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Infrared spectroscopic studies of the different solid products upon the chemical reactions between some transition metal ions/ ammonia/ urea with 1: 2: 10 ratios

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Abstract: There are different solid products (MnO , $Co(NCO)_2$, $ZnCO_3$ and CdO) were presented through the chemical reactions of $MnCl_2$, $Co(NO_3)_2$, $Zn(NO_3)_2$ or $CdCl_2$, ammonia and urea with molar ratio 1: 2: 10, respectively, at $\sim 100^{\circ}C$ for 3 hrs in aqueous media. The infrared spectra of the results indicate absence of the essential bands of urea, but existed of the characteristic bands of oxide and both of ionic carbonate, CO_3^{2-} and isocyanate, NCO^- . The reaction mechanisms of decomposition of urea in the presence of alkaline media using $Mn(II)$, $Co(II)$, $Zn(II)$ or $Cd(II)$ salts were described.

Keywords: carbonate CO_3^{2-} , isocyanate NCO^- , infrared spectra, transition metals, ammonia and urea.

I. INTRODUCTION

Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Urea has a melting point of $132^{\circ}C$, soluble in water and ethanol, but insoluble in ether. Urea is used for preparing formaldehyde-Urea resin (plastics) [1], barbiturates [2], and fertilizers [3-6]. Urea is also extensively used in the paper industry to soften cellulose and has been used to promote healing in infected wounds and many other applications in the field of biological and organic synthesis [7-10]. Yamaguchi and Stewart [11, 12] were assigned all of the observed frequencies in the spectra of urea and urea-d₄. The two vibrations of the frequencies at 1686 and 1603 cm^{-1} were assigned as the 1686 cm^{-1} band due to CO stretching vibration and the 1603 cm^{-1} band for NH₂ bending motion. The calculations studied by Yamaguchi showed that for the band at 1686 cm^{-1} , the contribution of the NH₂ bending motion is greater than that of CO stretching motion. The infrared bands of urea-d₄ observed at 1245 and 1154 cm^{-1} are assigned to ND₂ bending vibrations. This assignment is consistent with the observed depolarization degrees of the Raman lines. The 1464cm^{-1} frequency of urea is assigned to the CN stretching vibration. The corresponding frequency of urea-d₄ is observed at 1490cm^{-1} . The 1150cm^{-1} band is assigned to NH₂ rocking vibrations. The reactions between transition metal ions and urea at room temperature have been studied extensively [13-17]. The infrared spectra of these complexes clearly indicated that urea molecule behaves as a mono dentate ligand and coordinates to the metal ions through the oxygen atom and not the nitrogen atom. The nature of the reaction products depend strongly on the type of metal ions and so the metal salt used. The novelty in our previously studies [18-27] were oriented to the reaction of urea ligand with different metals such as $Co(II)$, $Pb(II)$, $Sn(II)$, $Cr(III)$, $Fe(III)$, $Au(III)$, $Sn(IV)$, $V(V)$ and $Mo(IV)$ at high temperature which demonstrate that the types of metal ions beside their anions have a pronounced effect on the nature

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of the reaction products. The published papers were trended for the reaction of urea with different metal salts at elevated temperature lead to discovering a novel method for preparation pbCO_3 and CoCO_3 [21], lanthanide carbonates [23,27], limonite, FeO(OH) [20], $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$ [19], $\text{SnOCl}_2 \cdot 2\text{H}_2\text{O}$ [18], (Cr_2O_3 , MnO_2 , MoO_3 and WO_3) oxides resulted from a novel oxidation reduction reaction between (K_2CrO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$), KMnO_4 , Na_2MoO_4 and Na_2WO_4 , respectively, with urea in an aqueous solution at $\sim 85^\circ\text{C}$ [27]. The aim of the work in this paper was directed to identify the nature of the reaction mechanisms of the products resulted during the reaction of (MnCl_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ or CdCl_2), ammonia and urea with molar ratio 1:2:10, respectively, at $\sim 100^\circ\text{C}$ for 3 hrs in aqueous media. The reaction products were isolated as solids and characterized by infrared spectroscopy technique.

II. EXPERIMENTAL

All chemicals used throughout this work were analytical pure. MCO_3 ($\text{M} = \text{Mn(II)}, \text{Co(II)}, \text{Zn(II)} \text{ or } \text{Cd(II)}$) were prepared by mixing an aqueous solutions (100 ml) of 0.1M of urea, 0.02 of ammonia with 0.01M of the respective MnCl_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ or CdCl_2 . The mixtures were heated at 100°C for 3 hrs in a hot plate. The solid products compounds were filtered off, washed several times with hot water, dried at 100°C in an oven for 3 hours and then placed in *vacuo* over anhydrous calcium chloride. The yields of the obtained were varied in the range 55-to-65% depending upon the type of metal as well as on the counter ions associated with the metal ion.

Carbonate content in the zinc(II) compound was determined by dissolving a sample of each product in excess standard HCl and the excess of HCl was determined using standard sodium carbonate [28]. The percentage of manganese(II), cobalt(II), zinc(II) and cadmium(II) in their compounds were determined gravimetrically method till constant weight and stable formula. The infrared spectra of urea, all reactants and products were recorded using a Bruker FT-IR Spectrophotometer.

III. RESULTS AND DISCUSSION

The chemical reactions of 0.1M of urea, 0.02 of ammonia with 0.01M of the respective MnCl_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ or CdCl_2 with molar ratio (10: 2: 1), respectively, at 100°C produces a dark brown, pink, white and white solid fine powders, respectively. The infrared spectra of urea as well as the reaction products of different manganese(II), cobalt(II), zinc(II) and cadmium(II) salts with urea at boiling point of water solvent (100°C) were obtained. The spectra of free urea ligand, manganese(II), cobalt(II), zinc(II) and cadmium(II) carbonates are shown in Fig. 1-5, respectively. The infrared spectra show no bands due to any of the reactants and of coordinated urea, but instead, a group of bands characteristic for the ionic carbonate, $(\text{CO}_3)^{2-}$, ionic isocyanate, NCO^- , and oxides for zinc(II), cobalt(II) and both cadmium and manganese(II) respectively, are appeared [29]. Based on this fact, the infrared spectra of the commercially obtained MnO , $\text{Co}(\text{NCO})_2$, ZnCO_3 and CdO are the same as that of the reaction products.

Previous studies [18-27] indicated that the nature of the reaction product obtained from the reaction of metal ions with urea at high temperature depends upon the type of metal ion and in some cases on the nature of the metal salts used. The manganese(II)-urea complexes have been studied extensively [30-33] and it was found that, these complexes are of high spin and possess octahedral structures. These investigation have also shown that, all of the studied Mn(II)-urea complexes are of the general formula MnU_2X_2 ($\text{X}=\text{Cl}^-$ or Br^- , $\text{U}=\text{Urea}$). They have a chain like structure with halogen bridges. This structure is supported by electronic spectral measurements and the magnetic susceptibility data [34] but could not be checked by infrared spectroscopy because of the Mn-X-M bridging vibration frequency lying below 200 cm^{-1} . The trans-octahedral complex $[\text{MnU}_4(\text{NCS})_2]$, ($\text{U}=\text{urea}$) has been prepared and investigated [35]. The ligand, urea is coordinated through its oxygen atom while the thiocyanate through the nitrogen atom. These results are supported by the crystallographic data of Tsintsadze et al [36] obtained or the $[\text{MnU}_4(\text{NCS})_2]$ complex. The trifluorobis(urea)manganese(III) trihydrate, $[\text{MnF}_3(\text{urea})_2] \cdot 3\text{H}_2\text{O}$ complex is prepared and its infrared spectrum is obtained [37]. The characteristic features of the infrared spectrum of this complex are the absorptions due to coordinated urea, coordinated fluoride and lattice water. The important bands of coordinated urea have been observed at 3425 and 1535cm^{-1} , assignable to $\nu(\text{NH}_2)$ and $\nu(\text{CO})$ modes, respectively. The unaltered position of $\nu(\text{NH}_2)$ and a

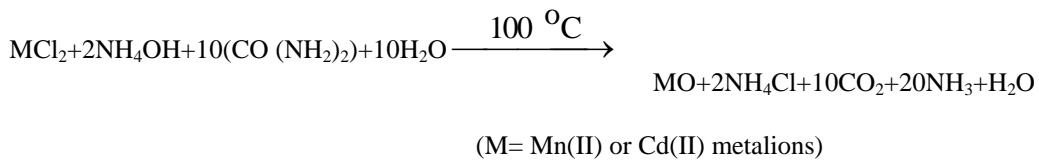
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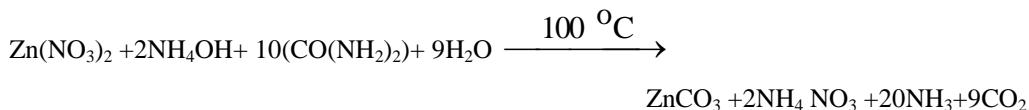
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significant lowering of $\nu(\text{C=O})$ band frequencies compared with those for the free urea suggest that urea is coordinated with the metal in an unidentate manner through its oxygen atom. However, there is a shift to the lower frequency in the position of the $\nu(\text{Mn-F})$ mode indicating that, the fluoro ligands are involved also in the formation of bridges among the contiguous Mn centers in the crystal lattice.

At high temperature the role of Mn(II) and Cd(II) ions in decomposing the coordinated urea in the presence of ammonia as alkaline media could be understood according to the following reactions;

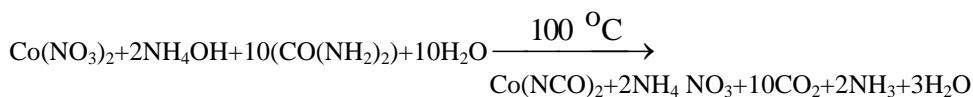


Adducts of $\text{ZnX}_2 \cdot 2\text{urea}$ ($X = \text{Cl, Br, I}$), $\text{CdX}_2 \cdot 2\text{urea}$ ($X = \text{Br, I}$), $\text{CdX}_2 \cdot \text{urea}$ ($X = \text{Cl, Br, I}$) and $\text{HgX}_2 \cdot \text{urea}$ ($X = \text{Cl, Br}$) have been characterized [38]. The shifts of the stretching vibrations to low frequency ($\nu(\text{CO})$) and to high frequencies ($\nu(\text{CN})$ and $\nu(\text{NH})$) indicated that urea is oxygen-bonded to the metals. At high temperature the role of Zn(II) ions in decomposing the coordination urea in presence of ammonia could be understood as follows;



The $(\text{CO}_3)^{2-}$ ion is planar and therefore, it belongs to the D_{3h} symmetry. It is expected to display four modes of vibrations, $A''_1 + A''_2 + 2E'$ (E' is a doubly degenerate motion). The vibration A''_1 is only Raman active while the other ν_2 , ν_3 and ν_4 are infrared active. The stretching vibrations of the type; $\nu(\text{C-O})$; $\nu_3(\text{E}')$ is observed as a strong broad band in the range of 1509 cm^{-1} while the stretching vibration $\nu(\text{C-O})$; $\nu_1(\text{A}'_1)$ is observed in the region $\sim 998 \text{ cm}^{-1}$ as a medium-to-weak band. It should be indicated here that this motion (A''_1) should be infrared inactive, its weak appearance in the spectrum of MCO_3 could be related to weak solid-solid interactions causes the symmetry of CO_3^{2-} to be lowered than D_{3h} . The out of plane of vibration $\delta(\text{OCO})$; $\nu_2(\text{A}''_2)$ is observed in the range of $\sim 834 \text{ cm}^{-1}$ as a strong band while, the angle deformation bending vibration $\delta(\text{OCO})$; $\nu_4(\text{E}')$ appear in the range of 691 cm^{-1} as a medium strong. The infrared spectra of metal(II) carbonate, MCO_3 show that, some these products are hygroscopic and its clearly have moisture water. The band related to the stretching vibration $\nu(\text{O-H})$ of uncoordinated H_2O is observed as expected in the range of $\sim 3362 \text{ cm}^{-1}$.

The x-ray studies on cobalt(II) salt-urea complexes [39-41] have confirmed the existence of the double compounds $\text{CoSO}_4 \cdot 6\text{CO}(\text{NH}_2)_2$, $\text{Co}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 4\text{CO}(\text{NH}_2)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{CO}(\text{NH}_2)_2$, and of the triple compound $\text{Co}(\text{NO}_3)_2 \cdot 4\text{Co}(\text{SO}_4)_2 \cdot 20\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 6\text{H}_2\text{O}$. Complexes of N-allyl urea (NAU) with cobalt(II) and nickel(II) halides and perchlorates have prepared and characterized by electrical conductance, magnetic susceptibility [42]. The infrared spectra of N-allyl urea complexes with Ni(II) and Co(II) salts, $[\text{Co}(\text{NAU})_2\text{X}_2]$; ($\text{X} = \text{Cl, Br, and I}$), $[\text{Ni}(\text{NAU})_4\text{X}_2]$; ($\text{X} = \text{Cl, Br}$), $[\text{Ni}(\text{NAU})_4](\text{ClO}_4)_2$ and $[\text{Ni}(\text{NAU})_6](\text{ClO}_4)_2$ are reported [43]. A negative shift in the frequencies of $\nu(\text{C=O})$ and $\delta(\text{NH}_2)$ bands, and a positive shift in the frequency of $\nu(\text{C-N})$ band, suggest that carbonyl oxygen is the donor site. Moreover, the negative shift of the N-H stretching frequency is arise from hydrogen bonding between N-H and halogen and not to coordination. A small negative shift of the double bond on coordination is probably due to drain of electrons towards oxygen. The role of Co(II) ions in the decomposing of coordinated urea at high temperature may be understood as follows.



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The $\nu(\text{N}\equiv\text{C})$ is observed as expected at 2202 cm^{-1} , while the $\nu(\text{C}-\text{O})$ and $\delta(\text{NCO})$ are assigned at $1479, 1356$ and $620, 517 \text{ cm}^{-1}$, respectively. These results for the NCO^- ions agree quite well with those known for isocyanato complexes [29]. The detected band, $\nu(\text{O}-\text{H})$, vibrations characteristic of uncoordinated water in the 3382 cm^{-1} region.

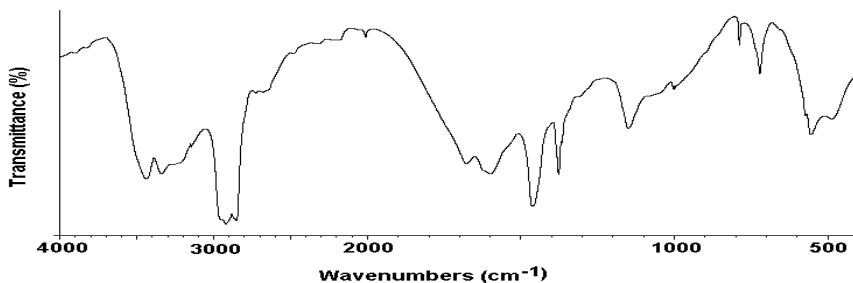


Fig. 1: Infrared spectrum of urea free ligand

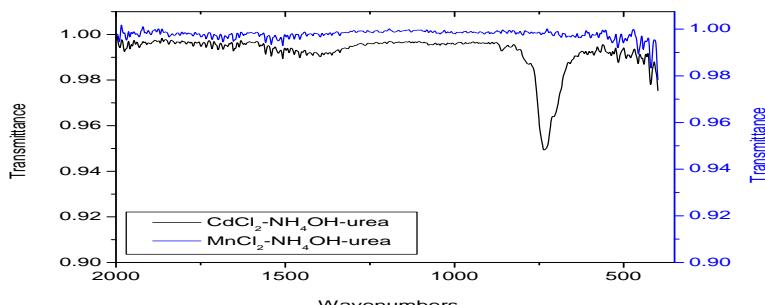


Fig. 2: Infrared spectrum of MnO and CdO compounds

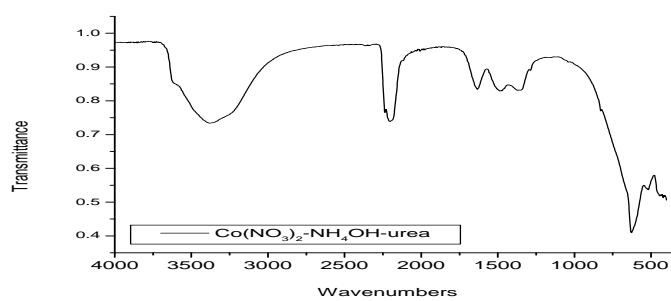


Fig. 3: Infrared spectrum of $\text{Co}(\text{NCO})_2\text{xH}_2\text{O}$ compound

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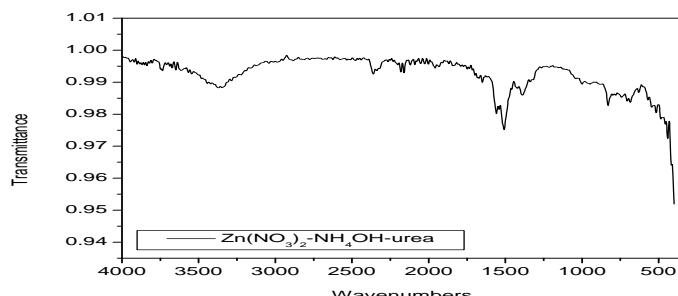


Fig. 4: Infrared spectrum of $\text{ZnCO}_3 \cdot x\text{H}_2\text{O}$ compound

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