ACETONITRILE, A CONVENIENT SOLVENT FOR INORGANIC FLUORIDES

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SUMMARY

    A procedure is described for the purification of acetonitrile to a
level suitable for synthetic, spectroscopic, and electrochemical work
involving high oxidation state fluorides. Lewis acid-base and redox
reactions in this solvent are discussed.

INTRODUCTION

    Although anhydrous hydrogen fluoride is the pre-eminent solvent
for inorganic fluorides, several other inorganic solvents, for example
sulphur dioxide, sulphuryl chloride fluoride, and bromine pentafluoride
are used in currently reported work. The purpose of this article is to
point out the use which can be made of Lewis base, aprotic, organic
solvents in inorganic fluorine chemistry. Acetonitrile is among the
most useful members of this class. Its volatility, mp. = -45.7;
bp. = 81.6°C, makes it ideal for vacuum line work at ambient temperatures,
and it can be handled easily in greaseless, Pyrex apparatus. Its di-
electric constant is relatively high, 37.5 at 25°C [1], and it is there-
fore a suitable solvent for many ionic compounds. It is a strong enough
Lewis base to solvate effectively many high oxidation state, covalent
fluorides and metal cations, particularly those of 3d and post transition
elements, but it can be readily displaced by stronger bases, for example
F^- ion. MeCN has a simple vibrational spectrum and is transparent in
the visible and u.v. regions. These properties, with the availability
of CD_3CN, make it an ideal solvent for spectroscopic work.

SOLVENT PREPARATION

For use with many high oxidation state fluorides MeCN must be care-
fully purified, acrylonitrile and benzene being particularly troublesome
impurities. Some Lewis acid fluorides react with impure MeCN to give
brown solids or viscous liquids. The purification procedure used in
these laboratories is an extension of that due to Walter and Ramaley[2],
and consists of multiple refluxes of HPLC or spectroscopic grade MeCN
in a Pyrex still equipped with a 0.75 m vacuum jacketed separating column,
and protected from atmospheric moisture. The following sequence of
reagents is used, quantities and times being given in parentheses:
(a) anhydrous $AlCl_3$ (15 gl^{-1}; 1 h), (b) $KMnO_4$ + Li_2CO_3 (both 10 gl^{-1};
0.25 h), (c) $KHSO_4$ (15 gl^{-1}; 1 h), (d) CaH_2 (20 gl^{-1}; 1 h), (e) P_2O_5 -
(1 gl^{-1}; 0.5 h), (f) as (e). The solvent is rapidly distilled after each
reflux and is topped and tailed at each step by approximately 3%. MeCN
is then transferred, without exposure to atmospheric moisture, to vessels
containing previously activated 3A molecular sieves. It is degassed
in vacuo, allowed to stand at room temperature for 24 h, then vacuum
distilled onto fresh 3A sieves. After standing over these it is ready
for use. Thus purified, MeCN has an absorbance at 200 nm of <0.05
(H_2O reference) and an apparent u.v. cut-off point ca. 175 nm. The
working potential range of purified $Et_4N^+BF_4^-$, 0.1 mol dm^{-3} in this
MeCN, is +3.0 to -2.7V vs Ag^+/Ag^o.

If these criteria are not quite met, trace impurities remaining
can often be removed by treatment of MeCN with activated alumina
(neutral, 60 mesh) in vacuo, prior to the final molecular sieve treat-
ment. Purification of GPR grade MeCN is seldom satisfactory as very large
losses are encountered at the $KMnO_4$, Li_2CO_3 step.

LEWIS BASE BEHAVIOUR TOWARDS BINARY FLUORIDES AND THEIR DERIVATIVES

Acetonitrile forms isolable, 1:1 complexes with the strong Lewis
acids, Sb, As, Nb, Ta, and Mo pentafluorides. Complete vibrational
spectroscopic studies of solid MF_5.NCMe, M=Sb, As, indicate local
C_{4v} symmetry for the MF_5N moieties [3], and the spectroscopic data
available for the remainder are consistent with a similar situation [4] .

Reactions of these pentafluorides in MeCN are likely to involve MF_5.NCMe rather than the free pentafluoride. One consequence of this is that AsF_5 in MeCN is an inferior oxidizing agent than is PF_5 [5]. UF_5 is stable with respect to disproportionation in MeCN, and a 1:1 complex is isolable [6]. Its structure is unknown, but both molecular [6] and ionic [7] formulations have been suggested.

Weaker Lewis acids such as BF_3 and PF_5 are likely to exist in MeCN in equilibrium with their 1:1 adducts. The n.m.r. spectra of PF_5 in MeCN are consistent with this view [5,8], and although BF_3.NCMe is isolable at low temperature [9], it is highly dissociated in the gas phase [10]. Raman spectra of IF_5, MeCN and WF_6.MeCN solutions indicate that the fluorides have C_{4v} and O_h symmetry respectively. Variations in the IF_5 Raman spectrum with dilution have been interpreted in terms of the progressive replacement of weak $I-F_{eq}$ --- I, intermolecular contacts by MeCN --- I contacts [11]. The behaviour of WF_6 in MeCN is similar to that in the ¶-donor solvent benzene where contact charge transfer has been suggested [12]. Similar considerations apply to MoF_6.

Due to the existence of MeCN --- fluoride interactions MeCN is a good solvent for studying the replacement of fluoro-ligands. For example U^V chloride fluoride mixtures, $UF_{5-n}Cl_n$.xNCMe, are obtained from reactions between UF_5 and Me_3SiCl or UCl_5 [13], and WF_4X.NCMe, X = NMe, O, are obtained from WF_6 and $(Me_3Si)_2X$ [14]. The reactions either do not occur, or are very slow, in the absence of the donor solvent. The ability of MeCN to solvate the products as well as the reactant fluorides is therefore crucial. Solvation of polymeric WF_4S by MeCN has also been demonstrated, the isolated product being monomeric WF_4S.NCMe [15].

FLUORIDE ION TRANSFER REACTIONS

Although the solubilities of ionic, metal fluorides in MeCN are very small, reactions with fluoride ion acceptors do occur in the presence of MeCN. An early example of this type of reaction is the formation of trifluoromethoxide salts from reactions of CsF, RbF, or KF with F_2CO [16]. Similar behaviour is observed between $R_FC(O)F$, $R_F = CF_3$, C_2F_5, C_3F_7, or $(CF_3)_2CO$ and CsF, RbF, or, in some cases, KF [17, 18].

[19]F n.m.r. measurements are consistent with the occurrence of exchange in solution between $R_FC(O)F$ and $R_FCF_2O^-$ [17, 18], and possibly also between $(CF_3)_2CO$ and $(CF_3)_2CFO^-$, although in this case the evidence is less strong [17]. The solubilities of $M^+OCF_3^-$, M = Cs, Rb, K, in MeCN are too small for [19]F n.m.r. observations, however the enhancement of ^{18}F exchange at 25^oC between [18]FFCO and CsF which is observed in the presence of MeCN may be due in part to a solution process [19].

This example highlights a commonly-found ambiguity, the relative importance of homogeneous vs. heterogeneous pathways in the acid-base reaction, and this consideration is particularly important when alkali metal fluorides, normally CsF or KF, are used as bases in organic reactions[20]. One of the methods used to 'activate' CsF is to make, then thermally decompose, $Cs^+OCF(CF_3)_2^-$. The resulting solid has a greatly increased surface area, and is a good heterogeneous catalyst[21].

Extension of acid-base reactions in MeCN to other ionic fluorides, for example CuF_2, FeF_2, and TlF, allows the preparation of a range of hexafluorometallates (V), MF_6^- where M^V = P, As, Ta, or U [5, 22, 23, 24] and two heptafluorotungstates (VI) [25]. In all cases the cations are solvated by MeCN. CuF_2 has been used most often [5, 23-25], complete transfer of F^- ion being observed in all cases except when IF_5 is used as the acceptor. In this case a molecular adduct, trans-$CuF_2(NCMe)_4 \cdot 4IF_5$, rather than an IF_6^- salt, is obtained [11]. Reactions involving CuF_2, and that between FeF_2 and PF_5 [22], are conveniently followed by observing the intensity increase in the appropriate $M(NCMe)_6^{2+}$ d-d band. Interestingly no reaction is observed between pentafluorides and CoF_2 or NiF_2, possibly for kinetic reasons[5].

Since the heavier alkali metal cations are not particularly well solvated by MeCN, the use of this solvent for the preparation of their fluorometallate salts offers no great advantage, although $NaUF_6$ and KUF_6 have been prepared from UF_5 in MeCN [7]. This is not the case for Li^+ salts however, for example $LiPF_6$ is readily prepared from LiF and PF_5 in MeCN, and its solubility is >0.1 mol dm^{-3}. Effective solvation of Cu^+, Ag^+ and Tl^+ by MeCN must also be one of the reasons for the high solubilities observed for their fluorometallates [5].

REDOX REACTIONS

Most attention has been given to the redox properties of MoF_6 and WF_6 in MeCN. Half-wave potentials for the couples MF_6/MF_6^-, M=Mo, W, have been determined by voltammetry. Due to its large, working-potential-range, 5.7V, MeCN is an ideal solvent for electrochemistry, and these measurements were made as part of an extensive programme in which the couples $MF_6^{z/z-1}$, Z = 0, -1, -2; M = Ta, W, Re, Os, Nb, Mo, and Ru, have been determined. Linear progressions in the couples are observed for electronic configurations up to, and including, d^3, and 5d elements are less oxidizing than their 4d counterparts in a given oxidation state by ca. 1V [26]. Synthetic work involving MoF_6 and WF_6 is in harmony with the electrochemical measurements. A number of 3d and post-transition metals are oxidized by the hexafluorides in MeCN to give solvated cation hexafluoro-molybdates(V) or -tungstates(V) [27, 22]. The greater oxidizing ability of MoF_6 is demonstrated by the oxidation of Tl metal to solvated Tl^{3+} or to $Tl^I Tl^{III}$ mixtures [27, 24], and by the oxidation of I^- anion to solvated I^+ [28]. Corresponding reactions of WF_6 yield solvated Tl^+ and I_2 respectively.

In all the reactions studied to date reduction of MoF_6 and WF_6 does not proceed beyond the +5 oxidation state, although the electrochemical work indicates that MoF_6^{2-} should be accessible[26]. Redox reactions involving WF_6 are complicated by the ability of WF_6^- to transfer a F^- ion to WF_6 giving WF_7^- as one product [25, 27, 22]. Similar behaviour appears to be possible for UF_6^- [29].

Synthetic work and cyclic voltammetry both indicate that WF_6 and solvated Cu^{2+} have similar oxidizing abilities in MeCN, and that both are inferior to the solvated NO^+ cation which in turn is inferior to MoF_6 [24]. Thus, solvated cations which are accessible by oxidation of the metal with WF_6 are equally so using NO^+ [30, 22]. The latter route can be advantageous if a kinetically inert counter anion such as PF_6^- is required.

Voltammetric measurements suggest that the oxidizing ability of UF_6 in MeCN should be significantly greater than that of MoF_6 [24], and unlike MoF_6, UF_6 undergoes a slow reduction in MeCN to give $UF_5 \cdot NCMe$ [6]. However in the redox reactions with metals so far studied [31, 24], its behaviour is identical to that of MoF_6.

Other useful oxidizing agents that can be handled at room temperature in MeCN include xenon difluoride and Rb^+ and Cs^+ fluoroxysulphates. XeF_2, 0.5 mol dm^{-3} in MeCN, decomposes slowly in daylight at room temperature [32], but is sufficiently stable kinetically for it to be used to perform oxidative fluorinations on inorganic [33] and organic compounds [34]. The solubilities of $RbSO_4F$ and $CsSO_4F$ in MeCN are 0.12 and ca.0.07 mol dm^{-3} respectively. The solutions are stable over the course of a day, and can be used to fluorinate aromatic compounds [35]. In an alternative procedure a suspension of $CsSO_4F$ in MeCN and BF_3 as a catalyst are used [36].

ACKNOWLEDGEMENT

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