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STUDIES ON THE STRUCTURE AND THERMAL BEHAVIOUR OF THE Mn–UREA COMPLEX

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ABSTRACT

The urea complex of manganese was synthesized and its structure established to be $[Mn(Urea)(H_2O)_3Cl_2]$ from elemental analyses, IR and UV and visible spectroscopy and magnetic susceptibility measurements. The thermal behaviour has been studied by thermogravimetry (TG) in nitrogen and air atmospheres and differential thermal analysis (DTA) in air. TG analysis shows three main steps of decomposition leading to oxide formation in the final stage when the complex is heated in air, and $MnCl_2$ formation when it is heated in nitrogen. The kinetics of decomposition of the complex have been studied. Plots of the Coats–Redfern equation show two breaks from which three values of the activation energy are reported. From the results, it is concluded that decomposition of the complex is a heterogeneous process.

INTRODUCTION

Metal–urea complexes are a very important class of compounds that find application in many fields such as fertilizers, medicines, etc. Moreover, most of the transition metal ions are recognised to be plant nutrients. Among these, manganese is used as a catalyst in the plant enzyme system [1] as well as an urease inhibitor [2]. In order to explain the mechanism of action of manganese–urea complexes in various physicochemical processes, it is necessary to have a complete knowledge of the molecular structure and thermal behaviour of the compounds. From the above viewpoint, the present work has been carried out. In an earlier communication [3], we reported the molecular structure and phase transformations of the copper–urea system.

The present paper describes the preparation of a manganese–urea complex, together with the results of thermal analysis, electronic spectra, IR spectra and magnetic measurements.

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PREPARATION OF THE COMPLEX

An ethanolic solution of manganese(II) chloride was prepared by dissolving 5 gm (0.025 mole) $MnCl_2 \cdot 4H_2O$ (BDH) in 100 ml ethanol. This solution was added to a nonaqueous solution of urea prepared by dissolving 10 gm in ~ 100 ml ethanol. The pH of the mixture was 4.2. The solutions were allowed to reflux on a water bath for ~ 3 h; the resultant solid was filtered and washed with ethanol and acetone to apparent dryness. The complex was stored in a vacuum desiccator over calcium chloride until used. The complex corresponds to the composition $[Mn(CN_2H_4O)(H_2O)_3Cl_2]$. Analysis of the complex gave Mn, 23.05%; C, 5.08%; H, 3.50%; N, 11.87%; and Cl, 30%. Calculated values for the complex are Mn, 22.91%; C, 5.0%; H, 3.34%; N, 11.60%; and Cl, 29.58%.

ANALYSIS

Analysis for carbon, hydrogen and nitrogen were carried out by the microanalytical laboratory, Science College, Calcutta. Manganese and chloride ion were determined by EDTA titration and silver chloride precipitation techniques [4], respectively.

APPARATUS

The IR spectra were recorded in the range 4000–250 cm^{-1} with a Beckman IR 20A infrared spectrophotometer using KBr discs.

Solid-state electronic spectra were recorded with a Cary 14 spectrophotometer provided with an automatic recording system. The spectra were taken in Nujol mull.

Magnetic susceptibility measurements were carried out by use of Gouy's method. Molecular susceptibility was corrected for diamagnetism of the component atoms by use of Pascal's constant [5].

Thermal studies were made as reported in an earlier paper [6].

RESULTS AND DISCUSSION

The complex gave a satisfactory elemental analysis and displayed a 1 : 1 Mn:urea stoichiometry with a composition of $[Mn(CN_2H_4O)(H_2O)_3Cl_2]$. To determine whether the H_2O is coordinated or crystalline, information from the TG results was taken. The decomposition step in the TG, which corresponds to H_2O loss from the complex is above 280°C. If the H_2O is crystalline, the weight loss would take place at lower temperatures, hence the

TABLE 1

Electronic spectral and magnetic susceptibility data of the complex

Complex	Electronic bands (cm^{-1})	Magnetic susceptibility (BM)
[Mn(Urea)$(H_2O)_3Cl_2$]	18500 21600 24000	5.90

H_2O in the complex must be water of coordination only.

The temperature-independent magnetic moment value of the complex, 5.90 BM, is very close to the spin value (i.e., for five unpaired electrons, $S = \frac{5}{2}$). The value is consistent with an octahedral stereochemistry around Mn(II) [7]. The electronic spectra (Table 1) show weak bands of low intensity. Mn(II) ion d^5 has a multiplicity $(1 + 2 \times \frac{5}{2})$ for the ground state [8]. The sextet term in an octahedral stereochemistry is $^6A_{1g}(^6S)$ for the electronic ground state. Since excited states have different multiplicities from the ground state, the transitions are spin-forbidden and are thus observed as weak transitions. The bands have been assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ (18500 cm^{-1}), $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, (21600 cm^{-1}) and $^6A_{1g} \rightarrow {}^4E_g(G)$, $^4A_{1g}(G)$ (24000 cm^{-1}).

Fig. 1 shows the IR spectrum of urea [Mn(Urea) $(H_2O)_3Cl_2$] and heated complexes at 180, 260, 300 and 400°C. The spectral data along with tentative assignments are given in Table 2. The free urea shows bands at 1670 cm^{-1} and 1600 cm^{-1} corresponding to $-C{=}O$ stretching and NH_2 bending and $+\nu(CO)$ frequencies, respectively. In the complex (Mn(Urea)$(H_2O)_3Cl_2$] spectra, these bands were found to be absent. Instead, weak intensity bands appeared at 1620 and 1570 cm^{-1}, indicating coordination of the carbonyl group with manganese ion. Thus, the bonding between monodentate urea

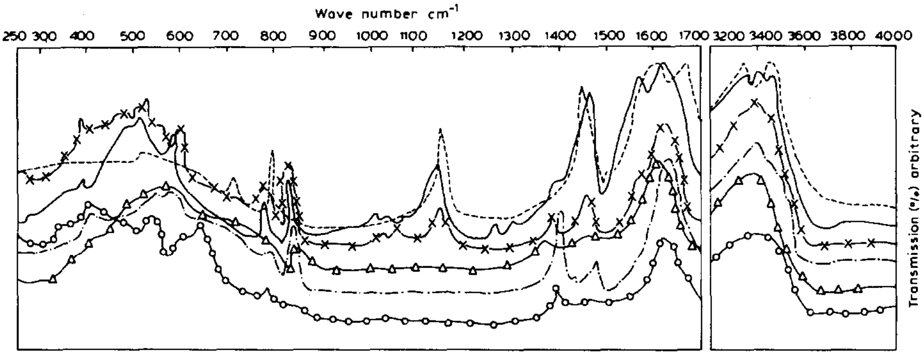


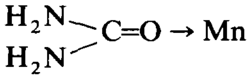
Fig. 1. IR spectra of urea (------), complex (————) and the residue obtained after heating in nitrogen at 180°C (×-×-×), 260°C (·—·—·), 300°C (△-△-△) and 400°C (○-○-○).

TABLE 2

IR data of urea, complex and complex heated at different temperatures [frequency (cm^{-1})]

Assignment of band	Urea	Complex	Complex heated at 180°C	Complex heated at 260°C	Complex heated at 300°C	Complex heated at 400°C
ν(NH)	3455 (bs)	3450 (bs)	3460 (vw)	3400 (bs)	3400 (bs)	
		3400 (bs)	3400 (bs)			
ν(NH)	3340 (bs)	3345 (bs)	3320 (sh)			
ν(CO)+NH_2 bending	1670 (ms)	1620 (bs)	1620 (bs)	1630 (bs)	1615 (bs)	1630 (mb)
$\nu(NH_2)$ bending + ν(CO)	1600 (bs)	1570 (s)				
ν(CN)	1450 (s)	1460 (s)	1460 (m)	1470 (w)		
		1300 (vw)	1390 (w)			
		1270 (w)				
$\nu(NH_2)$ rocking	1145 (s)	1140 (s)	1130 (m)	1400 (s)	1370 (w)	1400 (w)
			1050 (w)			
			1015 (vw)			
		820 (s)	815 (s)	830 (s)	830 (w)	
	790 (s)	780 (s)	780 (ms)			780 (ww)
	700 (w)		585 (w)	570 (w)	580 (w)	635 (w)
		580 (m)		540 (w)		530 (w)
			515 (w)			
	510 (w)	510 (bw)	480 (w)			
		470 (ww)	390 (w)	400 (w)	400 (wv)	390 (w)
		390 (w)				
		270 (vw)				

and manganese in the complex is represented by the structure



The broad absorption peak around 3400 cm^{-1} (indicative of asymmetric and symmetric stretches of H–O–H) [9], another around 1620 cm^{-1} (indicative of the bending mode of H–O–H) [10] and a strong absorption at 820 cm^{-1} in the spectrum of the complex confirms the presence of water in coordinated form [11]. The far infrared spectrum of the complex shows the presence of additional bands at 470 and 390 cm^{-1} due to Mn–O and Mn–Cl stretching frequencies. The values of the force constants calculated [12] for Mn–O and Mn–Cl bonds were found to be 2.01 and 1.81×10^{-5} dyn cm^{-1}, which are of the order of a single bond.

THERMAL STUDIES

The TG, DTG (in nitrogen atmosphere) and DTA (in air) curves of the complex are given in Fig. 2. The complex is thermally stable up to 80°C as

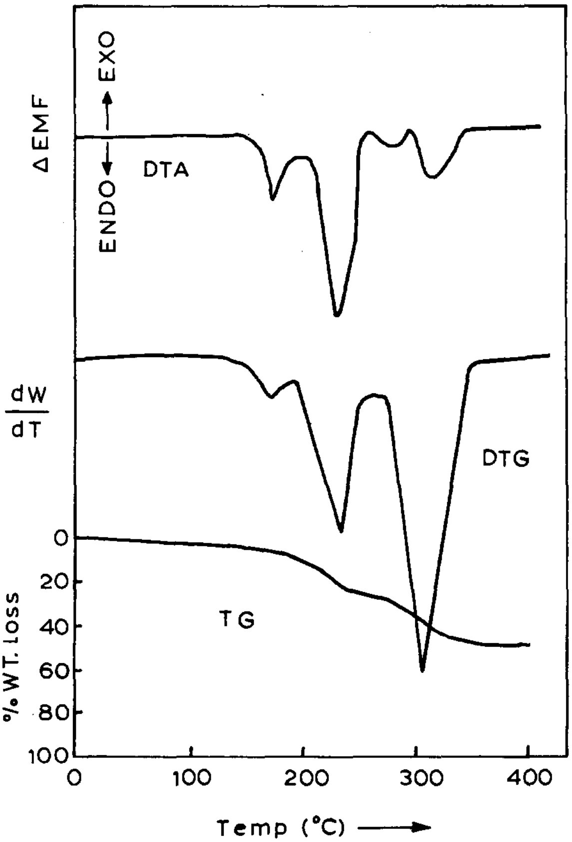


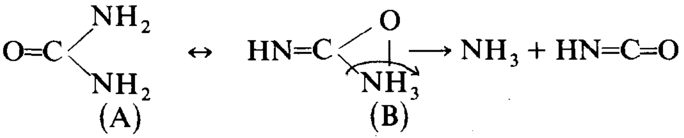
Fig. 2. TG, DTG (in nitrogen) and DTA (in air) curves of the complex.

indicated by a fairly horizontal plateau on the TG curve. From the pyrolysis curve it is clear that the continuous loss from 80 to 260° corresponds to the complete decomposition of the urea molecule [theoretical loss = 25.0%, experimental loss = 25.0%]. The DTG curve shows two peaks at 180 and 240°C, which reveal that the loss of urea takes place through formation of intermediates, which could be possibly due to decomposition of urea into ammonia (NH_3) and cyanic acid (HNCO) though the break of their formation are not clearly visible on the TG curve. The weight loss data, exptl. = 7.0%; theor. = 7.10% up to 180°C and exptl. = 18.0%; theor. = 17.90% up to 240°C, correspond to the loss of NH_3 and HNCO, respectively. In the DTA curve the stepwise decomposition of the urea ligand of the complex into NH_3 and HNCO is indicated by a small endothermic peak at 180°C and a sharp endothermic peak at 240°C. The most probable stepwise thermal decomposition of urea from the complex may be represented as

$$[Mn(Urea)(H_2O)_3Cl_2] \rightarrow Mn(H_2O)_3Cl_2 + Urea \tag{I}$$

$$Urea \rightarrow NH_3 + HNCO \tag{II}$$

The information reported here can be used to speculate on the reaction pathway (II) in the thermal loss of ammonia from urea compound. The schematic representation of the urea decomposition involves rearrangement through a cyclic aziridine intermediate (B). The slight decrease in intensity of ν(NH) and disappearance of the bending mode NH_2 frequency bands in the IR spectrum of the heated complex at 180°C (Fig. 1) indicate the loss of a NH_3 molecule. Between 200 and 260°C there is a large weight loss due to elimination of HNCO molecule. The IR spectrum of the complex heated at 260°C shows the absence of ν(NH) and ν(CO) frequencies, indicating complete loss of a urea molecule.



The intermediate $[Mn(H_2O)_3Cl_2]$, obtained after loss of urea, is insoluble and stable up to 280°C. This intermediate starts decomposing from 280°C to 360°C, the final residue corresponding to $MnCl_2$ [weight loss, exptl. = 47.40%, theor. = 47.50%], which is stable up to 450°C in nitrogen atmosphere. Such a great weight loss is associated with a strong DTG peak at 310°C. The DTA curve gives rise to two broad endothermic peaks at 295 and 310°C, indicating the loss of coordinated H_2O molecules in two steps. The observed weight loss in the TG curve up to 295°C is 7.85%, in reasonable agreement with the calculated value of 7.50% for removal of an H_2O molecule. The weight loss up to 360°C corresponds to the loss of two water molecules [exptl. = 15.30%, theor. = 15.0%]. The complex heated at

400°C (Fig. 2) does not retain the characteristic IR features of the original complex. The strong vibrational frequency of coordinated water at 780 cm^{-1} and stretching mode at 3400 cm^{-1} are found to be absent in the spectrum, suggesting thereby that all the water has been removed at this temperature. The decomposition stoichiometry of H_2O molecules may be expressed as

$$Mn(H_2O)_3Cl_2 \rightarrow Mn(H_2O)_2Cl_2 + H_2O \tag{III}$$

$$Mn(H_2O)_2Cl_2 \rightarrow MnCl_2 + 2H_2O \tag{IV}$$

Figure 3 shows the results obtained when $[Mn(Urea)(H_2O)_3Cl_2]$ is heated in air at a linear rate of 10°C min^{-1}. The portion of the TG curve which extends from room temperature to 450°C is parallel to the analogous region of the TG curve in nitrogen atmosphere. As the temperature is raised above 550°C, decomposition directly to Mn_2O_3 [weight loss exptl. = 70.06%, theor. = 69.50%] is completed by 650°C. Such a great weight loss is associated with a strong DTG peak at 640°C. The final stage (TG curve in air) represents the complete loss of chlorine as a volatile product and conversion to Mn_2O_3 [13]. This change appears to involve oxygen because no loss occurs after 400°C when TG is performed under nitrogen.

Based on thermogravimetric evidence, supported by the IR spectra of the intermediate compounds which are formed, we propose the following sequence of reactions to represent the thermal decomposition of

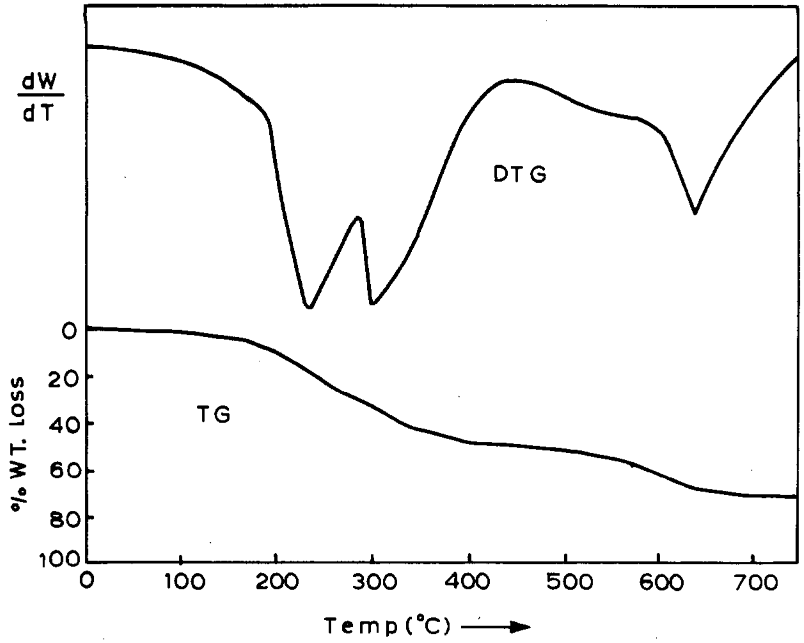


Fig. 3. TG and DTG (in air) curves of the complex.

$[Mn(Urea)(H_2O)_3Cl_2]$ in an inert atmosphere

$$[Mn(Urea)(H_2O)_3Cl_2] \rightarrow [Mn(H_2O)_3Cl_2] + Urea$$

$$[Mn(H_2O)_3Cl_2] \rightarrow [Mn(H_2O)_2Cl_2] + H_2O$$

$$[Mn(H_2O)_2Cl_2] \rightarrow MnCl_2 + 2\ H_2O$$

However the decomposition sequence in oxidizing atmosphere has one more step involving transformation to Mn_2O_3

$$[Mn(Urea)(H_2O)_3Cl_2] \rightarrow MnCl_2 \rightarrow Mn_2O_3$$

KINETIC PARAMETERS

Kinetic parameters of the thermal decomposition are calculated from the course of the TG curve. The Satava [14] simplified graphical method for the present sample has been applied. Out of nine equations for which log[g(α)] has been plotted against $1/T$, no single equation seems to satisfy the entire experimental data, which indicates that the decomposition reaction is complex in nature. The process is, therefore, clearly a heterogeneous one with a changing mechanism and activation energy during the course of reaction. Freeman and Carroll [15] and Coats and Redfern [16], like the Satava plot,

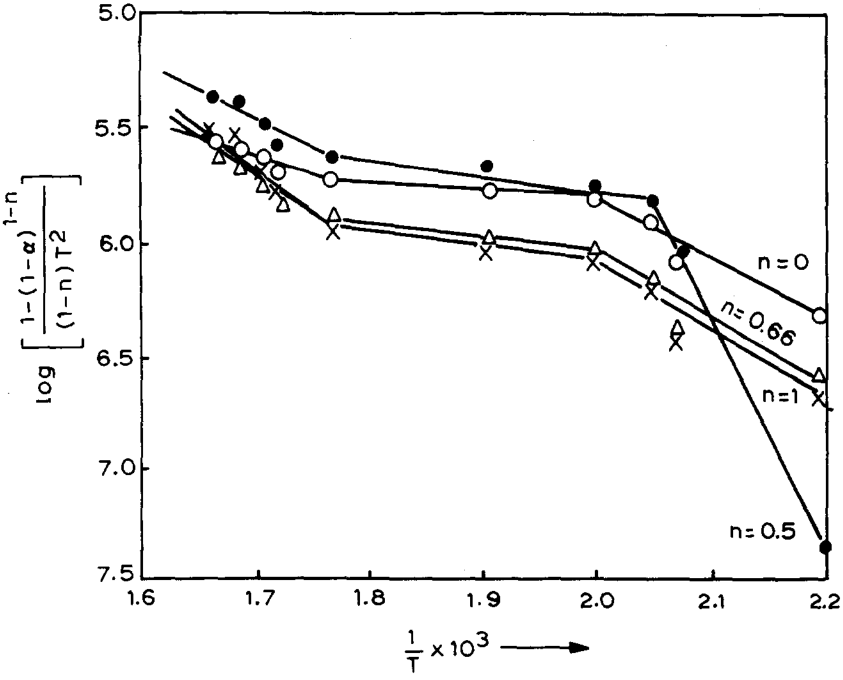


Fig. 4. Coats and Redfern's plot.

TABLE 3

Values of activation energy

n	E_1 (kcal $mole^{-1}$)	E_2 (kcal $mole^{-1}$)	E_3 (kcal $mole^{-1}$)
0	12.07	1.38	9.2
0.5	17.25	2.68	11.5
0.66	14.15	2.87	16.10
1.00	13.8	3.19	20.12

showed the three-step decomposition pattern for the system. The Coats and Redfern equation which appears to be more reliable when the order of reaction is known, has been applied here to obtain the activation energies for the decomposition of the complex. The plots (Fig. 4) of log $[1-(1-\alpha)^{1-n}]/[T^2(1-n)]$ against $1/T \times 10^3$ [where $\alpha = (W_0 - W)/(W_0 - W_k)$ (W_0, W_k and W are the initial, final and intermediate weight of the sample at temperature T (K) and n = order of reaction)] showed two breaks for each value of n. A number of such relationships are plotted for a number of assumed values of $n = 0$, 0.5, 0.66 and 1.0. Arora et al. [17] also reported a number of breaks in the kinetic studies of mixed oxide systems. The activation energy for each line is calculated from the equation $E = 2.3\, Rt_g\beta$ [where $t_g\beta$ = the slope of straight line and R = gas constant] and values are given in Table 3. In the complex, the decomposition is a three-step process since two breaks have been observed in Coats and Redfern's plots, thus three values for the activation energy have been reported. The activation energy of the first curve corresponds to the decomposition of urea molecules and the activation energy of the second and third curves are due to loss of the coordinated molecules, in two steps.

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