

THERMAL DECOMPOSITION OF ALUMINUM, IRON AND MANGANESE COMPLEXES OF UREA

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ABSTRACT

The thermal decomposition of the urea complexes $\text{Al(urea)}_6(\text{NO}_3)_3$, $\text{Fe(urea)}_6(\text{NO}_3)_3$ and $\text{Mn(urea)}_4\text{Cl}_2$ have been studied in air and argon by simultaneous recording of thermogravimetric (TG), differential thermal gravimetric (DTG) and differential thermal analysis (DTA) curves. The metal oxides formed by the decompositions have been identified by X-ray powder diffraction and decomposition stoichiometries have been proposed and discussed.

INTRODUCTION

Urea complexes with metals are well known, and the nature of coordination of some has been determined by IR spectrometry [1]. However, reports of thermal analysis of metal–urea compounds are limited to studies of complexes of uranyl nitrate [2]; chromium nitrate and chloride [3]; nickel nitrate [4]; brief reports on complexes with cobalt nitrate [5]; and cadmium, manganese and zinc acetates [6].

Metal salt–urea complexes are presently being investigated as possible intermediates for improving the efficiency of urea as a fertilizer and as a means of introducing required trace elements into the soil [7]. As part of this study, the thermal behavior of the complexes $\text{Al(urea)}_6(\text{NO}_3)_3$, $\text{Fe(urea)}_6(\text{NO}_3)_3$ and $\text{Mn(urea)}_4\text{Cl}_2$ has been examined using a Setaram thermal analyzer. This analyzer allows the simultaneous measurement of the thermogravimetric (TG), differential thermal gravimetric (DTG) and differential thermal analysis (DTA) curves. The thermal behavior of the complexes was examined in an inert atmosphere, argon, as well as in air, and the residues remaining after decomposition were identified by their X-ray diffraction patterns.

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TABLE I
Analytical data for urea complexes

Complex	Found (%)					Calculated (%)				
	C	H	N	Cl	M ^a	C	H	N	Cl	M ^a
Al(urea) ₆ (NO ₃) ₃	12.55	4.35	36.56	—	4.54	12.53	4.36	36.59	—	4.70
Fe(urea) ₆ (NO ₃) ₃	12.15	4.16	34.89	—	9.30	11.95	4.15	34.84	—	9.26
Mn(urea) ₄ Cl ₂	13.10	4.43	30.62	19.25	14.88	13.12	4.41	30.61	19.37	15.01

^a Metal.

EXPERIMENTAL

Preparation of the compounds

The aluminum and iron compounds were prepared by dissolving the metal salt hydrate and required molar ratio of urea in the minimum of warm water and allowing the complex to crystallize. The manganese complex could not be obtained by this procedure and was prepared by a solid-state reaction in which manganese chloride hydrate was ground with the required molar ratio of urea in a ball mill for several hours. The resulting paste was dried in a vacuum oven to give the desired complex. The compounds were characterized by elemental analysis (Table 1) and IR spectrometry (Table 2). The IR spectra were obtained as KBr pellets on a Perkin-Elmer 283 infrared spectrophotometer.

Thermal analysis

Thermal data were obtained using a Setaram thermal analysis system, which comprises a B-70 electronic balance, an RT 3000C temperature regulator with a PT 3000 temperature programmer, a DT 25 differentiator and a C3-ATD differential thermal analysis assembly. The curves were

TABLE 2

Infrared data for urea complexes

Complex	$\nu(\text{C-O})$ (cm^{-1})	$\nu(\text{C-N})$ (cm^{-1})
Urea	1682	1465
$\text{Al}(\text{urea})_6(\text{NO}_3)_3$	1662	1500
$\text{Fe}(\text{urea})_6(\text{NO}_3)_3$	1655	1500
$\text{Mn}(\text{urea})_4\text{Cl}_2$	1676	1494

TABLE 3

Composition of residues from thermal decompositions of urea complexes

Complex	Atmosphere	Residue	Weight percentage of residue	
			Found	Calc.
$\text{Al}(\text{urea})_6(\text{NO}_3)_3$	Argon	Al_2O_3	11.6	8.9
	Air	Al_2O_3	10.1	8.9
$\text{Fe}(\text{urea})_6(\text{NO}_3)_3$	Argon	Fe_3O_4	15.1	12.8
	Air	Fe_2O_3	15.0	13.3
$\text{Mn}(\text{urea})_4\text{Cl}_2$	Argon	MnO	18.6	19.4
	Air	Mn_3O_4	21.5	20.9

recorded on a Texas Instruments Servo/riter II potentiometric recorder. The measurements were made on 50 mg samples in a platinum crucible. The heating rate was $5^{\circ}\text{C min}^{-1}$ over the range of ambient to 1000°C . The atmosphere was flowing argon (99.995%, Matheson) or air (Ultra Zero, Matheson) at a flow rate of $6\text{ cm}^3\text{ min}^{-1}$. The chamber pressure was one atmosphere. Residues from the thermal decompositions were identified (Table 3) with a Siemens D-500 X-ray diffractometer (XRD) using $\text{Cu-K}\alpha$ ($\lambda = 1.541780\text{ \AA}$) radiation.

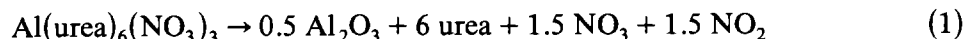
RESULTS

Infrared spectra

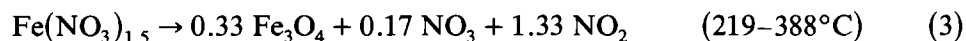
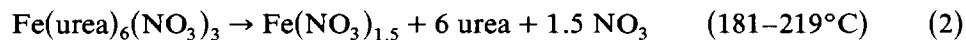
The shift of the (C–O) stretching frequency in urea to lower wavenumbers in the complexes and the shift of the (C–N) stretching frequency to higher wavenumbers (Table 2) indicate that the urea molecules are coordinated to the metals through the oxygen atom [1].

Decompositions in argon

The TG, DTG and DTA curves for the complexes (Fig. 1) show that the aluminum nitrate–urea complex loses all six urea molecules and nitric oxides in a single step in the range $205\text{--}533^{\circ}\text{C}$ and leaves a residue of Al_2O_3 . The DTA curve shows two peaks; the first at 236°C is an endothermic change and the second at 285°C is an exothermic change associated with the formation of Al_2O_3 . On the basis of the observed loss of all the urea and nitric oxides to give Al_2O_3 , the following stoichiometric decomposition is proposed



The iron nitrate–urea complex shows a two-stage decomposition where the first stage occurs in the range $181\text{--}219^{\circ}\text{C}$ and the second in the range $219\text{--}388^{\circ}\text{C}$. The residue is Fe_3O_4 , and the proposed stoichiometry for the two stages based on the weight losses (Table 4) is



The DTA curve shows an endothermic peak at 193°C and two exothermic peaks at 202°C and 248°C associated with the two decomposition steps.

The manganese chloride–urea complex shows a much more complicated decomposition pattern that involves four separate steps and leaves a final residue of MnO . The weight losses for each step are shown in Table 4. The

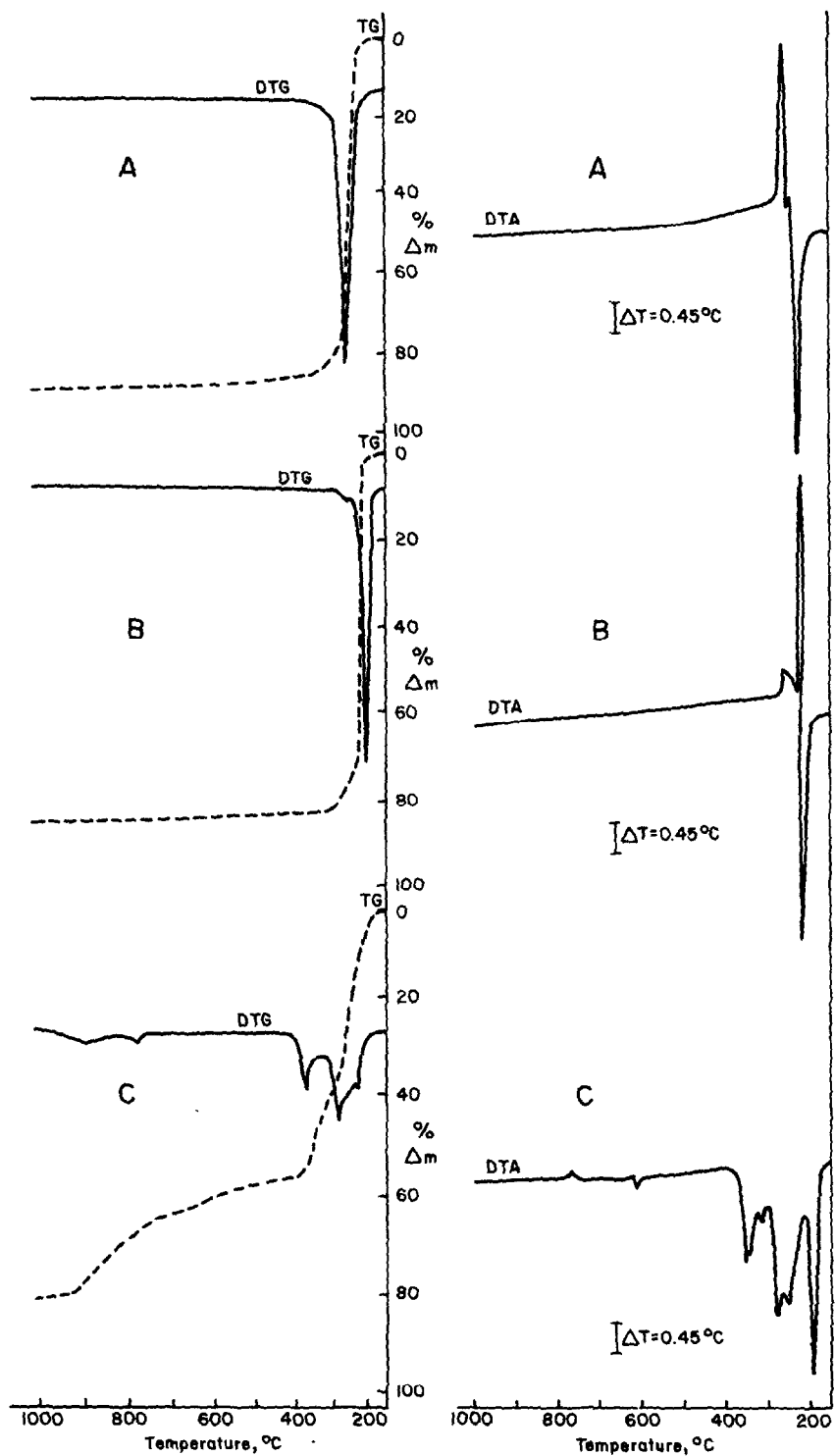


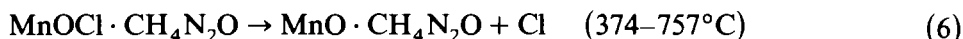
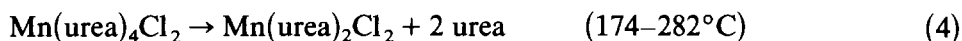
Fig. 1. TG, DTG and DTA of urea complexes in argon. (A) $\text{Al}(\text{urea})_6(\text{NO}_3)_3$; (B) $\text{Fe}(\text{urea})_6(\text{NO}_3)_3$; (C) $\text{Mn}(\text{urea})_4\text{Cl}_2$.

TABLE 4

Thermogravimetric data for $\text{Fe(urea)}_6(\text{NO}_3)_3$ and $\text{Mn(urea)}_4\text{Cl}_2$ in argon

Complex	Temperature range (°C)	% Weight loss	
		Found	Calc.
$\text{Fe(urea)}_6(\text{NO}_3)_3$	181–219	75.0	75.3
	219–388	9.9	11.8
$\text{Mn(urea)}_4\text{Cl}_2$	174–282	33.7	32.8
	282–374	21.3	21.7
	374–757	9.2	9.7
	757–937	17.2	16.4

steps correspond to the following stoichiometric reactions



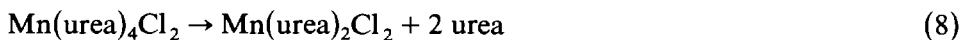
The DTA curve shows multiple endothermic peaks in the range 174–366°C, a small endothermic peak at 637°C and an exothermic peak at 781°C, which is probably associated with the formation of MnO.

Decompositions in air

The TG, DTG, and DTA curves for the three complexes (Fig. 2) show that the aluminum nitrate–urea complex loses all six urea molecules and nitric oxides in one step in the range 219–385°C and leaves a residue of Al_2O_3 . The DTA curve shows two strong peaks; an endothermic peak at 230°C and an exothermic peak at 315°C. The proposed stoichiometry for this decomposition is the same as that in argon.

The iron nitrate–urea complex shows a single-stage decomposition in air in the range 174–251°C that leaves a residue of Fe_2O_3 . The proposed stoichiometry for the decomposition is the same as that proposed for the aluminum complex. The DTA curve shows two peaks; an endothermic change at 189°C and an exothermic change at 201°C.

The manganese chloride–urea complex exhibits a multistep decomposition whose steps are shown in Table 5. The XRD shows the final residue to be Mn_3O_4 . The first two decomposition steps overlap and cannot be separated on the TG curve, but they do show separate DTG peaks. The steps correspond to the following proposed reactions



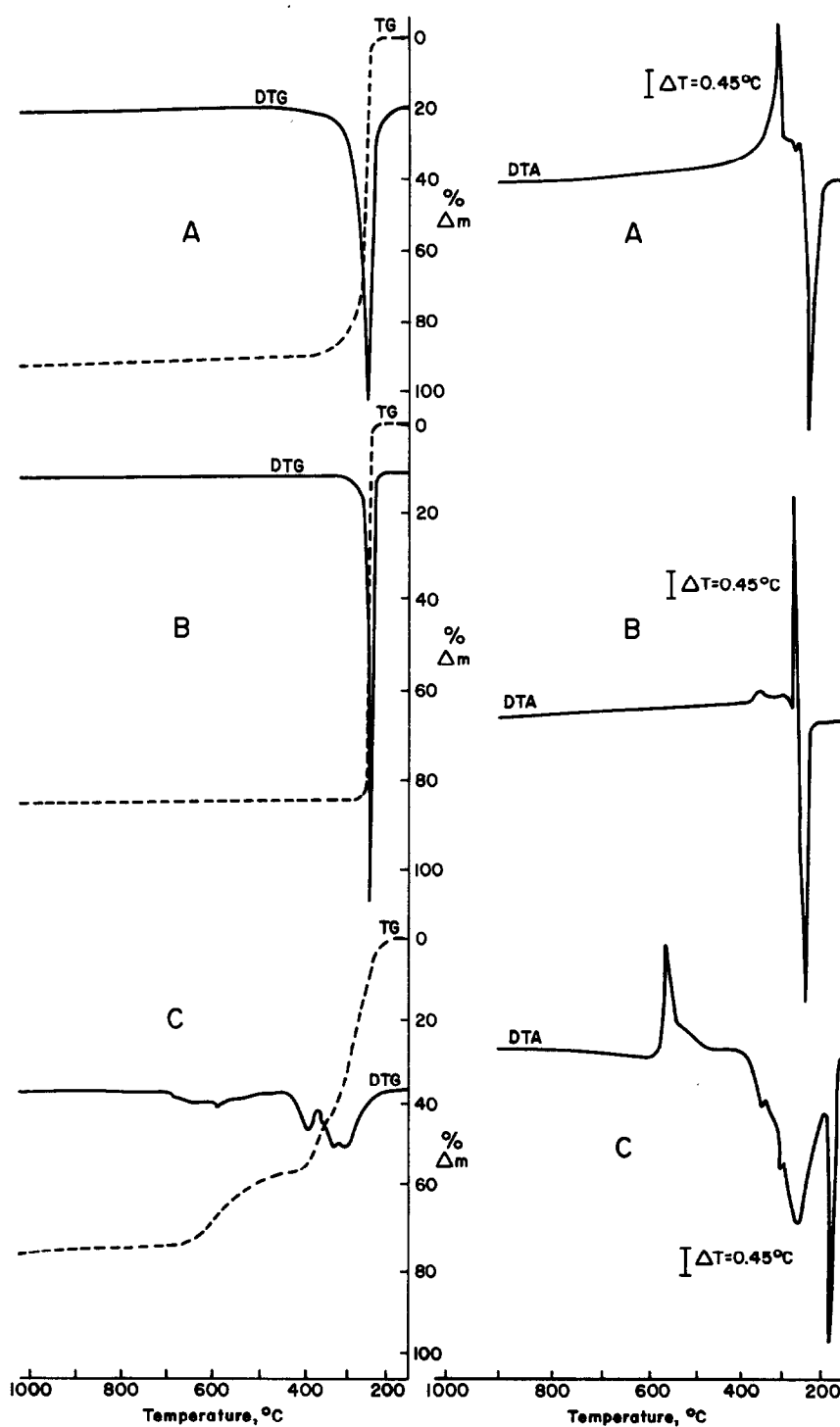


Fig. 2. TG, DTG and DTA of urea complexes in air. (A) $\text{Al}(\text{urea})_6(\text{NO}_3)_3$; (B) $\text{Fe}(\text{urea})_6(\text{NO}_3)_3$; (C) $\text{Mn}(\text{urea})_4\text{Cl}_2$.

TABLE 5

Thermogravimetric data for $\text{Mn(urea)}_4\text{Cl}_2$ in air

Temperature range (°C)	% Weight loss	
	Found	Calc.
180–390	55.7	54.5
390–648	20.5	21.7
648–897	2.3	2.7



The DTA curve shows multiple endothermic peaks and a strong exothermic peak at 563°C that is probably associated with the formation of MnO_2 . The decomposition of MnO_2 to Mn_3O_4 is in the range of 648–897°C, which corresponds with data given by Duval [8] although no intermediate Mn_2O_3 was identified.

DISCUSSION

The use of the Setaram thermal analysis system allows the simultaneous recording of TG, DTG and DTA curves with the resulting benefit that the thermogravimetric and differential thermal analysis curves are obtained under identical atmospheric conditions and heating rates.

The thermal decompositions of the aluminum and iron nitrate–urea complexes show basically the same pattern of an initial endothermic change that can be attributed to melting and a strong exothermic effect associated with loss of urea and nitric oxides and the formation of the metal oxides. This general pattern agrees well with the thermal decomposition of $\text{Cr(urea)}_6(\text{NO}_3)_3$ in air as reported by Janicki et al. [3]. In the aluminum and iron complexes, as well as the chromium [3], weight loss begins before melting. The loss of urea and nitric oxides from the aluminum and iron complexes occurs over a wider temperature range in argon than in air. The only oxide form of aluminum, Al_2O_3 , is formed in both argon and air. However, the iron complex decomposes in argon to the mixed Fe(II)–Fe(III) oxide Fe_3O_4 while decomposition in air gives the Fe(III) oxide Fe_2O_3 .

The decomposition of the chloride complex $\text{Mn(urea)}_4\text{Cl}_2$ is a multistep process involving loss of urea molecules, as well as part of the urea and chlorine, with the oxygen for MnO (in argon) coming from the urea molecule. In air the stepwise decomposition occurs over a smaller tempera-

ture range with formation of MnO_2 . MnO_2 decomposes further in the range of 648–897°C to give Mn_3O_4 , as reported previously [8].

These results support previous studies on the effect of the anion on the thermal decomposition pattern of urea–metal salt complexes [3,5]. The nitrate complexes decompose in a single-stage process, whereas the chloride complex decomposes in a multistep process.

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