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Formation of Metal Chelates in Solid State Reaction between 8-Hydroxyquinoline and Carbonates of Cadmium and Zinc

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The solid state reactions between 8-hydroxyquinoline (8-HQ) and $CdCO_3$ and $ZnCO_3$ have been studied. The Brounshtein–Ginstling rate equation is followed in both cases. The activation energy for $CdCO_3$–8-HQ and $ZnCO_3$–8-HQ are respectively 92.3 ± 3.3 and 86.6 ± 0.6 kJ mole^{-1}. The reaction products were characterized by elemental analysis, X-ray diffraction, and IR studies. Metal (Zn and Cd) carbonates and 8-HQ react in 1:2 molar ratio and the reaction proceeds via surface migration of 8-HQ.

Introduction

Chelating agents have long been in analytical use, but it is only in the last few decades that chelation has been recognized as a prominent chemical principle. The formation of coordination complexes in solution is well understood, so is the case with chelation. However, general solid state coordination chemistry has not yet picked up, and references to reactions leading to chelate formation in the solid state are few. Solid state reactions involving inorganic compounds like the formation of ferrites (*1, 2*), mercurates (*3*), silicates (*4*), and titanates (*5, 6*) have been extensively studied. Likewise, solid state reactions involving organic solids have been studied at great length (*7*). However, the solid state reactions involving inorganic and organic solids have been rarely studied. The strong chelating action of 8-HQ in solution has been extensively studied and used for analytical determination of several metals for a long time, but its chelate-forming reaction in solid state seems to be unreported. The object of the present study is to investigate the kinetics and mechanism of solid state reaction between 8-HQ and some of the transition metal carbonates.

Experimental

Materials. BDH reagent grade cadmium carbonate and zinc carbonate and 8-HQ (Aldrich Chemical Company, Inc.), melting point 74.9°C, were used without further purification. The reactants were powdered and sieved to above 300 mesh size.

Kinetic Measurements

The kinetics of the reactions were studied at different temperatures by determining the amount of metal carbonates reacting at different intervals of time. The amount of

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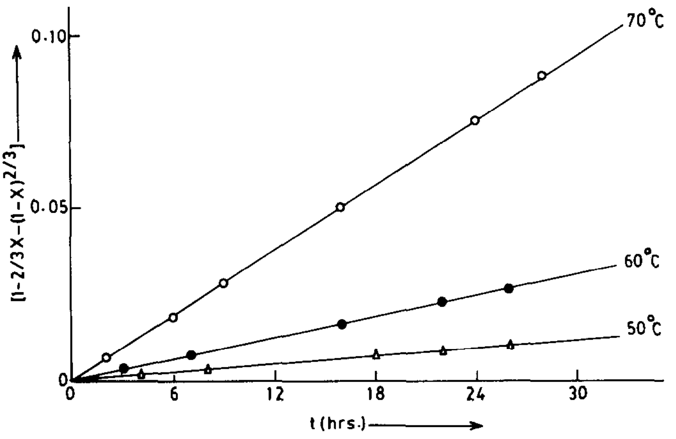


FIG. 1. Kinetic data for the reaction between $CdCO_3$ and 8-HQ.

unreacted metal carbonate was determined by measuring the CO_2 gas evolved from the reaction mixture by the action of dilute hydrochloric acid. It has been ascertained that the product is unaffected by the action of HCl. The particle size of the reactants were always maintained above 300 mesh. The reactions follow (Figs. 1 and 2) the Brounshtein–Ginstling rate equation (*8*)

$$kt = 1 - \tfrac{2}{3}x - (1 - x)^{2/3} \qquad (1)$$

where x is the fraction of metal carbonate

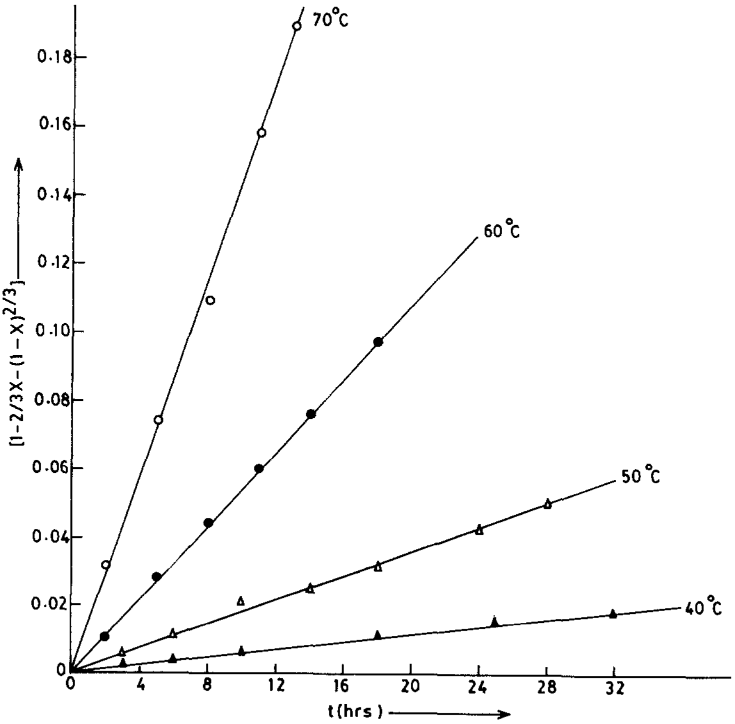


FIG. 2. Kinetic data for the reaction between $ZnCO_3$ and 8-HQ.

reacted at time t. The values of k at different temperatures for the two reactions are reported in Table I.

The reaction products in either of the reactions being yellow, the lateral diffusion technique (*9*) for the kinetic studies was attempted. But the growth of the product layers were too heterogeneous to allow precise rate measurement.

Elemental Analysis of the Reaction Products

Solid cadmium carbonate or zinc carbonate was finely ground with a large excess of 8-HQ and heated to 60°C. The reaction products thus obtained were washed repeatedly with acetone to remove unreacted 8-HQ. The products were dried and the metal content (cadmium or zinc) was estimated gravimetrically (*10*). Nitrogen was estimated by microanalytical technique. The elemental analyses are as follows:

$CdCO_3$–8-HQ

Cd (Calculated) = 24.29% Cd (Observed) = 23.90%
N (Calculated) = 6.05% N (Observed) = 6.20%

$ZnCO_3$–8-HQ

Zn (Calculated) = 15.73% Zn (Observed) = 15.65%
N (Calculated) = 6.74% N (Observed) = 6.79%

IR Studies

Infrared spectra were taken in KBr with a Beckman IR-20 spectrophotometer.

TABLE I

Parameters of Equation (1)

Temperature (°C)	$CdCO_3$–8-HQ ($k \times 10^{-3}$ mole/h)	$ZnCO_3$–8-HQ ($k \times 10^{-3}$ mole/h)
40	—	0.591
50	0.385	1.785
60	1.000	5.400
70	3.125	14.000

Thermal Studies

Metal carbonates and 8-HQ were mixed thoroughly in 1 : 2 molar ratios, and poured immediately into a Dewar flask, and the raise in temperature as a function of time was recorded using a Beckman thermometer calibrated to 0.01°C. The plot of temperature against time is shown in Fig. 3.

X-Ray Diffraction Studies

Powder X-ray diffractograms of the reaction product, obtained as a result of mixing metal carbonates and 8-HQ in solid state in 1 : 2 molar ratio, and the solid–solid reaction product washed with acetone were taken with a Norelco Geiger X-ray diffractometer using Cu$K\alpha$ radiation with a Ni filter. Lack of sharpness in diffractograms show that all the products were noncrystallized solids.

Results and Discussion

Product analyses show that metal carbonates and 8-HQ react in the molar ratio of 1 : 2. Thermal studies suggest that both are one-step reactions (Fig. 3). No evidence was obtained for the evolution of CO_2 gas and H_2O vapor during the reaction at room temperature. Chemical analyses of the products also reveal that metal carbonates and 8-HQ react in the afore mentioned ratio. IR spectra of the products, obtained by the reaction of metal carbonate with 8-HQ in solution, and those of the products of solid state reactions obtained (1) by mixing the carbonate with excess 8-HQ and removing the unreacted 8-HQ by treating with acetone and (2) by mixing the carbonate with 8-HQ in 1 : 2 molar ratio in mortar are the same.

In lateral diffusion experiments carried out with an air gap in between the reactants, the product is on the side of the metal carbonates, indicating that the diffusing species in both reactions is 8-HQ.

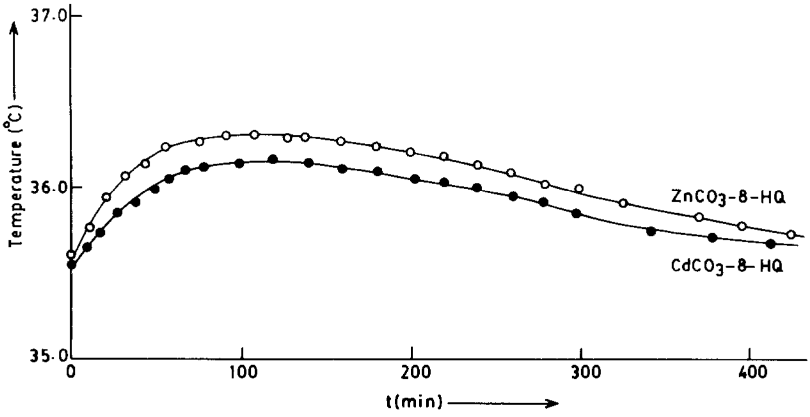


FIG. 3. Temperature rise as a function of time for the reactions (i) $CdCO_3$–8-HQ and (ii) ZnCO–8-HQ in 1 : 2 molar ratio.

The kinetic data best fit the Brounshtein–Ginstling rate equation

$$kt = 1 - \tfrac{2}{3}x - (1 - x)^{2/3} \qquad (1)$$

The plots of time versus the right hand side of Eq. (1) are straight lines (Figs. 1 and 2) and values of k at different temperatures are reported in Table I. The k's show the Arrhenius dependence. The energy of activation for the $CdCO_3$–8-HQ reaction is calculated to be 92.3 ± 3.3 kJ $mole^{-1}$, and for the $ZnCO_3$–8-HQ reaction it is 86.6 ± 0.6 kJ $mole^{-1}$. The rate decreased with increasing thickness of the product layer.

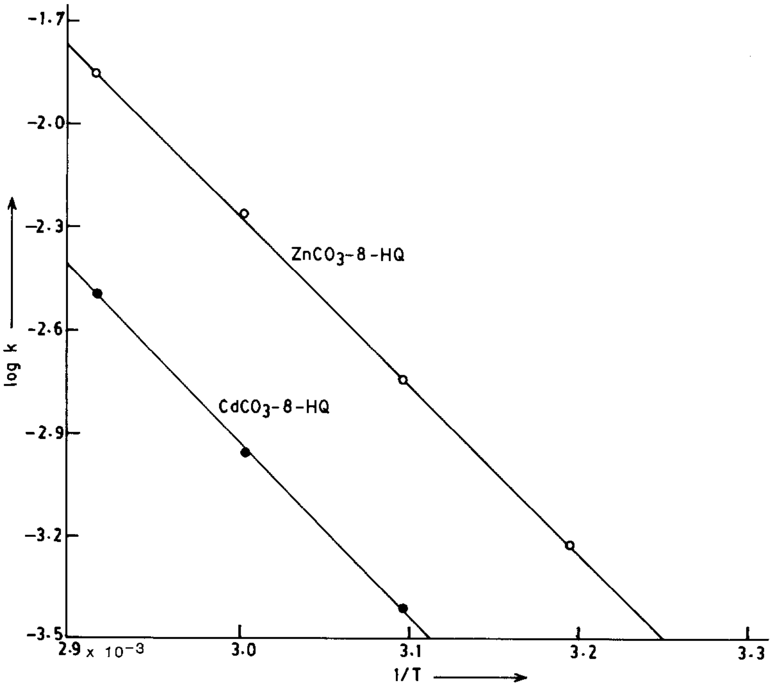


FIG. 4. Arrhenius plots for the reactions (i) $CdCO_3$–8-HQ and (ii) $ZnCO_3$–8-HQ.

TABLE II

IR SPECTRA

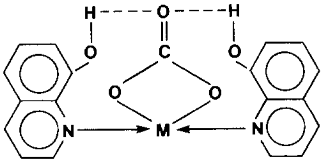
Compound/ frequency	ν_1	ν_2	ν_3	ν_4	Ring vib.	C–O–H
$ZnCO_3$	1050 cm^{-1}(m)	835 cm^{-1}(s)	1550 cm^{-1}(s) 1420 cm^{-1}(s)	735 cm^{-1}(m)	—	—
$CdCO_3$	1075 cm^{-1}(m)	865 cm^{-1}(s)	1500–1440 cm^{-1}(bs)	730 cm^{-1}(s)	—	—
8-HQ	—	—	—	—	1590 cm^{-1}(s) 1495 cm^{-1}(vs) 1465 cm^{-1}(s)	1265 cm^{-1}(s)
Reaction product ($CdCO_3$ + 8-HQ)	1060 cm^{-1}(m)	840 cm^{-1}(m)	1410 cm^{-1}(bs) 1385 cm^{-1}(s)	750 cm^{-1}(m)	1595 cm^{-1}(m) 1500 cm^{-1}(s)	1230 cm^{-1}(m)
Reaction product ($ZnCO_3$ + 8-HQ)	1040 cm^{-1}(m)	820 cm^{-1}(m)	1470 cm^{-1}(s) 1380 cm^{-1}(s)	750 cm^{-1}(m)	1590 cm^{-1}(m) 1500 cm^{-1}(s)	1235 cm^{-1}(m)

From the high values of activation energies, it can be concluded that 8-HQ diffuses into the metal (Zn and Cd) carbonate grains by a defect mechanism. When the reactants were separated by air gaps, the rate decreased with increasing length of the air gap. This suggests that penetration inside the carbonate grain is preceded by surface migration of 8-HQ. Experiments suggest that 8-HQ can migrate on the glass surface (*11*).

Elemental analyses of the reaction products indicate that two molecules of 8-hydroxyquinoline react with one molecule of metal (Zn or Cd) carbonate. IR spectra of the reaction products obtained by solid state reactions and of those extracted in acetone showed that the two products are the same. The products obtained in solid–solid interactions when treated with dilute HCl did not evolve CO_2 gas which implies that the carbonate group of the metal carbonate is not free and forms a part of the chelate.

The IR spectra of $CdCO_3$ and $ZnCO_3$ (Table II) show bands which are compatible with a bidentate involvement of the carbonate anion (*12*). The ligand, 8-HQ, exhibited a broad band in the region 3100–3450 cm^{-1} due to the presence of the hydrogen-bonded —OH group in the molecule in addition to the characteristic ring vibrations. The peaks in IR spectra of metal quinolinolates are less sharp as compared to those of metal carbonates and 8-HQ due to the non-xalline character of the former ones.

The ring vibrations of the 8-HQ are not much affected in the reaction product. However, the C–OH vibration is shifted down by 35 and 30 cm^{-1} in the reaction products with $CdCO_3$ and $ZnCO_3$, respectively, thus suggesting the involvement of OH hydrogen in a sort of hydrogen bonding with the $CdCO_3$ or $ZnCO_3$ moiety. This is further confirmed by observing a considerable decrease in the characteristic carbonate stretching vibrations as indicated in Table II. The probable structure of the reaction product, in the light of the above observations, may be given as shown below:



(where M = Cd or Zn).

Acknowledgments

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