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Solid State Reactivity of Organic Compounds with Inorganic Compounds

I. Reactions of Cupric Acetate and Copper Carbonate with 2-, 3-, and 4-Aminobenzoic Acids

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The reactions of 2-, 3-, and 4-aminobenzoic acids with copper acetate and basic copper carbonate were studied in the solid state. The products have been identified as bis(aminobenzoato) copper(II) complexes. Kinetic data for the reactions have been recorded at various temperatures for fixed sizes of the particles at constant compaction. The order of reactivity is 2- > 4- > 3-aminobenzoic acid and copper acetate is more reactive than copper carbonate. These observations have been explained in terms of structural characteristics of the reactants. © 1986 Academic Press, Inc.

Introduction

Solid state reactions among inorganic solids are being studied extensively (*1*) while reactions between organic solids (*2*) continue to be a subject of extreme current interest. However, the study of solid state reactions between inorganic and organic solids has been rudimentary. There has been only one report (*3*) in which the solid phase synthesis and mechanism of formation of Cu(II) carboxylates have been studied from the reaction of copper carbonate with benzoic and salicylic acids.

Chelate complexes of amino benzoic acids with copper have attracted considerable attention because they help in understanding the processes occurring *in vivo*. The structure (*4*), magnetic properties, infrared (*5*) and also electronic spectra have been studied. There has been no attempt to prepare these complexes in the solid state. Present investigations report the synthesis and kinetics of formation of Cu(II) aminobenzoates from reactions of $Cu(CH_3COO)_2$ and $CuCO_3 \cdot Cu(OH)_2$ with 2-, 3-, and 4-aminobenzoic acids in the solid state. This method does not involve the adjustment of pH or the use of solvent, etc.

Experimental

Basic copper carbonate and the organic acids were of Analar grade and were used without further purification. The purity of organic acids was checked from melting points, which were sharp and agree with the literature values. Anhydrous copper acetate was prepared by drying the hydrated form at 393 K. Both copper acetate and copper carbonate were used in the anhydrous form because their hydrated species are reported to lose water at temperatures at which these reactions have been studied

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and hence cause complications in the study of kinetics of solid–solid reactions. The composition of the anhydrous samples was checked by analysing for copper volumetrically with EDTA: percentage found for copper acetate, 32.3 (calculated for $CuC_4H_6O_4$, 32.4); percentage found for copper carbonate 55.8 (calculated for $Cu_2CH_2O_5$, 57.5). All the reactants were sieved to obtain fixed particle size (<42 μm). The materials were always dried at 393 K immediately before use.

The copper(II) carboxylates were synthesized in the solid state by mixing copper acetate or basic copper carbonate with the organic acid in molar ratio of 1 : 2 or 1 : 4, respectively. After grinding for about 10 min, the mixture was kept in a thermostat at 393 K for 1 day.

The reflectance spectra of the samples were recorded on a VSU-2P type spectrophotometer in the region 200–1000 nm using magnesium oxide as reference material. The IR spectra were done on a SP3-300 Pye-Unichem instrument in the range 200–4000 cm^{-1} in potassium bromide disks. Magnetic studies were done on a Guoy balance. DTA studies were carried out on a unit coupled with DC microvoltmeter and *XY* recorder model BW-11, both of Rikadenki Kogyo and Eurotherm temperature programmer, in air with a heating rate of 5° min^{-1}.

The products from the solution phase were also prepared. Pure acids were first converted into their corresponding sodium salts and mixed with a solution of copper acetate in methanol. The complexes, precipitated immediately were filtered and washed with alcohol.

Kinetics

Since the vapor pressure, melting point, and rate of reaction depend on particle size for small particles, an estimate of the size of the powder particles for all reactants was made with a Carl-Zeiss microscope having magnification of 1250. The longest and the shortest sides of the smallest particles (in μm) are for 2-aminobenzoic acid, 22,15; 3-aminobenzoic acid, 6,2; 4-aminobenzoic acid, 7,4; copper acetate, 15,7; and copper carbonate, 12,5, respectively. The melting points of these particles as calculated using the Kelvin equation (*6*) modified by Thomson (*7*) do not differ by more than a fraction of a degree from the ones for a macroscopic crystal. This shows that the reactants do not melt at temperatures at which the reactions were studied and also that contribution to reaction of small and large crystals is not different.

The colors of products for 3- and 4-aminobenzoic acids are parrot green and dark green, respectively, and are distinctly different from those of reactants; so rates were measured from noting the increase in thickness of the product layer. Since the color of the product with 2-amino benzoic acid is not visually distinguishable from that of the reactant the kinetics for its reactions were not studied by this method.

Kinetics for these reactions were studied by two methods:

1. The capillary technique (*8*) was used to study the kinetics of the reactions of copper acetate and copper carbonate with 3- and 4-aminobenzoic acids. Glass capillaries (i.d. 2.5 mm, l = 6 cm) were packed with reactants (<42 μm) from either side of the capillary using steel rods, so as to have a sharp boundary at the interface of the two reactants, under a pressure of 8000 g/cm^2. These capillaries were kept in a thermostat (±0.1 K) and the movement of the colored boundary in it was noted with a microscope (least count ± 0.002 cm) as a function of time. Each reported measurement is a mean of three experiments with a standard deviation of 0.0042 cm.

2. Mass loss method: Fine powders of the reactants (<42 μm) were intimately mixed

in appropriate molar ratio and compressed into pellets of diameter 2 cm and thickness 1 mm under a pressure of 100 kP/cm^2. These pellets were taken in previously weighed dishes and kept in a thermostat. Change in weight which is due to loss of gaseous acetic acid for reactant copper acetate, and carbon dioxide and water for reactant copper carbonate, was recorded with time and each reported measurement is an average of four runs with a standard deviation of 5 × 10^{-4} g.

Results and Discussion

The solid–solid reactions of 2-, 3-, and 4-aminobenzoic acids with copper acetate and basic copper carbonate give bis(aminobenzoato) copper(II) complexes,

$$\underset{(s)}{\mathrm{Cu(CH_3COO)_2}} + \underset{(s)}{\mathrm{2C_7H_7NO_2}} \rightarrow \underset{(s)}{\mathrm{Cu(C_7H_6NO_2)_2}} + \underset{(g)}{\mathrm{2CH_3COOH}} \quad [1]$$

$$\underset{(s)}{\mathrm{CuCO_3 \cdot Cu(OH)_2}} + \underset{(s)}{\mathrm{4C_7H_7NO_2}} \rightarrow \underset{(s)}{\mathrm{2Cu(C_7H_6NO_2)_2}} + \underset{(g)}{\mathrm{CO_2}} + \underset{(g)}{\mathrm{3H_2O}}. \quad [2]$$

These reactions go to completion if the reactants are intimately mixed at room temperature and then kept in a thermostat. Reaction rate is very slow when the reaction mixture is kept in a thermostat without grinding. However, in the reaction of copper acetate with 2-aminobenzoic acid grinding is not necessary even at room temperature. Mechanical pressure applied during grinding was far below, either to lower the melting points of the reactants by any significant amount or to generate frictional heat to cause melting of the reactants. The effect of grinding is thus to ensure close contact so that reaction occurs in a short time.

The products have been characterized from reflectance spectra, IR spectra, magnetic moment, and thermoanalytical techniques. The reflectance spectra of the starting materials, the freshly mixed reactants and the products of solid phase and solution phase reactions were recorded. The reflectance spectra for the systems copper acetate-4-aminobenzoic acid and copper carbonate-4-aminobenzoic acid are shown in Figs. 1 and 2, respectively. The spectra give only the band positions and not the relative intensities. Products obtained from reactions with copper acetate and copper carbonate give identical spectra. The spectra of the freshly mixed components resemble those of the starting material, which indicates that insignificant amount of reaction occurs immediately after mixing. There is complete correspondence between the spectra for products obtained in solid phase as well as solution phase reactions.

Further evidence of the formation of Cu(II) carboxylates in the solid state is given by infrared spectral studies. The positions of the absorption maximas for the chelates are given in Table I. The N–H stretching frequency in the product is lower

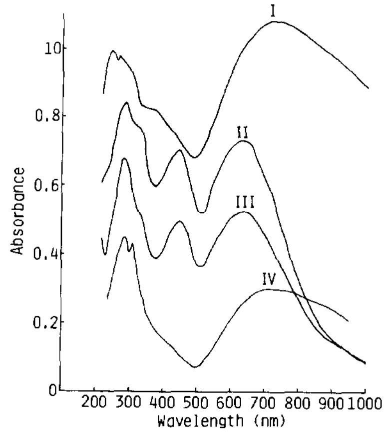

FIG. 1. Reflectance spectra of (I) $\mathrm{Cu(CH_3COO)_2}$; (II) $\mathrm{Cu(4\text{-}C_7H_6NO_2)_2}$ solution product; (III) $\mathrm{Cu(4\text{-}C_7H_6NO_2)_2}$ from the solid state reaction between $\mathrm{Cu(CH_3COO)_2}$ and $\mathrm{4\text{-}C_7H_7NO_2}$; (IV) freshly mixed reactants.

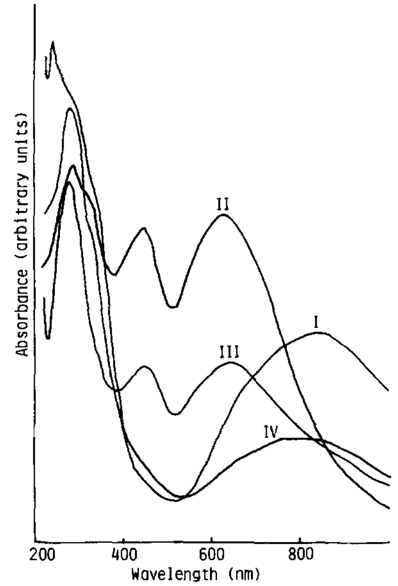

FIG. 2. Reflectance spectra of (I) $CuCO_3 \cdot Cu(OH)_2$; (II) $Cu(4\text{-}C_7H_6NO_2)_2$ solution product; (III) $Cu(4\text{-}C_7H_6NO_2)_2$ from the solid state reaction between $CuCO_3 \cdot Cu(OH)_2$ and $4\text{-}C_7H_7NO_2$; (IV) freshly mixed reactants.

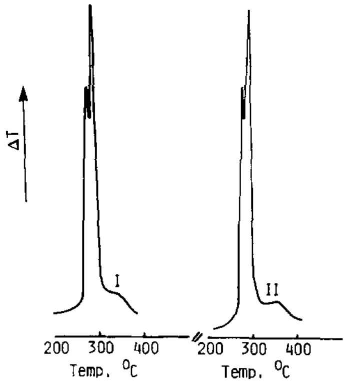

FIG. 3. DTA traces of the solid product of the reaction between $Cu(CH_3COO)_2$ and $4\text{-}C_7H_7NO_2$; $Cu(4\text{-}C_7H_6NO_2)_2$ solution product.

by about 150 cm^{-1} than in the corresponding free acid, the characteristic carbonyl band around 1650 cm^{-1} in the free acid is absent in the product spectra. Two additional peaks appear around 1630–1550 cm^{-1} and 1385–1410 cm^{-1} due to asymmetric and symmetric stretching vibrations of the carboxylate ion. The IR data shows that the coordination to the metal atom is through the two carboxyl oxygens and nitrogen of the $-NH_2$ moiety.

The DTA of the solid products and solution phase products are exactly identical (Fig. 3). No new or additional thermal effects were noted. The area under the DTA curves for the product obtained in the solid phase and solution phase reactions is same showing thereby that the reaction is quantitative and goes to completion even in the solid state. The magnetic moment values lie in the range 1.4–1.7 B.M which correspond to octahedral copper(II) with slight amount of antiferromagnetic coupling. The analysis of the products for Cu, C, H, and N are in

TABLE I

POSITION AND ASSIGNMENT OF INFRARED SPECTRAL BANDS (cm^{-1}) OF THE PRODUCTS OF SOLID STATE REACTIONS

$Cu(CH_3COO)_2$ +			$CuCO_3 \cdot Cu(OH)_2$ +			
o-$C_7H_7NO_2$	m-$C_7H_7NO_2$	p-$C_7H_7NO_2$	o-$C_7H_7NO_2$	m-$C_7H_7NO_2$	p-$C_7H_7NO_2$	Assignment
3270(m)	3240(m)	3230(m)	3280(m)	3230(m)	3275(m)	NH_2 asym. str.
3120(m)	3140(m)	3140(m)	3115(m)	3140(m)	3125(m)	NH_2 sym. str.
1540(vs)	1570(vs)	1592(vs)	1565(vs)	1575(vs)	1590(m)	COO^- asym. str.
1380(vs)	1400(vs)	1385(vs)	1385(vs)	1400(vs)	1380(vs)	COO^- sym. str.

Note. m = medium, vs = very strong.

TABLE II

Elemental Analysis Results of the Solid Products of Solid State Reactions

Reactants	C	H	N	Cu
1. $Cu(CH_3COO)_2$ + 2-$C_7H_7NO_2$	50.76	3.70	8.58	18.73
2. $Cu(CH_3COO)_2$ + 3-$C_7H_7NO_2$	49.28	2.80	9.05	18.78
3. $Cu(CH_3COO)_2$ + 4-$C_7H_7NO_2$	49.70	4.05	8.90	19.02
4. $CuCO_3 \cdot Cu(OH)_2$ + 2-$C_7H_7NO_2$	50.39	3.96	9.40	18.96
5. $CuCO_3 \cdot Cu(OH)_2$ + 3-$C_7H_7NO_2$	48.90	4.76	7.70	19.35
6. $CuCO_3 \cdot Cu(OH)_2$ + 4-$C_7H_7NO_2$	51.80	3.32	7.79	18.69
Theoretical value	50.07	3.58	8.35	18.93

accordance with the respective products (Table II).

Kinetic data for the reactions of copper acetate and copper carbonate with 3- and 4-aminobenzoic acids, obtained by the capillary technique at temperatures 388, 393, 398, and 403 K are best fitted to the equation.

$$\xi^2 = kt \qquad (1)$$

where ξ is the thickness of the colored product layer, t is the time, k is a constant. The plot of ξ^2 vs t for the reactions of copper acetate and copper carbonate with 3- and 4-aminobenzoic acids are given in Figs. 4–7. The values of energy of activation for the reactions of copper acetate with 3- and 4-aminobenzoic acids are 76.5 and 58.3 and for the reactions of copper carbonate with 3- and 4-aminobenzoic acid are 92.7 and 78.8 kJ mole^{-1}, respectively. In these reactions there are important contributions from surface migration of the more labile reaction component on the surface of the other and penetration into the interior of

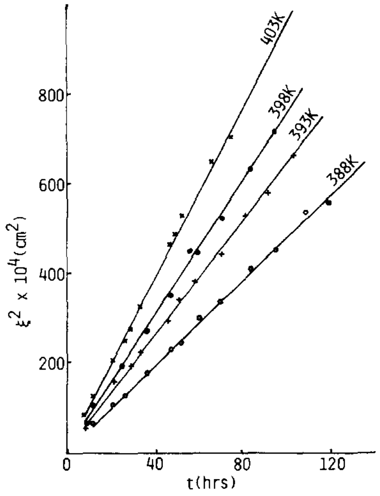

Fig. 4. Kinetic data for the reaction between $Cu(CH_3COO)_2$ and 3-$C_7H_7NO_2$ at different temperatures by capillary technique.

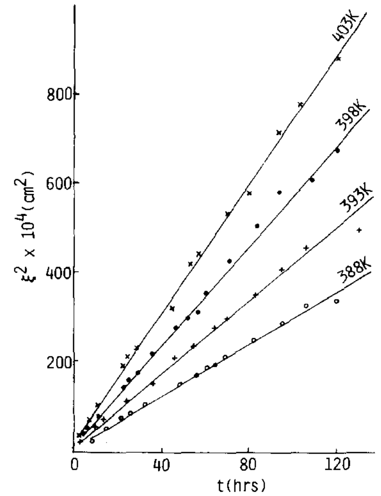

Fig. 5. Kinetic data for the reaction between $Cu(CH_3COO)_2$ and 4-$C_7H_7NO_2$ at different temperatures by capillary technique.

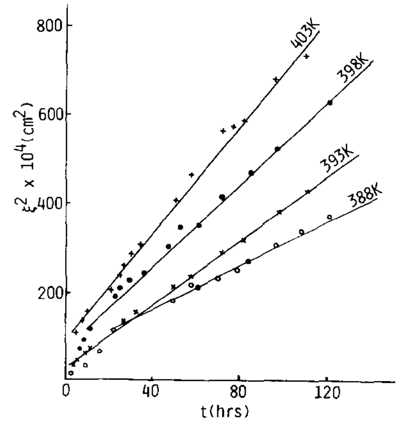

Fig. 6. Kinetic data for the reaction between $CuCO_3 \cdot Cu(OH)_2$ and 3-$C_7H_7NO_2$ at different temperatures by capillary technique.

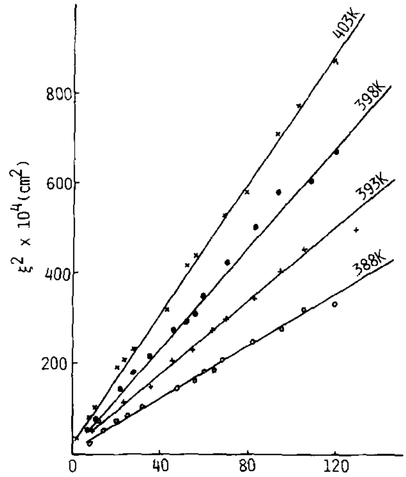

FIG. 7. Kinetic data for the reaction between $CuCO_3 \cdot Cu(OH)_2$ and $4\text{-}C_7H_7NO_2$ at different temperatures by capillary technique.

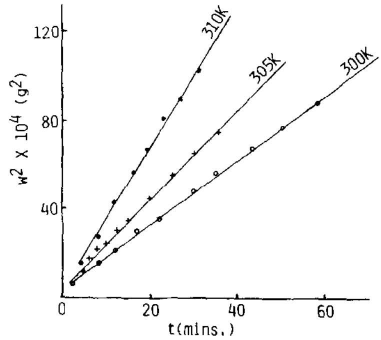

FIG. 8. Kinetic data for the reaction between $Cu(CH_3COO)_2$ and $2\text{-}C_7H_7NO_2$ at different temperatures by weight loss.

crystalline particles by a defect mechanism. These reactions are diffusion controlled. From the direction of the movement of the colored boundary the diffusing species through the product layer was found to be the organic acid. Copper acetate and copper carbonate have a polymeric network in their crystals and the binding forces in these are very strong being covalent throughout the crystals. Their diffusion will thus require the breaking of many covalent bonds, whereas aminobenzoic acids are dimers, held together by weak inter or intramolecular hydrogen bonds and their diffusion requires very small amount of energy which is available at the temperatures at which these reactions have been studied.

The rate measurements for the reactions of copper acetate and copper carbonate with 2-aminobenzoic acid have been done at 300–310 K and 353–373 K, respectively, by monitoring the weight loss with time after the reactants have been compressed into pellets. The reactions follow Eq. (2), where w is the weight loss at time t, and

$$w^2 = k't \qquad (2)$$

k' is the rate constant. In Figs. 8 and 9 straight lines are obtained for the plot of w^2 vs t for the two reactions. The values of energy of activation as determined from the Arrhenius plots are 61.8 and 80.0 kJ mole^{-1}, respectively. The kinetic studies for the other reactions could not be done by this method as the rate is very slow for the reactions of 4-aminobenzoic acid and in the case of 3-aminobenzoic acid the amount of weight loss is still smaller, e.g., the rate constant for the reactions of copper acetate

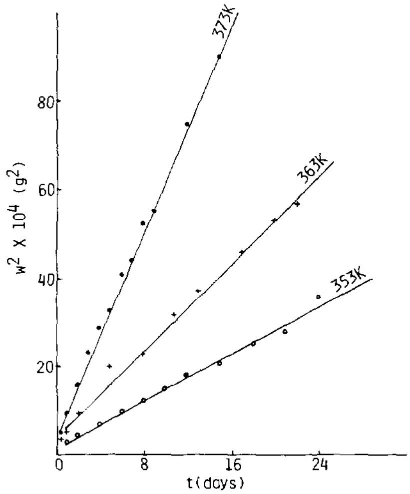

FIG. 9. Kinetic data for the reaction between $CuCO_3 \cdot Cu(OH)_2$ and $2\text{-}C_7H_7NO_2$ at different temperatures by weight loss.

with 3- and 4-aminobenzoic acids are 3.75 $\times 10^{-5}$ and 5.75 $\times 10^{-5}$ g^2/day at 388 K, respectively. In Figs. 4–9, some of the plots when interpolated give positive intercept on the *Y* axis. This behavior is expected from reactions in which phase boundary process is fast. At the start, since the phase boundary process is dominant and fast and therefore certain initial points may not lie on kinetic plots which represent diffusion.

From these reactions the order of reactivity for the corresponding reactions is found to be 2- > 4- > 3-aminobenzoic acid and copper acetate reacts faster than copper carbonate. The reactivity can be considered to be dependent mainly on two factors:

1. The relative rate of diffusivities of the diffusing species through the product layer and its penetration into the other reactant lattice, and
2. The ease of formation of the products when the reactants come sufficiently close to each other.

The diffusion coefficients (*9*) of the aminobenzoic acids have been determined in the solution phase and are 0.968, 0.775, and 0.927 $\times 10^{-5}$ cm^2 sec^{-1} for 2-, 3-, and 4-aminobenzoic acids respectively. Similar pattern is expected for the solids also. 4-aminobenzoic acid, being a symmetrical species, diffuses easily. In 2-aminobenzoic acid diffusion does not require the breaking of intramolecular hydrogen bonds, which counteracts the retarding force due to the presence of groups in the 1,2 position, while in 3-aminobenzoic acid the combined effect of the proximity of the groups and the intermolecular hydrogen bonds gives a low value of diffusion coefficient.

These are anion exchange reactions on Cu^{2+} wherein carbonate or acetate is replaced by the more favourable aminobenzoate; the –COOH function of the acid carries the advantage of an electron source from the delocalized system of the aromatic nucleus, which is in turn, reinforced by the electron releasing $-NH_2$ substituent. As such pK_a (*10*) of acetic acid (4.734) is lower than that of any benzoic acid (4.97, 4.79, and 4.92 for 2-, 3-, and 4-aminobenzoic acid), but electrostatic shift of Cu^{2+} from acetate to the carboxylate of aminobenzoate makes possible this counter shift of the benzoic acid proton to acetate. Consequently the reaction [1] proceeds to the right. Of the 2-, 3-, and 4-aminobenzoic acids, the first isomer proves exceptionally a strong base in view of the coordination of $-NH_2$ to the COO^- paired Cu^{2+} to give a six-membered chelate ring which is a very stable structure. X-ray structural analysis (*4*) has revealed that 2-aminobenzoate interacts with Cu^{2+}, both through $-NH_2$ and $-COO^-$, which reflects the comparative cation affinity of the aminobenzoate over the acetate (*11, 12*).

The electron supply of the 4- and 3-amino function to the aromatic nucleus is increasingly poor, and they are also incapable of chelating to the carboxylate bound Cu^{2+} in a manner similar to 2-isomer, so that solid state anion exchange for the corresponding aromatic acids is accordingly poor as found.

In the basic carbonate (*13*), Cu^{2+} is fairly strongly bound by the doubly charged carbonate oxygens and the bridging hydroxide ions. As such the probability of anion exchange at the basic carbonate with the aminobenzoate appears highly diminished because it becomes difficult for the diffusing aminobenzoic acid molecule to penetrate into its crystal lattice, which is essential for the reaction to occur. We, however, noted that it does occur; understandably, therefore, the proton exchange in favor of carbonate serves to trigger the Cu^{2+} exchange in favor of aminobenzoate.

The presence or absence of polar axis in solids (*14*) may also determine its reactivity. Crystal structures which have a polar axis are more reactive than those in which it is absent. The room-temperature modification of 2-aminobenzoic acid (*15*) has $P2_1cn$ space group which is noncentrosymmetric and possesses a polar axis whereas 3-aminobenzoic acid (*16*) with space group $P2_1/c$ and 4-aminobenzoic acid (*17*) with space group $P2_1/n$ are both centrosymmetric and do not have polar axis. This also accounts for the enhanced reactivity of 2-aminobenzoic acid.

These reactions may involve features of certain solid–gas reactions which have already been reported (*18*)—reaction at the surface of a crystalline particle leading to disruption of the structure as product is formed and then diffusion through the partially disordered region by the penetrating reagent. Experiments performed with single crystals of either reactant immersed in the powder of the other showed uniform surface attack on the crystal. The product layer was found to be microcrystalline and there was no evidence of anisotropic attack.

Out of the various modes of diffusion possible, the most feasible one is by surface migration. The values of heat of sublimation (*19*) for 2-, 3-, and 4-aminobenzoic acids are 99.0, 121.5, and 113.0 kJ mole^{-1} at 393 K, respectively, and are higher than the values of energy of activation for these reactions. The low values of frequency factors which lie in the range 10^1–$10^{1.5}$ for these reactions, and energy of activation rule out the possibility of vapour phase or bulk diffusion. However surface migration and grain boundary diffusion may be predominant.

All observations support that the initial reaction occurs at the phase boundary of the reactants and that further reaction is propagated by the surface migration of the reacting molecules. The gaseous products which are produced diffuse away from the reaction zone through the voids between the particles of the reacting species and do not influence the phase boundary processes because the reactions are very slow and isothermal.

Acknowledgments

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