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The Direct Electrochemical Synthesis of Neutral and Anionic Halogeno Complexes of Uranium(IV) and Uranium(VI)

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The electrochemical oxidation of anodic uranium into acetonitrile solutions of X_2 ($X = Cl, Br$) under nitrogen gives rise to $UCl_4 \cdot 4CH_3CN$ or $UBr_4 \cdot 2CH_3CN$ in good yield. These compounds are easily converted to other UX_4 adducts. In the presence of oxygen, solutions of UO_2X_2 are produced by the electrolysis, and the parent halide, or neutral addition compounds, are readily obtained from these. Addition of R_4NX to the cell results in the direct synthesis of $(R_4N)_2UX_6$ under nitrogen, or $(R_4N)_2UO_2X_4$ under oxygen. The only iodo compound which could be formed by electrolysis into N,N-dimethylformamide (=dmf) was $UI_4 \cdot 4dmf$.

Introduction

The electrochemical oxidation of a metal into a non-aqueous solution phase containing elemental halogen (Cl_2, Br_2, I_2) has been shown to be a simple and direct route to the neutral and anionic halogeno complexes of a number of metals [1–12]. One interesting feature of the method is that the complexes produced under these oxidising conditions are frequently those in which the metal is in a low oxidation state (*e.g.*, indium(I) [1], vanadium(II) [3], chromium(III) [6], copper(I) [9], gallium(II) [11] and thorium(II) [12], and possible reasons for this have been discussed in terms of the mechanism of the anode reactions [13].

Following recent studies of the oxidation of thorium metal to ThX_4, ThX_6^{2-} (X = Cl, Br) [10] or ThI_2 [12] derivatives, we have now extended the investigations to uranium. In a nitrogen atmosphere, products based on UX_4 (X = Cl, Br) or UX_6^{2-} were obtained, while in the presence of oxygen UO_2X_2 and $UO_2X_4^{2-}$ derivatives were formed. Results with iodine systems were not very encouraging. The influence of oxygen is closely parallel to that observed in syntheses of uranium chelate complexes [14].

Experimental

General

Uranium was in the form of discs, approximately 1 cm diameter and 1 mm thickness (Atomic Energy of Canada Ltd.). Acetonitrile was dried over phosphorus pentoxide and distilled under nitrogen before use. Diethyl ether was dried over sodium, and acetone over anhydrous magnesium sulphate. Neutral ligands, and tetraalkylammonium halides, were dried at 105 °C for 3–4 h. All other materials were used as supplied.

Uranium was determined gravimetrically as U_3O_8, and halogen by the Volhard method.

Infrared spectra were recorded on a Perkin-Elmer instrument over the range 3000–100 cm^{-1}.

Electrochemical

The electrochemical methods were essentially those used in previous work [8]. Uranium formed the anode of a cell whose liquid phase consisted of acetonitrile solutions of either X_2 (X = Cl, Br, I), or $X_2 + R_4NX$. In the case of X = Cl, chlorine gas diluted with dry nitrogen was bubbled through the solution during electrolysis [6]. Reaction took place either under nitrogen, or with a stream of dry oxygen bubbling through the solution. Experimental conditions are summarised in Table I.

Preparation of Adducts of UX_4 ($X = Cl, Br$)

The electrochemical oxidation of uranium into CH_3CN/X_2 solution under nitrogen results in the precipitation of green UX_4 compounds, which were recrystallised from hot acetonitrile to yield $UCl_4 \cdot 4CH_3CN$ or $UBr_4 \cdot 2CH_3CN$. These compounds are readily soluble in acetone, and the addition of a twofold excess of suitable neutral ligands (dmso, Ph_3PO, 2,2′-bipyridine, 1,10-phenanthroline) precipitated the appropriate UX_4 adducts, which were washed and recrystallised from hot acetonitrile.

Preparation of Adducts of UO_2X_2 ($X = Cl, Br$)

When uranium was oxidised anodically into CH_3CN/X_2 in thes presence of dry oxygen, a yellow (X =

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TABLE I. Experimental Conditions for the Electrochemical Preparation of Neutral and Anionic Uranium Complexes.

Product	CH_3CN vol (mL)	Mass of halogen (g)	Mass of R_4NX (g)	Initial		Time of electrolysis (h)	Mass of metal dissolved (g)	Electrochemical efficiency (mol F^{-1})
				Voltage (v)	Current (mA)			
$UCl_4 \cdot 4CH_3CN$	50	–	–[a]	12	30	4	1.1	1.0
$UBr_4 \cdot 2CH_3CN$	50	2	–[a]	4	10	12	1.3	1.2
$UI_4 \cdot 4dmf$	50(b)	0.6	–[a]	40	30	2	0.26	0.43
UO_2Cl_2	50	–	–[a]	16	30	3.7	0.48	0.5
UO_2Br_2	50	2	–[a]	10	30	4	0.56	0.5
$(Et_4N)_2UCl_6$	50	–	1.8	4	30	3	0.9	1.1
$(Et_4N)_2UBr_6$	50	2	1.9	2	30	3	0.85	1.0
$(Et_4N)_2UO_2Cl_4$	60	–	1.2	2	30	2.5	0.62	0.9
$(Et_4N)_2UO_2Br_4$	50	2	1.0	2	30	1.5	0.50	1.2

[a] 30 mg of Et_4NClO_4 added in these experiments. [b] N,N-dimethylformamide (=dmf).

HCl) or red (X = Br) solution was obtained. Removal of solvent *in vacuo*, followed by recrystallisation from 60/40 (v/v) petroleum ether/diethyl ether mixtures, gave solid UO_2X_2. Adducts were prepared by adding a twofold excess of the appropriate ligand in solution to an electrochemically prepared solution of UO_2X_2. Precipitation occurred immediately with Ph_3PO and 1,10-phenanthroline for both UO_2Cl_2 and UO_2Br_2, and with 2,2′-bipyridine and UO_2Cl_2. Mixing solutions of 2,2′-bipyridine and UO_2Br_2 produced an initial deposit of bright golden crystals subsequently shown to be $(bpyH_2)UO_2Br_4$ (see below). After removal of this material, the solution was reduced in volume by about 50%, when a powder of $(bpyH)_2UO_2Br_4$ precipitated.

Addition of dimethylsulphoxide to solutions of UO_2Cl_2 or UO_2Br_2 produced a clear solution, but evaporation of solvent gave oils which solidified on trituration with acetone.

Preparation of Salts of UX_6^{2-} and $UO_2X_4^{2-}$ (X = Cl, Br)

The oxidation of uranium anodes into acetonitrile solutions of $Et_4NX + X_2$ gave solutions containing UX_6^{2-} anions in a nitrogen atmosphere, and $UO_2X_4^{2-}$ anions in the presence of oxygen. In each case, nitrogen was subsequently bubbled through the solution to remove excess halogen, and the volume then reduced by about 40%, at which point crystals deposited. The solid products were washed with diethyl ether and recrystallised from hot acetonitrile.

Electrolysis in the Presence of I_2

The electrochemical oxidation of uranium with acetonitrile solutions of iodine (~1 g) gave a black suspension. Attempts to purify this resulted in a black oil, and this work was not pursued further. Electrolysis in N,N-dimethylformamide (dmf) gave a dark red solution, which was filtered to remove impurities and then treated with excess (200 mL) diethyl ether. The dark red oil which came down solidified on standing overnight; analysis (Table II) gave values close to those for $UI_4 \cdot 4dmf$. Treatment of acetone solutions of this compound with either 2,2′-bipyridine or 1,10-phenanthroline did not yield adducts of these ligands and $UI_4 \cdot 4dmf$ was subsequently recovered. The addition of an eightfold excess of triphenylphosphine oxide produced orange crystals of $UO_2I_2 \cdot 2Ph_3PO$ in 40% yield (Found U = 22.4, I = 22.8%; calcd. U 22.0, I 23.5%; the infrared spectrum confirmed the presence of Ph_3PO, $\nu(P{=}O)$ 1055 cm^{-1}, $\nu(U{=}O_2)$ 930 cm^{-1}). It appears that Ph_3PO oxidises UI_4 to UO_2I_2, which then complexes with excess Ph_3PO. The presence of Ph_3P in the reaction mixture was confirmed by t.l.c.

The oxidation of uranium in the presence of I_2 in dmf under oxygen gave a black solid, analysing as U 53% I 12%. No further work was done on this system.

Results and Discussion

General

As in previous studies of this type, the electrochemical oxidation of uranium provides a convenient, one-step room temperature synthesis of uranium(IV) and (VI) halide species. The avoidance of high temperatures is certainly a striking advantage over the methods in the literature [15], many of which involve high temperature (>400 °C) halogenation of uranium oxides to obtain uranium(IV) halides, which are themselves the source of uranium(VI) oxyhalides by reaction with UO_2 at temperatures of 475 °C or above. A widely used route to UCl_4 involves the treatment (6 h, 160 °C) of $UO_3 \cdot 2H_2O$ with hexachloropropene.

The present method yields acetonitrile adducts of UX_4 (X = Cl, Br) which easily lose acetonitrile on heating [17]. Even without such treatment,

TABLE II. Analytical and Related Results for Uranium Complexes.

Product[a]	Yield[b] (%)	Colour	M.Pt. (°C)[c]	Uranium %		Halogen %	
				Found	Calcd	Found	Calcd
$UCl_4 \cdot 4CH_3CN$	72	Bluish green	–	43.2	43.8	25.8	26.1
$UBr_4 \cdot 2CH_3CN$	50	Deep green	–	37.5	37.2	50.6	50.0
$UI_4 \cdot 4dmf$	60	Deep red	–	23.2	22.5	47.0	48.0
UO_2Cl_2	61	Yellow	–	68.9	69.8	20.6	20.8
UO_2Br_2	70	Red	–	55.0	55.3	41.2	41.8
$UCl_4 \cdot 2Ph_3PO$	86	Bluish green	>300 (318)	24.6	25.4	d	–
$UBr_4 \cdot 2Ph_3PO$	78	Green	212 (210)	21.1	21.4	–	–
$UO_2Cl_2 \cdot 2Ph_3PO$	74	Yellow	298 (297)	25.9	26.5	–	–
$UO_2Br_2 \cdot 2Ph_3PO$	61	Yellow	>300 (307)	24.3	24.1	–	–
$UCl_4 \cdot 3dmso$	86	Green	180–82	38.3	38.7	22.6	23.0
$UBr_4 \cdot 6dmso$	80	Green	152–54	22.2	23.2	31.0	31.1
$UO_2Cl_2 \cdot 3dmso$	60	Yellow	124	41.6	41.4	12.4	12.3
$UO_2Br_2 \cdot 4dmso$	58	Yellow	90–92	31.8	32.1	22.0	21.5
$UCl_4 \cdot 2bpy$	75	Green	224	33.6	34.4	21.0	21.5
$UCl_4 \cdot 2phen$	68	Green	295	31.1	32.2	18.3	19.2
$UO_2Cl_2 \cdot 2bpy$	50	Yellow	>300 (dec)	35.6	36.4	10.3	10.8
$UO_2Cl_2 \cdot 2phen$	59	Yellow	>300 (dec)	33.0	33.9	10.5	10.1
$(bpyH)_2UO_2Br_4$	45	Gold	235	25.8	26.4	36.0	35.4
$(phenH)_2UO_2Br_4$	52	Yellow	300	25.4	25.0	33.8	33.6
$(Et_4N)_2UCl_6$	50	Green	–	33.7	33.5	29.6	29.9
$(Et_4N)_2UBr_6$	61	Green	–	25.1	24.6	48.8	49.0
$(Et_4N)_2UO_2Cl_4$	82	Yellow	–	35.6	35.4	21.6	21.1
$(Et_4N)_2UO_2Br_4$	56	Yellow	–	27.6	28.0	37.8	37.6

[a] dmso = dimethylsuphoxide; bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline. [b] Based on quantity of metal dissolved electrochemically. [c] Literature values in parentheses. [d] Found C 46.3, H 3.01%; calcd C 46.2, H 3.20%.

the primary products are easily converted to other adducts. Similarly, the anionic $UX_6{}^{2-}$ and $UO_2X_4{}^{2-}$ complexes are directly obtained from the electrochemical oxidation, as opposed to conventional methods which involve the prior preparation of the corresponding neutral halides [18, 19]. The yields of the electrochemical procedures are as good as, or better than, those quoted in the literature. One further advantage of the method is that either uranium(IV) or uranium(VI) species can be generated simply by excluding or adding oxygen to the cell.

Neutral and Anionic Chloro- and Bromo-Complexes

The products obtained (Table II) are in general those described by previous workers. With acetonitrile, $UX_4 \cdot 4CH_3CN$ (X = Cl, Br) have been described by Bagnall, Brown and Jones [17]; the compound $UBr_4 \cdot 2CH_3CN$ has not apparently been reported previously. The triphenylphosphine oxide adducts of UCl_4, UO_2Cl_2 and UO_2Br_2 have been prepared by Gans and Smith [20] and Day and Venanzi [19], and the UBr_4 compound can now be added to this group. Dimethylsulphoxide complexes with UCl_4 (3dmso [21]) and UBr_4 (6dmso [22]) are known, but the corresponding UO_2Cl_2 and UO_2Br_2 compounds do not appear to have been prepared previously. Adducts of the bidentate donors 2,2'-bipyrdine and 1,10-phenanthroline with UCl_4 have been reported by Gans and Smith [22] and the analogous bromo-complexes are reported here for the first time.

The compounds formed by UO_2X_2 (X = Cl, Br) and these bidentate donors present a different problem. The 1:1 complexes $UO_2Cl_2 \cdot phen$ and $UO_2Cl_2 \cdot bpy \cdot 2H_2O$ were prepared by Markov and Tsapkin [23] via non-aqueous solution, but reaction in aqueous acidic media gave the salts $(bpyH)_2UO_2Cl_4$, $(phenH)_2UO_2Cl_4$ or $bpyH_2 \cdot UO_2Cl_4 \cdot 3H_2O$, depending on the conditions [23, 24]. The $(bpyH)^+$ and $(phenH)^+$ salts were later obtained by the oxidation of $UCl_4 \cdot L_2$ (L = bpy, phen) [20], and other salts of $UO_2Cl_4{}^{2-}$ and $UO_2Br_4{}^{2-}$ are now known [19, 20]. The neutral 1:2 compounds reported here (Table II) are apparently different from those described earlier [23]. We also note that the first material which appeared in the 2,2'-bipyridine/UO_2Br_2 reaction was highly crystalline, in contrast to the powdery nature of the bulk product. An X-ray crystallographic investigation of these crystals [25] showed them to be $(bpyH_2)[UO_2Br_4]$, in which the structure of the anion is essentially identical to that recently reported [26]. The bulk product analysed as $(bpyH)_2UO_2Br_4$, and the 1,10-phenanthroline system yielded the analogous $(phenH)_2UO_2Br_4$. No neutral adducts of these ligands and UO_2Br_2 were obtained. The source of the protons which form the $bpyH^+$ *etc.* cations is not immediately obvious.

The salts of UX_6^{2-} and $(UO_2X_4)^{2-}$ (X = Cl, Br) with the tetraethylammonium cation are clearly analogous to the compounds prepared by Day and Venanzi [18, 19], and Gans and Smith [20].

The Uranium/Iodine System

Given the paucity of iodine derivatives of the actinide elements, the negative results obtained in the iodine/acetonitrile system are perhaps not surprising. The compound $UI_4 \cdot 4CH_3CN$ has been reported, but such compounds are easily reduced [27], and cathodic reduction may induce decomposition *in situ* of any UI_4 species formed electrochemically. With N,N-dimethylformamide as solvent, $UI_4 \cdot 4dmf$ is obtained, but other adducts of UI_4 could not be prepared; with excess triphenylphosphine oxide, oxidation of UI_4 to UO_2I_2 occurs, yielding the known compound $UO_2I_2 \cdot 2Ph_3PO$ [19]. No anionic iodo complexes were obtained.

Infrared Spectroscopy

The infrared spectra of the compounds served in part to confirm their identity. For the acetonitrile adducts of UCl_4 and UBr_4, $\nu(C{\equiv}N)$ is at 2310 + 2282 cm^{-1}, and 2305 + 2280 cm^{-1} respectively (*cf.* ref. 17). The $\nu(PO)$ mode in the triphenylphosphine oxide compounds is in the region 1060–1065 cm^{-1}, and $\nu(SO)$ in the dimethylsulphoxide adducts is at 990–995 cm^{-1}. The other vibrations of these ligands, and of the ligands 2,2′-bipyridine and 1,10-phenanthroline, are as described in the literature.

The frequencies of the $\nu(U{-}X)$ modes, and of $\nu(UO_2)$, are given in Table III. Where comparisons are possible, we find values in agreement with those of previous workers.

Electrochemical Efficiency

The electrochemical efficiency (E_F) of the cell is given by moles of uranium dissolved per Faraday of electricity, and has been determined in non-preparative experiments for the various systems used by us (Table I). For those systems which yield neutral uranium(VI) chloride or bromide, anionic uranium(IV), and anionic uranium(VI) species, the E_F values are 1.0 ± 0.2 mol F^{-1}. Following previous arguments, in which the current carrier is identified as X^- in the $X_2 + X^-$ systems, and (tentatively) X_2^- otherwise, we suggest that the anode reactions are

TABLE III. Far Infrared Absorptions for Uranium Halide Complexes (cm^{-1}).

Compound	$\nu(M{-}X)$	$\nu(M{-}O)$
$UCl_4 \cdot 4CH_3CN$	254	–
$UBr_4 \cdot 2CH_3CN$	184	–
UO_2Cl_2	245–265 br	960
$UCl_4 \cdot 2Ph_3PO$	250–256 br	–
$UBr_4 \cdot 2Ph_3PO$	170–190 br	–
$UO_2Cl_2 \cdot 2Ph_3PO$	259	918
$UO_2Br \cdot 2Ph_3PO$	169	930
$UCl_4 \cdot 3dmso$	250	–
$UBr_4 \cdot 6dmso$	–	–
$UO_2Cl_2 \cdot 3dmso$	–	915
$UO_2Br \cdot 4dmso$	184	900 sh
$UCl_4 \cdot 2bpy$	242	–
$UCl_4 \cdot 2phen$	244	–
$UO_2Cl_2 \cdot 2bpy$	232	925
$UO_2Cl_2 \cdot 2phen$	226	910
$(bpyH)_2UO_2Br_4$	173 br	930
$(phenH)_2UO_2Br_4$	178, 167, 156	915
$(Et_4N)_2UCl_6$	254	–
$(Et_4N)_2UBr_6$	186	–
$(Et_4N)_2UO_2Cl_4$	255 br	918
$(Et_4N)_2UO_2Br_4$	174	930

$$M + X^- \longrightarrow MX + e \qquad (1)$$

$$MX + {}^3/_2 X_2 \longrightarrow MX_4 \qquad (2)$$

$$MX + {}^1/_2 X_2 + {}^1/_2 O_2 \longrightarrow MO_2X_2 \qquad (3)$$

or

$$M + X_2^- \longrightarrow MX_2 + e \qquad (4)$$

$$MX_2 + X_2 \longrightarrow MX_4 \qquad (5)$$

The fate of the species formed in eqns. (2), (3) or (5) then depends on the nature of the complexing species in solution (CH_3CN, X^-). No explanation is forthcoming for the E_F value of 0.5 mol F^{-1} in those experiments which yield UO_2Cl_2 or UO_2Br_2, but it is noteworthy that identical values were found in studies of both uranium(IV) and (VI) chelate complexes [14]. Further work on these systems is planned.

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References

1 J. J. Habeeb and D. G. Tuck, *Chem. Commun.*, 808 (1975).
2 J. J. Habeeb, L. Neilson and D. G. Tuck, *Synth. React. Inorg. Metal-org. Chem.*, *6*, 105 (1976).
3 J. J. Habeeb, L. Neilson and D. G. Tuck, *Can. J. Chem.*, *55*, 2631 (1977).
4 J. J. Habeeb, F. F. Said and D. G. Tuck, *Can. J. Chem.*, *55*, 3882 (1977).
5 J. J. Habeeb, L. Neilson and D. G. Tuck, *Inorg. Chem.*, *17*, 306 (1978).
6 J. J. Habeeb and D. G. Tuck, *Inorg. Synth.*, *19*, 123, 257 (1979).
7 J. J. Habeeb, F. F. Said and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1161 (1980).
8 C. Oldham and D. G. Tuck, *J. Chem. Ed.*, *59*, 420 (1982).
9 M. Khan, C. Oldham and D. G. Tuck, *Can. J. Chem.*, *59*, 2714 (1981).
10 N. Kumar and D. G. Tuck, *Can. J. Chem.*, *60*, 2579 (1982).
11 M. J. Taylor and D. G. Tuck, *Inorg. Synth.*, *22*, 135 (1983).
12 N. Kumar and D. G. Tuck, *Inorg. Chem.*, *22*, 1951 (1983).
13 D. G. Tuck, *Pure Applied Chem.*, *51*, 2005 (1979).
14 N. Kumar, L. Matassa and D. G. Tuck, unpublished results.
15 K. W. Bagnall, 'Halogen Chemistry', V. Gutmann, Academic Press, London, Vol. 3, p. 304, 1972.
16 J. A. Hermann and J. F. Suttle, *Inorg. Synth.*, *5*, 143 (1957).
17 K. W. Bagnall, D. Brown and P. J. Jones, *J. Chem. Soc., (A)*, 1762 (1966).
18 J. P. Day and L. Venanzi, *J. Chem. Soc., (A)*, 197 (1966).
19 J. P. Day and L. Venanzi, *J. Chem. Soc., (A)*, 1363 (1966).
20 P. Gans and B. C. Smith, *J. Chem. Soc., (A)*, 4172 (1964).
21 G. Bombieri and K. W. Bagnall, *J. Chem. Soc., Chem. Comm.*, 188 (1975).
22 P. Gans and B. C. Smith, *J. Chem. Soc., (A)*, 4177 (1964).
23 V. P. Markov and V. V. Tsapkin, *Zh. Neorg. Khim.*, *4*, 2261 (1959).
24 V. P. Markov and V. V. Tsapkin, *Zh. Neorg. Khim.*, *6*, 2059 (1961).
25 M. Khan and D. G. Tuck, unpublished results.
26 Y. N. Mikhailov, G. M. Lobanova, A. S. Kanishcheva, G. T. Boltova, V. V. Tsapkin, A. Y. Nuikin and R. N. Shchelokov, *Zh. Neorg. Khim.*, *28*, 2051 (1983).
27 D. Brown, 'Comprehensive Inorganic Chemistry', A. F. Trotman-Dickenson, Pergamon, Oxford, Vol. V., p. 203, 1973.