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Reactions of Uranium Metal with Alcohols

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Two new routes for the synthesis of uranium alkoxides are reported. One is based on the reaction of uranium metal with a mixture of carbon tetrachloride/alcohol and the other on the anodic 'dissolution' of uranium metal in alcohol.

Introduction

Pitts [1] has reported reactions of plutonium and uranium metals in mixtures of CCl_4/alcohols, as part of a study of the dissolution of irradiated fuel elements. Although the author reports the formation of alkoxides, no products were isolated and characterized. In this work we describe the reaction of uranium metal with CCl_4/C_2H_5OH (1:1). We also report preliminary results obtained on the direct electrochemical synthesis of uranium alkoxides, in particular the electrosynthesis of $U(OC_2H_5)_4$. Little has been published [2] concerning the electrosynthesis of metal alkoxides, the most recent work being made by Shreider *et al.* [3].

Experimental

All reactions were carried out under an inert atmosphere of nitrogen on Schlenk apparatus or vacuum line. All the compounds were handled in an inert atmosphere glove box in which the water and oxygen contents were lower than 20 ppm.

Uranium metal was obtained from a pilot-plant in our laboratories and was used as metal turnings. The oxide layer was removed by dissolution in nitric acid and the metal was further washed with water, alcohol and acetone. All solvents were dried by conventional methods [4] prior to use. Lithium chloride was vacuum dried at 50 °C.

IR spectra were obtained as mujol mulls on CsI plates with a Perkin-Elmer 577 spectrometer. Electronic spectra were recorded on a Cary 17 Varian spectrophotometer. ^1H NMR spectra were run on a Perkin Elmer R32 spectrometer. C, H, N elemental analyses were performed on an automatic Perkin Elmer 240C analyser. Cl and U were determined gravimetrically by standard methods.

Reaction of Uranium Metal with CCl_4/C_2H_5OH (1:1)

The reaction was carried out in a double Schlenk apparatus, which consisted of two Schlenk compartments separated by a glass frit [5]. 10 ml of the mixture CCl_4/C_2H_5OH (1:1) were added to about 1 g of uranium metal. The reactants were stirred at room temperature.

The reaction started with evolution of hydrogen and a green solution was formed. After the reaction was complete, the solution was filtered and evaporated under vacuum. The green solid obtained was formulated as $UCl_2(OC_2H_5)_2 \cdot xC_2H_5OH$ on the basis of U, Cl, C, H analysis, I.R. and U.V. spectroscopy. Ethanol was always present in the compound even after further washings with pentane and drying under vacuum.

Anodic 'Dissolution' of Uranium in Ethanol

The electrolyses were run at about 0 °C in ethanol with LiCl as electrolyte (~0.1 *M*), the uranium metal as anode and a cathode of platinum. The applied currents ranged from 10 to 30 mA. At the beginning of the electrolysis and close to the uranium electrode, a deep red coloration was formed which quickly turned green. Hydrogen evolution occurred near the cathode, and after some time a green precipitate was formed. The electrolysis was interrupted after 1 to 2 hours, the solution filtered and the precipitate washed with ethanol by the Schlenk technique and vacuum dried. This compound was extremely sensitive to moisture and oxygen. *Anal.* Calcd. for $U(OC_2H_5)_4$: U, 56.91; C, 22.97; H, 4.19%. Found: U, 56.77; C, 20.75; H, 4.33%. Infrared spectrum (Nujol mull, cm^{-1}): 1120s; .1090w; 1070s; 1030s; 910m; 880m; 460m; 435m; 345m; 315m.

Results and Discussion

The ^1H n.m.r. spectrum of the solution obtained after the reaction of uranium metal with CCl_4/

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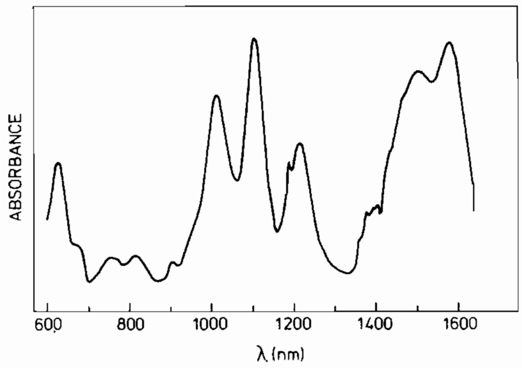

Fig. 1. Electronic spectrum of the reaction solution of U metal with CCl_4/C_2H_5OH (1:1).

C_2H_5OH (1:1) shows evidence of the formation of chloroform (also reported by Pitts [1]), suggesting the existence of intermediate radicals of the type $CCl_3^{\bullet}$. The electronic absorption spectrum of the same solution is shown in Fig. 1, and is identical to that of the isolated compound which is characteristic of an U(IV) species. The main features of its i.r. spectrum are: absorption bands relative to the alkoxide groups at 1100(s), 1060(s), 1020(s) and 920(m) cm^{-1}, assigned to C–O stretching vibrations; bands at 535(m), 470(m) and 450(m) cm^{-1} assigned to U–O vibrations; a weak band at about 250 cm^{-1} which is attributed to the U–Cl stretching vibration and a broad band at 3300 cm^{-1} (O–H stretching vibration) indicates coordinated ethanol. On the basis of these observations, elemental analysis and a U/Cl ratio of 1:2, the compound was formulated as $UCl_2(OC_2H_5)_2 \cdot xC_2H_5OH$ ($x \sim 0.5$). The compound is a dark green solid, sparingly soluble in toluene, benzene and dichloromethane.

At present, the reactions of U metal with methanol and isopropanol are being undertaken in our laboratories and the products isolated are being studied.

In the anodic 'dissolution' of U metal in ethanol, the mechanism of the uranium alkoxide formation is not yet clear. In order to identify the uranium intermediate species, a cell with separated cathodic and anodic compartments was used. No precipitate was formed but a clear green solution was obtained. Comparison of the electronic spectra of various solutions taken at different electrolysis times with those of UCl_4 and $U(OC_2H_5)_4$ in ethanol led us to assume that the intermediate species should be of the type $UCl_{4-n}(OC_2H_5)_n$. The anodic reaction would be the oxidation of uranium metal with the formation of the soluble $UCl_{4-n}(OC_2H_5)_n$ species, which will be later reduced at the cathode. The cathodic reduction of $UCl_{4-n}(OC_2H_5)_n$ may involve the formation of radicals, elimination of the chloride ion, subsequent interaction with the alcohol and evolution of hydrogen, as suggested by Shreider *et al.* [3] in electrosyntheses of other metal alkoxides.

References

1 S. H. Pitts Jr., *Canadian Patent,* 963024 (1975).
2 H. Lehmkuhl and M. Eisenbach, *Ann. Chem.*, 672 (1975).
3 V. A. Shreider, E. P. Turevskaya, N. I. Koslova and N. Ya. Turova, *Inorg. Chim. Acta, 53,* L-73 (1981).
4 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 'Purification of Laboratory Chemicals', Pergamon Press, 1969.
5 D. F. Shriver, 'The Manipulation of Air-sensitive Compounds', McGraw-Hill Book Company, New York 1969, p. 153.