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A Novel Method for the Synthesis of Metal Carbonates. I. Synthesis and Infrared Spectrum of Manganese Carbonate, $MnCO_3.H_2O$, Formed by the Reaction of Urea with Manganese(II) Salts

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A NOVEL METHOD FOR THE SYNTHESIS OF METAL CARBONATES. I. SYNTHESIS AND INFRARED SPECTRUM OF MANGANESE CARBONATE, $MnCO_3.H_2O$, FORMED BY THE REACTION OF UREA WITH MANGANESE(II) SALTS

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ABSTRACT

Manganese(II) carbonate, $MnCO_3.H_2O$, is obtained by a new synthetic method involving the reaction of aqueous solutions of $MnCl_2$, $Mn(NO_3)_2$, $MnSO_4$ or $Mn(CH_3COO)_2$ with urea at ~ 80°C. The infrared spectrum of the formed product clearly indicates the absence of bands due to urea and shows the characteristic bands of carbonate ion. A general mechanism describing the formation of manganese carbonate, $MnCO_3.H_2O$, is suggested.

INTRODUCTION

The reactions between transition metal ions and urea at room temperature, have been studied extensively[1-6] and many metal-urea complexes have been isolated and characterized. Obviously, it is clear that urea may coordinate either via its oxygen or its nitrogen atoms, depending on the type of metal ion[6-7]. Studies on the nature of the reaction of urea with metal ions at high temperature are rare in the literature, and the available investigations[8-11] show an interesting feature, the reaction products depend not only on the type of metal ion but also on the metal salt used in the reaction. The present investigation was undertaken to study the course of the reaction of urea with manganese(II) ions, $MnCl_2$, $Mn(NO_3)_2$, $MnSO_4$ or $Mn(CH_3COO)_2$, in aqueous media at ~ 80°C. The reaction products were characterized by elemental analyses, infrared spectra as well as thermal analysis. The study of the urea complexes is of interest due to the utility of urea complexes as micronutrients and complex fertilizers.

EXPERIMENTAL

Reagent grade chemicals were used throughout. $MnCO_3.H_2O$ was prepared by mixing equal aqueous solutions (100 mL) of 0.01 mol of manganese(II) salts, $MnCl_2.4H_2O$, $Mn(NO_3)_2.4H_2O$, $MnSO_4.H_2O$ or $Mn(CH_3COO)_2.2H_2O$ with (100 mL) of 0.1 mol urea. The mixtures were heated to *ca.* 80°C for 1-2 h in a water bath. The precipitated brown complex was filtered, washed several times with hot water, dried at 80°C in an oven for 3 h, and then *in vacuo* over silica gel. The yields were 67,71,72 and 76%, for the following manganese salts used: chloride (67%), nitrate (71%), sulphate (72%) and acetate (76%), respectively. The elemental analyses for $MnCO_3.H_2O$ formed in all experiments using different manganese salts were almost the same and indicate the absence of nitrogen. Analysis of $MnCO_3.H_2O$ obtained using $Mn(CH_3COO)_2.2H_2O$ is as follows: (CH_2MnO_4): C, 10.4 (9.03); H, 1.65 (1.5); Mn 41.53 (41.32). The calculated values are shown in parentheses. Carbonate in $MnCO_3.H_2O$ was determined by titration with standard HCl solution, while Mn^{+2} was determined gravimetrically as manganese dioxide, MnO_2. The IR spectra of urea and all reactants and products were recorded in KBr discs using a Perkin - Elmer 1430 Ratio - Recording Infrared Spectrophotometer.

RESULTS AND DISCUSSION

The reaction of aqueous solutions of urea and manganese(II) salts at *ca.* ~ 80°C produces a brown solid crystalline product. The infrared spectrum of the solid product is shown in Fig. 1 and its band assignments are given in Table I.

The infrared spectrum of the obtained product shows no bands due to coordinated urea, but instead, a group of bands characteristic for ionic carbonate,[12] CO_3^{2-}, appeared. Based on this fact, along with that obtained from elemental analysis data as well as the determination of CO_3^{2-} with HCl and that the infrared spectrum of commercially obtained $MnCO_3.H_2O$ is the same as that of the reaction product, the product obtained was identified as $MnCO_3.H_2O$. The IR assignments agree quite well with those generally known for the ionic carbonate, $MnCO_3$. Previous studies[8-11] indicate 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 salt used. However, in this investigation, we have obtained the same reaction product, $MnCO_3.H_2O$ by using manganese(II) ions with different counter ions, e. g., $MnCl_2$, $Mn(NO_3)_2$, $MnSO_4$ or $Mn(CH_3COO)_2$. The role of Mn(II) ions in decomposing the coordinated urea at high temperature may be understood as follows.

Table I

Infrared Frequencies (cm^{-1}) and Assignments for $MnCO_3.H_2O$ Formed in the Reaction of $Mn(CH_3COO)_2.2H_2O$ with Urea at 80°C.

(cm^{-1})[a]	Assignments[b]
3446 s, br	ν(O-H); H_2O
1637 sh	δ(H_2O); H_2O
1400 s, br, 1050 w	ν(C-O); CO_3^{2-}
858 s, 721 ms	δ(OCO); CO_3^{2-}

a: br, broad; m, medium; sh, shoulder; s, strong; w, weak
b: ν, stretching; δ, bending.

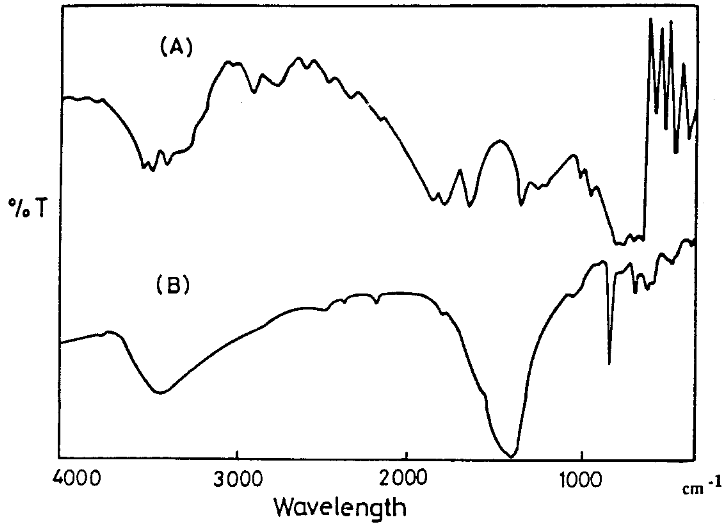

Fig. 1. Infrared Spectra of (A) Urea and (B) $MnCO_3.H_2O$ formed in the reaction of $Mn(CH_3COO)_2.2H_2O$ with Urea at 80°C.

At room temperature, manganese(II) ions react with urea to form the complex[5] $[Mn(urea)_4]X_2$. At high temperature, the following reaction may take place:

$$[Mn(urea)_4]X_2 + 5H_2O \xrightarrow{ca\ 80^0\ C} MnCO_3 + 3CO_2 + 2NH_4X + 6NH_3$$

$$(X = Cl^-, NO_3^-, CH_3COO^-, \text{or } 1/2\ SO_4^{2-})$$

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