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THERMAL DECOMPOSITION OF THE SOLVENT EXTRACTED CHLORO COMPLEXES OF URANIUM(VI) WITH TRIOCTYLAMINE AND TRIOCTYLMETHYLAMMONIUM CHLORIDE

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ABSTRACT

The complexes, $(R_3NH)_2UO_2Cl_4$ and $(R_3R'N)_2UO_2Cl_4$, prepared by drying in vacuo the organic solutions from the extraction of aqueous UO_2Cl_2 solution with trioctylamine (TOA, R_3N) and trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) in benzene have been examined by thermogravimetry and differential thermal analysis under an atmosphere of N_2, and their thermally decomposed products such as volatile matters and residues by gas chromatography, X-ray diffraction study and infrared spectroscopy. As a result, it is found that the complexes with TOA and TOMAC thermally decompose to UO_2 at 320-360 and 280-325 °C via UO_2Cl_2 formed by cracking of the complexes at 205-320 and 200-280 °C, respectively.

INTRODUCTION

The solvent extraction of metals with long-chain aliphatic amines has been investigated by a number of researchers, but the properties of the complexes isolated from their organic solutions have recieved little attention. In order to obtain further information concerning their composition, studies on the thermal decomposition of such complexes have been made of the chloro complexes of Cu(II) (1), Zr(IV) (2), V(IV) (3) and U(VI) (4) in air and of Mn(II), Co(II), Cu(II) and Zn(II) under an atmosphere of N_2 (5). Therefore the present paper extends the work to examine the thermal behaviour of chloro complexes of U(VI) with trioctylamine (TOA, R_3N) and trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) under an atmosphere of N_2 in comparison with air (4).

EXPERIMENTAL

Chemicals TOA and TOMAC (both > 99 %, Koei Chemical Co., Ltd., Osaka) of high purity were used without further purification and diluted with benzene. Aqueous solution of U(VI) was prepared by dissolving $UO_2Cl_2 \cdot 2H_2O$ in 0.06 M HCl. All chemicals used were of analytical reagent grade.

Preparation and Analysis of Complexes On the basis of the distribution results, the organic solutions saturated with U(VI) were prepared as follows: 0.05 M TOA and TOMAC in benzene were shaken for 10

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min with aqueous solutions of 0.1 M UO_2Cl_2 in 3 or 7 M HCl, respectively, at 20 °C; the organic phases separated from aqueous phases by centrifuge were heated in vacuo at 50-60 °C to remove benzene. The benzene-freed complexes with TOA and TOMAC have the stoichiometric compositions, $(R_3NH)_2UO_2Cl_4$ and $(R_3R'N)_2UO_2Cl_4$, respectively.

Analysis The complexes were examined by thermogravimetry (TG) and differential thermal analysis (DTA), and their thermally decomposed products such as volatile matters and residues were checked by gas chromatography, X-ray diffraction study and infrared spectroscopy. The TG and DTA were examined under an atmosphere of N_2 at a heating rate of 5 °C min^{-1} and a flow rate of N_2 of 50 ml min^{-1}. The TG and DTA were carried out on an automatic recording thermobalance and DTA apparatus, made by the Agne Research Centre, using alumel-chromel thermocouples, forty milligrams of the samle and α-alumina as reference material for the measurement of differential thermal electromotive force. The residues were derived from the complex by heating to the required temperatures at a rate of 5 °C min^{-1} under the same atmosphere. Infrared spectra were recorded on Japan Spectroscopic Co., Ltd. Model IRA-1 (4000-650 cm^{-1}) and IR-F (700-200 cm^{-1}) grating spectrometers. X-ray powder diffraction diagrams were obtained on Geigerflex recording X-ray diffractometer with filtered copper radiation. The volatile matters generated during the DTA were collected with 2 ml syringe at the gas outlet of the DTA apparatus and analyzed with a Shimazu Model GC-6AMPTF gas chromatograph under the following analytical conditions: carrier gas He at 40 ml min^{-1}; column, Porapak Q of 80/100 mesh; column temperature, 140 °C; detector, FID. Each component detected was identified by gas chromatograph-mass spectrometry (GC-MS). HCl in the volatile matter was trapped in 0.05 M $AgNO_3$ solution in an interval of 10 °C at a temperature between 200 and 350 °C by passing it through the solution for 3 min. For chemical analysis, the resulting materials were dissolved in benzene, and the chloride concentration and water content in portions of the solution were determined by Volhard and Karl-Fischer titrations. In addition the benzene solutions were washed with 1 M HCl and the U(VI) in the acidic layers was detemined by EDTA with XO as indicator (6).

RESULTS AND DISCUSSION

In the complex with TOA, the TG curve exhibits the weight-loss of 73.4 % at 200-300 °C and 3.6 % at 300-470 °C, and the DTA curve gives the endothermic reactions at 270, 305 and 330 °C. The complex with TOMAC reveals the weight-losses of 74.3 % at 200-350 °C in the TG curve and the endotherms at 250, 265, 280 and 305 °C, in the DTA curve. Additionally, it is observed that the endothermic reactions in the DTA curve occur at he point near the change of shape in the TG curves.

The volatile matters generated by the thermal decomposition of the uranyl complexes with TOA and TOMAC contain aliphatic compounds such as C_3H_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, 1-C_4H_8, 2-C_4H_8 and CH_3Cl, identified by GC-MS, and HCl, trapped in $AgNO_3$ solution. In addition, the change in the molar ratios, [Cl]/[U], was examined for the residues obtained by heating the complexes with TOA and TOMAC. From these it is seen that the amount of components detected above 250 °C increases with increasing the temperature, in accordance with the weight-loss in the TG curve, and the maximal amounts of their volatile matters correspond to the endotherms in the DTA curve. On the one hand, it is found that HCl evolved from the complex with TOA is detected above 200 °C (before the detection of the organic components) and its maximal amount is obtained at about 250 °C, as identified in the thermal decomposition of divalent metal complexes (5). It is thus inferred that the thermal decomposition is initiated by the release of HCl, followed by the decomposition of TOA. This implies that in the DTA curve the endotherm at 270 °C are assigned to the release of HCl accompanied by the decomposition of TOA. Because the TG curve reveals the weight-loss corresponding to the theoretical value for the thermal reaction of the complex with TOA. In addition, it is considered that the endotherms at 305 and 330 °C arise from the cracking of alkyl group and dechlorination, respectively.

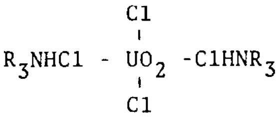
The volatile matters for the complex with TOMAC contain the same organic components as those for the complex with TOA, although the former complex contains much CH_3Cl more than the latter complex. Moreover it is found that the distribution of CH_3Cl is different from that of hydrocarbons; The maximal amount of CH_3Cl is detected at 250-275 °C, and those of hydrocarbons at 275-400 °C. These components are greatly generated in the begining of the thermal decomposition, implying that the decomposition of the complex with TOMAC at first releases CH_3Cl. From this the endotherms at 250 and 265 °C are assigned to the release of CH_3Cl, and those at 280 and 305 °C to cracking and dechlorination, respectively.

In the infrared spectrum of the uranyl complex with TOA, the absorption assigned to the asymmetric stretching frequency of the UO_2^{2+} group appears at 910 cm^{-1}; the NH^+ stretching vibration at 2350 cm^{-1} in TOA·HCl shifts to a broad band centered around 3000 cm^{-1}. On heating at 250 °C, the NH^+ band, the C-H stretching bands at 2920 and 2860 cm^{-1}, the CH_3 degenerate (and CH_2 scissoring) and symmetrical bonding modes at 1465 and 1380 cm^{-1} decrease in intensity, and at 400 °C disappear. The uranyl complex with TOMAC gives an infrared spectrum similar to the complex with TOA, except the absence of the NH^+ stretching band. In addition the changes in the infrared spectra of the thermally decomposed residues derived from the TOMAC complex are almost the same as those from the TOA complex. Furthermore the X-ray diffraction results for the residues produced by heating the uranyl complexes with TOA and TOMAC indicated the following patterns: UO_2Cl_2, $UO_2Cl_2 + UO_2$ and UO_2 from the complex with TOA at 250, 300 and 350 °C, respectively; UO_2Cl_2, $UO_2Cl_2 + UO_2$ and UO_2 from the complex with TOMAC at 200, 250 and 350 °C, respectively. It is thus presumed that UO_2Cl_2 and UO_2 are formed during the decomposition process of their complexes under an atmosphere of N_2. Accordingly it is concluded that the thermal decomposition of the uranyl complexes with TOA and TOMAC proceeds in the sequences:

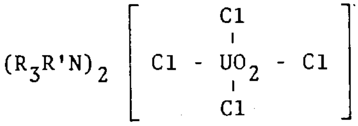
$$(R_3NH)_2UO_2Cl_4 \xrightarrow[\text{-HCl and cracking}]{250\text{-}320°C} UO_2Cl_2 \xrightarrow[\text{dechlorination}]{320\text{-}360°C} UO_2;$$

and
$$(R_3R'N)_2UO_2Cl_4 \xrightarrow[\text{-}CH_3Cl\text{ and cracking}]{200\text{-}280°C} UO_2Cl_2 \xrightarrow[\text{dechlorination}]{280\text{-}325°C} UO_2.$$

supporting the proposed structures, [I] and [II], for the uranyl complexes with TOA and TOMAC



$$R_3NHCl - \overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{UO_2}} - ClHNR_3 \quad ;$$



$$(R_3R'N)_2 \left[Cl - \overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{UO_2}} - Cl \right]$$

[I] [II]

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