

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 ($X = \text{Cl}, \text{Br}$) under nitrogen gives rise to $\text{UCl}_4 \cdot 4\text{CH}_3\text{CN}$ or $\text{UBr}_4 \cdot 2\text{CH}_3\text{CN}$ 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 $(\text{R}_4\text{N})_2\text{UX}_6$ under nitrogen, or $(\text{R}_4\text{N})_2\text{UO}_2\text{X}_4$ under oxygen. The only iodo compound which could be formed by electrolysis into N,N -dimethylformamide (=dmf) was $\text{UI}_4 \cdot 4\text{dmf}$.

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-} ($X = \text{Cl}, \text{Br}$) [10] or ThI_2 [12] derivatives, we have now extended the investigations to uranium. In a nitrogen atmosphere, products based on UX_4 ($X = \text{Cl}, \text{Br}$) or UX_6^{2-} were obtained, while in the presence of oxygen UO_2X_2 and $\text{UO}_2\text{X}_4^{2-}$ 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].

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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 ($X = \text{Cl}, \text{Br}, \text{I}$), or $X_2 + \text{R}_4\text{NX}$. In the case of $X = \text{Cl}$, 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 ($X = \text{Cl}, \text{Br}$)

The electrochemical oxidation of uranium into $\text{CH}_3\text{CN}/X_2$ solution under nitrogen results in the precipitation of green UX_4 compounds, which were recrystallised from hot acetonitrile to yield $\text{UCl}_4 \cdot 4\text{CH}_3\text{CN}$ or $\text{UBr}_4 \cdot 2\text{CH}_3\text{CN}$. 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 ($X = \text{Cl}, \text{Br}$)

When uranium was oxidised anodically into $\text{CH}_3\text{CN}/X_2$ in the presence of dry oxygen, a yellow ($X =$

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

Product	CH ₃ CN vol (mL)	Mass of halogen (g)	Mass of R ₄ NX (g)	Initial		Time of electrolysis (h)	Mass of metal dissolved (g)	Electrochemical efficiency (mol F ⁻¹)
				Voltage (v)	Current (mA)			
UCl ₄ ·4CH ₃ CN	50	—	— ^a	12	30	4	1.1	1.0
UBr ₄ ·2CH ₃ CN	50	2	— ^a	4	10	12	1.3	1.2
UI ₄ ·4dmf	50(b)	0.6	— ^a	40	30	2	0.26	0.43
UO ₂ Cl ₂	50	—	— ^a	16	30	3.7	0.48	0.5
UO ₂ Br ₂	50	2	— ^a	10	30	4	0.56	0.5
(Et ₄ N) ₂ UCl ₆	50	—	1.8	4	30	3	0.9	1.1
(Et ₄ N) ₂ UBr ₆	50	2	1.9	2	30	3	0.85	1.0
(Et ₄ N) ₂ UO ₂ Cl ₄	60	—	1.2	2	30	2.5	0.62	0.9
(Et ₄ N) ₂ UO ₂ Br ₄	50	2	1.0	2	30	1.5	0.50	1.2

^a30 mg of Et₄NClO₄ added in these experiments. ^bN,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 UO₂X₂. Adducts were prepared by adding a twofold excess of the appropriate ligand in solution to an electrochemically prepared solution of UO₂X₂. Precipitation occurred immediately with Ph₃PO and 1,10-phenanthroline for both UO₂Cl₂ and UO₂Br₂, and with 2,2'-bipyridine and UO₂Cl₂. Mixing solutions of 2,2'-bipyridine and UO₂Br₂ produced an initial deposit of bright golden crystals subsequently shown to be (bpyH₂)UO₂Br₄ (see below). After removal of this material, the solution was reduced in volume by about 50%, when a powder of (bpyH)₂-UO₂Br₄ precipitated.

Addition of dimethylsulphoxide to solutions of UO₂Cl₂ or UO₂Br₂ produced a clear solution, but evaporation of solvent gave oils which solidified on trituration with acetone.

Preparation of Salts of UX₆²⁻ and UO₂X₄²⁻ (X = Cl, Br)

The oxidation of uranium anodes into acetonitrile solutions of Et₄NX + X₂ gave solutions containing UX₆²⁻ anions in a nitrogen atmosphere, and UO₂-X₄²⁻ 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 I₂

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 UI₄·4dmf. Treatment of acetone solutions of this compound with either 2,2'-bipyridine or 1,10-phenanthroline did not yield adducts of these ligands and UI₄·4dmf was subsequently recovered. The addition of an eightfold excess of triphenylphosphine oxide produced orange crystals of UO₂I₂·2Ph₃PO in 40% yield (Found U = 22.4, I = 22.8%; calcd. U 22.0, I 23.5%; the infrared spectrum confirmed the presence of Ph₃PO, $\nu(\text{P}=\text{O})$ 1055 cm⁻¹, $\nu(\text{U}=\text{O}_2)$ 930 cm⁻¹). It appears that Ph₃PO oxidises UI₄ to UO₂I₂, which then complexes with excess Ph₃PO. The presence of Ph₃P in the reaction mixture was confirmed by t.l.c.

The oxidation of uranium in the presence of I₂ 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 UO₂ at temperatures of 475 °C or above. A widely used route to UCl₄ involves the treatment (6 h, 160 °C) of UO₃·2H₂O with hexachloropropene.

The present method yields acetonitrile adducts of UX₄ (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 ·4CH ₃ CN	72	Bluish green	—	43.2	43.8	25.8	26.1
UBr ₄ ·2CH ₃ CN	50	Deep green	—	37.5	37.2	50.6	50.0
UCl ₄ ·4dmf	60	Deep red	—	23.2	22.5	47.0	48.0
UO ₂ Cl ₂	61	Yellow	—	68.9	69.8	20.6	20.8
UO ₂ Br ₂	70	Red	—	55.0	55.3	41.2	41.8
UCl ₄ ·2Ph ₃ PO	86	Bluish green	> 300 (318)	24.6	25.4	d	—
UBr ₄ ·2Ph ₃ PO	78	Green	212 (210)	21.1	21.4	—	—
UO ₂ Cl ₂ ·2Ph ₃ PO	74	Yellow	298 (297)	25.9	26.5	—	—
UO ₂ Br ₂ ·2Ph ₃ PO	61	Yellow	> 300 (307)	24.3	24.1	—	—
UCl ₄ ·3dmso	86	Green	180–82	38.3	38.7	22.6	23.0
UBr ₄ ·6dmso	80	Green	152–54	22.2	23.2	31.0	31.1
UO ₂ Cl ₂ ·3dmso	60	Yellow	124	41.6	41.4	12.4	12.3
UO ₂ Br ₂ ·4dmso	58	Yellow	90–92	31.8	32.1	22.0	21.5
UCl ₄ ·2bpy	75	Green	224	33.6	34.4	21.0	21.5
UCl ₄ ·2phen	68	Green	295	31.1	32.2	18.3	19.2
UO ₂ Cl ₂ ·2bpy	50	Yellow	> 300 (dec)	35.6	36.4	10.3	10.8
UO ₂ Cl ₂ ·2phen	59	Yellow	> 300 (dec)	33.0	33.9	10.5	10.1
(bpyH) ₂ UO ₂ Br ₄	45	Gold	235	25.8	26.4	36.0	35.4
(phenH) ₂ UO ₂ Br ₄	52	Yellow	300	25.4	25.0	33.8	33.6
(Et ₄ N) ₂ UCl ₆	50	Green	—	33.7	33.5	29.6	29.9
(Et ₄ N) ₂ UBr ₆	61	Green	—	25.1	24.6	48.8	49.0
(Et ₄ N) ₂ UO ₂ Cl ₄	82	Yellow	—	35.6	35.4	21.6	21.1
(Et ₄ N) ₂ UO ₂ Br ₄	56	Yellow	—	27.6	28.0	37.8	37.6

^admso = dimethylsulphoxide; bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline. ^bBased on quantity of metal dissolved electrochemically. ^cLiterature values in parentheses. ^dFound 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 UX₆²⁻ and UO₂-X₄²⁻ 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, UX₄·4CH₃CN (X = Cl, Br) have been described by Bagnall, Brown and Jones [17]; the compound UBr₄·2CH₃CN has not apparently been reported previously. The triphenylphosphine oxide adducts of UCl₄, UO₂Cl₂ and UO₂Br₂ have been prepared by Gans and Smith [20] and Day and Venanzi [19], and the UBr₄ compound can now be added to this group. Dimethylsulphoxide complexes with UCl₄ (3dmso [21]) and UBr₄ (6dmso [22]) are known,

but the corresponding UO₂Cl₂ and UO₂Br₂ compounds do not appear to have been prepared previously. Adducts of the bidentate donors 2,2'-bipyridine and 1,10-phenanthroline with UCl₄ have been reported by Gans and Smith [22] and the analogous bromo-complexes are reported here for the first time.

The compounds formed by UO₂X₂ (X = Cl, Br) and these bidentate donors present a different problem. The 1:1 complexes UO₂Cl₂·phen and UO₂Cl₂·bpy·2H₂O were prepared by Markov and Tsapkin [23] via non-aqueous solution, but reaction in aqueous acidic media gave the salts (bpyH)₂UO₂Cl₄, (phenH)₂UO₂Cl₄ or bpyH₂·UO₂Cl₄·3H₂O, depending on the conditions [23, 24]. The (bpyH)⁺ and (phenH)⁺ salts were later obtained by the oxidation of UCl₄·L₂ (L = bpy, phen) [20], and other salts of UO₂Cl₄²⁻ and UO₂Br₄²⁻ 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/UO₂Br₂ 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 $(\text{bpyH}_2)[\text{UO}_2\text{Br}_4]$, in which the structure of the anion is essentially identical to that recently reported [26]. The bulk product analysed as $(\text{bpyH})_2\text{UO}_2\text{Br}_4$, and the 1,10-phenanthroline system yielded the analogous $(\text{phenH})_2\text{UO}_2\text{Br}_4$. 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 $(\text{UO}_2\text{X}_4)^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) 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 $\text{UI}_4 \cdot 4\text{CH}_3\text{CN}$ 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, $\text{UI}_4 \cdot 4\text{dmf}$ 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 $\text{UO}_2\text{I}_2 \cdot 2\text{Ph}_3\text{PO}$ [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 , $\nu(\text{C}\equiv\text{N})$ is at $2310 + 2282 \text{ cm}^{-1}$, and $2305 + 2280 \text{ cm}^{-1}$ respectively (*cf.* ref. 17). The $\nu(\text{PO})$ mode in the triphenylphosphine oxide compounds is in the region $1060\text{--}1065 \text{ cm}^{-1}$, and $\nu(\text{SO})$ in the dimethylsulphoxide adducts is at $990\text{--}995 \text{ cm}^{-1}$. The other vibrations of these ligands, and of the ligands 2,2'-bipyridine and 1,10-phenanthroline, are as described in the literature.

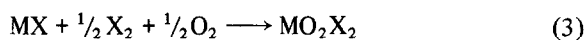
The frequencies of the $\nu(\text{U-X})$ modes, and of $\nu(\text{UO}_2)$, are given in Table III. Where comparisons are possible, we find values in agreement with those of previous workers.

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 $1.0 \pm 0.2 \text{ mol F}^{-1}$. Following previous arguments, in which the current carrier is identified as X^- in the $\text{X}_2 + \text{X}^-$ systems, and (tentatively) X_2^{2-} otherwise, we suggest that the anode reactions are

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

Compound	$\nu(\text{M-X})$	$\nu(\text{M-O})$
$\text{UCl}_4 \cdot 4\text{CH}_3\text{CN}$	254	—
$\text{UBr}_4 \cdot 2\text{CH}_3\text{CN}$	184	—
UO_2Cl_2	245–265 br	960
$\text{UCl}_4 \cdot 2\text{Ph}_3\text{PO}$	250–256 br	—
$\text{UBr}_4 \cdot 2\text{Ph}_3\text{PO}$	170–190 br	—
$\text{UO}_2\text{Cl}_2 \cdot 2\text{Ph}_3\text{PO}$	259	918
$\text{UO}_2\text{Br}_2 \cdot 2\text{Ph}_3\text{PO}$	169	930
$\text{UCl}_4 \cdot 3\text{dmso}$	250	—
$\text{UBr}_4 \cdot 6\text{dmso}$	—	—
$\text{UO}_2\text{Cl}_2 \cdot 3\text{dmso}$	—	915
$\text{UO}_2\text{Br}_2 \cdot 4\text{dmso}$	184	900 sh
$\text{UCl}_4 \cdot 2\text{bpy}$	242	—
$\text{UCl}_4 \cdot 2\text{phen}$	244	—
$\text{UO}_2\text{Cl}_2 \cdot 2\text{bpy}$	232	925
$\text{UO}_2\text{Cl}_2 \cdot 2\text{phen}$	226	910
$(\text{bpyH})_2\text{UO}_2\text{Br}_4$	173 br	930
$(\text{phenH})_2\text{UO}_2\text{Br}_4$	178, 167, 156	915
$(\text{Et}_4\text{N})_2\text{UCl}_6$	254	—
$(\text{Et}_4\text{N})_2\text{UBr}_6$	186	—
$(\text{Et}_4\text{N})_2\text{UO}_2\text{Cl}_4$	255 br	918
$(\text{Et}_4\text{N})_2\text{UO}_2\text{Br}_4$	174	930



or



The fate of the species formed in eqns. (2), (3) or (5) then depends on the nature of the complexing species in solution ($\text{CH}_3\text{CN}, \text{X}^-$). 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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