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THERMAL DECOMPOSITION OF METAL COMPLEXES

VII. URANYL NITRATE–UREA SYSTEM: SYNTHESIS AND DECOMPOSITION

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ABSTRACT

The thermal synthesis of the known complexes $UO_2(NO_3)_2(urea)_2$, $UO_2(NO_3)_2(urea)_3$, $UO_2(NO_3)_2(urea)_4$ and $UO_2(NO_3)_2(urea)_5$[II]–[V] and the unreported complexes $UO_2(NO_3)_2(urea) \cdot H_2O$[I] and $UO_2(NO_3)_2(urea)_6$[VI] has been carried out by solid–solid interaction in a thermoanalyzer and the enthalpy changes of formation have been calculated. Two different thermal behaviours have been exhibited from [I]–[IV] and from [V]–[VI] complexes, as shown also from the "activation energy" values. In each case, the thermal decomposition does not occur through a stepwise release of urea molecules.

INTRODUCTION

In previous works, some of us have studied the thermal decomposition of metal complexes in order to correlate, within the described limits, the strength of the metal–ligand bond with E_a^* or ΔH_d parameters obtained from thermoanalytical curves[1–6].

Considering the usefulness of solid–solid reactions for the preparation of complexes[7–11], in this work we use this technique, carrying out the syntheses directly in a thermoanalyzer, by introducing into the crucible stoichiometric mixtures of the reactants with the following purposes: (i) to observe by DTA curve the complex formation, calculating the associated enthalpy change; (ii) to investigate, in continuity with our previous works, the subsequent thermal decomposition of the reaction products.

This work concerns the uranyl nitrate–urea system which, as known[7], gives rise to some adducts by solid–solid interaction. Here, we extend the study to other stoichiometric ratios between the reactants, obtaining in this way also the formation of the two new species $UO_2(NO_3)_2urea \cdot H_2O$ and $UO_2(NO_3)_2urea_6$.

We have considered the thermal synthesis and decomposition of the following systems:

(1) $UO_2(NO_3)_2 \cdot 6H_2O + urea \rightarrow UO_2(NO_3)_2urea \cdot H_2O + 5H_2O$

(2) $UO_2(NO_3)_2 \cdot 6H_2O + n\ \text{urea} \rightarrow UO_2(NO_3)_2(\text{urea})_n + 6H_2O$
$(n = 1; 2; 3; 4; 5; 6)$
(3) $UO_2(NO_3)_2(\text{urea})_n + m(\text{urea}) \rightarrow UO_2(NO_3)_2(\text{urea})_{n+m}$
$(n = 2; m = 1; 2; 3; 4)$
$(n = 3; m = 1; 2; 3)$
$(n = 4; m = 1; 2)$
$(n = 5; m = 1)$

Therefore, the following complexes have been prepared and characterized:
$UO_2(NO_3)_2\text{urea} \cdot H_2O$ [I]; $UO_2(NO_3)_2(\text{urea})_2$ [II];
$UO_2(NO_3)_2(\text{urea})_3$ [III]; $UO_2(NO_3)_2(\text{urea})_4$ [IV];
$UO_2(NO_3)_2(\text{urea})_5$ [V]; $UO_2(NO_3)_2(\text{urea})_6$ [VI].

The complexes [I] and [VI] are unreported in literature.

EXPERIMENTAL

Materials

Reagent grade uranyl nitrate hexahydrate and urea were used without further purification.

Thermal analysis measurements

Simultaneous TG, DTG and DTA were carried out with a Mettler thermoanalyzer at heating rates between 0.5 and 4°C min^{-1} in dynamic nitrogen atmosphere (10 l h^{-1}). A Mettler T-TD3 crucible holder, 0.3 ml platinum microcrucibles and thermally inactive Al_2O_3 as reference material were used. The reactions were performed by introducing into the thermoanalyzer closely powdered stoichiometric mixtures of the reactants, the total weight of the system being about 25 mg. The ΔH of the formation process of the complexes has been evaluated by measuring the area of DTA peak with a planimeter, for at last five experiences, calibrating the apparatus by melting ΔH. The kinetic parameter, E_a^*, for the decomposition reactions was calculated by literature methods (12, 13).

The simultaneous analysis of evolved gases was performed with a Balzers QMG 311 spectrometer.

I.R. spectra (4000–625 cm^{-1})

They were performed with a Perkin-Elmer 257 spectrophotometer using KBr pellets and hexachlorobutadiene or Nujol mulls between NaCl plates.

RESULTS AND DISCUSSION

The analytical data for the new [I] and [VI] complexes are reported in Table 1. Properties and analytical data of [II]–[V] compounds agree with those reported[7].

The water molecule in [I] is confirmed by thermogravimetric analysis and infrared measurements; the I.R. spectrum shows in the region 3500–3200 cm^{-1} a

TABLE 1

ANALYTICAL DATA FOR THE [I] AND [VI] COMPLEXES

Complex	*U(%)*		*C(%)*		*H(%)*		*N(%)*	
	Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
[I]	50.43	50.12	2.54	2.58	1.28	1.19	11.86	11.51
[VI]	31.56	31.39	9.55	9.30	3.21	3.16	25.99	25.93

broad band assigned to the OH_2 stretching coupled with the NH_2 stretching modes. In the region 2000–625 cm^{-1}, the I.R. spectra of the [I] and [VI] complexes are correspondingly analogous to those of the complexes [II] and [V]; in each case the spectra show the band amide I at 1680 cm^{-1} in the free ligand, shifted to longer wavelengths, thus indicating cation–oxygen bond formation.

THERMAL SYNTHESIS

For the investigated reactant system

$UO_2(NO_3)_2 \cdot 6H_2O + \text{urea}$ (1)

the first weight loss, due to the release of five water molecules, occurs in the range 25–150 °C; the DTA curve shows a very broad endothermic peak which covers this temperature range entirely. If the product $UO_2(NO_3)_2\text{urea} \cdot H_2O$ is cooled and heated again no weight loss or DTA peak is observed in the range 25–150 °C.

The thermoanalytical curves of the investigated reacting system:

$UO_2(NO_3)_2 \cdot 6H_2O + p(\text{urea})$ (2)

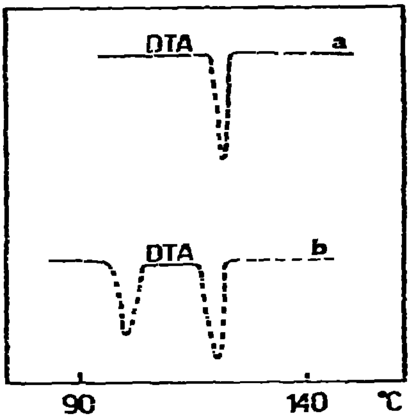
show, in the temperature range 25–150 °C, a weight loss, due to the release of the six water molecules, beginning at room temperature, and a broad DTA endothermic peak.

The thermoanalytical curves of the anhydrous reacting system:

$UO_2(NO_3)_2(\text{urea})_n + m(\text{urea})$ (3)

show, before a weight loss takes place at about 200 °C, two DTA endothermic peaks in the range 80–130 °C.

It is interesting that the thermoanalytical curves from about 200 °C, coincide for the two different systems (2) and (3) when $m + n = p$. In both cases, the same complex $UO_2(NO_3)_2(\text{urea})_{m+n=p}$ is formed. For reaction (2), after the end of the broad peak, when the sample is cooled and then heated again, the first weight loss and the broad DTA peak are not observed. The DTA curve shows only a peak coinciding with the latter DTA one of the corresponding system (3). This endothermic peak is due to the melting process of the obtained complex that takes place without decomposition whereas the former DTA peak in system (3) arises from complex formation. Examples of DTA curves are reported in Fig. 1.



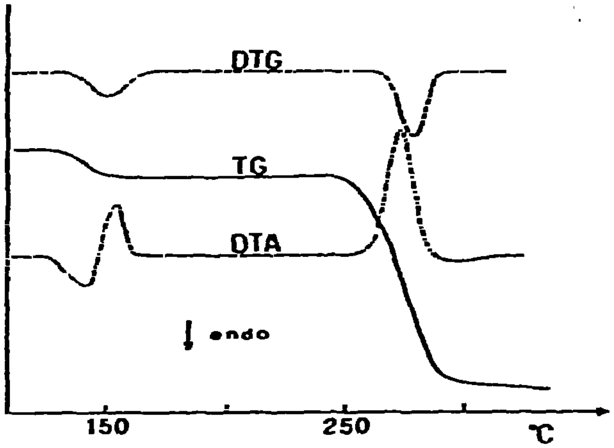


Fig. 1. (a) DTA curve of the product $UO_2(NO_3)_2(urea)_3$; (b) DTA curve of the system $UO_2(NO_3)_2(urea)_2$ + urea in the temperature range 70–150°C.

Fig. 2. Thermal decomposition of complex [I].

TABLE 2

STARTING TEMPERATURES (°C) OF COMPLEX FORMATION (T_1) AND COMPLEX MELTING (T_2), AND VALUES OF ENTHALPY OF FORMATION (kcal mol^{-1}) OF COMPLEXES [I]–[VI] BY THE REACTION: $UO_2(NO_3)_2(urea)_n$ + *m* urea

Value of n	*Value of m*	T_1	T_2	ΔH	*Reaction product*
2	0	—	202	—	—
2	1	74	114	1.2	[III]
2	2	80	110	2.7	[IV]
2	3	80	118	4.5	[V]
2	4	78	120	8.7	[VI]
3	1	80	110	1.6	[IV]
3	2	80	118	3.4	[V]
3	3	78	120	7.6	[VI]
4	1	74	118	1.7	[V]
4	2	76	120	6.1	[VI]
5	1	80	120	4.3	[VI]

In reaction (2), the water substituted by urea in the coordination sphere, endothermically evolves. This is the only exhibited process, and it covers the entire thermal range in which the DTA curve should show the formation and melting peaks of the compounds. The temperatures at which the two DTA peaks begin and the ΔH values for reaction (3) are reported in Table 2.

Reaction (3) involves the substitution of one or more bonds U–O of nitric group with bonds U–O of urea. It appears that the formation of all the complexes is enthalpically unfavored.

The first step of the thermal decomposition of $UO_2(NO_3)_2urea \cdot H_2O$ corresponds to the following stoichiometry:

$$UO_2(NO_3)_2urea \cdot H_2O\ (s) \rightarrow UO_2(NO_3)_2urea\ (s) + H_2O\ (v)$$

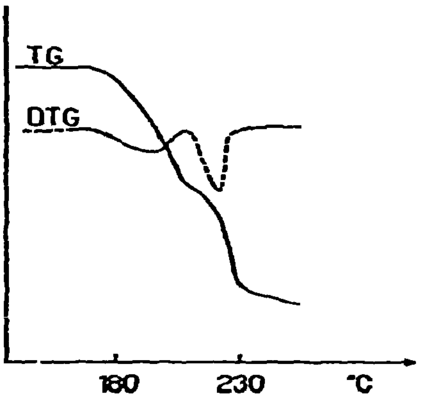
The DTA curve (see Fig. 2) shows that an exothermic process follows the endothermic one before the dissociation is completed, in agreement with the occurrence of simultaneous structural rearrangements. Probably, oxygen atoms of the nitric group, that are not engaged in the formation of the initial units, can fill the coordination sphere of adjacent uranium atoms giving rise to polymeric structures.

For the complexes [II]–[IV], the first reaction is:

$$UO_2(NO_3)_2urea_n\ (s) \rightarrow UO_2(NO_3)_2urea\ (s) + (n - 1)\ urea\ (v)$$

This is the stoichiometry of the overall process. However, when n is greater than two, DTG curves do not exhibit a regular behaviour, thus suggesting that a stepwise release of urea occurs, though the different steps are overlapped and unseparable in the described experimental conditions. An example is reported in Fig. 3. Owing to the impossibility to separate the successive steps, this is not a method to obtain one complex from another by release of the required number of moles of urea.

$[UO_2(NO_3)_2urea]_n$ obtained from [II], [III], and [IV] shows the same thermoanalytical behaviour of that obtained from [I] and, therefore, it is assumed to be polymeric too. This complex decomposes exhibiting only an exothermic DTA peak, giving rise to UO_3 and unidentified products. It is probable that ox–red reactions involving urea molecule and nitric groups occur. This conclusion is supported by the mass spectra of the evolved gases: the recorded spectra show, during the decomposition, peaks corresponding to NO and CO_2. At temperatures above 500°C, UO_3 gives, as known, U_3O_8.



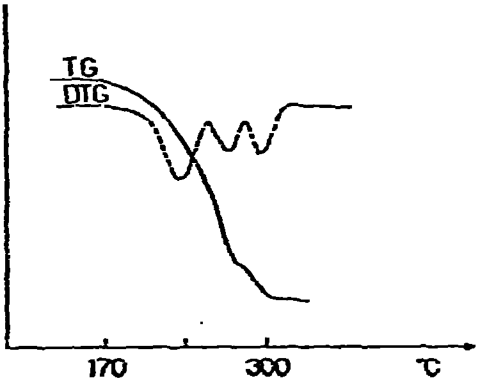


Fig. 3. Thermal decomposition of complex [III].

Fig. 4. Thermal decomposition of complex [V].

TABLE 3

"ACTIVATION ENERGY", E_a^*, (kcal mol^{-1}) VALUES OF THE TWO PROCESSES OF DECOMPOSITION OF [I]–[VI] COMPLEXES

Complex	E_{a1}^*	E_{a2}^*
[I]	21.9	106
[II]	41.6	106
[III]	25.8	106
[IV]	14.9	106
[V]	29.7	57
[VI]	32.8	63

For the complexes [V] and [VI]. the decomposition process is quite different (Fig. 4). In neither of these cases there is formation. as intermediate product, of $[UO_2(NO_3)_2\text{urea}]$, and it is impossible to follow the stoichiometry of the processes by thermoanalytical curves. Some indications were obtained by mass spectroscopic analysis of the evolved gases: a sharp increase of 17 peak was observed at the beginning of the weight loss. It is known, on the other hand, that processes of deamination of urea may occur through the condensation of urea molecules. It is therefore reasonable to suppose that the steric and electronic situation achieves the condensation of five or six molecules of urea giving rise to very unstable complexes. Only after the end of deamination. the decomposition of nitric groups was observed by mass spectra.

The "activation energies", E_{a1}^*, reported in Table 3, concerning the release of urea molecules for the complexes [II]. [III], and [IV] show that the replacement of nitric groups with urea molecules in the coordination sphere of uranyl ion, increases the weakness of the U–O bonds involved in this first step of decomposition. This is in agreement with the endothermicity of the formation process of the same complexes.

The E_{a2}^* values (see Table 3) of the second step of decomposition, are equal for the complexes [II], [III], and [IV], but different for [V] and [VI], confirming the two observed thermal behaviours.

It has been reported[7] that the complex [IV] must be considered as a mixture, in the 1 : 1 stoichiometric ratios of the complexes [III] and [V]. The described thermoanalytical results do not agree with this conclusion. However, it cannot be excluded that the complexes [III] and [V], present in the 1 : 1 stoichiometric ratio, during the melting, give actually rise to the complex [IV].

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