



## **A new procedure for synthesis of copper(II) carbonate by the chemical reactions between three cupric salts and urea at elevated temperature: Microanalytical and infrared spectroscopic investigations**

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### **Abstract**

The main purpose of this article was to study the coordinated decomposition method of urea in copper-urea complexes in aqueous media at high temperature. This enables us to compare the degradation pathway of coordinated urea known as free urea. It was shown that the reaction products obtained during the reaction of urea with metal ions depend not only on the type of metal ion but also on the nature of the metal salt used in the reaction. Cupric (II) carbonate,  $\text{CuCO}_3$  was synthesized by a new simple method during the reaction of aqueous solutions of  $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{ClO}_4)_2$  with urea at  $\sim 90^\circ\text{C}$  for about 10 hrs. The green solid reaction products were characterized by elemental analysis and infrared spectroscopy. The IR spectra clearly indicate the characteristic bands of the ionic carbonates and the absence of all band characteristics of the coordinated urea. A general mechanism describing the coordinated decomposition of urea and formation of cupric(II) carbonate at high temperature has been proposed.

**Keywords:** Cupric(II) salt;  $\text{CuCO}_3$ ; urea; aqueous media; infrared spectra; elemental analysis; new procedure.

### **1. Introduction**

Raman and infrared spectra of urea have been observed by many researchers [1-6]. The natural vibrations of the urea molecule were calculated by Kellner [7] assuming the non-planar model. However, based on the coupled measurement of the infrared band arising from the N-H stretching vibration by Waldron and Badger [8] and the proton magnetic resonance absorption measurement performed by Andrew and Hyndman [9], it was concluded that the urea molecule has a planar structure. Yamaguchi et al. [10] calculated the natural vibrations of the  $\text{C}_{2v}$  model of the urea molecule as an eight-body problem using a potential function of the Urey-Bradley force field and obtained the force constants that were refined

by the least squares method. Based on the result of these calculations, Yamaguchi [10] assigned all observed frequencies in the spectra of urea and urea-d<sub>4</sub>. For the 1686 and 1603  $\text{cm}^{-1}$  frequency vibrations, there are significant contributions of both CO stretching motions and  $\text{NH}_2$  bending motions, while Stewart [11] assigned the 1686  $\text{cm}^{-1}$  band to the CO stretching vibration and the 1603  $\text{cm}^{-1}$  band to the  $\text{NH}_2$  bending motion. Calculations studied by Yamaguchi showed that for a band with a length of 1686  $\text{cm}^{-1}$  the contribution of the bending motion of  $\text{NH}_2$  is greater than that of the extending motion of CO. The band at 1629  $\text{cm}^{-1}$  corresponds to the bending vibration of almost pure  $\text{NH}_2$ . The bending motion of  $\text{NH}_2$  type A<sub>1</sub> is equal to the bending motion of type

B2. The A1 band frequency should be about  $1630\text{ cm}^{-1}$  if there is no coupling between the bending motions of  $\text{NH}_2$  and the stretching of CO. On the other hand, the observed frequency of  $1610\text{ cm}^{-1}$  of urea- $d_4$  is for almost pure skeletal vibration. Therefore, the interaction between the  $1630$  and  $1610\text{ cm}^{-1}$  vibrations gives rise to the observed bands at  $1686$  and  $1603\text{ cm}^{-1}$ . The IR bands of urea- $d_4$  observed at  $1245$  and  $1154\text{ cm}^{-1}$ , respectively, were assigned to A1-type, B2-type and ND2 bending vibrations. This assignment is consistent with the degrees of depolarization observed for the Raman lines. The large frequency difference between the A1 and B2 vibrations is because in the A1 vibration, the cross term associated with the CN stretching vibration is large. The urea frequency of  $1464\text{ cm}^{-1}$  was assigned to the B2 type CN extension vibration. The corresponding frequency for urea- $d_4$  is observed at  $1490\text{ cm}^{-1}$ . The band  $1150\text{ cm}^{-1}$  was assigned to the  $\text{NH}_2$  rocking vibrations of both types A1 and B2. Calculating normal vibration results in approximately the same values for these frequencies.

Urea has two types of potential donor atoms, carbonyl oxygen and amide nitrogen. Penland et al. [12] studied the infrared spectra of urea complexes to determine whether coordination occurs through oxygen or nitrogen atoms. Coordination spectra of urea complexes with Pt(II) and Cr(III), where coordination occurs through nitrogen and oxygen atoms, respectively [12]. The way urea coordinates with metal ions appears to depend on the type and nature of the metal. Pd(II) coordinates with nitrogen, while Fe(III), Zn(II), and Cu(II) coordinate with urea oxygen [12]. IR spectra of urea complexes Zn(II) and Cu(II) [13-17],  $[\text{Cu}(\text{urea})_2\text{Cl}_2]$ ,  $[\text{Zn}(\text{urea})_2\text{Cl}_2]$  and  $[\text{Zn}(\text{urea})_2(\text{CH}_3\text{COO})_2]$  [18], very similar to the spectra of  $[\text{Cr}(\text{urea})_6]\text{Cl}_3$  and  $[\text{Fe}(\text{urea})_6]\text{Cl}_3$ . This similarity reveals the presence of O-M coordinate bonds in Cu(II) and Zn(II) urea complexes. The current research was carried out to study the effect of changing metal ion anions on the nature of the products of the reaction of urea with three copper (II) salts at a high temperature  $\sim 90\text{ }^\circ\text{C}$  in aqueous media. The reaction products were characterized by elemental analysis and infrared spectra analysis.

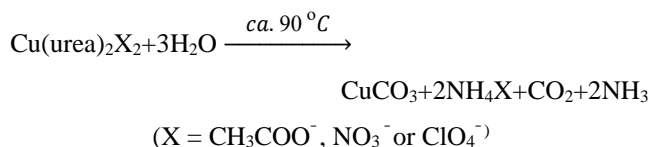
## 2. Experimental

Reagent chemicals were used throughout.  $\text{CuCO}_3$  was prepared by mixing equal amounts of aqueous solution (100 mL) of 2 mmol of copper(II) salts,  $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{ClO}_4)_2$ , with 100 mL of aqueous solution (16 mmol) of urea. The reaction mixtures were heated to approximately  $90\text{ }^\circ\text{C}$  for 10 h in a water bath. The green precipitate products were filtered, washed several times with hot water, dried at  $90\text{ }^\circ\text{C}$  in an oven for three hours, and then in vacuo over anhydrous  $\text{CaCl}_2$ . The yield of cupric carbonate obtained is in the range of 80 to 87% depending on the type of anion bound to the cupric ion. Elemental analysis (C, H and N contents were measured using a Perkin Elmer CHN 2400 (USA)) of cupric carbonate obtained during the reaction of urea with cupric acetate, nitrate or perchlorate were almost the same and indicated the absence of nitrogen. Analysis of the obtained products:  $\text{CuCO}_3$  (123.55 g/mol) C, 9.69(9.71); Copper, 51.24 (51.44). The calculated values are shown in parentheses. The carbonate content of the  $\text{CuCO}_3$  product was

determined using a standard hydrochloric acid solution, [19] while cupric(II) was determined gravimetrically as cupric oxide which is stable after ignition. The infrared spectra of urea and chemical products in potassium bromide tablets were recorded using a Gensis II FT IR spectrophotometer. The contents of copper(II) in the compound solutions were determined using the atomic absorption technique. An atomic absorption spectrometer model PYE-UNICAM SP 1900 and corresponding lamps were used for this purpose.

## 3. Results and discussions

A green solid product is produced during the reaction of urea with copper(II) salts at a temperature of about  $90\text{ }^\circ\text{C}$  in aqueous media. The infrared spectra of the free urea and the solid product are shown in Figure 1, and their band assignments are given in Table 1. The infrared spectrum of the green solid product shows no bands due to the coordinated urea but a set of bands characteristic of the ionic carbonate,  $[\text{CO}_3]^{2-}$  present. Accordingly, to the data obtained from the elemental analysis of the products, with their IR spectrum as well as the determination of  $\text{CO}_3^{2-}$  with HCl and that the IR spectrum of commercially obtained  $\text{CuCO}_3$  is the same as that of the reaction product. The obtained product is defined as  $\text{CuCO}_3$ . The infrared assignments agree well with those generally known for carbonate ionic  $\text{CuCO}_3$ . However, in some cases [21], the same metal carbonate products,  $\text{MnCO}_3$ ,  $\text{CoCO}_3$  and  $\text{PbCO}_3$  were obtained regardless of the associated counter ions of cadmium(II), zinc(II), cobalt(II), and manganese(II) ions. In this study, we obtained the same reaction product,  $\text{CuCO}_3$ , using copper ions with different counter ions, for example  $(\text{CH}_3\text{COO}^-)$ ,  $(\text{NO}_3^-)$ ,  $(\text{ClO}_4^-)$ . The formation of this compound when heating an aqueous mixture of copper (II) acetate, nitrate and perchlorate can be understood as follows. At room temperature, the compound  $[\text{Cu}(\text{urea})_2\text{X}_2]$  [18] is formed where urea coordinates with the Cu(II) ion via its oxygen atom. At high temperatures the following reactions may occur giving the corresponding metal carbonate.

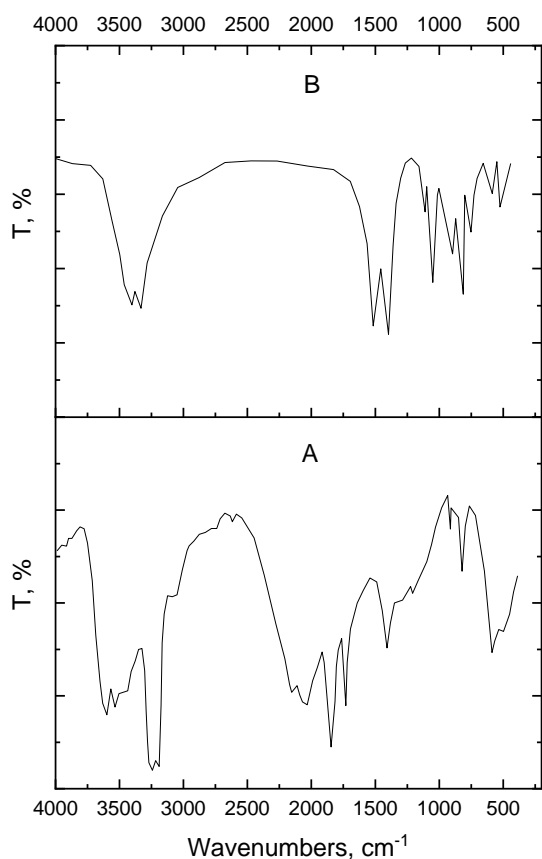


**Table 1.** Infrared frequencies<sup>a</sup> ( $\text{cm}^{-1}$ ) and assignments<sup>b</sup> for  $\text{CuCO}_3$  formed in the reaction of  $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{ClO}_4)_2$ , with urea at  $\sim 90\text{ }^\circ\text{C}$ .

$\text{cm}^{-1}$ <sup>a</sup>	Assignments <sup>b</sup>
1518 vs 1398 vs 1055 s	$\nu(\text{C-O})$ ; $\text{CO}_3$
815 s 747 ms	$\delta(\text{OCO})$ ; $\text{CO}_3$
584 w 524 ms	$\nu(\text{Cu-O})$ ; $\text{CuCO}_3$

<sup>a</sup> br, broad; m, medium; sh, shoulder; s, strong; w, weak

<sup>b</sup>  $\nu$ , stretching;  $\delta$ , bending.



**Fig. 1.** Infrared spectra of A: urea free ligand; B:  $\text{CuCO}_3$  formed in the reaction of  $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{ClO}_4)_2$ , with urea at  $\sim 90^\circ\text{C}$ .

## References

1. T. J. Bhoopathy, M. Baskaran and S. Mohan, *Indian J. Phys.*, 62 B (1), 47 (1988).
2. A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, Columba Curran and J. V. Quagliano, *J. Amer. Chem. Soc.*, 80, 527 (1958).
3. J. L. Duncan, *Spectrochim. Acta, Part A*, 27, 1197 (1970).

4. G. B. Aitken, J. L. Duncan and G. P. Mc Quillan, *J. Chem. Soc. A*, 2695, (1971).
5. D. Hadzi, J. Kidric, Z. V. Knezevic and B. Barlic, *Spectrochim. Acta, Part A*, 32, 693 (1976).
6. Sib Sankar Bala and Pradip N. Ghosh, *J. of Molecular Structure*, 101, 69 (1983).
7. L. Kellner, *Proc. Roy. Soc., A* 177, 456 (1941).
8. R. D. Waldron and R. M. Badger, *J. Chem. Phys.*, 18, 566 (1950).
9. E. R. Andrew and D. Hyndman, *Proc. Phys. Soc., A* 66, 1187 (1953).
10. A. Yamaguchi, T. Miyazawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, 10, 170 (1957).
11. J. E. Stewart, *J. Chem. Phys.*, 26, 248 (1957).
12. R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, *J. Amer. Chem. Soc.*, 79, 1575 (1957).
13. Yu. Ya. Kharitonov and T. N. Gushchina, *Zh. Neorg. Khim.*, 33(3), 808 (1988).
14. M. Koman, E. Jona and D. Nagy, *Z. Kristallogr.*, 210(11), 873 (1995).
15. Z. Ye, H. Zhang, R. Yang, M. Cai, W. Chen and W. He, *Fuzhou Daxue Xuebao, Ziran Kexueban*, 22(5), 97 (1994).
16. K. Gyoryova and V. Balek, *J. Therm. Anal.*, 40(2), 519 (1993).
17. V. F. Resnyanskii, D. K. Sulaimankulova, V. A. Kuznetsov, K. S. Sulaimankulov and M. D. Davranov, *Kristallografiya*, 38(5), 212 (1993).
18. O. Yar and L. Lessinger, *Acta Crystallogr., Sect. C Cryst. Struct. Commun. C* 51(11), 2282 (1995).
19. Vogel, "Qualitative Inorganic Analysis", John Wiley & Sons, Inc. New York (1987).
20. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Wiley, New York, (1978).
21. Ghaferah H. Al-Hazmi, Khuloud A. Albrahim, M.S. Refat, Omar B. Ibrahim, Abdel Majid A. Adam, Sonam Shakya, *Bulletin of the Chemical Society of Ethiopia*, 36(2), 363-372 (2022).

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