Charge-transfer Interactions involving High Oxidation State Transition-metal Fluorides

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Charge-transfer interactions have been observed between NbF_5, MoF_6, and WF_6 and the Group IV compounds MX_4 (M = Si, Ge, Sn, X = alkyl; M = C, Si, Sn, X = Cl) and between WF_6 and C_6H_6, $C_6H_5CH_3$, and C_6F_5. WF_5OMe behaves similarly to WF_6 but the spectra of phenoxotungsten(VI) fluorides are solvent independent. Photolysis of solutions of WF_6 in C_6H_6, $C_6H_5CH_3$, and Me_4Sn, leads to reduction of tungsten but pure products are not obtained.

SOLUTIONS of tungsten hexafluoride in organic π- and n-donor solvents, *e.g.* benzene and acetonitrile, are intensely coloured [1,2] but their Raman and ^{19}F n.m.r. spectra indicate that the octahedral symmetry of WF_6 is unperturbed.[2] Halides, oxides, and oxohalides of elements in high oxidation states behave similarly towards π donors, and this has been ascribed [3] to contact charge-transfer [4] interactions. We find that the phenomenon is not restricted to solutions in what would normally be described as donor solvents, and report the electronic spectra and some photolysis studies of high oxidation state transition-metal fluorides in Group IV tetra-alkyls and tetrachlorides and in organic, aromatic solvents. A preliminary report of the spectra has been given.[5]

RESULTS

Solutions in Group IV Tetra-alkyls.—Dilute solutions of niobium pentafluoride, molybdenum and tungsten hexafluorides, and methoxotungsten(VI) pentafluoride in these solvents are yellow, and are characterised by broad absorptions ($\varepsilon_{molar} = 5 \times 10^4$—$10^5$) in the u.v. region (Table 1), where MoF_6, WF_6, and R_4M are transparent. Their colours arise from 'tailing' of the bands into the visible region. The MoF_6, WF_6, and WF_5OMe solutions become red with increasing concentration due to increases in the 'tail' intensities, although no additional bands could be detected, and their colours almost disappear on freezing. NbF_5 solutions were too dilute for colour changes to be detected, and a blue solid is rapidly deposited from MoF_6 in tetramethyltin, therefore no spectrum of the solution could be recorded.

TABLE 1

Electronic spectra of transition-metal fluoride, Group IV tetra-alkyl solutions: $\nu_{max.} \times 10^{-3}$ cm^{-1}

	NbF_5	MoF_6	WF_6	WF_5OMe
Me_4Si	43·5, 37·9sh	27·9	40·3	40·3
Me_4Ge	42·9	43·4	34·8	
Me_4Sn	36·3	Reaction	29·8	
$Pr^n{}_4Sn$			43·7, 34·5sh	
$Bu^n{}_4Sn$			41·3, 31·7	

The spectrum of WF_6 in tetra-n-butyltin consists of two peaks and the variation of optical density with concentration is consistent [6] with a 1 : 1 interaction which has a near-zero equilibrium constant. The spectrum of WF_6 in tetra-n-propyltin has a pronounced shoulder in addition to the main peak, and in both spectra the absorptions are at higher energies than $\nu_{max.}$ for the Me_4Sn solution.

The products from photolysis of a liquid WF_6–Me_4Sn mixture are methane, a small quantity of methyl fluoride, and a light brown solid, containing carbon, hydrogen, tin, and tungsten, which could not be identified. Oxidation-state titrations indicate that tungsten or tin has been reduced and it is considered that the former is most likely. Similar behaviour is observed for solutions in $Pr^n{}_4Sn$ and $Bu^n{}_4Sn$, and no breakdown occurs when R_4Sn is irradiated alone under similar conditions.

Solutions in Group IV Tetrachlorides.—Molybdenum hexafluoride reacts slowly with carbon and silicon tetrachlorides to form $CCl_{4-n}F_n$, SiF_4, and a mixed halide formulated as $(Mo_3{}^{IV}Cl_9)(Mo^{V}F_6)_3$.[7] A yellow solution of MoF_6 in $SiCl_4$ has absorptions at 21,400, 26,900sh and >33,300 cm^{-1}. With time, the low-energy peak, which may be compared with a peak at 21,500 cm^{-1} in the spectrum of $(Mo_3Cl_9)(MoF_6)_3$,[7] rapidly increases in intensity while the shoulder disappears. The spectrum of MoF_6 in CCl_4 consists of a very broad absorption between 29,900 and 50,000 cm^{-1} which rapidly increases in intensity with time. Although no bands due to MoF_6–solvent interactions can be positively identified in these solutions, it seems likely that such interactions are present initially.

Tungsten hexafluoride does not react with carbon, silicon, or tin tetrachlorides, and the spectra of its colourless solutions in those compounds consist of broad bands at 37,200, 41,800, and 42,900 cm^{-1} respectively, which are not present in the spectra of the components. WF_5OMe behaves similarly, $\nu_{max.}$ for a solution in CCl_4 being 37,200 cm^{-1}.

Solutions in Aromatic Organic Solvents.—The spectra of (red) tungsten hexafluoride solutions in benzene and toluene and (yellow) WF_6 and WF_5OMe solutions in hexafluorobenzene contain absorptions which tail into the visible region. The $\nu_{max.}$ positions are >33,900 cm^{-1}, but accurate values could not be obtained due to overlap with solvent bands. The spectra of phenoxotungsten(VI) pentafluoride and *cis*-diphenoxotungsten(VI) tetrafluoride in C_6H_6 and C_6F_6 all consist of a band at 27,800 cm^{-1} ($\varepsilon_{molar} \sim 10^4$),

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[1] H. F. Priest and W. C. Schumb, *J. Amer. Chem. Soc.*, 1948, **70**, 2291.

[2] H. J. Clase, A. M. Noble, and J. M. Winfield, *Spectrochim. Acta*, 1969, **25A**, 293.

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

[4] L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839.

[5] R. R. McLean, D. W. A. Sharp, and J. M. Winfield, *Chem. Comm.*, 1970, 452.

[6] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

[7] T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.*, 1966, **5**, 1434; *Nature*, 1966, **210**, 836.

but as identical spectra are also obtained in Me_4Si, they are assigned to intramolecular charge-transfer transitions.

Photolysis of WF_6 solutions in benzene or toluene produces small quantities of dark brown, viscous liquids which contain reduced tungsten and apparently co-ordinated C_6H_6 or $C_6H_5CH_3$. No fluorocarbons are detected and the only volatile product appears to be HF. A similar liquid is obtained ftom a thermal reaction between WF_6 and C_6H_6. Tungsten tetrafluoride, which has been previously reported to be a product,[8] was not observed.

DISCUSSION

It is considered that charge-transfer interactions, arising from simple molecular contacts, exist in the NbF_5, MoF_6, WF_6, and WF_5OMe solutions. The interactions will be very weak, and equilibrium constants are not quoted because values obtained using the Benesi–Hildebrand method are unreliable for weak complexes.[9] The most obvious description of the charge-transfer process is that it involves transitions to metal, non-bonding orbitals from π orbitals of the aromatic molecules, non-bonding $1t_1$ orbitals of the chlorides, or t_2, σ carbon–Group IV element orbitals of the tetra-alkyls. n-Hexane and cyclohexane have recently been classified as σ donors to MoF_6 and WF_6 from similar work.[10]

The electron affinity of WF_6 is estimated to be 120 ± 5 kcal mol^{-1} (ref. 11) and the reactions of MoF_6 suggest that it has a greater electron affinity than WF_6.[12] The ionisation potentials of Group IV tetra-alkyls vary in the order $Si > Ge > Sn$,[13] and those of the non-bonding $1t_1$ electrons in the tetrachlorides, in the order $C < Si < Sn$.[14] These trends correspond to the trends in $\nu_{max.}$ for the WF_6,Me_4M, WF_6,MCl_4, and NbF_5,Me_4M solutions, although the NbF_5 results are ambiguous as its molecular state in Me_4M is not known.

This simple model does not account for all the observed features of the spectra. The additional absorptions in the spectra of WF_6 in tetra-n-butyl- and tetra-n-propyltins may be due to transitions involving C–C framework orbitals and the spectra clearly indicate that both the size and the electronic properties of the alkyl groups are significant. $\nu_{max.}$ for MoF_6 in tetramethylgermane would be expected to occur at a lower energy than is observed, and the implication from the spectra, that WF_5OMe and WF_6 have identical electron affinities, seems unlikely. Charge transfer from solvent to the transition-metal fluoride is believed to be dominant in these solutions, but the possibility of a synergic process, whereby the fluoride behaves also as a donor to non-bonding orbitals localised on Si, Ge, or Sn, cannot be excluded.

EXPERIMENTAL

All operations were carried out *in vacuo* or in a dry box. Molybdenum and tungsten hexafluorides (Matheson Co. and Alfa Inorganics) were purified by low-temperature trap-to-tap distillation and stored over NaF. Niobium pentafluoride, prepared from Nb and F_2, was sublimed several times before use. WF_5OMe, WF_5OPh, and *cis*-$WF_4(OPh)_2$ were prepared as reported previously.[15] The Group IV tetra-alkyls and tetrachlorides, benzene, toluene, and hexafluorobenzene were commercial products and were distilled, degassed under reduced pressure, and dried over 4A molecular sieves or Na as appropriate.

Electronic Spectra.—Solutions were prepared *in vacuo* using a manifold equipped with Teflon-glass stopcocks (Ace Glass Co.). A silica cell fitted with a side-arm in which components were mixed, and stopcock was attached to the manifold by a Kel-F waxed (3M) joint. Solutions were made up by weight, using a calibrated bulb and manometer to determine small quantities of volatile fluorides. Hydrolysis of these solutions leads to the formation of oxofluorides which absorb strongly in the u.v. region. Prolonged degassing of the apparatus was necessary to avoid hydrolysis, particularly for the MoF_6 solutions. Spectra were recorded on Pye–Unicam SP 700 and SP 800 spectrometers using 5 and 10 mm path-length cells. Reproducible spectra were obtained in each case and the solutions could be kept for at least 1 h before any spectral change was detected. Optical densities obtained for WF_6, $Bu^n{}_4Sn$ solutions of different concentrations (Table 2) were analysed by the Benesi–Hildebrand method.[6]

TABLE 2

Optical densities of tungsten hexafluoride solutions in tetra-n-butyl tin

Mol fraction of $WF_6 \times 10^2$	Optical density	
	at 41,300 cm^{-1}	at 31,700 cm^{-1}
0·20	0·64	0·56
0·94	0·68	0·60
1·83	0·91	0·88
2·42	0·98	0·96
4·06	1·02	1·04
5·48	1·07	1·20
8·70	1·17	1·28
13·2	1·42	1·89

Irradiations.—Equimolar mixtures of WF_6 and tetra-alkyltins, benzene, or toluene were irradiated in Pyrex ampoules for periods of up to 10 days, using a medium-pressure Hg lamp (Hanovia). Significantly different results were not obtained if silica ampoules and different stoicheiometries were used. Volatile products were identified by i.r. spectroscopy using a Perkin-Elmer 457 instrument. ^1H and ^{19}F N.m.r. spectra were recorded using a Perkin-Elmer R10 instrument. Tungsten was determined as WO_3 using cinchonine hydrochloride, oxidation states by $KMnO_4/Fe^{II}$ titrations, and microanalyses were by Laboratorium Beller, Göttingen.

Tungsten Hexafluoride and Tetramethyltin.—The products were methane, a small quantity of methyl fluoride,

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[9] S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, 1965, 2048.

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

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[13] B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, 1961, **65**, 2186; 1962, **66**, 155.

[14] P. J. Bassett and D. R. Lloyd, *J. Chem. Soc.* (*A*), 1971, 641.

[15] A. M. Noble and J. M. Winfield, *J. Chem. Soc.* (*A*), 1970, 2574.

and an involatile, pale brown solid (Found: C, 11·3; H, 2·9; F, 20·5; Sn, 36·6; W, 28·4%; apparent oxidation state of tungsten = +5). Its i.r. spectrum suggested that Me–Sn and W–F groups were present, and its *X*-ray powder photograph indicated that it did not contain Me_3SnF.

Similar solid products were obtained from WF_6 and tetra-n-butyl- or tetra-n-propyl-tin, the other products being respectively butane and propane. Irradiation of R_4Sn alone under similar conditions had no effect.

Tungsten Hexafluoride and Aromatic Hydrocarbons.—The products from WF_6 and benzene or toluene were small quantities of involatile, dark brown, viscous liquids, BF_3, and SiF_4. Composition of the liquids was variable, typical analyses were as follows. For WF_6,benzene, Found: C, 23·9; H, 2·0; F, 23·2; W, 47·9%; W : F $\simeq$ 1 : 4·7. For WF_6,toluene, Found: C, 10·3; H, 1·2; F, 24·8; W, 52·9%; W : F $\simeq$ 1 : 4·5. The apparent oxidation states of tungsten were 4·5—5. Their i.r. spectra indicated the presence of aromatic hydrocarbons. The ^1H and ^{19}F n.m.r. spectra of the WF_6,benzene product consisted of a broad singlet at $\tau = 3·4$ (*cf.* benzene at $\tau = 2·7$), and two broad singlets at 74 and 70 p.p.m. downfield from CCl_3F. The n.m.r. spectra of the WF_6,toluene product consisted of two singlets at $\tau = 4·6$ and 9·05 (relative intensity 5 : 3) which were shifted to $\tau = 3·1$ and 7·4 in acetonitrile solution (*cf.* toluene at $\tau = 2·9$ and 7·6), and two broad singlets at 71 and 63 p.p.m. downfield from CCl_3F.

A brown liquid with similar properties was obtained from WF_6 and benzene at 110 °C in glass or metal ampoules.

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