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# Study of alkaline earth metal chloride-urea complexes in aqueous media at boiling point in presence of potassium iodide: New equation for preparation of calcium(II), strontium(II) and barium(II) carbonates

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**Abstract:** The carbonate salts of Ca(II), Sr(II), and Ba(II), respectively, were synthesized by a new simple and cheap materials via the chemical reaction of an aqueous solutions of metal chloride ions (CaCl<sub>2</sub>, SrCl<sub>2</sub> and BaCl<sub>2</sub>), potassium iodide and urea with molar ratio 1:2:10, respectively, at ~ 100 °C for 3 hrs. The infrared spectra of the results indicate absence of the essential bands of urea, but existed of the characteristic bands of ionic carbonate, CO<sub>3</sub><sup>2-</sup>. An important chemical mechanisms discussed the preparation of Ca(II), Sr(II), and Ba(II) carbonate compounds were suggested.

**Keywords:** carbonate CO<sub>3</sub><sup>2-</sup>, infrared spectra, alkaline earth metals, potassium iodide, urea.

## I. INTRODUCTION

Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Urea has a melting point of 132°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-d<sub>4</sub>. The two vibrations of the frequencies at 1686 and 1603cm<sup>-1</sup> were assigned as the 1686 cm<sup>-1</sup> band due to CO stretching vibration and the 1603 cm<sup>-1</sup> band for NH<sub>2</sub> bending motion. The calculations studied by Yamaguchi showed that for the band at 1686 cm<sup>-1</sup>, the contribution of the NH<sub>2</sub> bending motion is greater than that of CO stretching motion. The infrared bands of urea-d<sub>4</sub> observed at 1245 and 1154 cm<sup>-1</sup> are assigned to ND<sub>2</sub> bending vibrations. This assignment is consistent with the observed depolarization degrees of the Raman lines. The 1464cm<sup>-1</sup> frequency of urea is assigned to the CN stretching vibration. The corresponding frequency of urea-d<sub>4</sub> is observed at 1490cm<sup>-1</sup>. The 1150cm<sup>-1</sup> band is assigned to NH<sub>2</sub> 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

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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 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  $\text{pbCO}_3$  and  $\text{CoCO}_3$  [21], lanthanide carbonates [23,27], limonite,  $\text{FeO(OH)}$  [20],  $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$  [19],  $\text{SnOCl}_2 \cdot 2\text{H}_2\text{O}$  [18], ( $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{MoO}_3$  and  $\text{WO}_3$ ) oxides resulted from a novel oxidation reduction reaction between ( $\text{K}_2\text{CrO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ ),  $\text{KMnO}_4$ ,  $\text{Na}_2\text{MoO}_4$  and  $\text{Na}_2\text{WO}_4$ , respectively, with urea in an aqueous solution at  $\sim 85^\circ\text{C}$  [27]. The aim of this paper was focused to identify the nature of the reaction mechanisms of the products resulted during the reaction of ( $\text{CaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$ ), potassium iodide 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.  $\text{MCO}_3$  ( $\text{M} = \text{Ca(II)}$ ,  $\text{Sr(II)}$  or  $\text{Ba(II)}$ ) were prepared by mixing an aqueous solutions (100 ml) of 0.1M of urea, 0.02 of potassium iodide with 0.01M of the respective  $\text{CaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$ . The mixtures were heated at  $100^\circ\text{C}$  for 3 hrs in a hot plate. The solid products compounds were filtered off, washed several times with hot water, dried at  $100^\circ\text{C}$  in an oven for 3 hours and then placed in *vacuo* over anhydrous calcium chloride. The yields of the obtained Ca(II), Sr(II) and Ba(II) carbonates were varied in the range 75-to-80% depending upon the type of metal as well as on the counter ions associated with the metal ion.

Carbonate content in the four compounds were 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 calcium(II), strontium(II), and barium(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 potassium iodide with 0.01M of the respective  $\text{CaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$  with molar ratio (10: 2: 1), respectively, at  $100^\circ\text{C}$  produces a white fine solid powders. The infrared spectra of urea as well as the reaction products of different  $\text{CaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$  salts with urea at boiling point of water were obtained. The spectra of free urea ligand, calcium(II), strontium(II) and barium(II) carbonates are shown in Fig. 1-4, respectively. The band assignments for the products are given in Table 1. 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,  $(\text{CO}_3)^{2-}$ , is appeared [29]. Based on this fact, along with that obtained data from the volumetric determination of  $(\text{CO}_3)^{2-}$  group with standard solution of HCl and beside that the infrared spectra of the commercially obtained  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$  are the same as that of the reaction products. The products obtained were identified as  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$ . The infrared assignments agree quite well with those known [29] for the ionic carbonate  $(\text{CO}_3)^{2-}$ .

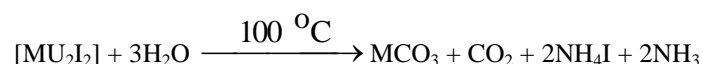
The inhibiting action of amides and alkaline earth element acetates on the corrosion of metals gives a practical importance to the investigation of their reaction in aqueous solutions. The reaction of urea with alkaline-earth metals in aqueous solutions has been studied by a number of workers [30-34]. In case of  $\text{CO(NH}_2)_2\text{-M(CH}_3\text{COO)-H}_2\text{O}$  ( $\text{M} = \text{Mg}$ ,  $\text{Ca}$ ,  $\text{Sr}$  or  $\text{Ba}$ ) systems [35,36], the tendency of the alkaline earth elements to form complexes with urea decreases as its ionic radius increases. Thus magnesium(II) forms a complex with two molecules of urea, calcium(II) forms a complex with one molecule of urea, while strontium and barium acetates don't react. The complexes  $[\text{2CO(NH}_2)_2 \cdot \text{Mg(CH}_3\text{COO)}_2]$  and  $[\text{CO(NH}_2)_2 \cdot \text{Ca(CH}_3\text{COO)}_2]$ , are identified by elemental, X-ray phase, thermogravimetric analysis. The system  $\text{MgCl}_2\text{-CO(NH}_2)_2\text{-H}_2\text{O}$  has been studied [30]. Its solubility isotherm at  $0^\circ$  consists of three branches. The two branches on the outside correspond to the crystalline of urea and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,

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while the middle branch corresponds to  $MgCl_2 \cdot 4CO(NH_2)_2$ . With a further temperature rise to  $15^\circ$ , the hydrated complex  $MgCl_2 \cdot CO(NH_2)_2 \cdot 4H_2O$  is formed. At  $30^\circ$  another complex,  $[MgCl_2 \cdot 6CO(NH_2)_2]$  is formed. All of these complexes are congruently soluble and are precipitated in crystalline forms. At  $45^\circ$  the complex  $[MgCl_2 \cdot 10CO(NH_2)_2]$  is formed. The bond between  $MgCl_2$  and urea is formed through the oxygen of the carbonyl group, as indicated by infrared spectroscopy. The role of M(II) (Ca, Sr or Ba(II)) ions in decomposing the coordinated urea at high temperature may be understood as follows.



The  $(CO_3)^{2-}$  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  $v_2, v_3$  and  $v_4$  are infrared active. The stretching vibrations of the type;  $\nu(C-O); v_3(E)$  is observed as a strong broad band in the range of  $1473-1416\text{ cm}^{-1}$  while the stretching vibration  $\nu(C-O); v_1(A_1)$  is observed in the region  $\sim 1060-1080\text{ cm}^{-1}$  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  $\delta(OCO); v_2(A_2)$  is observed in the range of  $\sim 850\text{ cm}^{-1}$  as a strong band while, the angle deformation bending vibration  $\delta(OCO); v_4(E)$  appear in the range of  $691-711\text{ cm}^{-1}$  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  $\nu(O-H)$  of uncoordinated  $H_2O$  is observed as expected in the range of  $\sim 3351-3198\text{ cm}^{-1}$  Table 1.

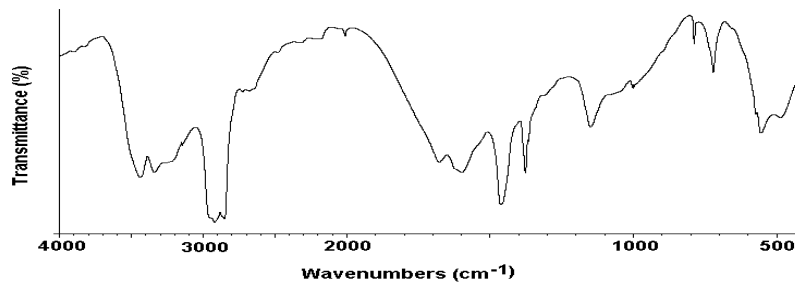
**Table 1:** Infrared frequencies ( $\text{cm}^{-1}$ ) and assignments of the products obtained from the reaction of (a):  $CaCl_2$ , (b):  $SrCl_2$  or (d):  $BaCl_2$  with potassium iodide and urea at  $100^\circ C$  temperature.

Frequencies*, $\text{cm}^{-1}$			Assignments
a	b	c	
3211 3198	3351 3198	3331 3203	$\nu(O-H); H_2O$
1473 1080	1455 1070	1419 1060	$\nu(C-O); CO_3^{2-}$
850 711	853 705	853 691	$\delta(OCO); CO_3^{2-}$

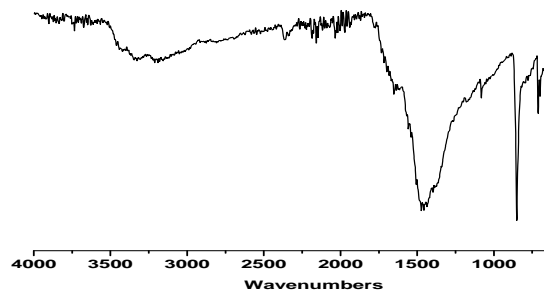
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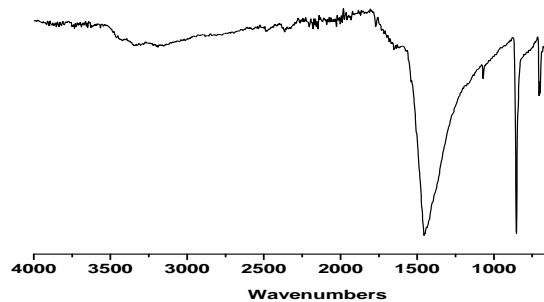
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**Fig. 1:** Infrared spectrum of urea free ligand



**Fig. 2:** Infrared spectrum of CaCO<sub>3</sub>.xH<sub>2</sub>O compound



**Fig. 3:** Infrared spectrum of SrCO<sub>3</sub>.xH<sub>2</sub>O compound

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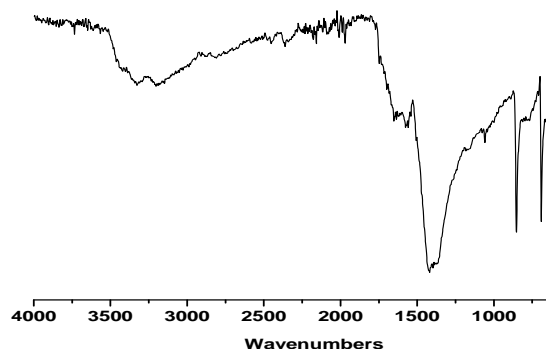


Fig. 4: Infrared spectrum of  $\text{BaCO}_3 \cdot x\text{H}_2\text{O}$  compound

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