

## REACTIONS OF UREA WITH OXIDES OF Mo(VI), V(V) AND Se(IV), AT HIGH TEMPERATURE

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### Abstract

The molybdenum(VI) nitrate salt,  $[V_2(O)_4(OH)(NH_2)]$  complex and selenium metal were obtained by a new reaction of urea with  $MoO_3$ ,  $V_2O_5$  and  $SeO_2$ , respectively, in aqueous media at  $\sim 90^\circ C$ . The solids formed  $Mo(NO_3)_6$ ,  $[V_2(O)_4(OH)(NH_2)]$  and Se metal were characterized through elemental analysis and infrared spectroscopy. Thermo-gravimetric(TG) and differential thermal analysis (DTA) measurements of the  $Mo(NO_3)_6$  salt and the  $[V_2(O)_4(OH)(NH_2)]$  complex, along with the infrared spectra of the final decomposition products were also recorded. The data obtained are in agreement with the detected structures and shows that the  $Mo(NO_3)_6$  salt and the  $[V_2(O)_4(OH)(NH_2)]$  complex were decomposed to form  $MoO_3$  and  $V_2O_5$ .

### Resumen

Nitrato de molibdeno (VI), conjuntamente con el complejo  $[V_2(O)_4(OH)(NH_2)]$  y selenio metálico fueron sintetizados mediante la reacción entre urea y los reactivos  $MoO_3$ ,  $V_2O_5$  y  $SeO_2$ , respectivamente, en medio acuoso a  $\sim 90^\circ C$ . Los sólidos obtenidos,  $Mo(NO_3)_6$ ,  $[V_2(O)_4(OH)(NH_2)]$  y Se metálico fueron caracterizados mediante análisis elemental y espectroscopia de Infrarrojo. Termogravimetría (TG) y análisis térmico diferencial (DTA) de la sal  $Mo(NO_3)_6$  y del complejo  $[V_2(O)_4(OH)(NH_2)]$  fueron complementados con espectros infrarrojo de los correspondientes productos de la descomposición final. Los datos obtenidos concuerdan con las estructuras propuestas y confirman que la sal  $Mo(NO_3)_6$  y el complejo  $[V_2(O)_4(OH)(NH_2)]$  se descomponen para formar  $MoO_3$  y  $V_2O_5$ .

### Introduction

Many coordination complexes in which the donor bases are urea or thiourea have been reported. Quagliano and co-workers [1] have established that among the urea complexes, some coordinated through one of the nitrogen atoms and others through the oxygen atom of the urea molecule. The reaction of urea with transition metal ions at room temperature has been extensively studied [2-7].

The reaction of urea with these metal ions at high temperature is rare in the literature. However, the available publications describe an interesting feature: the reaction products depend not only on the type of metal ions but also on the metal salt used in the

reaction [8-12]. Free urea is known to decompose in aqueous media to  $\text{CO}_2$  and  $\text{NH}_3$  and the decomposition increases with temperature. The new idea in this investigation relates to the role of metal ions on the decomposition of urea.

The aim of this work was to study the nature of the reaction products of urea with  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{SeO}_2$  in aqueous solutions at high temperature  $\sim 90^\circ\text{C}$ , in order to investigate the mechanism of their decomposition. The final reaction products (oxides) were well characterized through elemental analysis, infrared spectra as well as thermogravimetric (TGA) and differential thermal (DTA) analyses. The final decomposition products were identified by means of infrared spectra.

## Experimental

Reagent grade chemicals were used throughout this investigation. The blue solid salt,  $\text{Mo}(\text{NO}_3)_6$ , orange solid complex,  $[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$ , and dark brown selenium metal were prepared by addition of 0.1M of each solid oxides ( $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{SeO}_2$ ) to 50 mL of an aqueous solution of 1.0M urea. The mixtures were heated with stirring on a water bath to approx.  $90^\circ\text{C}$  for about 18 h. The solid products were precipitated, (in the case of  $\text{MoO}_3$  - urea mixture, it gave a blue liquid product which precipitated by adding ethanol), filtered off, washed several times with hot water for  $\text{V}_2\text{O}_5$  - urea;  $\text{SeO}_2$  - urea and with ethanol for  $\text{MoO}_3$  - urea, dried at  $70^\circ\text{C}$  in an oven for 3h., and then in vacuo over silica gel. The solid reaction products were characterized by elemental analysis, infrared spectra and thermal analysis (DTA, TGA).

The elemental analysis data of the solid products are summarized as follows: (calculated values are shown in parenthesis)

- i)  $\text{MoO}_3$  - urea system,  $\text{Mo}(\text{NO}_3)_6$ ; N, 17.63% (17.95%) ; Mo, 19.89% (20.50%).
- ii)  $\text{V}_2\text{O}_5$  - urea system,  $[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$ ; H, 1.48% (1.51%); N, 6.97% (7.04); V, 50.94% (51.21%).
- iii)  $\text{SeO}_2$  - urea system, Se metal, the elemental analysis demonstrates the absence of carbon, hydrogen and nitrogen.

Molybdenum(VI), vanadium(V) and selenium contents in the three solid reaction products were determined gravimetrically as metal oxides, and also determined by using atomic absorption. A spectrometer model PYE-UNICAM SP 1900 fitted with a suitable lamp was used for this purpose. The metal percentages obtained by using atomic absorption gave values within expected limits.

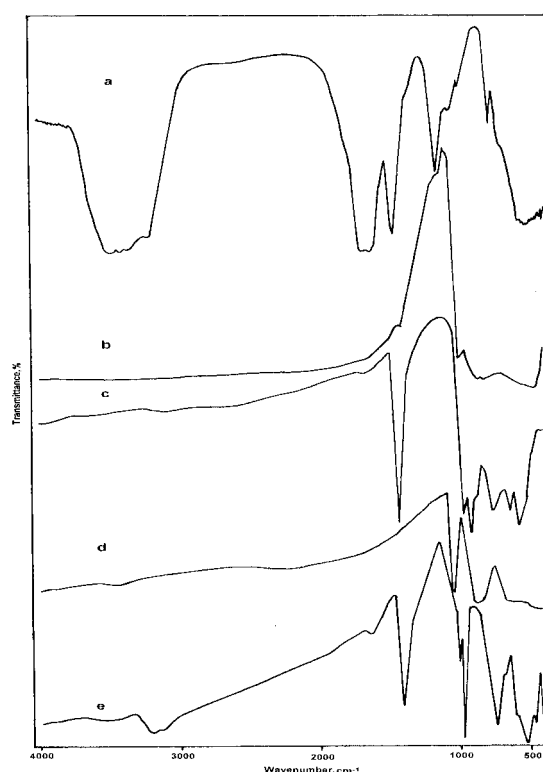
The infrared spectra of urea, reactants and solid reaction products were recorded with KBr discs using a Genesis II FT IR spectrophotometer. Thermogravimetry (TG), and differential thermal analysis were carried out under a  $\text{N}_2$ -atmosphere using detectors Shimadzu TG-50 H and DTA - 50H, respectively.

## Results and discussion

The interaction between metal oxides and urea has not yet been studied. The solid products molybdenum (VI) nitrate salt,  $[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$  complex and selenium metal

are produced during the aqueous reaction of urea with  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{SeO}_2$ , respectively. The infrared spectra of urea, reactants and the solid products mentioned above are shown in Figure 1. Band assignments of the two products  $\text{Mo}(\text{NO}_3)_6$  and  $[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$ , are given in Table 1.

**1-  $\text{Mo}(\text{NO}_3)_6$  Salt:** This compound was obtained through the reaction of  $\text{MoO}_3$  with urea at high temperature, approx.  $90^\circ\text{C}$ . Based on elemental analysis data together with a qualitative black-ring test for ionic nitrate using freshly prepared  $\text{FeSO}_4$  solution and concentrated sulfuric acid, a black ring of  $\text{FeSO}_4 \cdot \text{NO}$  is formed and the infrared spectrum of the obtained compound led to its identification as molybdenum(VI) nitrate,  $\text{Mo}(\text{NO}_3)_6$ .



**Figure 1.** Infrared spectra of a: Urea; b:  $\text{MoO}_3$ ; c:  $\text{Mo}(\text{NO}_3)_6$ ; d:  $\text{V}_2\text{O}_5$  and e:  $[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$

The infrared spectrum for this product (Figure 1c) clearly indicates the absence of any bands arising from coordinated urea, instead a group of bands characteristic of ionic nitrate [13]  $\text{NO}_3^-$ , are observed. The formation of  $\text{Mo}(\text{NO}_3)_6$  is greatly supported by comparison with the infrared spectrum of the commercially molybdenum(VI) nitrate. The two spectra are very similar indicating the obtained product is  $\text{Mo}(\text{NO}_3)_6$ .

In order to be sure about the proposed formula and structure for the simple salt,  $\text{Mo}(\text{NO}_3)_6$ , thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out for this salt under a  $\text{N}_2$  flow. DTA and TGA thermograms are shown in Figure 2. Table 2 gives the maximum temperature values,  $T_{\text{max}}/(^{\circ}\text{C})$ , together with the correspond-

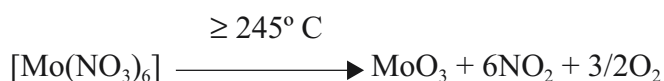
ing weight loss for each step of the decomposition of the salt. The obtained data strongly support the structure proposed for the salt under investigation as follows.

**Table 1.** Infrared frequencies ( $cm^{-1}$ ) and tentative assignments for  $Mo(NO_3)_6$  and  $[V_2(O)_4(OH)(NH_2)]$  compounds.

$Mo(NO_3)_6$		$[V_2(O)_4(OH)(NH_2)]$	
Frequency	Assignments	Frequency	Assignments
3438 s,br	$\nu(O-H); H_2O$ of KBr	3485 ms,br	$\nu(O-H); OH^-$
1405 vs	$\nu_{as}(N-O); NO_3$	3202 s,br	$\nu_{as}(N-H); NH_2^-$
949 s	$\nu_s(N-O); NO_3$	3118 w,sh	$\nu_s(N-H); NH_2^-$
902 s	$\delta_b(NO_3)$	1630 ms	$\delta(H_2O); H_2O$ of KBr
855 sh		1400 vs	$\delta_b(NH_2^-)$
750 s	$\delta_r(NO_3)$	1007 ms	$\delta_w(NH_2^-) + \nu(V=O)$
630 s		970 vs	$\delta_t(NH_2^-) + \nu(V=O)$
557 s	$\delta_w(NO_3)$	740 vs	$\delta(V-OH-V)$
515 sh		672 sh	$\delta_r(NH_2^-)$
		598 sh	$\nu(V-N); NH_2^-$
		525 s	
		467 ms	$\nu(V-O); OH^-$
		405 s	

**Key:** *s* = strong; *w* = weak; *m* = medium; *sh* = shoulder; *v* = very; *br* = broad;  $\nu$  = stretching;  $\delta$  = bending;  $\delta_w$  = wagging;  $\delta_t$  = twisting;  $\delta_r$  = rocking.

The thermal decomposition of the molybdenum (VI) nitrate salt proceeds approximately with one main degradation step. The only one stage occurs at a maximum temperature of 245°C. The weight loss associated with this stage is 69.05% which is closer to the theoretical value of 69.32% corresponding to the loss of  $6NO_2 + 3/2 O_2$  as will be described by the mechanism of the decomposition. The final thermal product obtained at 600°C is  $MoO_3$ , judging from its measured infrared spectrum shown in Figure 1b.



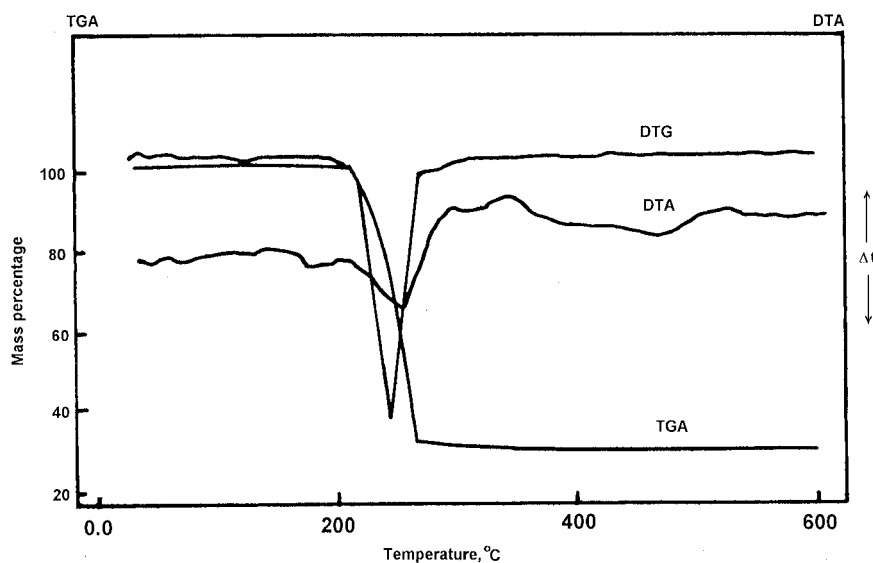


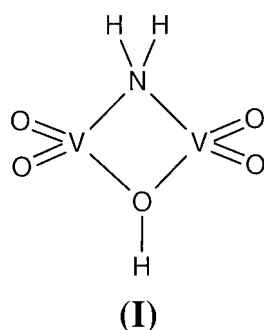
Figure 2. Thermal analysis TGA, DTG and DTA for  $\text{Mo}(\text{NO}_3)_6$  salt.

Table 2. Maximum temperatures,  $T_{\text{max}}/^\circ\text{C}$ , and weight loss values of the decomposition stages for the  $\text{Mo}(\text{NO}_3)_6$  and  $[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$  compounds.

Complexes	Decomposition	$T_{\text{max}}/^\circ\text{C}$	Lost species	% weight losses	
				Found	Calc.
$\text{Mo}(\text{NO}_3)_6$	First stage	$\geq 245^\circ\text{C}$	$6\text{NO}_2 + 3/2\text{O}_2$	69.05%	69.32%
	Total loss			69.05%	69.32%
	Residue			30.95%	30.68%
$[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$	First stage	$\geq 230^\circ\text{C}$	$\text{NH}_3$	8.48%	8.55%
	Total loss			8.48%	8.55%
	Residue			91.52%	91.45%

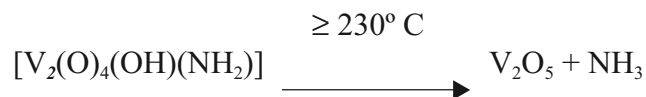
## 2- $\text{V}_2(\text{O})_4(\text{NH})(\text{OH})$ Complex:

The infrared spectrum of the new complex,  $[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$ , in a KBr disc, is shown in Figure 1e, its band assignments are given in Table 1. The spectrum shows no bands due to coordinated urea, whereas characteristic signals arising from coordinated  $\text{O}_2^-$ ,  $\text{NH}_2^-$  and  $\text{OH}^-$  groups are observed. Accordingly, the most probable geometrical structure for this complex is shown in structure (I) where both  $\text{NH}_2^-$  and  $\text{OH}^-$  exist as bridging ligands.

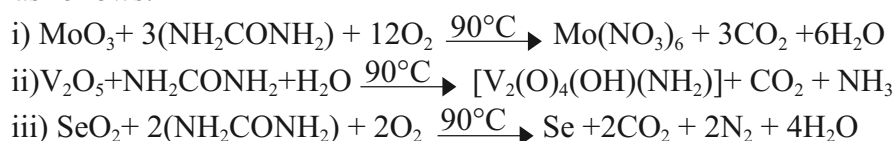


The coordination  $\text{-NH}_2$  group shows a set of bands that agree with those previously reported [1,13-15] for related complexes. The two bands at  $3202$  and  $3118\text{ cm}^{-1}$  are assigned to the N-H stretching modes corresponding to the antisymmetric and symmetric modes, respectively. The four bands at  $1400$ ,  $1007$ ,  $970$  and  $672\text{ cm}^{-1}$  are due to the bending, wagging, twisting and rocking vibration of the coordinated  $\text{-NH}_2$  group, respectively. The V-N stretching frequency is of particular interest, because it provides direct information about the coordination bond. According to Nakamoto [13], the bands at  $525$  and  $598\text{ cm}^{-1}$  are attributed to the  $\nu(\text{V-N})$  stretching mode. The  $\nu(\text{O-H})$  vibration of the bridged hydroxide,  $\text{OH}^-$  ligand was assigned to the weak intensity band at  $3485\text{ cm}^{-1}$ . Like many other compounds containing the  $\text{M=O}$  groups, that exhibit the  $\text{M=O}$  vibration bands in  $1050 - 800\text{ cm}^{-1}$  region [16, 17], the stretching frequency of the type  $\nu(\text{V=O})$  in our complex is assigned to the doublet bands that observed at  $1007$  and  $970\text{ cm}^{-1}$ . The bending OH ( $\text{V-OH-V}$ ) appears at ca.  $740\text{ cm}^{-1}$  [18], while V-O (oxygen of  $\text{OH}^-$ ) is observed at  $467$  and  $405\text{ cm}^{-1}$  [19].

The thermal degradation of  $[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$  complex take place in one degradation stage, Figure 3. This stage of decomposition occurs at the maximum temperature of  $230^\circ\text{C}$ , accompanied by a weight loss  $8.48\%$  corresponding to the loss of  $\text{NH}_3$  in agreement with the theoretical weight loss value of  $8.55\%$ . This mechanism of decomposition is supported by the infrared spectrum of the final thermal decomposition product,  $\text{V}_2\text{O}_5$ , Figure 1 d.



The formation of selenium metal upon the reaction of urea with selenium dioxide at high temperature indicates that the reduction process of  $\text{Se(IV)}$  oxide occurs during the decomposition of urea into  $\text{NH}_3 + \text{CO}_2$ . Finally, the formation of these three solid reaction products,  $\text{Mo}(\text{NO}_3)_6$ ,  $[\text{V}_2(\text{O})_4(\text{OH})(\text{NH}_2)]$  and  $\text{Se}$  metal upon the reaction of urea with  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{SeO}_2$  respectively, in aqueous media at high temperature is proposed to occur as follows:



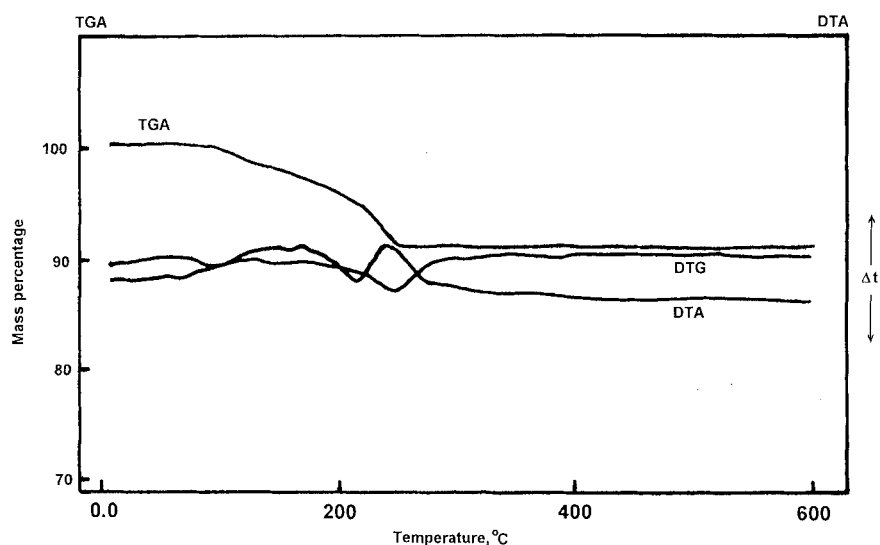


Figure 3. Thermal analysis TGA, DTG and DTA for the  $[V_2(O)_4(OH)(NH_2)]$  complex.

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