Cluster Formation in the Fast Atom Bombardment (FAB) Mass Spectra of Dioxouranium(VI) Dinitrate and Diacetate

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Fast atom bombardment (FAB) mass spectrometry [1] has been applied widely to gain information concerning relative molecular masses (RMMs) and certain structural information on involatile materials [2], particularly polar organic solids but also, and increasingly, inorganic salts and organometallic compounds of high RMM [3]. The emphasis has therefore been on species such as MH^+ and M^+ (M = parent molecule) and their breakdown products, although a few studies [4, 5] have either noted or been directed towards products of aggregation of mononuclear compounds, while others have dealt with FAB spectra of polynuclear compounds of, for example, platinum metals [6, 7] and polyoxotungstates [8]. The general subject of clusters of main group metals has been reviewed recently [9] and the mass spectrometric detection of all types of clusters has also been summarised [10]. Stimulated by a recent report [11] of metal–oxygen clusters generated by sputtering surfaces of metal oxides and metal foils with 8 keV Xe atoms, followed in the latter case by reaction with O_2, we report series of clusters generated in the FAB of solutions of uranyl nitrate and acetate using a beam of 8 keV argon atoms.

A typical spectrum produced from uranyl nitrate in sulpholane solution (0.1 mol dm^{-3}) is shown in Fig. 1 and assignments of the major ions are given in Table 1. Both in this series and in that found for uranyl acetate (Table 2), the strongest peaks are due to the simple oligomers $(UO_2)_n^+$ (n = 1–5), although the clusters based on O atom adducts to $(UO_2)_n^+$ are significant for both uranyl nitrate and acetate, especially for $n = 1$ when m in $(UO_2)_nO_m^+$ reaches 5 for both salts. The oxygen-loss species $(UO_2)_n(UO)^+$ (n = 0, 1, 2, 4) are also prominent, and mirror the major product $[TiO(TiO_2)_{x-1}]^+$ in the metal foil sputtering experiments at higher oxygen pressures [11] and in analogous experiments with vanadium. Reaction of Fe clusters with O_2 yields product ions $[Fe_nO_n]^+$ and $[Fe_nO_{n+1}]^+$ when $3 \leqslant n \leqslant 9$; $[Fe_nO_{n+1}]^+$ when $10 \leqslant n \leqslant 13$; $[Fe_nO_{n+2}]^+$ when $14 \leqslant n \leqslant 22$; and $[Fe_nO_{n+3}]^+$ when $23 \leqslant n \leqslant 31$ [12]; the 'iron deficiency' reaches 6 in $[Fe_{59}O_{65}]^+$. (Another study [13] reports $[Fe_nO_2]^+$ ($2 < n < 18$) and $[Fe_nS]^+$ in reactions of Fe_n^+ with O_2 and H_2S respectively [13].) More complex spectra were exhibited by aqueous uranyl acetate (0.1 mol dm^{-3}) due to complexation by the organic ligand or its components of the cluster (Fig. 2). Assignments of the more important ions are summarised in Table 2. However, the simple cationic metal–oxygen clusters are strongly featured as for uranyl nitrate.

What seems to be unique in the FAB experiments with uranyl salts is the appearance of the species $[(UO_2)_nO_m]^+$ (m = 0–5), which poses interesting structural problems. We are currently examining analogous oxo–cation salts of V, Nb and Eu, and preliminary results in the latter case indicate long

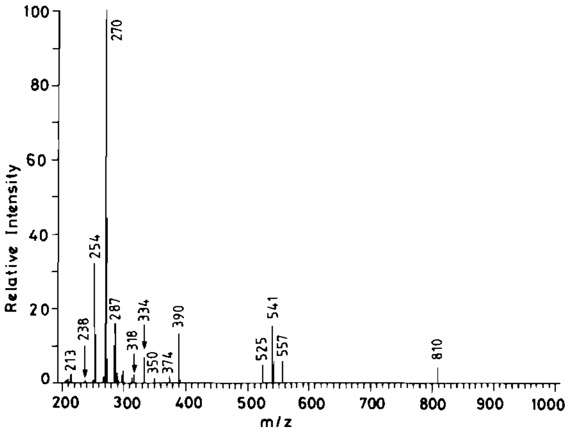

Fig. 1. Cluster pattern in the positive ion FAB spectrum of uranyl nitrate (0.1 mol dm^{-3}) in sulpholane solution.

TABLE 1. Cluster Peaks Obtained in the Positive Ion FAB Spectrum of Uranyl Nitrate (0.1 mol dm^{-3}) in Sulpholane Solution

m/z (% internal reference)	Molecular formula and RMM of species	Designation of structure
810(2.3)	$U_3O_6^+$(810)	$(UO_2)_3^+$
557(4.8)	$U_2O_5^+$(556)	$(UO_2)_2^+$
541(15.1)	$U_2O_4^+$(540)	$(UO_2)_2^+$
525(32)	$U_2O_3^+$(524)	$(UO_2)(UO)^+$
390(14.8)	UO_2M^+(390)[a]	$(UO_2)(M)^+$
374(1.1)	UOM^+(374)	$(UO)(M)^+$
349(1.1)	UO_7^+(350)	$(UO_2)O_5^+$
334(6.9)	UO_6^+(334)	$(UO_2)O_4^+$
318(1.9)	UO_5^+(318)	$(UO_2)O_3^+$
287(15.7)	UO_3^+(286)	$(UO_2)O^+$
270(100)	UO_2^+(270)	$(UO_2)^+$
254(31.0)	UO^+(254)	$(UO)^+$
238(0.8)	U^+(238)	U^+

[a] M = sulpholane (RMM = 120).

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TABLE 2. Cluster Peaks Obtained in the Positive Ion FAB Spectrum of Aqueous Uranyl Acetate (0.1 mol dm^{-3})

m/z (% internal reference)	Molecular formula and RMM of species	Designated molecular formula
1415(6.8)	$U_5O_{14}^+$(1414)	$(UO_2)_5O_4^+$
1409(8.4)	$U_5O_{12}C_2H_3^+$(1409)	$(UO_2)_5(CH_3COO)^+$
1398(6.8)	$U_5O_{13}^+$(1398)	$(UO_2)_5O_3^+$
1394(10.6)	$U_5O_{12}C^+$(1394)	$(UO_2)_5(CO_2)^+$
1393(10.3)	$U_5O_{11}C_2H_3^+$(1393)	$(UO_2)_5(CH_3CO)^+$
1383(14.6)	$U_5O_{12}^+$(1382)	$(UO_2)_5O_2^+$
1367(28.8)	$U_5O_{11}^+$(1366)	$(UO_2)_5O^+$
1351(39.9)	$U_5O_{10}^+$(1350)	$(UO_2)_5^+$
1333(3.0)	$U_5O_9^+$(1334)	$(UO_2)_4(UO)^+$
1230(5.3)	$U_4O_{14}C_4H_6^+$(1230)	$(UO_2)_4(CH_3COO)_2O_2^+$
1198(5.5)	$U_4O_{12}C_4H_6^+$(1198)	$(UO_2)_4(CH_3COO)_2^+$
1182(4.1)	$U_4O_{11}C_4H_6^+$(1182)	$(UO_2)_4(CH_3CO)_2O^+$
1167(14.7)	$U_4O_{11}C_3H_3^+$(1167)	$(UO_2)_4(CH_3COO)(CO)^+$
1166(7.6)	$U_4O_{10}C_4H_6^+$(1166)	$(UO_2)_4(CH_3CO)_2^+$
1159(5.6)	$U_4O_{13}^+$(1160)	$(UO_2)_4O_5^+$
1151(5.7)	$U_4O_{10}C_3H_3^+$(1151)	$(UO_2)_4(CH_3CO)(CO)^+$
1139(11.9)	$U_4O_{10}C_2H_3^+$(1139)	$(UO_2)_4(CH_3COO)^+$
1123(13.1)	$U_4O_9C_2H_3^+$(1123)	$(UO_2)_4(CH_3CO)^+$
1112(12.6)	$U_4O_{10}^+$(1112)	$(UO_2)_4O_2^+$
1107(4.9)	$U_4O_9C^+$(1108)	$(UO_2)_4(CO)^+$
1096(48.2)	$U_4O_9^+$(1096)	$(UO_2)_4O^+$
1080(36.6)	$U_4O_8^+$(1080)	$(UO_2)_4^+$
1064(7.4)	$U_4O_7^+$(1064)	$(UO_2)_3(UO)^+$
911(4.0)	$U_3O_9C_4H_6^+$(912)	$(UO_2)_3(CH_3CO)_2O^+$
897(5.4)	$U_3O_9C_3H_3^+$(897)	$(UO_2)_3(CH_3COO)(CO)^+$
896(6.7)	$U_3O_8C_4H_6^+$(896)	$(UO_2)_3(CH_3CO)_2^+$
880(17.4)	$U_3O_8C_3H_3$(881)	$(UO_2)_3(CH_3CO)(CO)^+$
873(3.8)	$U_3O_{10}^+$(874)	$(UO_2)_3O_4^+$
869(8.6)	$U_3O_8C_2H_3^+$(869)	$(UO_2)_3(CH_3COO)^+$
855(12.7)	$U_3O_8C^+$(854)	$(UO_2)_3(CO_2)^+$
852(31.3)	$U_3O_7C_2H_3^+$(853)	$(UO_2)_3(CH_3CO)^+$
842(7.0)	$U_3O_8^+$(842)	$(UO_2)_3O_2^+$
826(52.2)	$U_3O_7^+$(826)	$(UO_2)_3O^+$
810(55.0)	$U_3O_6^+$(810)	$(UO_2)_3^+$
794(7.4)	$U_3O_5^+$(794)	$(UO_2)_2(UO)^+$
642(7.0)	$U_2O_7C_4H_6^+$(642)	$(UO_2)_2(CH_3CO)_2O^+$
637(6.8)	$U_2O_{10}^+$(636)	$(UO_2)_2O_6^+$
626(5.8)	$U_2O_7C_3H_3^+$(627)	$(UO_2)_2(CH_3COO)(CO)^+$
625(5.2)	$U_2O_6C_4H_6^+$(626)	$(UO_2)_2(CH_3CO)_2^+$
611(12.5)	$U_2O_6C_3H_3^+$(611)	$(UO_2)_2(CH_3CO)(CO)^+$
598(20.0)	$U_2O_6C_2H_3^+$(599)	$(UO_2)_2(CH_3COO)^+$
584(14.6)	$U_2O_6C^+$(584)	$(UO_2)_2(CO_2)^+$
583(9.5)	$U_2O_5C_2H_3^+$(583)	$(UO_2)_2(CH_3CO)^+$
555(79.0)	$U_2O_5^+$(556)	$(UO_2)_2O^+$
539(100.0)	$U_2O_4^+$(540)	$(UO_2)_2^+$
523(10.1)	$U_2O_3^+$(524)	$(UO_2)(UO)^+$

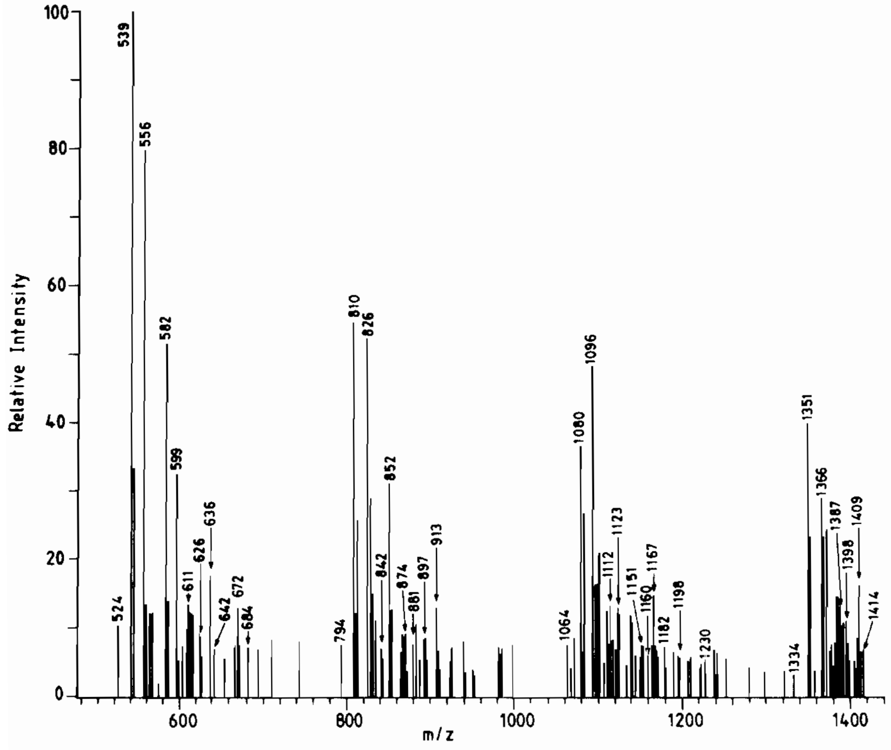

Fig. 2. Cluster pattern in the positive ion FAB spectrum of aqueous uranyl acetate (0.1 mol dm^{-3}); average of five scans.

sequences of analogous clusters reaching nine Eu atoms, *i.e.* the limit of our current detection instrumentation, a Kratos Model MS 50 mass spectrometer equipped with a DS-55 data station.

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