

Bromide Alkoxides of Uranium

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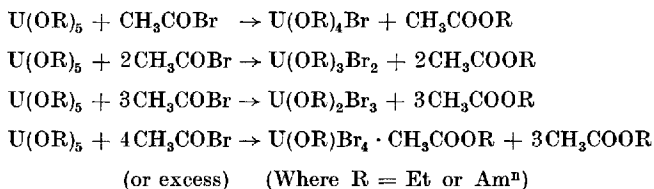
Summary

The reactions of uranium pentaalkoxides (ethoxide and n-amylxide) with acetyl bromide in different molar ratios yield the products, $U(OEt)_4Br$, $U(OEt)_3Br_2$, $U(OEt)_2Br_3$, $U(OEt)Br_4 \cdot CH_3COOEt$, $U(OAm^n)_4Br$, $U(OAm^n)_3Br_2$, $U(OAm^n)_2Br_3$ and $U(OAm^n)Br_4 \cdot CH_3COOAm^n$. All these bromide alkoxides are soluble in benzene.

Introduction

Much work has been carried out on the chloride and bromide alkoxides of niobium¹⁾ and tantalum^{2) 3)}. The only reference in the literature however concerning the uranium chloride alkoxides is the formation of uranium alkoxide chlorides by the reactions of uranium pentaethoxide with dry hydrogen chloride gas^{4) 5)}.

It is therefore considered of interest to find a more convenient method for the preparation of bromide alkoxides of uranium and to study their properties. The reaction between uranium pentaethoxide and acetyl bromide was therefore investigated in detail. These reactions were found to be exothermic and can be represented by the following equations:



¹⁾ R. C. MEHROTRA and P. N. KAPOOR, *J. Less-Common Metals* **10**, 348 (1966).

²⁾ R. N. KAPOOR and S. PRAKASH, *Ind. J. Chem.* (In Press).

³⁾ R. N. KAPOOR and S. PRAKASH, *Aust. J. Chem.* (In Press).

⁴⁾ R. G. JONES, E. BINDSCHADLER, D. BLUME, G. KARMA, G. A. MARTIN, J. R. THIRTLE, and H. GILMAN, *J. Amer. chem. Soc.* **78**, 6027 (1956).

⁵⁾ A. M. BHANDARI and R. N. KAPOOR, *J. chem. Soc.* (In Press).

The reactions of uranium pentaethoxide and penta n-amyloxiide with acetyl bromide are straightforward but to ensure completion, the reaction mixture was refluxed for an hour. The bromide alkoxides so obtained exhibit an increasing tendency to add on a molecule of organic ester. This is easily understandable as the replacement of the alkoxide group by a more electronegative bromide group would cause to decrease the electron density around the uranium atom and thus increases the acceptor property of the central metal atom. The bromide alkoxides are soluble in benzene and are isolated by drying under reduced pressure.

Experimental

Uranium pentaethoxide was prepared as a mobile brown liquid, b.p. $180^{\circ}/0.1$ mm. (yield 88%) from uranium tetrachloride and sodium ethoxide⁶). Anhydrous uranium tetrachloride was prepared from uranium trioxide and hexachloropropene⁷). Uranium n-amyloxiide was prepared from the reaction of uranium pentaethoxide with an excess of n-amyl alcohol in boiling benzene⁸).

Acetyl bromide was B.D.H. Analar product and was distilled (b.p. 76.5°C) before use. Benzene (B.D.H.) was dried by keeping over sodium metal and distilling it. Finally it was dried azeotropically with ethanol. An all glass apparatus were used with precautions to exclude moisture.

Uranium and bromide were determined gravimetrically as U_3O_8 and AgBr . The valency of uranium 5.0 in each case was confirmed by the double oxidation with ceric sulphate solution⁹).

Reaction between uranium pentaethoxide and acetyl bromide in molar ratio of 1:1

Acetyl bromide (0.54 g) was added to a solution of uranium pentaethoxide (2.02 g) in benzene (40 g) when an exothermic reaction took place at room temperature. The mixture was refluxed for about one hour at $80-90^{\circ}\text{C}$. The excess solvent and the ester were removed under reduced pressure at $30^{\circ}\text{C}/0.5$ mm. for three hours. A brown viscous liquid was obtained. On heating under reduced pressure it decomposes.

Found: U, 47.48%; Br, 15.92%. $\text{U}(\text{OEt})_4\text{Br}$
requires: U, 47.79%; Br, 16.09%.

Reaction between uranium penta n-amyloxiide and acetyl bromide in molar ratio of 1:1

An exothermic reaction took place when acetyl bromide (0.42 g) was admitted to a benzene solution of uranium penta n-amyloxiide (2.26 g). The contents of the mixture was refluxed at a temperature of about $80-90^{\circ}\text{C}$. for half an hour after which excess

⁶) R. G. JONES, E. BINDSCHANDLER, G. KARMA, F. A. YOEMAN, and H. GILMAN, *J. Amer. chem. Soc.* **78**, 4287 (1956).

⁷) J. A. HERMAN and J. F. SUTTLE, *Inorg. Synth.* **5**, 143 (1957).

⁸) D. C. BRADLEY, R. N. KAPOOR, and B. C. SMITH, *J. chem. Soc.* 1023 (1963).

⁹) D. C. BRADLEY, B. N. CHAKRAVARTI, and A. K. CHATTERJEE, *J. Inorg. Nucl. Chem.* **3**, 367 (1957).

Table 1
Reactions of Uranium Pentaalkoxides with Acetyl Bromide

Molar Ratio	Alkoxide (g)	Acetyl- bromide (g)	Product and State	Found		Analysis		Calcd.	
				U (%)	Br (%)	U (%)	Br (%)	U (%)	Br (%)
U(OEt)₅									
1 : 1	2.02	0.54	U(OEt) ₄ Br Brown liquid	47.48	15.92	47.79	16.09	47.79	16.09
1 : 2	2.12	1.13	U(OEt) ₃ Br ₂ Brown viscous liquid	44.64	30.32	44.66	30.02	44.66	30.02
1 : 3	1.88	1.50	U(OEt) ₂ Br ₃ Brown viscous liquid	41.96	42.00	41.91	42.26	41.91	42.26
1 : 4	1.58	1.68	U(OEt)Br ₄ · CH ₃ COOEt Reddish Brown viscous liquid	34.28	45.92	34.44	46.30	34.44	46.30
1 : excess	1.55	2.22	U(OEt)Br ₄ · CH ₃ COOEt Reddish brown viscous liquid	34.08	46.14	34.44	46.30	34.44	46.30
U(OAmⁿ)₅									
1 : 1	2.26	0.42	U(OAm ⁿ) ₄ Br Dark brown liquid	35.33	12.24	35.74	12.01	35.74	12.01
1 : 3	1.84	1.00	U(OAm ⁿ) ₂ Br ₃ Dark brown liquid	36.28	36.88	36.51	36.81	36.51	36.81
1 : excess	1.80	1.86	U(OAm ⁿ)Br ₄ · CH ₃ COOAm ⁿ Dark brown liquid	30.77	41.00	30.71	41.21	30.71	41.21

solvent and the ester were removed under reduced pressure at 40°C/1.0 mm. for 2–3 hours. A dark brown liquid was obtained.

Found: U, 35.33%; Br, 12.24%. $U(OAm^a)_4Br$
requires: U, 35.74%; Br, 12.01%.

The analytical data are recorded in the Table 1.

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