Journal of Fluorine Chemistry, 23 (1983) 403–404

Received: July 25, 1983; accepted: August 11, 1983

PRELIMINARY NOTE

The Redox Reaction between Molybdenum Hexafluoride and Iodine in Acetonitrile. Isolation of Bis(acetonitrile) iodine(I) Hexafluoromolybdate(V)

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SUMMARY

Iodine is oxidized by molybdenum hexafluoride in acetonitrile at ambient temperature, the product being bis(acetonitrile)iodine(I) hexafluoromolybdate(V).

Oxidation of iodide anion to iodine by excess molybdenum or tungsten hexafluoride in liquid sulphur dioxide is the standard route to hexafluorometallates(V) of these elements [1], and if excess I^- anion is used, hexafluoromolybdates(IV) can be isolated [2]. However in acetonitrile solution the oxidizing abilities of MoF_6 and WF_6 towards I^- can be differentiated. With MoF_6 further oxidation of I_2 occurs to give bis(acetonitrile) iodine(I) hexafluoromolybdate(V). Although the feasibility of I_2 oxidation in MeCN has been demonstrated previously by voltammetry, $E_{\frac{1}{2}}$ = ca. 1.1 V vs. Ag^+/Ag^0 [3], the formation of I^+, solvated by MeCN, via a chemical route has apparently not been reported.

Addition of MoF_6 to a frozen solution of I_2 in MeCN (MoF_6:I_2 mole ratio >>1:1) results in a rapid colour change, red → yellow-green, as the mixture is allowed to warm to ambient temperature. A white, moisture-sensitive solid is isolated by removal of volatile material. The solid reacts with aqueous I^- anion to give I_2 and is identified as $[I(NCMe)_2][MoF_6]$ on the basis of its analysis (Found: C, 11.35; H, 1.5; F, 27.4; I, 30.5; N, 6.6; Mo, 22.75. $C_4H_6F_6IN_2Mo$ requires C, 11.5; H, 1.45; F, 27.2; I, 30.3; N, 6.7; Mo, 22.9%) and physical properties.

0022-1139/83/$3.00

Its vibrational spectrum shows the presence of coordinated MeCN, ν_{max} : 2312, 2299, 2280 (comb. + ν CN), 949 (ν CC), 383 cm^{-1} (δ CCN), and MoF_6^-, ν_{max} : 675 pol (ν_1), 425 (ν_2), 640 (ν_3), 250 (ν_4), 232 cm^{-1} (ν_5). Cyclic voltammetry of the compound in MeCN shows quasi-reversible waves at $E_{\frac{1}{2}}$ = 1.60 and -0.40 V vs. Ag^+/Ag^o which are characteristic of the redox couples MoF_6/MoF_6^- and MoF_6^-/Mo^{IV} respectively [4]. Two waves identical to those observed for I_2 or I^- in MeCN, and assigned [3] to the couples I_2/I_3^- and I_3^-/I^-, are also observed, however $[I(NCMe)_2][MoF_6]$ in MeCN decomposes on standing to give I_2 as one product.

The $I(NCMe)_2^+$ cation is presumably analogous to the cations IL_2^+, L = pyridine or thiourea, which are prepared by direct reaction between I_2 and L, and which have linear L-I-L skeletons [5]. A strong band at 174 cm^{-1} in the low temperature (< 50K) Raman spectrum of $[I(NCMe)_2][MoF_6]$ is tentatively assigned to ν_s(NIN) and a strong band at 220 cm^{-1} in its i.r. spectrur to ν_a(NIN). Its Raman spectrum at room temperature is dominated by the resonance Raman spectrum of I_2 vapour.

In contrast to the polynuclear iodine cations formed in acidic solvents [6], a Lewis base solvent is required to stabilize I^+. However the oxidizing ability of WF_6 in MeCN, $E_{\frac{1}{2}}$ for WF_6/WF_6^- = 0.70 V vs. Ag^+/Ag^o [4], is insufficient to perform the oxidation.

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