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Solid State Reaction between Thallous Carbonate and 8-Hydroxyquinoline

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The solid state reaction between thallous carbonate and 8-hydroxyquinoline has been studied. The energy of activation for surface migration was found to be 8.8 kcal/mole whereas for inner penetration it was 14.6 kcal/mole. The reaction product was characterized by elemental analysis and ir spectral studies.

Introduction

The formation of coordination complexes in solution is well understood. Reaction in the solid state, giving rise to a coordination complex as the reaction product, is perhaps unknown. 8-Hydroxyquinoline, a very good complexing reagent, forms complex compounds with various metal ions in solution. We observed that it also reacts with some metal carbonates in the solid state forming yellow-colored products.

This paper reports the study of the kinetics of the solid state reaction between 8-hydroxyquinoline and thallous carbonate. The reaction product is also characterized by using various techniques.

Experimental

Materials

Thallous carbonate (AR, BDH) was used without purification. 8-Hydroxyquinoline (BDH) was purified by repeated distillation under reduced pressure. The purified sample melts at 75.4°C.

Procedures

1. Study of the kinetics in solid state. The kinetics of the reaction in the solid state were studied by a capillary technique (*1*). A glass capillary was half-filled with thallous carbonate, and the other half was filled with 8-hydroxyquinoline and kept in a thermostat at a constant temperature. The reaction started with the formation of yellow-colored product at the junction of the two reactants. The kinetics of the reaction were followed by measuring the thickness of the reaction product as a function of time with a microscope. The experiment was performed at different temperatures for fixed particle size.

2. Study of the kinetics in capillaries when the reactants are separated by an air gap. The two components were kept in glass capillaries with air gaps of different lengths. The reaction occurred at the surface of thallous carbonate, showing that 8-

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hydroxyquinoline is the diffusing species. The thickness of the product layer was measured at different intervals of time and for different lengths of the air gap.

3. Gravimetric study. The gravimetric study was performed in a way described earlier (*1*). A known amount of thallous carbonate was taken in a glass tube fitted with a B_{19} female joint and 8-hydroxyquinoline was taken in another glass tube fitted with a B_{19} male joint. The two tubes were then joined together and kept in a thermostat at constant temperature. The increase in weight in thallous carbonate was measured as a function of time at different temperatures.

Elemental Analysis of the Reaction Product

Solid thallous carbonate was ground with a large excess of 8-hydroxyquinoline solution in acetone several times and the reaction product obtained was washed several times with acetone in order to remove the excess amount of 8-hydroxyquinoline. The product thus obtained was dried and the thallium was estimated gravimetrically as thallium chromate. N was estimated by a microanalytical technique in the Chemistry Department, B.H.U., Varanasi.

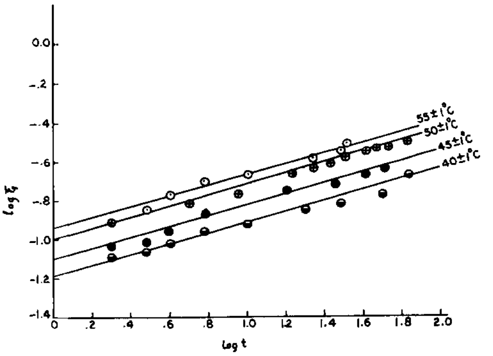


FIG. 1. Kinetic data for the reaction between thallous carbonate and 8-hydroxyquinoline at different temperatures (capillary technique).

TABLE I

PARAMETERS OF EQ. (1)[a]

Temperature (°C)	$k_1 \times 10^2$ (cm/hr)	n
40 ± 1	6.5	0.3
45 ± 1	7.9	0.3
50 ± 1	10.0	0.3
55 ± 1	11.5	0.3

[a] Particle size 100–140 mesh.

Infrared Spectral Studies

Infrared spectra of the reaction product and 8-hydroxyquinoline were taken in nujol mull with a Carl–Zeiss UR 10 spectrophotometer.

X-Ray Diffraction Studies

Powder X-ray diffraction patterns of the reaction product prepared as above and the product obtained by solid state reaction as in the gravimetric study were taken with an X-ray apparatus using Cu$K\alpha$ radiation.

Electrical Conductivity in Solution

Electrical conductivity of the reaction

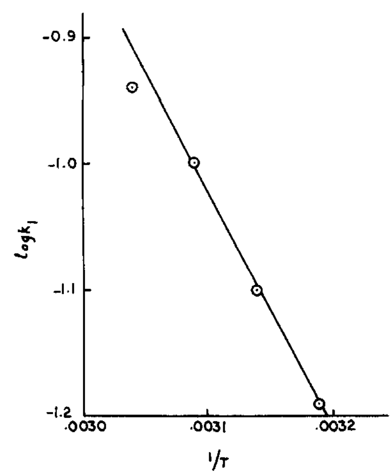


FIG. 2. Dependence of rate constant for the reaction between thallous carbonate and 8-hydroxyquinoline at different temperatures (capillary technique).

product in nitrobenzene was measured with a Toshniwal conductivity bridge, type CL01/01 A.

Results and Discussion

The growth of the product layer on one side of the original boundary, i.e., on the side of thallous carbonate, indicates that 8-hydroxyquinoline is the diffusing species. The kinetic data where the reactants are kept side by side in the capillary were fitted by the following equation:

$$\xi = k_1 t^n, \quad (1)$$

where ξ is the thickness of the product layer at any time t, k_1 is the rate constant, and n is a constant. The validity of Eq. (1) is tested by plotting log ξ vs log t, where straight lines are obtained (Fig. 1). The values of k_1 and n, calculated from the graph, are given in Table I.

When the logarithm of the rate of reaction is plotted as a function of the reciprocal of the absolute temperature, a straight line (Fig. 2) is obtained. This indicates that the Arrhenius equation is obeyed. From the graph, the formal activation energy is derived as 8.8 kcal/mole. A low value of the energy of activation indicates some easier way of diffusion; it may be surface migration. When the reactants are separated by air gaps, the kinetic data were

TABLE II
DEPENDENCE OF RATE CONSTANT ON THE LENGTH OF AIR GAP d[a]

d (cm)	$k_2 \times 10^2$ (cm/hr)
0.115	2.5
0.518	1.0
0.770	0.7
1.164	0.3

[a] Particle size 100–140 mesh; temperature = 50 ± 1°C.

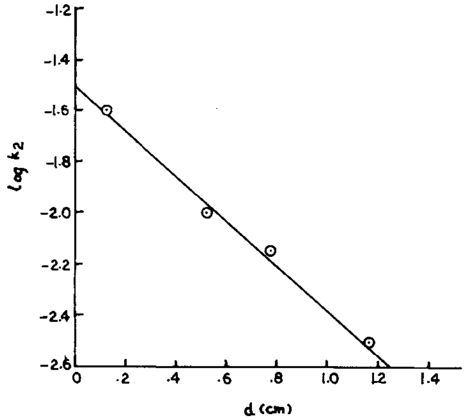


FIG. 3. Dependence of rate constant for the reaction between thallous carbonate and 8-hydroxyquinoline at different lengths of air gaps (capillary technique).

again followed by Eq. (1) and the rate constant (k_2) varies with the length of the air gap (Table II) in the following way:

$$k_2 = A_e^{-pd}, \quad (2)$$

where d is the length of the air gap and A and p are constants. When log k_2 is plotted against d, a straight line (Fig. 3) is obtained. Analysis of Eq. (2) shows that when $d = 0$, $k_2 = A$ and when $d = \infty$, $k_2 = O$. This simply indicates that when the reactants are separated by air gaps, vapor-phase diffusion is not the only probability. In addition to vapor-phase diffusion, surface migration of 8-hydroxyquinoline may also take place. Separate experiments have indicated that solid 8-hydroxyquinoline can migrate on glass surfaces (*2*).

When the reaction kinetics were followed by measuring the change in weight of thallous carbonate, the kinetic data fitted the following equation

$$W = k_3 t, \quad (3)$$

where W is the change in weight at any time t and k_3 is the rate of the reaction. The plot of W against t gives straight lines (Fig. 4). The values of k_3 at different temperatures are given in Table III. An Arrhenius plot

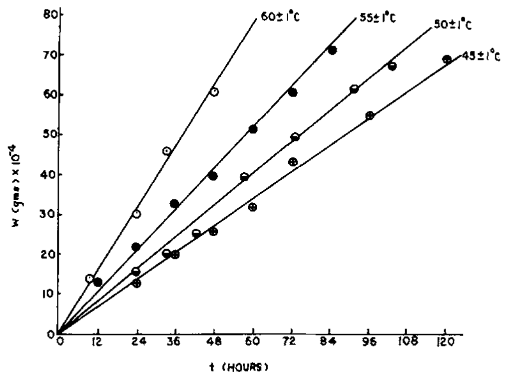


FIG. 4. Kinetic data for the reaction between thallous carbonate (solid) and 8-hydroxyquinoline (vapor) at different temperatures (gravimetric method).

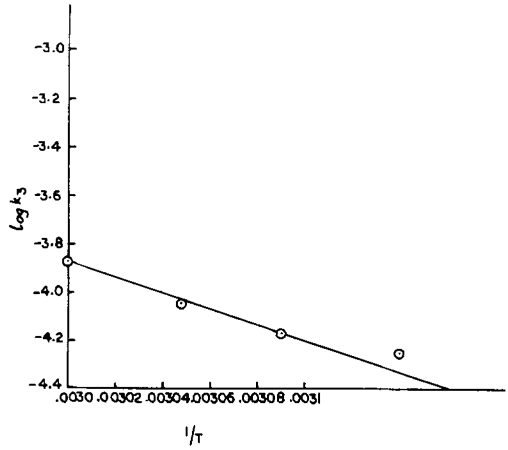


FIG. 5. Dependence of rate constant for the reaction between 8-hydroxyquinoline and thallous carbonate at different temperatures (gravimetric method).

gives a straight line (Fig. 5) and from the slope of the graph, the formal energy of activation (14.6 kcal/mole) is nearly 1.5 times the energy of activation for the reaction when the reactants were kept side by side in the capillary. This simply shows that, in addition to surface migration, penetration of 8-hydroxyquinoline molecules is also taking place inside the grains of Tl_2Co_3. Diffusion inside the grains might be taking place through some imperfections present in the grains of Tl_2Co_3 and this may require comparatively higher activation energy. Further, Eq. (3) shows that the rate of the reactions continuously increases with time (Fig. 4), which means, during the course of reaction, the reaction product does not offer any hindrance for diffusion. In other words we can say that as soon as the first layer of reaction product is formed, cracks and voids are developed, through which the 8-hydroxyquinoline molecule diffuses and comes in contact with fresh surfaces of Tl_2CO_3 molecules. This process continues until the completion of the reaction.

TABLE III

PARAMETERS OF EQ. (3)[a]

Temperature (°C)	$k_3 \times 10^{-4}$ (cm/hr)
45 ± 1	0.57
50 ± 1	0.67
55 ± 1	0.87
60 ± 1	1.30

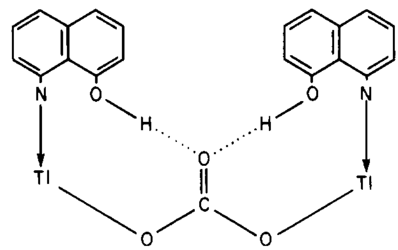
[a] Particle size 100–140 mesh.

Elemental analysis of the reaction product,

$$Tl^+_{obs} = 53.20\%,\ Tl^+_{cal} = 53.80\%;$$
$$N_{obs} = 4.02\%,\ N_{cal} = 3.69\%,$$

shows that one molecule of thallous carbonate reacts with two molecules of 8-hydroxyquinoline. Powder X-ray diffraction patterns of the reaction product obtained by solid state reaction and that obtained in acetone were identical, showing that the two products are the same. Electrical conductivity of the reaction product in nitrobenzene at room temperature shows that the product is a nonelectrolyte. The product does not evolve CO_2 gas on reaction with dilute acids, showing thereby that the carbonate group of thallous carbonate is involved in the bonding.

Infrared spectra of 8-hydroxyquinoline and the reaction products were examined in order to know the mode of linkage. A broad band observed between 3100 and 3300 cm^{-1} in the case of 8-hydroxyquinoline shows the presence of a hydrogen-bonded OH group in the molecule. The weak band observed at 3200 cm^{-1} in the case of the reaction product may be assigned to ν (OH). The broadness and its occurrence at lower frequency indicate the presence of a considerable amount of hydrogen bonding in the complex. A band occurring at ~1270 cm^{-1} in 8-hydroxyquinoline may be assigned to the ν(C–OH) group. This band is also observed in the reaction product at lower frequency, ~1260 cm^{-1}, indicating the presence of this group. A band observed at 1690 cm^{-1} in the spectrum of the reaction product may be assigned to ν (C=O) of the carbonate group. The occurrence of two bands at 1580 and 1300 cm^{-1} due to splitting of the ν_3 band and a band at 1020 cm^{-1} (ν_1) is indicative of the presence of a bidentate carbonate group (*3*). On the basis of analytical data, the following structure may be proposed for the molecule.



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