of alkaline hypochlorite hydrolysis at 298 K, the standard enthalpies of formation of $KWF_6$, $RbWF_6$, $CsWF_6$, $KMoF_6$, $RbMoF_6$, and $CsMoF_6$ have been derived. They are −2224 ± 6, −2236 ± 9, −2258 ± 6, −2075 ± 9, −2099 ± 8, and −2117 ± 7 kJ mol$^{-1}$ respectively. Values for the electron affinities ($\Delta H_E$) of gaseous tungsten hexafluoride and molybdenum hexafluoride have thence been estimated as $\Delta H_E[WF_{6(g)}] = -490 \pm 5$ and $\Delta H_E[MoF_{6(g)}] = -517 \pm 6$ kJ mol$^{-1}$, at 298 K. For the reactions $MF_{5(c)} + F^-_{(g)} \longrightarrow MF_6{}^-_{(g)}$ the fluoride ion affinities ($\Delta H_F$) of tungsten pentafluoride and molybdenum pentafluoride are estimated to be −491 ± 5 and −412 ± 6 kJ mol$^{-1}$ respectively.

Few thermochemical data for complex fluorides are available. Present information is insufficient either to enable estimates of the stabilities of known complex fluorides to be made, or to allow the calculation of derived data such as electron affinities [equation (1)] and fluoride ion affinities [equation (2)]. Knowledge of these affinities would be useful in predicting the possible existence and reactions of as yet unknown compounds.

$$MF_6 + e^- = MF_6{}^- \quad \Delta H_E \qquad (1)$$

$$MF_5 + F^- = MF_6{}^- \quad \Delta H_F \qquad (2)$$

Qualitative estimates of the minimum values of electron affinities of a number of transition metal hexafluorides, based upon the reactivity of the hexafluorides towards oxidisable molecules such as nitric oxide, nitrogen dioxide, or oxygen, have been made by Bartlett[1] with values ranging from $\Delta H_E = -90$ kcal mol$^{-1}$ for $ReF_6$ to $-156$ kcal mol$^{-1}$ for $PtF_6$. Magnetron experiments, in which the equilibrium $MF_6 + e^- \rightleftharpoons MF_6{}^-$ is set up and monitored at a heated metal surface, led to a surprisingly small estimate for $\Delta H_E$ of $-68{\cdot}2$ kcal mol$^{-1}$ for the electron affinity of $WF_6$.[2]

Studies[3] of the chemical reactions of molybdenum and tungsten hexafluorides with lower fluorides of non-

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[1] N. Bartlett, *Angew. Chem. Internat. Edn.*, 1968, **7**, 433.

[2] G. C. Goode, Ph.D. Thesis, University of Aston, 1969, pp. 45—47.

[3] T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.*, 1966, **5**, 1434; J. R. Geichmann, E. A. Smith, S. S. Trond, and P. R. Ogle, *ibid.*, 1962, **1**, 661.

metallic elements, nitric oxide, and nitrosyl chloride have illustrated the relative inertness of tungsten hexafluoride. Hammond [4-6] has suggested, from a study of band positions in the charge-transfer spectra of these hexafluorides with organic donors, that the molecular electron affinity of molybdenum hexafluoride is greater than that of tungsten hexafluoride.

In a preliminary communication from this laboratory,[7] the heat of alkaline oxidative hydrolysis of $KWF_6$ was reported, and a value of $\Delta H_E = ca.\ -120$ kcal mol$^{-1}$ ($-500$ kJ mol$^{-1}$) was estimated for the electron affinity of tungsten hexafluoride. We have now measured the heats of oxidative alkaline hydrolysis of the potassium, rubidium, and caesium salts of the hexafluoromolybdate(V) and hexafluorotungstate(V) anions, and thence calculated values for the heats of formation of these compounds and for the respective hexafluorometallate anions. From the results we have deduced the electron affinities of the hexafluorides, and the fluoride ion affinities of the pentafluorides, of molybdenum and tungsten.

TABLE 1

Unit cell dimensions of potassium, rubidium, and caesium hexafluoromolybdates(V) and hexafluorotungstates(V)

| Compound | Unit cell parameters/Å | $r_0$/Å * |
|---|---|---|
| $KWF_6$ | $a_0 = 10{\cdot}21,\ c_0 = 10{\cdot}09$ | $4{\cdot}40_5$ |
| $RbWF_6$ | $a_0 = 5{\cdot}14\ (\alpha_0 = 97{\cdot}3°)$ | $4{\cdot}42_8$ |
| $CsWF_6$ | $a_0 = 5{\cdot}31\ (\alpha_0 = 95{\cdot}3°)$ | $4{\cdot}57_0$ |
| $KMoF_6$ | $a_0 = 10{\cdot}17,\ c_0 = 9{\cdot}97$ | $4{\cdot}37_5$ |
| $RbMoF_6$ | $a_0 = 5{\cdot}11\ (\alpha_0 = 96{\cdot}5°)$ | $4{\cdot}39_9$ |
| $CSMoF_6$ | $a_0 = 5{\cdot}29\ (\alpha_0 = 96{\cdot}0°)$ | $4{\cdot}54_9$ |

* Unit length, defined in text.

TABLE 2

Analyses and thermochemical results for $AMoF_6$ and $AWF_6$ series

| | Analyses/% | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Alkali metal | | W or Mo | | | | | |
| Compound | Found | Calc. | Found | Calc. | No. of hydrolyses | Mean $\Delta H_{hydr}$ [a] /kJ mol$^{-1}$ | $\sigma$[b]/kJ mol$^{-1}$ | $\Delta H_f^{\ominus}$ (298) /kJ mol$^{-1}$ |
| $KWF_6$ | 11·4 | 11·6 | 54·9 | 54·6 | 6 | −517 | 6 | −2224 |
| $RbWF_6$ | 22·3 | 22·2 | 47·8 | 48·0 | 6 | −505 | 9 | −2236 |
| $CsWF_6$ | 30·3 | 30·9 | 42·8 | 42·7 | 6 | −495 | 6 | −2258 |
| $KMoF_6$ | 16·1 | 15·7 | 38·1 | 38·5 | 6 | −592 | 9 | −2083 |
| $RbMoF_6$ | 28·9 | 29·5 | 32·7 | 32·5 | 6 | −577 | 8 | −2099 |
| $CsMoF_6$ | 39·1 | 38·7 | 27·7 | 28·0 | 6 | −569 | 7 | −2117 |

[a] Heat of alkaline hypochlorite hydrolysis. [b] Standard deviations, from which standard errors of the means and their confidence limits can be calculated by standard procedures (see, *e.g.*, E. S. Swinbourne, ' Analysis of Kinetic Data,' Nelson, London, 1971, pp. 7—9).

EXPERIMENTAL

*Preparations*.—The compounds $AWF_6$ and $AMoF_6$ (A = K, Rb, Cs) were prepared by established procedures.[8] From *X*-ray diffraction patterns (Debye–Scherrer), the lattice constants (Table 1) were derived for each compound. These values show satisfactory agreement with those published earlier.[8] The presence of the hexafluorotungstate(V) ion ($\nu_3 = 594$ cm$^{-1}$) [8] and the hexafluoromolybdate(V) ion ($\nu_3 = 615$ cm$^{-1}$) [8] in each sample was confirmed by i.r. spectra recorded on a Perkin-Elmer 225 spectrometer. For each salt the alkali metal was determined by precipitation with sodium tetraphenylborate; [9] tungsten was precipitated as the tannin–cinchonine complex, ignited and weighed as the trioxide; [10] and molybdenum was estimated as the oxine derivative as appropriate.[9] The analyses are recorded in Table 2.

*Calorimetry*.—The calorimeter was a modified version of the one described by Myers and Brady,[11] and was operated at 298·2 K. A frangible glass bulb containing a known mass (between 0·13 and 0·21 g) of the compound was broken into 150 cm$^3$ of a solution of sodium hydroxide (0·1M) and sodium hypochlorite (1·5%) contained in a glass Dewar. The temperature change of the calorimeter's contents was followed by a thermistor (Type F-23 supplied by Standard Telephone and Cable Company Limited), whose changing resistance was monitored by a Kipp–Zonen BD 5 recorder incorporated in a Wheatstone bridge circuit. The recorder was calibrated by supplying a known amount of current through a constantan wire of known resistance for a specified time. The performance of the calorimeter was periodically checked by standardisation with tris(hydroxymethyl)-methylamine.[12]

RESULTS

Three heats of hydrolysis were recorded for each of two individual samples, yielding a total of six results, for each compound. The experimental calorimeter results are summarised in Table 2. The hydrolysis of $AMoF_6$ and $AWF_6$ (A = K, Rb, Cs) by alkaline hypochlorite solution occurs quantitatively according to equation (3), with A = K, Rb, or Cs, and M = Mo or W. The standard enthalpy of formation of ($\Delta H_f^{\ominus}$) of each compound was calculated from the

$$2AMF_{6(c)} + OCl^-{}_{(aq)} + 14OH^-{}_{(aq)} \longrightarrow 2A^+{}_{(aq)} + 2MO_4{}^{2-}{}_{(aq)} + Cl^-{}_{(aq)} + 15H_2O_{(l)} + 12F^-{}_{(aq)} \quad (3)$$

heat of hydrolysis and the appropriate ancillary thermochemical data.* The results are incorporated in Table 2.

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* Standard enthalpies of formation have been taken from the sources cited in the previous paper, plus D. A. Johnson, ' Some Thermodynamic Aspects of Inorganic Chemistry,' Cambridge, 1968, pp. 208—216 [$K^+$(g), $Rb^+$(g), $Cs^+$(g), and $F^-$(g)]; J. Schröder and F. J. Sieben, *Chem. Ber.*, 1970, **103**, 76 [$WF_6$(g) and $WF_5$(c)]; and I. Haigh, Ph.D. Thesis, Leicester, 1973 {$\Delta H_f^{\ominus}$[$MoF_5$ (c)] = 331 kcal mol$^{-1}$}.

[4] P. R. Hammond, *J. Phys. Chem.*, 1970, **74**, 647.

[5] P. R. Hammond and R. R. Lake, *Chem. Comm.*, 1968, 987.

[6] P. R. Hammond and W. S. McEwan, *J. Chem. Soc.* (*A*), 1971, 3812.

[7] J. Burgess, I. Haigh, and R. D. Peacock, *Chem. Comm.*, 1971, 977.

[8] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1957, 4212.

[9] A. I. Vogel, ' Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961.

[10] D. A. Lambie, *Analyst*, 1945, **70**, 124.

[11] O. E. Myers and A. P. Brady, *J. Phys. Chem.*, 1960, **64**, 591.

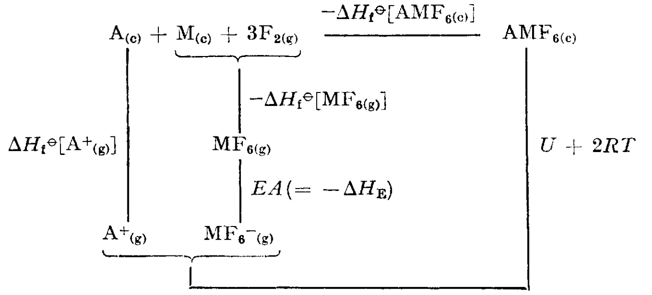
[12] J. O. Hill, G. Öjelund, and I. Wadsö, *J. Chem. Thermodynamics*, 1969, **1**, 111.

## DISCUSSION

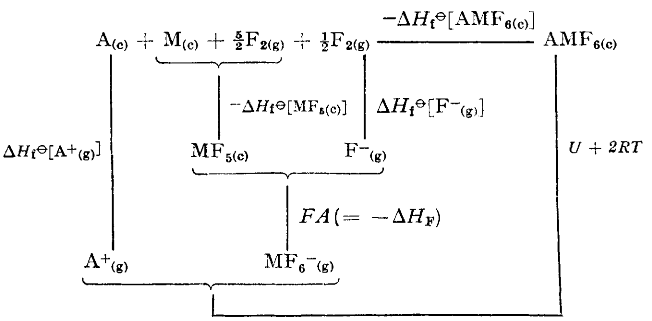
The main purpose of this work has been to obtain estimates for the electron affinities of the hexafluorides and the fluoride ion affinities of the pentafluorides. These quantities may be obtained,* *via* enthalpies of formation of the gaseous $MF_6^-$ ions, from the thermochemical data of Table 2 and the lattice enthalpies of the respective salts. The thermochemical cycles used are shown in Schemes 1 and 2; lattice energies ($U$) can be calculated from the known structures.[8] All six salts have distorted caesium chloride structures with the alkali metal and transition metal ions occupying the caesium and chloride positions respectively. The potassium salts have a tetragonal modification with either 4 or 8 molecules in the unit cell; the rubidium and caesium salts are rhombohedrally distorted with 1 molecule in the unit cell. These distortions are not large, but they could lead to a significant lowering of the Madelung constant. A further reduction of the lattice energy could be caused by the (almost certain) presence of partial charges on the fluorine and transition metal atoms leading to multipole interactions. For the present purpose, the simplest assumption has been made, *viz.* that the lowering of the lattice energy from these causes will be balanced by the van der Waals forces, which lead to an increase in the lattice energy and which are likely to be significant in these complex salts. This is close to the Kapustinskii assumptions[13] and is illustrated by recent calculations[14] of the lattice energies of the complex chlorides $K_2TeCl_6$ and $K_2SnCl_6$, where the gross cancellation of errors is clearly shown. We have therefore used the normal Born–Meyer expression [equation (4)], with the cube root of the volume of one formula unit as the unit length ($r_0$), and a ρ value of

$$U = \frac{N_0 A z_1 z_2 e^2}{r_0}\left(1 - \frac{\rho}{r_0}\right) \qquad (4)$$

0·345. The resultant lattice energies, calculated from the crystal parameters of Table 1, are listed in Table 3.



SCHEME 1



SCHEME 2

TABLE 3

Estimated lattice energies ($U_{298}$) of $AMF_6$ salts

| | $U_{298}$/kJ mol$^{-1}$ | | $U_{298}$/kJ mol$^{-1}$ |
|---|---|---|---|
| $KWF_6$ | −531 | $KMoF_6$ | −535 |
| $RbWF_6$ | −520 | $RbMoF_6$ | −525 |
| $CsWF_6$ | −504 | $CsMoF_6$ | −507 |

The assumptions are at least partly justified by the consistency of the calculations of the enthalpies of formation of the anions, of electron affinities, and of fluoride ion affinities (Table 4). The results indicate that the electron affinity of $MoF_6$ is greater (more exothermic) than that of $WF_6$ by *ca.* 30 kJ mol$^{-1}$, in accordance with the difference in observed chemical properties, but that $WF_5$ is a considerably better fluoride ion acceptor than $MoF_5$ (*ca.* 80 kJ mol$^{-1}$ difference). It should be noted that as the heats of formation of gaseous $MoF_5$ and $WF_5$ are not known, the fluoride ion affinities refer to $MF_{5(c)}$ and not, more conventionally, to gaseous pentafluoride. Interestingly, the reported lack of reaction[1] between NO and $WF_6$ is borne out by the present observations. If it is assumed that $NOWF_6$ has the CsCl type of structure proposed for $NOMoF_6$,[3] then it can easily be estimated that for the reaction shown in equation (5) $\Delta G_{298}$ is positive to the extent of *ca.* 20 kJ mol$^{-1}$.

TABLE 4

Enthalpies of formation of $MF_6^-$ anions, electron affinities of $MF_6$, and fluoride ion affinities of $MF_5$, for M = W or Mo

| Compound | $\Delta H_f^\ominus[MF_6^-(g)]$ /kJ mol$^{-1}$ | $\Delta H_E[MF_6(g)]$ /kJ mol$^{-1}$ | $\Delta H_F[MF_5(c)]$ /kJ mol$^{-1}$ |
|---|---|---|---|
| $KWF_6$ | −2209 | −487 | −488 |
| $RbWF_6$ | −2213 | −491 | −492 |
| $CsWF_6$ | −2213 | −493 | −494 |
| Mean | −2212 ± 5 [a] | −490 ± 5 [a] | −491 ± 5 [a] |
| $KMoF_6$ | −2063 | −512 | −407 |
| $RbMoF_6$ | −2070 | −520 | −415 |
| $CsMoF_6$ | −2070 | −519 | −414 |
| Mean | −2068 ± 6 [a] | −517 ± 6 [a] | −412 ± 6 [a] |

[a] Standard deviation.

$$NO_{(g)} + WF_{6(g)} \longrightarrow NOWF_{6(c)} \qquad (5)$$

The two fluoride ion affinities of $\Delta H_F = -414$ kJ mol$^{-1}$ for $MoF_{5(c)}$ and $\Delta H_F = -494$ kJ mol$^{-1}$ for $WF_{5(g)}$ may be compared with the only other fluoride ion affinity available, *viz.*, that of $\Delta H_F = -385$ kJ mol$^{-1}$ for $BF_{3(g)}$.[15] Clearly, these are of the same order, and it is possible, so far as the gaseous molecules are concerned, that $BF_3$ would be at least as good a fluoride ion acceptor as $WF_5$.

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* Our values for electron affinities and fluoride ion affinities are at 298 K, not, as they should ideally be, at 0 K. While we have, or can extrapolate, values for some of our thermochemical quantities at 0 K, this is not the case for others.

[13] A. F. Kapustinskii, *Quart. Rev.*, 1956, **10**, 283.
[14] M. Webster and P. H. Collins, *J.C.S. Dalton*, 1973, 588.
[15] J. L. Bills and F. A. Cotton, *J. Phys. Chem.*, 1960, **64**, 1477.