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Thermoanalytical and pyrolysis–MS studies on dioxouranium(VI) complexes of sodium 1,2-naphthoquinone-1-monoxime-7-sulfonate

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Abstract

A solid dioxouranium(VI) complex of sodium 1,2-naphthoquinone-1-monoxime-7-sulfonate (HL) has been synthesized and characterized. According to elemental analysis its metal to ligand molar ratio was 3. The analysis of potentiometric data obtained from a simulated synthesis by the MINIQUAD program showed that the main component of synthetic product was $(UO_2)_3(OH)_4L$ although the species $(UO_2)_3(OH)_5L$ made up about one fifth of the product.

TG, DTG and DSC techniques have been used at 39–900°C to analyze the thermal decomposition of the synthetic product in dynamic air and nitrogen atmosphere. The gaseous decomposition products were identified at 50–400°C by the pyrolysis–MS technique.

Some weakly bonded water was eliminated before 90°C; the product also contained 4.8 moles coordinated water which was released at 90–260°C. The decomposition proceeded at 260–800°C in several, partially simultaneous processes, releasing CO_2 together with some minor species. The residues, containing mostly U_3O_8, were 75.1% and 78.7% of the dry mass of the sample in dynamic air and nitrogen atmosphere, respectively. The theoretical amount of U_3O_8 is 72.0%.

INTRODUCTION

Nitrosonaphthols are compounds which may exist in tautomeric equilibria with naphthoquinone oximes [1, 2].

Previously [3, 4] it was shown that in aqueous solution and also in the solid state 1-nitroso-2-naphthol sulfonates exist mainly as 1,2-naphthoquinone-1-monoxime sulfonates. Although in the conditions during the complexation the strong sulfonic acid group of these ligands exists

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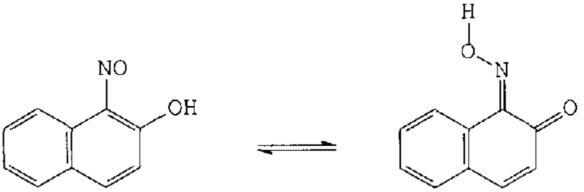
in the deprotonated form, the deprotonation of the oximic group controls the formation of complexes [1].



The formation of multinuclear hydroxo species is typical to dioxouranium(VI) ion in aqueous solution, as is well documented in the literature [1, 5–8]. In the circumstances of this study, in moderately acidic solutions, it is especially important to take into account the formation of these species as side products and also because they may act as an acceptor in coordination with ligands. The pure hydrolysis of dioxouranium(VI) can be estimated with the known formation of the $[(UO_2)_2(OH)_2]^{2+}$ and $[(UO_2)_3(OH)_5]^{+}$ species [1]. Both of these are hydroxo bridged, but the trinuclear species also has staggered equilateral triangular structure [1] for which reason it cannot accept this type of ligand as easily as species with an open chain structure. In addition, the unusual bonding capabilities of dioxouranium(VI) based on the availability of 5f orbitals may have an effect on the structures to be formed.

The sulphonic acid derivatives of nitrosonaphthols and their water soluble complexes with metals have been extensively investigated [1–4, 9–12]. There are, however, very few documents concerning the complexes of nitrosonaphthols with f-transition metals such as dioxouranium(VI).

In this work a solid dioxouranium(VI) complex of sodium 1,2-naphthoquinone-1-monoxime-7-sulfonate (HL) has been synthesized. The structure of the complex formed was characterized and its thermoanalytical behavior studied using elemental analysis, potentiometric titrations and TG, DTG, DSC and pyrolysis–MS techniques [1, 3, 13, 14]. Because of the hydrolysis of dioxouranium(VI) the crystallization of the complex did not succeed and the exact single crystal could not be determined.

EXPERIMENTAL

The ligand sodium 1-nitroso-2-naphthol-7-sulfonate (HL), was synthesized and purified as described earlier [2]. The elemental analysis was carried out by using a Carlo Erba Elemental Analyzer 1106.

The complex was prepared by adding sodium hydroxide solution to a hot solution containing dioxouranium(VI) ions and the ligand in molar ratio 2:1. The pH was adjusted to the area where also water soluble hydroxo-species of dioxouranium(VI) are formed. The solution was refluxed for at least 1 h, concentrated and cooled down. The solid product separated, was washed with ice cold water and dried in air. The crystallization of the solid was unsuccessful.

The TG, DTG and DSC curves were obtained on a Perkin-Elmer PC series TGA-7 thermogravimetric analyzer and DSC-7 differential scanning calorimeter. The TG curves were run from 1–18 mg of the samples in platinum-pans in dynamic air or nitrogen with a flow rate of 40–60 $cm^3 min^{-1}$. The heating rate was 5°C min^{-1} in the temperature range 30–900°C. DSC experiments were carried out at a heating rate of 5°C min^{-1} from 30 to 550°C using aluminum pans with holes, in dynamic air or nitrogen atmosphere.

Pyrolysis–mass spectrometry was used to determine the composition of evolved gases by heating the solid sample in a quartz capillary tube in the direct inlet on a Jeol JMS 300D mass spectrometer equipped with JMA 2000H data system. The spectra were measured under electron ionization, typical experimental conditions being, sample heating rate 5°C min^{-1}, electron energy 70 eV, aceleleration voltage 3 kV, ionization current 300 μA and ion source temperature 170°C.

RESULTS AND DISCUSSION

Carbon and nitrogen elemental analysis was used as the first tool to characterize the structure of the complex formed from sodium 1,2-naphthoquinone-1-monoxime-7-sulfonate and dioxouranium(VI) ion. All products obtained using slightly different synthetic conditions gave rise to the same result: the ratio of the metal to the ligand in the complex was 3:1. Based on the information obtained in previous works [1,3,5–9] for dioxouranium(VI) and the *ortho*-naphthoquinone monoxime sulfonates and their behavior in complexation in aqueous solutions, the formula of solid complex was expected to be $Na[(UO_2)_3(OH)_4L]$, if possible constitutional water molecules are neglected.

To confirm this result the formation of the complex species was simulated with potentiometric titrations in aqueous 0.1 M $NaClO_4$ solutions using values 2 and 1 for the metal:ligand ratio. The titration data of four titrations containing 83 titration points from the pH region 3.9–5.1 was analyzed by the MINIQUAD program [15]. The formation of hydroxo-complexes of dioxouranium(VI) was estimated in computation with known formation constants of $[(UO_2)_2(OH)_2]^{2+}$ and $[(UO_2)_3(OH)_5]^+$, $-\log \beta_{2\text{-}20} = 5.830$ and $-\log \beta_{3\text{-}50} = 16.162$ [1]. The known protonation constant of the ligand, $-\log \beta_{011} = -7.265$ was also used. The results pointed out that besides $[(UO_2)_3(OH)_4L]^+$, $[(UO_2)_3(OH)_5L]$was also formed. At final pH the concentration ratio of these complexes was about 5:1. As the result of MINIQUAD analysis the values of the formation constants of those complexes with error limits (3σ) were $-\log \beta_{3\text{-}41} = 4.23 \pm 0.02$ and

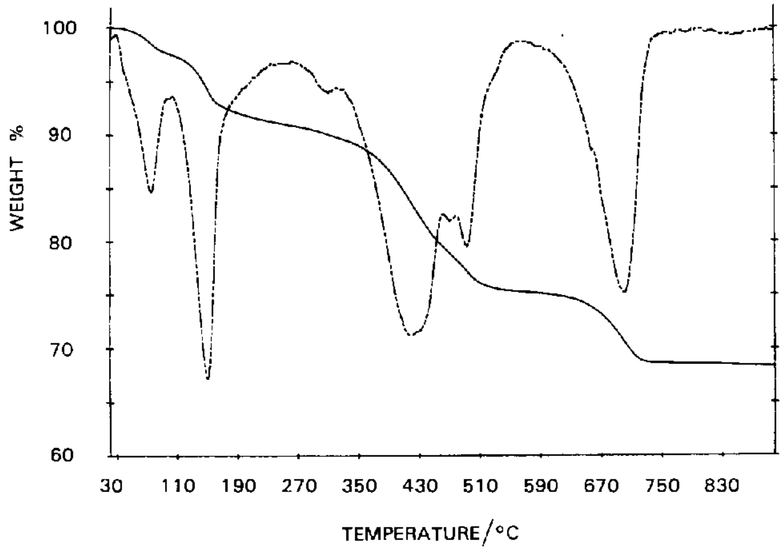


Fig. 1. TG (——) and DTG (-- —— --) curves of solid sample (6.105 mg) in air.

$-\log \beta_{3\text{-}51} = 9.91 \pm 0.16$. The statistical quantities of error analysis were $U = 5 \times 10^{-9}$, $s = 0.39$, $k = 3.73$, $\chi^2 = 12.6$ and $R = 0.007$.

TG analyses of the synthetic product were carried out in dynamic air and nitrogen atmosphere to give possible differences in decomposition processes and in the final products. In both cases the solid air-dry product was washed slightly with ethanol. Before TG measurement in nitrogen atmosphere the product was treated with dry nitrogen for about 12 h to remove humidity and oxygen.

The analyses of TG–DTG curves both in air and nitrogen, presented in Figs. 1 and 2, showed that the product contained both weakly bonded water, released at 30–90°C and coordinated water, released at 90–260°C. Proportional to one mole of complex in the air, the amount of weakly bonded water was 1.5 mole and that of coordinated water 4.8 mole. In nitrogen the related amounts were 0.4 mole and 4.8 mole, respectively, showing clearly the effect of nitrogen used for drying. Both of the detaching processes of water were endothermic, which can be seen from the qualitative enthalpy changes presented in DSC curves in Fig. 3. The amount of constitutional water obtained is in good agreement with the structure based on the coordination number 5 to dioxouranium(VI) in both complex species; this means five H_2O molecules in $[(UO_2)_3(OH)_4L]^+$ and four in $[(UO_2)_3(OH)_5L]$.

In air the decomposition of the complex proceeded at 260–760°C in partly simultaneous processes, which were exothermic before 450°C and endothermic after that (Fig. 3). According to the mass losses, the breaking of the OH-bridged part of the complex took place at about 700°C (Fig. 1.)

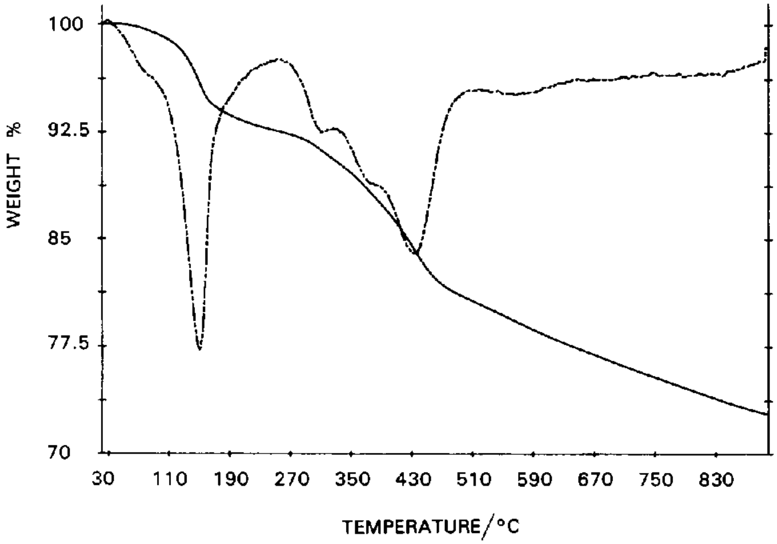


Fig. 2. TG (——) and DTG (-- —— --) curves of solid sample (8.300 mg) in nitrogen.

In nitrogen there were also several simultaneous decomposition processes at 260–650°C, but at 650–898°C the decomposition produced quite a linear loss of mass. It can be seen from Fig. 3 that in nitrogen the only exothermic decomposition took place at around 300°C, which means that the opening of the ring structure of the ligand in the complex must happen at this temperature. The same exothermic process can also be found in air. In the pure ligand the exothermic opening of the oxime-substituted ring also takes place at nearly the same temperature [3].

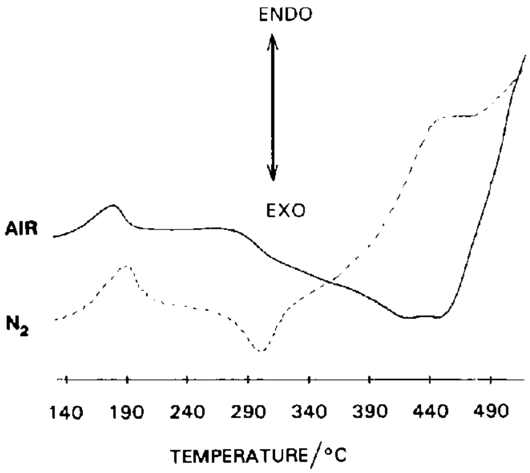


Fig. 3. DSC curves of solid samples in air (——) and in nitrogen (---).

The appearance and the composition of the final residue depended on the circumstances of decomposition. The residue in dynamic air at 898°C was 75.1% of the dry mass of the sample. The corresponding amount in nitrogen was 78.7%. In both cases, the residue contained all the uranium from the original sample, which is about 72.1% calculated as U_3O_8. The slightly yellow residue in the air contained all the sodium and some of the sulfur as Na_2O, Na_2SO_4 and S. The nearly black residue in nitrogen at 898°C contained some carbon besides sodium as Na_2O, Na_2SO_4 and Na_2S. The existence of carbon is understandable because at this temperature the endothermic processes had not yet ended.

The pyrolysis–MS technique made it possible to identify gaseous products formed at any point of the decomposition process of the synthetic product at 50–400°C in vacuum. The mass chromatograms for selected ions from the characteristic mass spectra of the decomposition products of the complex are presented in Fig. 4. The only species, which detached before 260°C, was H_2O. This loss took place in two separate processes as can be seen in mass chromatogram. In the region 260–400°C the decomposition took place in several simultaneous processes related to those observed in the DTG curve. However, the only notable products were CO_2 (at m/z 44) and CO (at m/z 28) as presented in Fig. 4. The absence of the $NO^{+\bullet}$ ion peak at m/z 30 shows that the ligand must coordinate to the dioxouranium(VI) through the oxime group as described in the literature [16]. Under similar conditions the pure ligand clearly eliminates NO [3].

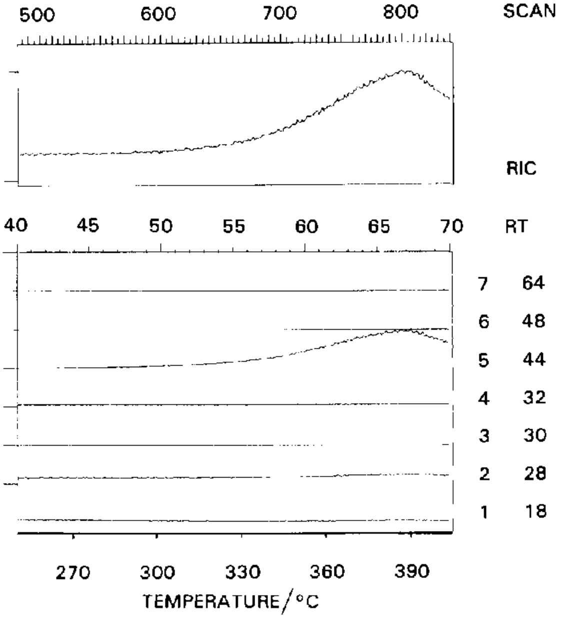


Fig. 4. Mass chromatograms with selected ion monitoring of studied complex species.

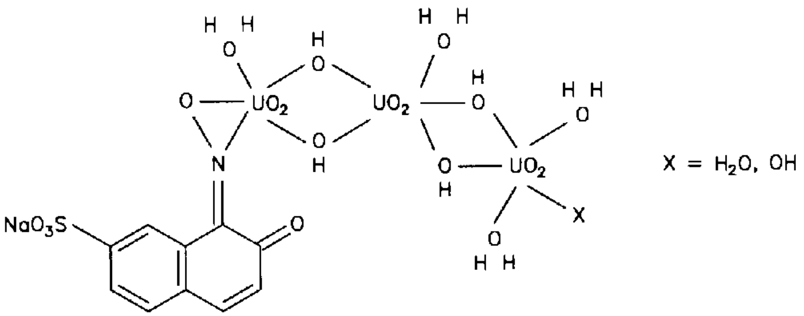


Fig. 5. The proposed structure of the complexes formed.

However, the existence of the $CO_2^{+\bullet}$ and $CO^{+\bullet}$ ion peaks in the spectrum proves the carbonyl group to be outside the coordination.

The results of this study, the constitutional water molecules, the metal to ligand molar ratio and CO_2 as the main decomposition product, in addition to the absence of the $NO^{+\bullet}$ peak in the mass spectra combined with the known μ-OH bridged pentagonal bipyramidal structure of dioxouranium(VI) compounds can be accounted for by the structure of the complex displayed in Fig. 5.

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