Mechanism of formation of Cu(II) carboxylates in the solid state 1. Kinetics of reactions between benzoic acid, salicylic acid and CuCO$_3$ Cu(OH)$_2$

P S BASSI, B R GUPTA and I B SHARMA

Department of Chemistry, University of Jammu, Jammu 180 001, India

Abstract. The kinetic data for reactions between aromatic acids, i.e. benzoic acid, salicylic acid and basic copper carbonate in the solid state have been recorded. The measurements have been made at various temperatures for fixed sizes of the particles at constant compression. The products are characterised by infrared and reflectance spectra. The reactions are diffusion-controlled with activation energy of 71.8 and 115.0 $\pm$ 5 kJ mol^{-1} for the formation of Cu(II) benzoate and Cu(II) salicylate respectively.

Keywords. Benzoic acid ; salicylic acid ; copper carbonate ; solid state reactions ; kinetics.

1. Introduction

In recent years metal carboxylates and their adducts have attracted considerable attention in chemistry because of their importance in industry and their interesting structures. The crystal structure (William and Toland 1961; Koizumi *et al* 1963) and the thermal decompositions (Bassi and Kalsi 1976; Bassi *et al* 1977; Nagase *et al* 1975; Borel *et al* 1976) of some of the copper (II) carboxylates have been a subject of considerable recent interest. Ordinarily these carboxylates are prepared in a solvent such as water from the reaction between carboxylic acid or its sodium salt with transition metal salt at an adjusted pH (Lewis and Mabb 1965). For example Cu(II) (C$_6$H$_5$COO)$_2$ is prepared by warming a concentrated solution (pH = 5) of sodium benzoate and CuSO$_4$ in water (Lewis *et al* 1965). Recently it has been reported that thermal decompositions of solid Cu(II) benzoate and salicylate give CuCO$_3$ · Cu(OH)$_2$ as an intermediate (Bassi and Kalsi 1976; Bassi *et al* 1977). It was therefore considered interesting to prepare these carboxylates from CuCO$_3$ · Cu(OH)$_2$ and acids in the solid state. The present paper reports a new technique for the preparation of Cu(II) carboxylates when the reactants are mixed in the solid state. In this method the adjustment of pH and the use of a solvent etc. are avoided in solid state reactions and thus facilitating the

determination of the mechanism of a reaction. This paper reports the kinetics of formation of Cu(II) carboxylates from $CuCO_3 \cdot Cu(OH)_2$ and the organic acids in the solid state. Since the colour of the products formed is quite different from the colour of the reactants, the kinetics are determined from the movement of the coloured boundary.

2. Experimental

2.1. *Materials*

$CuCO_3 \cdot Cu(OH)_2$ and the organic acids of AR grade were used without further purification. The purity of the organic acids was checked by comparing their melting points with those given in literature. The materials were dried at 373 K before use.

2.2. *Preparation of carboxylates in the solid state*

A small but equimolar amount of previously dried reactants as loose powders, i.e. $CuCO_3 \cdot Cu(OH)_2$ and organic acids were thoroughly mixed in small china crucibles and were kept in an oven set at a constant temperature, with $\pm 0 \cdot 1$ K variation at any temperature well below the melting points or eutectic points of the reactants to avoid any liquid formation. $CuCO_3 \cdot Cu(OH)_2$ reacted with C_6H_5COOH, $C_6H_4(OH)COOH$, $COOH(CH_2)_2COOH$, $COOH(CH_2)_4COOH$ and $C_6H_5CH : CHCOOH$ (trans) and gave products of different colours such as sky blue, green, light blue, greenish blue. No reactions were however noticed between $CuCO_3 \cdot Cu(OH)_2$ and $COOH \cdot COOH$, $COOHC_2H_2COOH$, $COOH(CH_2)_3COOH$ and phthalic acid even after keeping the reaction mixtures for days together in an oven. The products were characterised by reflectance spectra (spectrophotometer VSU–2P using MgO as the reference material) and infrared spectra (SP–2,000 Pye-unicam).

2.3. *Kinetic study of solid state reactions*

Kinetics of reactions between $CuCO_3 \cdot Cu(OH)_2$ and C_6H_5COOH and between $CuCO_3 \cdot Cu(OH)_2$ and $C_6H_4(OH)COOH$ were studied in detail by capillary technique (Rastogi *et al* 1963; Rastogi and Dubey 1967). A small amount of reactant $CuCO_3 \cdot Cu(OH)_2$ was pushed in a clean and dry glass capillary tube (inside bore 5 mm) and was held at constant pressure (5090 g/cm²) in an oven. Plugs of C_6H_5COOH and $C_6H_4(OH)COOH$ were prepared at known pressure (5090 g/cm²) and were pushed successively in different tubes from the other end. The two reactants formed a sharp boundary.

Since powder packing affects the reaction rate, all reactions were studied under similar packing and in capillaries of similar dimensions and held at the same pressure. Evidence for the formation of the products at the boundary came when a specified coloured product (sky blue in the case of C_6H_5COOH and green with $C_6H_4(OH)COOH$ was formed. The growth of the coloured boundary was noticed through a microscope (least count $\pm 0 \cdot 002$ cm) measured after known intervals of time.

3. Results and discussion

This is not a simple addition or double decomposition type of solid state reaction. The first stage of the reaction involves the formation of the Cu(II) carboxylates at the phase boundary of $CuCO_3 \cdot Cu(OH)_2/C_6H_5COOH$ and $CuCO_3 \cdot Cu(OH)_2/ C_6H_4(OH)COOH$ with the evolution of CO_2 and H_2O as gaseous products. The evolution of these gases will not disturb the phase boundary reaction at this stage or even at a later stage because the reaction is very slow and is isothermal. The small amounts of the gaseous products will move away from the reaction zone through the sides of the capillary tube and the voids between the particles of the plugs.

The second stage of the reaction involves the diffusion of certain species through the product layer to react at the interfaces. It follows the equation:

$$\zeta^2 = kt + c, \tag{1}$$

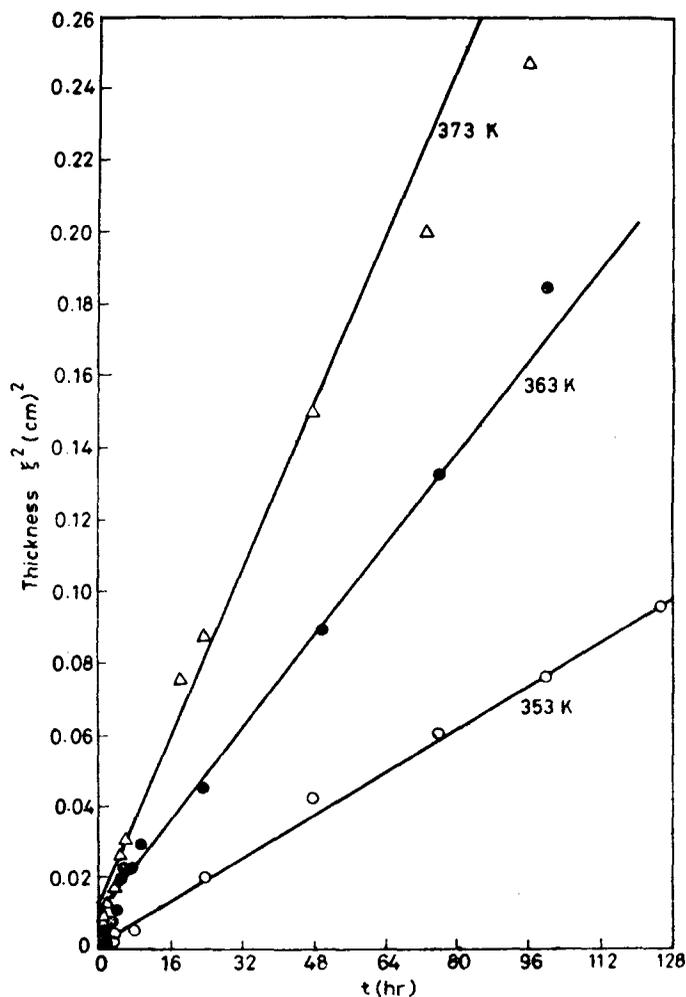where ζ is the thickness of the coloured boundary, t is time, k and c are constants.

Figure 1. Kinetic data for reaction between $CuCO_2Cu(OH)_2$ and C_6H_5 COOH.
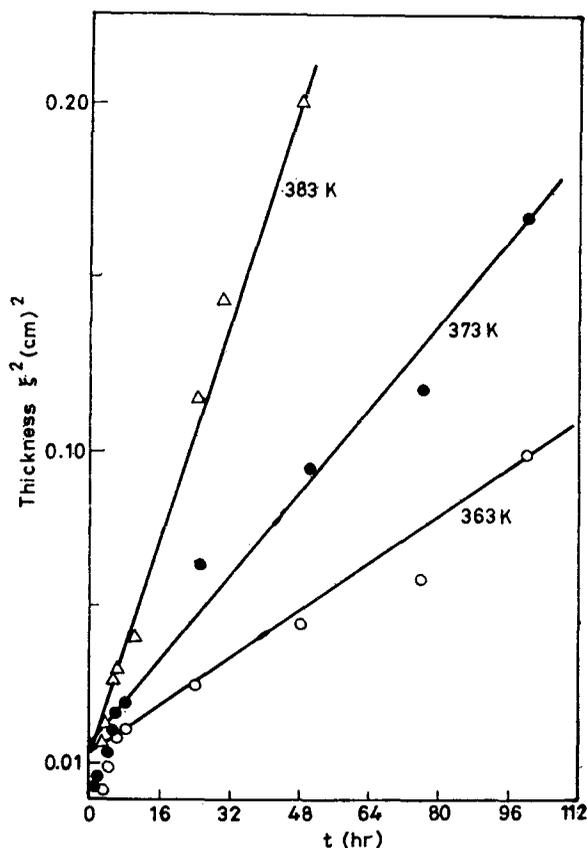
Figure 2. Kinetic data for reaction between $CuCo_3Cu(OH)_2$ and $C_6H_4(OH)COOH$.

The diffusion of the organic acid molecule or ion is highly unlikely as they are bulky as compared to that of other ions. However Cu^{2+} ions and protons will diffuse through the product layer in opposite directions. The Cu(II) carboxylate is formed at the carboxylate/organic acid interface while CO_2 and H_2O are formed and escape from the carboxylate/$CuCO_3 \cdot Cu(OH)_2$ interface. Figures 1 and 2 show the results for reactions between $CuCO_3 \cdot Cu(OH)_2$ and C_6H_5COOH and between $CuCO_3 \cdot Cu(OH)_2$ and $C_6H_4(OH)COOH$ at different intervals of time for fixed particle size (80–120 mesh) at different temperatures. It has been observed that the initial points do not lie on the straight line. However, after about 4 hr, the process becomes diffusion-controlled (equation (1)). The energy of activation of the process was determined from the equation $k = A \exp(-E/RT)$, i.e. Arrhenius plot. It comes out to be 71·85 kJ mol^{-1} and 115·0 kJ mol^{-1} for the formation of Cu(II) benzoate and Cu(II) salicylate respectively. This difference in reactivity is due to the difference in diffusivities of Cu^{2+} ions and protons through the two-product layers. Cu(II) benzoate is a relatively simpler compound than Cu (II) salicylate; therefore, the diffusion of these ions will be easier through Cu(II) benzoate than through Cu(II) salicylate. Thus Cu(II) benzoate should be formed with better ease as compared to Cu(II) salicylate. The comparison of k values (table 1) for both the reactions also substantiates this argument.

Table 1. Parameters of equation (1) for the reaction between $CuCO_3 \cdot Cu(OH)_2$ and benzoic acid and $CuCO_3 \cdot Cu(OH)_2$ and salicyclic acid.

k (cm²/hr) Temp. (K)	353	363	373	383
Cu(II) benzoate	75×10^{-5}	16×10^{-4}	31×10^{-4}	..
Cu(II) salicylate	..	87×10^{-5}	11×10^{-4}	35×10^{-4}

The formation of the products, i.e. Cu(II) benzoate and Cu(II) salicylate is seen in the reflectance spectra (figure 3) of the compounds. It is seen that in the region 500–1000 nm there is a band which shows greater reflectance with the peak shifted towards lower wavelength in Cu(II) salicylate and decreased reflectance in Cu(II) benzoate without any characteristic peak. In the region 500–200 nm is seen the formation of certain new peaks in Cu(II) benzoate and disappearance of peaks in Cu(II) salicylate. Besides a shallow reflectance band between 375–550 nm is converted into an absorption region for Cu(II) salicylate and Cu(II) benzoate.

Further confirmation of the formation of Cu(II) benzoate and Cu(II) salicylate in the solid was established by comparing the IR spectra (200–4000 cm⁻¹) of the $CuCO_3 \cdot Cu(OH)_2$, Cu(II) benzoate prepared in solution and Cu(II) benzoate prepared in the solid state. The IR spectra of Cu(II) benzoates completely matched with each other. Similarly the IR spectra of Cu(II) salicylates prepared in solution (Kishita and Kubo 1963) and in the solid state exactly matched with each other. These observations prove that the two methods of preparing the Cu(II) carboxylates give identical results.
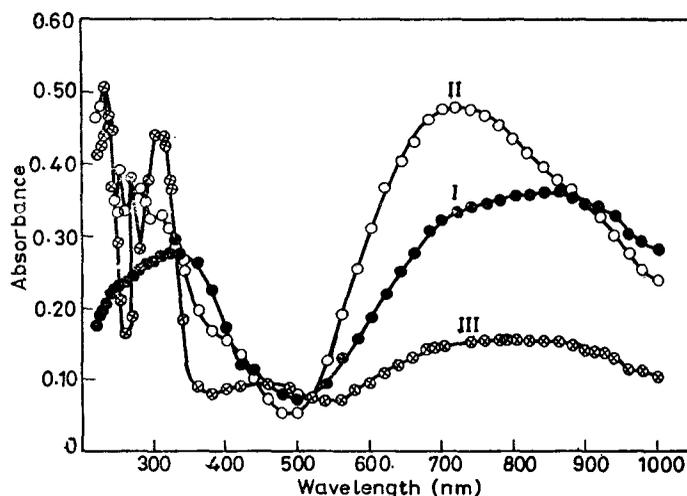

Figure 3. Reflectance spectra of I. $CuCO_3Cu(OH)_2$. II. $(C_6H_5COO)_2Cu$ from the solid state reaction between $CuCO_3Cu(OH)_2$ and C_6H_5 COOH. III. $(C_6H_4OH\ COO)_2Cu$ from the solid state reaction between $CuCO_3Cu(OH)_2$ and $C_6H_4(OH)$ COOH.

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