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STUDIES IN SOLID STATE REACTIONS BETWEEN BASIC COPPER CARBONATE WITH CINNAMIC, SUCCINIC AND ADIPIC ACIDS

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ABSTRACT

Solid–solid reactions of basic copper carbonate with cinnamic, succinic and adipic acids give the corresponding copper(II) carboxylate chelates with the elimination of carbon dioxide and water. Products were characterized by spectral and magnetic studies. The kinetic measurements were made at various temperatures for fixed particle size of the reactants under constant compression. The reactions are diffusion controlled with activation energies of 19.9, 8.8 and 15.9 kJ mol^{-1} for the formation of Cu(II) cinnamate, Cu(II) succinate and Cu(II) adipate, respectively.

INTRODUCTION

Copper carboxylate complexes have been studied extensively. These complexes have been obtained from solution by different synthetic methods, but only a few attempts have been made to prepare them from the solid phase. In solution the reaction is very fast and it is difficult to determine the kinetic parameters for the formation of the complexes, compared to the reactions in solids in which the reaction is quite slow. The kinetics and formation of the complexes of benzoic, salicylic, 2-, 3-, and 4-aminobenzoic acids with copper carbonate have already been reported [1,2]. A relationship between reactivity and the position of the amino group in the benzene nucleus has been observed. Here we report the formation and kinetic studies of the complexes of succinic, adipic and cinnamic acids with copper(II) by the reaction of these acids with basic copper carbonate in the solid state. The reactivity of different organic compounds can be correlated with their acidity constants, provided the nature and crystal structures of the reacting acids are similar. The structure of adipic, succinic and cinnamic acids have been reported [3–5]. The synthesis and properties of corresponding copper(II) carboxylates have also been reported in the solution phase [6,7].

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MATERIALS AND METHODS

Basic copper carbonate (BDH) and organic acids of AnalaR grade were used as such. The composition of copper carbonate was determined volumetrically: the percentage of copper found was 55.8 (calculated 57.5%). The products from the solid phase were prepared by mixing copper carbonate and the respective acids in the molar ratio 1 : 2 using agate pestles and mortars. The mixtures were kept in a thermostat (373 K) for 24 h. Products from the solution phase were prepared by known methods [6,7].

Kinetics

The solid state reactions between copper carbonate and cinnamic, succinic and adipic acids (particle size 125–177 μm) were studied by the capillary technique [8]. A small amount of copper carbonate was pushed into a glass capillary tube with the help of glass rods and held at constant pressure (5090 g cm^{-2}). Plugs of acids were pushed from the other end and held at the same pressure. The reactants formed a sharp boundary. The capillary tube was then placed in a thermostat and the growth of the product boundary was studied with time using a microscope (accuracy ± 0.002 cm).

RESULTS AND DISCUSSION

The solid–solid reactions of cinnamic, adipic and succinic acids with basic copper carbonate give the corresponding copper(II) carboxylates. In the reflectance spectra (Fig. 1), copper carbonate absorbs at 840 nm (**I**), freshly mixed $CuCO_3 \cdot Cu(OH)_2$ and succinic acid have absorption bands at 850 nm (**II**). The absorption maxima in the spectra of Cu(II) succinate synthesized from solid (**III**) and solution phase (**IV**) reactions are at 700 and 695 nm respectively. These clearly show the formation of Cu(II) succinate in the solid state. Similar behaviour is observed for reactions with cinnamic and adipic acids also. From the band positions it is clear that the spectra of the freshly mixed components are very similar to the spectrum of pure copper carbonate, and the spectra of the products obtained from the reactions in solid and solution phase are identical. This shows that the extent of reaction on immediate mixing is negligible, but the reaction goes to completion on prolonged contact between the reactants at higher temperatures (below the eutectic and melting points of the reactants).

The infrared spectra of the solid products show strong absorptions at 1550 and 1390 cm^{-1} due to the asymmetric and symmetric carboxylate stretching vibrations (Table 1). Bands due to unreacted carboxylic acids are completely absent from the spectra of the final products. The infrared spectra of solid and solution phase products are superimposable. The

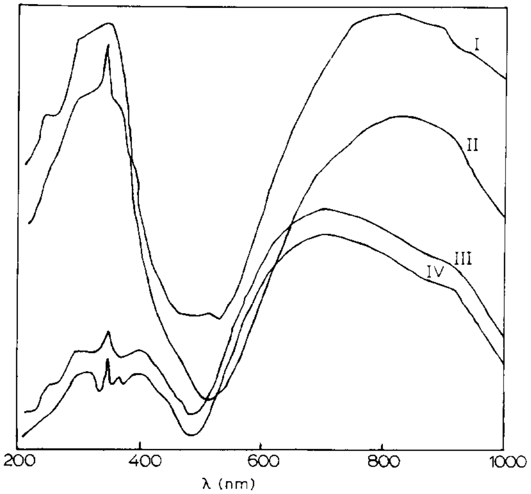

Fig. 1. Reflectance spectra of basic copper carbonate and succinic acid.

magnetic moment values of the complexes are in the range 1.4–1.7 B.M. These observations prove that the two methods of preparing Cu(II) carboxylates give identical results.

The kinetics of these reactions have been determined by the capillary technique at 353, 363 and 373 K. The kinetic data are best fitted to the parabolic equation $\xi^2 = kt + c$ where ξ is the thickness of the coloured product layer at time t and k and c are constants. The parabolic nature of the equation indicates that the reactions are diffusion controlled. Copper(II) carboxylate is formed at the carboxylate/organic acid interface with the evolution of carbon dioxide and water as gaseous products which diffuse away from the reactant/product interface along the sides of the capillary tube and the voids between the reacting particles. The evolution of these gases will not disturb the phase boundary reaction at any stage, because the

TABLE 1

Spectral data for the products obtained from solid and solution phase reactants

Complex	Phase	Reflectance (nm) λ_{max}	Infrared (cm^{-1}) νCOO asym	νCOO sym
Cu(II) cinnamate	Solid	720	1550	1390
	Solution	700	1550	1390
Cu(II) adipate	Solid	730	1570	1330
	Solution	740	1580	1325
Cu(II) succinate	Solid	700	1580	1325
	Solution	695	1575	1325

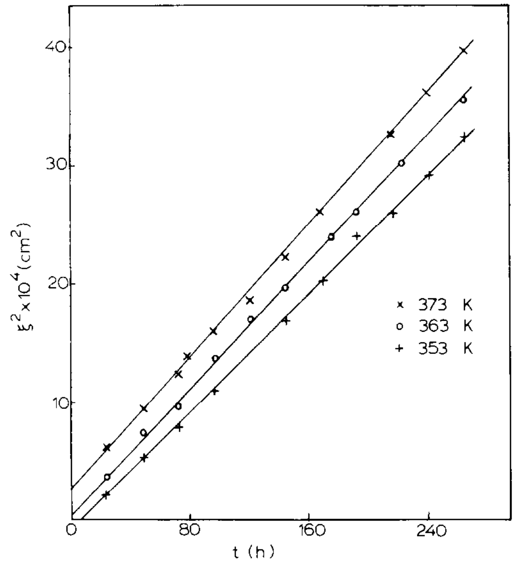

Fig. 2. Kinetic data for the reaction between basic copper carbonate and succinic acid.

reaction is very slow and isothermal. Figures 2–4 show the results for the reactions of copper carbonate with succinic, adipic and cinnamic acids, respectively at different intervals of time for fixed particle size (125–177 μm) under constant compaction at different temperatures. The values of energy of activation for these reactions as determined from Arrhenius plots are given in Table 2.

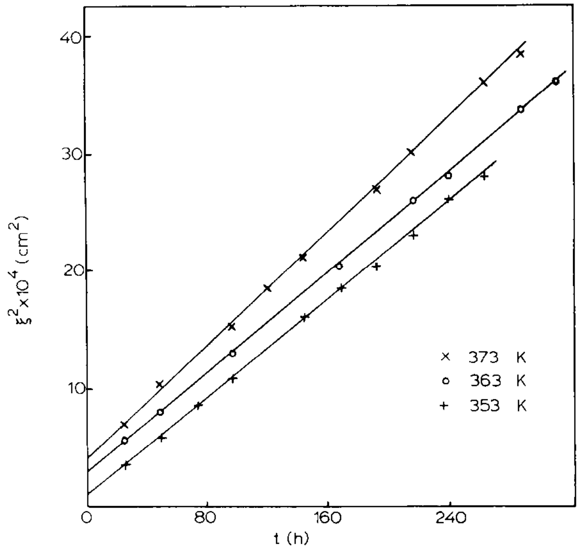

Fig. 3. Kinetic data for the reaction between basic copper carbonate and adipic acid.

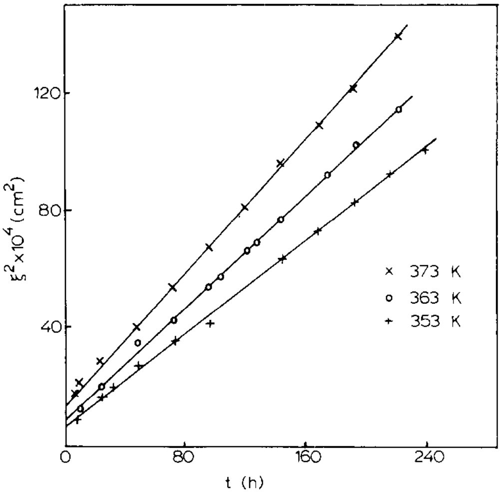

Fig. 4. Kinetic data for the reaction between basic carbonate and cinnamic acid.

From the E_a values the reactivity order for the acids is cinnamic > adipic > succinic acid. These reactions are anion exchange reactions in which the weakly acidic carbonate and hydroxyl groups on Cu^{2+} are replaced by more favourable carboxylate anions. These reactions occur by proton transfer from the organic acid which combines with carbonate and hydroxyl ion to liberate carbon dioxide and water as gaseous products. The acid–base reaction is favoured because of the basic nature of copper carbonate ($pK_a = 6.38$) compared to the greater acidic character of succinic acid (4.21), cinnamic acid (4.44) and adipic acid (4.43). The difference in reactivity may be due to the difference in the proton transfer capabilities of the reacting acids when the reactants come into contact with each other. If the structures

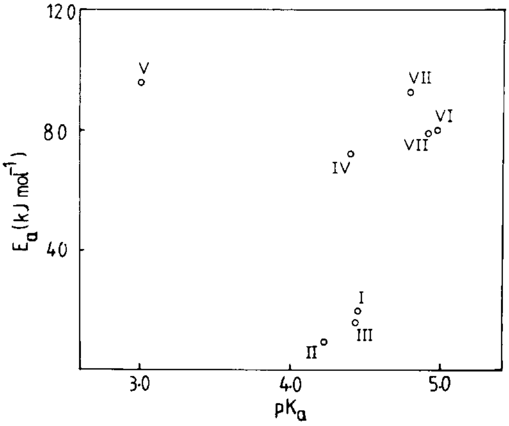

Fig. 5. Plot of pK_a against E_a.

TABLE 2

Kinetic and other data for the copper carboxylate complexes and free reactant acids

Complex	E_a (kJ mol^{-1})	A (s^{-1})	Heat of sublimation [a] (kJ mol^{-1})	pK_a [a]	Space group [a]
Cu(II) cinnamate	19.9	$10^{1.5}$	–	4.44	$P2_1/a$
Cu(II) succinate	8.8	$10^{3.6}$	116.9 [b]	4.21	$P2_1/a$
Cu(II) adipate	15.9	$10^{2.8}$	128.7 [b]	4.43	$P2_1/c$
Cu(II) benzoate	71.8	$10^{8.0}$	91.0 [b]	4.40	$P2_1/c$
Cu(II) salicylate	95.8	$10^{7.3}$	94.7 [b]	3.00	$P2_1/a$
Cu(II)-2-amino-benzoate	80.0	$10^{1.0}$	99.0 [c]	4.97	$P2_1cn$
Cu(II)-3-amino-benzoate	92.7	$10^{1.2}$	121.3 [c]	4.79	$P2_1/c$
Cu(II)-4-amino-benzoate	78.8	$10^{1.1}$	113.0 [c]	4.92	$P2_1/n$

[a] Data for corresponding pure acids.
[b] From ref. 10.
[c] From ref. 11.

of the reacting species in a series are similar, then a relationship between parameters characteristic of ligand acidity with reactivity has been observed [9].

There is no correlation between pK_a of the organic acid and E_a values for their reactions with basic copper carbonate (Table 2). Due to the differences in the nature and crystal structures of the carboxylic acids, the differences in reactivity are not quantitatively dependent on the acidity constants of these acids.

Out of the various possible modes of diffusion, bulk diffusion is not possible, as large amounts of energy would be involved. The values of activation energy for the formation of these carboxylates are significantly lower than the heats of sublimation of the reacting organic acids which are given in Table 2 [10,11]. Also the vapour pressures [10] are very low at the temperatures at which these reactions have been studied. The low values of frequency factors also support the observation that the contribution of vapour phase diffusion is not significant in these reactions. Vapour phase reaction will have very high frequency factors, as is known in homogeneous reactions or even in heterogeneous gas–solid reactions. The only mode of reaction, therefore, in these reactions is surface diffusion. The reaction first occurs at the point of contact of the two reactants, followed by surface migration over the grains. The reaction within the grains occurs via diffusion through line or planar defects and also through cracks which will develop in the product layer as a result of very large differences between the molecular sizes of the product and reactant.

REFERENCES

1 P.S. Bassi, B.R. Gupta and I.B. Sharma, Proc. Ind. Acad. Sci. (Chem. Sci.), 89 (1980) 125.
2 P.S. Bassi and G.S. Chopra, J. Solid State Chem., 62 (1986) 253 and references therein.
3 J. Housty and M. Hospital, Acta Crystallogr., 18 (1965) 697.
4 J.S. Broadley, D.W.J. Cruickshank, J.D. Morrison, J.M. Robertson and H.M.M. Shearer, Proc. Roy. Soc. London, Ser. A, 251 (1959) 441.
5 G.M.J. Schmidt, J. Chem. Soc., (1964) 2014.
6 L. Dubicki, C.M. Harris and R.L. Martin, Inorg. Chem., 5 (1966) 93.
7 V.G. Zaletov and A.D. Samenov, Teor. Eksp. Khim., 6 (1970) 275.
8 R.P. Rastogi, P.S. Bassi and S.L. Chaddha, J. Phys. Chem., 67 (1963) 2569.
9 P.S. BAssi and G.S. Chopra, J. Solid State Chem., 61 (1986) 103.
10 Robert Weast, Handbook of Chemistry and Physics, The Chemical Rubber Company, Ohio, 1972.
11 R. Sabbah, R. Chastel and M. Laffitte, Can. J. Chem., 52 (1974) 2201.