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Organic Solid-State Reactions

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The role of voids and cracks in solid-state reaction between 8-hydroxyquinoline and phthalic anhydride has been investigated. 8-hydroxyquinoline reacts with phthalic anhydride both in solution and in solid state, forming a 1:1 yellow-colored complex. X-ray diffraction studies prove that the complex obtained from the solid-state reaction is the same as that obtained from solution. Several techniques have been used to study the kinetics of the reaction in the solid state. Kinetic studies by capillary technique showed that surface migration is the mode of diffusion of reactant concerned. Dilatometric technique confirms the formation of cracks and voids in the systems and shows that the reaction is propagated through the channels.

Introduction

Powder reactions are of practical interest although single-crystal studies provide deeper insight into the mechanism of reactivity in the solid state (*1–4*). When powder solid particles of two species A and B are kept close to each other, the reaction would proceed as follows if A diffuses toward B. We designate it as *process I* (Fig. 1). The molecules of A cross the boundary EF by surface migration or vapor-phase diffusion. If the product AB is colored, a colored zone is formed which advances in the course of time. The length of the colored zone can be measured and mechanistic conclusions can be drawn. After a certain time, the colored boundary does not move. However, such data are not meaningful when penetration of A into the crystal grains of B is also a fast process. The penetration of A into the crystal grains of B would be a necessary component of a powder reaction. We can visualize this occurrence in two steps.

(i) Diffusion of the species A through the channels and cracks created in crystal grains occurs because of shrinkage or expansion of the lattice. We designate it as *process II* (Fig. 2).

(ii) In the second stage the penetration of A into the lattice occurs. We designate it as *process III* (Fig. 3).

In addition to the above, the reactions between powders are complicated by the fact that the reactions are localized. Kinetic features of such reactions can therefore be understood by a combination of various

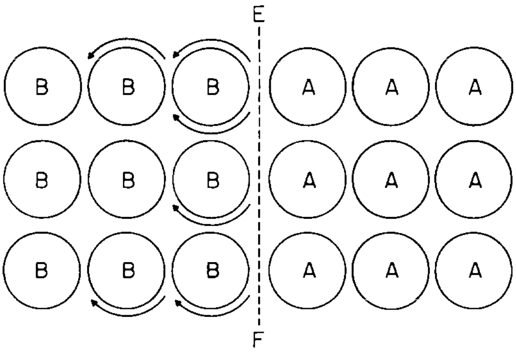

FIG. 1. Process I, diffusion of A towards B in powdered particles.

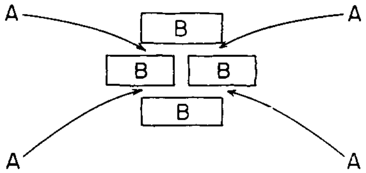

FIG. 2. Process II, diffusion of A through the channels and cracks in the crystal.

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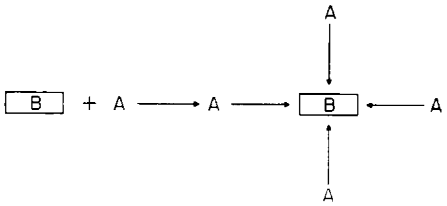

FIG. 3. Process III, penetration of A into the lattice B.

experimental techniques. Study of the moving boundary can provide information about surface migration. Study of solid–gas reactions yields additional information since the solid-solid interface would be excluded in such a reaction system. Similarly, dilatometric technique can be used to study the propagation of the reaction through cracks and voids.

In the present investigation, reaction between phthalic anhydride and 8-hydroxyquinoline has been investigated from the above angles. X-ray studies confirm that a complex is formed in the solid state. The nature of the complex has also been investigated. Detailed kinetic studies have been undertaken and a dilatometric technique is described.

Experimental

Materials and purification. Both phthalic anhydride and 8-hydroxyquinoline (BDH grade) were purified by repeated distillation. The melting points of the purified samples were 131 and 75.5°C, respectively (literature values are 131.16 and 75–76°C, respectively).

Elemental analysis. Phthalic anhydride and 8-hydroxyquinoline in an equimolar ratio were mixed in acetone and the complex which formed was crystallized twice. Elemental analysis was as follows (observed percentage of $C = 69.4$, $H = 3.8$, $N = 4.79$; the calculated percentage of $C = 69.6$, $H = 3.75$, $N = 4.77$).

Ultraviolet spectra in solution. The ultraviolet spectra of the components and the complex of equal concentrations in CCl_4 (0.01 *M* each) were taken with a Cary-14 spectrophotometer.

Infrared. Infrared spectra of the components and the complex in Nujol mull were also taken.

Reflectance spectra. The reflectance spectra of the components and the complex in the solid state were taken with a Hilger and Watts spectrophotometer using $MgCO_3$ as reference.

Electrical conductivity in solution. Electrical conductivity of 0.2 *M* solutions of phthalic anhydride, 8-hydroxyquinoline, and the 1:1 complex in acetone were determined at 37°C using the conventional conductivity bridge.

Electrical conductivity in solid state. The electrical conductivity of the complex prepared from the solution was measured in the form of a pellet at different temperatures. The pellet was kept between platinum electrodes and the conductivity was measured with the help of a conductivity bridge.

X-ray diffraction study. X-ray diffraction patterns of phthalic anhydride, 8-hydroxyquinoline, the product obtained from solid-state reaction of phthalic anhydride and 8-hydroxyquinoline, and the complex separated from the solution were obtained from X-ray diffractographs using CuK α radiation. The lines of the diffraction pattern of the complex obtained from solutions were indexed for the tetragonal system using the Hesse–Lipson method. The agreement between observed and calculated $\sin^2\theta$ (*hkl*) values (Table I) is satisfactory.

Density measurement. The density of the complex was determined at 35°C by pyknometric method using cyclohexane as the displacing liquid.

Kinetic study: capillary technique. The kinetics of the reaction between phthalic anhydride and 8-hydroxyquinoline in the solid state were studied using the procedure of Rastogi and co-workers (*5*). Phthalic anhydride and 8-hydroxyquinoline were placed separately in a glass capillary such that the two components were in contact with each other. The thickness of the growing product layer was measured as a function of time with a traveling microscope. The experiments were performed at different temperatures for a fixed particle size. It was observed that 8-hydroxyquinoline diffuses into phthalic anhydride resulting in the formation of a yellow-colored complex.

Kinetics of the reaction in a capillary when

TABLE I

X-RAY DIFFRACTION PATTERN OF 1:1 8-HYDROXYQUINOLINE–PHTHALIC ANHYDRIDE COMPLEX (PREPARED FROM SOLUTIONS)

Serial number	$\sin^2\theta_{obs}$	$h\ k\ l$	$\sin^2\theta_{cal}$	I/I_0
1	0.0153	1 0 2	0.0145	41
2	0.0180	2 0 0	0.0180	38
3	0.0189	1 1 2	0.0190	6
4	0.0203	2 0 1	0.0205	24
5	0.0224	0 0 3	0.0225	91
6	0.0267	1 0 3	0.0270	6
7	0.0308	1 1 3	0.0315	20
8	0.0320	2 1 2	0.0325	14
9	0.0361	2 2 0	0.0360	6
10	0.0407	2 0 3	0.0405	50
11	0.0447	3 1 0	0.0450	27
12	0.0465	2 2 2	0.0460	36
13	0.0502	3 0 2	0.0505	100
14	0.0585	3 2 0	0.0585	62
15	0.0627	0 0 5	0.0625	7
16	0.0683	3 2 2	0.0685	9
17	0.0705	1 1 5	0.0715	14
18	0.0741	4 0 1	0.0745	5
19	0.0793	4 1 1	0.0790	10

the reactants are separated by an air gap. The two components were kept in glass capillaries with an air gap of different lengths. It was observed that the reaction occurred only toward the side of phthalic anhydride. The thickness of the product layer was measured at different intervals of time and for various lengths of the air gap.

Gravimetric study. A gravimetric study was performed in a way similar to that described earlier (*6*). A known amount of phthalic anhydride was taken in a glass tube fitted with B_{19} female joint and was connected with another tube fitted with B_{19} male joint containing 8-hydroxyquinoline. The assembly was kept in an incubator maintained at constant temperature. The vapors of 8-hydroxyquinoline interacted with the solid phthalic anhydride forming a yellow-colored complex. The tube containing phthalic anhydride was weighed at different intervals of time.

Dilatometric technique. Powdered phthalic anhydride and 8-hydroxyquinoline in a 1:1 molar ratio (0.5 g phthalic anhydride and 0.4898 g 8-hydroxyquinoline) were mixed and made in the form of a pellet (length was 1.65 cm and diameter was 1.0 cm). The pellet was kept in a mercury dilatometer. As the reaction proceeded, the contraction in the volume of the pellet took place. The decrease in volume was measured at different intervals of time by noting the fall in the mercury column. The experiment was repeated for a definite particle size at different temperatures and also for particles of different sizes. (Particles of different sizes were obtained by passing them through sieves of different mesh sizes. In this manner, particles with a definite range of sizes were obtained.) Blank runs were also made for individual components but no change in volume was observed.

Results and Discussion

Nature of the Interaction

(a) *Complex from solution.* When solutions of phthalic anhydride and 8-hydroxyquinoline are mixed in 1:1 molar ratio, a yellow-colored molecular complex is found to separate. X-ray diffraction studies prove that the complex is a definite chemical species since new lines are obtained in the diffraction pattern which are not observed in the corresponding patterns of the parent components. The diffraction lines were indexed for tetragonal symmetry. The calculated and observed values of $\sin^2 \theta$ are given in Table I. The agreement is satisfactory. The analysis showed that $a = 11.61$ Å, $c = 15.42$ Å, and $Z = 6$. The density of the complex was found to be 1.40 g/c.c. whereas the X-ray density was calculated to be 1.33 g/c.c. According to de Wolff's (*7*) criteria M_{20} was found to be 14. This shows that the indexing of the lines is correct.

One may guess that the complex is a CT complex. In order to examine this point, uv spectrum of the complex in solution was investigated. The uv spectrum does not show any new band, which shows that probably a charge transfer interaction is not involved (*8*). It is also likely that the complex is dissociated in solution and hence a CT band is not obtained. If this is so, the electrical conductivity of complex in solution would be more than that of the solutions of the parent components. In order to investigate this point, conductance measurements were made. The electrical conductivities of 0.2 *M* 8-hydroxyquinoline, 0.2 *M* phthalic anhydride, and 0.2 *M* complex in acetone were measured at 37°C and were found to be 0.08×10^{-4}, 0.11×10^{-4}, and 0.165×10^{-3} mhos, respectively. These results again show that the complex undergoes dissociation in solution. The ir spectra simply gave the composite spectra of the individual components.

In order to avoid the complication due to the dissociation of the complex, reflectance spectra of the solids were taken (Fig. 4). The presence of a new band at 380 mμ and a broad maximum between 420 and 440 mμ in the case of the complex shows the formation of a new compound. This clearly indicates that probably charge transfer interaction is involved in the formation of the complex.

Electrical conductivity of the complex in the form of a pellet was measured between 100–120°C. The electrical conductivity increases with rise in temperature and obeys the following equation,

$$\sigma = \sigma_0 e^{-E/RT} \qquad (1)$$

where σ is the specific conductivity, σ_0 is a constant, E is the energy of activation for conduction, R is gas constant, and T is the absolute temperature. The energy of activation for conduction was found to be 4.5 kcal/mole. The results are inconclusive because in the temperature range in which measurements have been made, surface conduction (due to adsorbed molecules) may be a prominent process (*9*).

(b) *Complex obtained from solid-state*

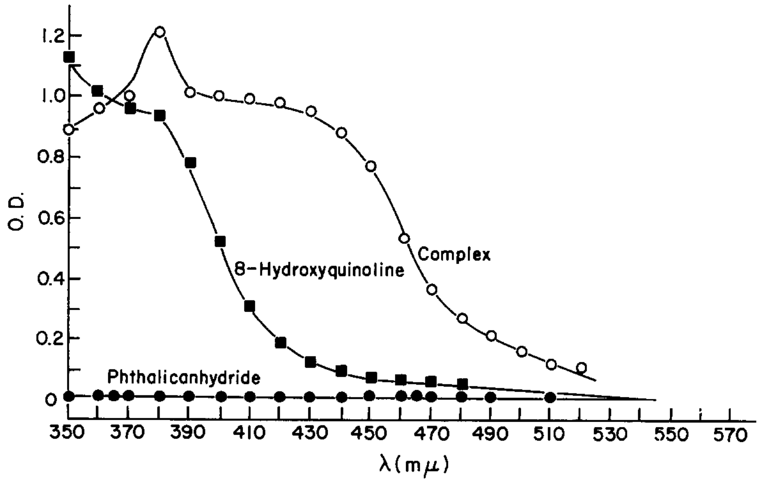

FIG. 4. Reflectance spectra of 8-hydroxyquinoline, phthalic anhydride, and the complex.

reaction. X-ray diffraction patterns of the complex prepared from the solution and obtained by solid-state reaction were compared. All the stronger lines observed in the diffraction pattern of the complex prepared from solution were found to be in the diffraction pattern of the complex prepared by solid-state reaction. (The weak lines observed in the diffraction pattern of the complex prepared from solution were not found in the complex prepared by solid-state reaction since the reaction does not go to completion in the solid state.) In addition, the diffraction pattern of the latter contained some of the lines of the components also, showing that the reaction does not go to completion in solid state (Table II). The X-ray study clearly shows that 1:1 complex is formed both in solid state as well as in solution.

Kinetic Studies

We first examine the kinetic data to have an insight into process I. The kinetic data for the solid–solid reaction obtained from capillary experiments are found to fit the following equation,

$$\zeta = k_1 t^n \tag{2}$$

where ζ is the thickness of the product layer at any time t and k_1 and n are constants. The validity of Eq. (2) was tested by plotting log ζ against log t (Fig. 5) whereby straight lines

TABLE II

COMPARISON OF d VALUES OF THE COMPLEX OBTAINED FROM SOLUTION AND THAT OBTAINED BY SOLID STATE REACTION

Serial number	$d_{\text{solid–state}}$ reaction product	I/I$_0$	d_{complex} from solution	I/I$_0$
1	9.4082[a]	38	—	—
2	7.1379[a]	16	—	—
3	6.2369	40	6.1935	41
4	5.7535	35	5.7535	38
5	—	—	5.5737	6
6	5.3723	5	5.3723	24
7	5.1257	87	5.1257	91
8	—	—	4.6952	6
9	4.3744	18	4.3959	20
10	4.3322	14	4.3959	14
11	4.1907[b]	29	—	—
12	—	—	4.0836	6
13	3.9864[b]	30	—	—
14	3.8015	46	3.8176	50
15	3.6479	26	3.6479	27
16	3.5900	35	3.5758	36
17	3.4399	100	3.4399	100
18	3.3022[b]	73	—	—
19	3.1865	59	3.1865	62
20	—	—	3.0789	7
21	2.9497	7	2.9497	9
22	2.9122	41	2.9029	45
23	—	—	2.8312	5
24	2.7385	8	2.7385	10

[a] Lines due to 8-hydroxyquinoline.

[b] Lines due to phthalic anhydride.

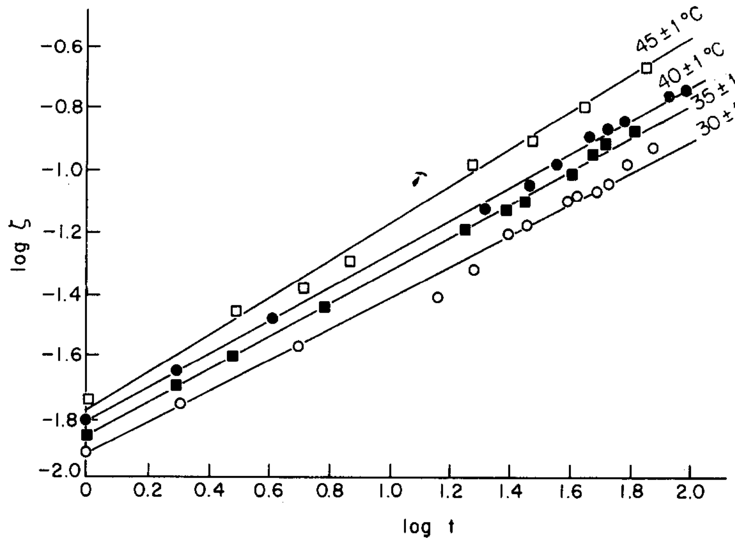

FIG. 5. Kinetic data for the reaction between 8-hydroxyquinoline and phthalic anhydride studied by capillary technique.

TABLE III

EFFECT OF TEMPERATURE ON k_1 WHERE PARTICLE SIZE = 300–350 MESH[a]

Temperature (°C)	k_1 (cm/hr)	n
30 ± 1	$(1.24 \pm 0.01) \times 10^{-2}$	0.51 ± 0.03
35 ± 1	$(1.33 \pm 0.01) \times 10^{-2}$	0.52 ± 0.01
40 ± 1	$(1.56 \pm 0.01) \times 10^{-2}$	0.52 ± 0.04
45 ± 1	$(1.69 \pm 0.01) \times 10^{-2}$	0.59 ± 0.04

[a] The plot of log k_1 against $1/T$ gave a straight line showing the validity of Arrhenius equation (Fig. 6).

are obtained. The parameters of Eq. (2) are given in Table III. The energy of activation was found to be 4.5 kcal/mole. Such a low value of energy of activation indicates that diffusion in the solid state is occurring via surface migration (see Fig. 6).

The rates of diffusion when the two reactants are kept in contact and when they are separated by an air gap are not the same. As the length of the air gaps increases, the rate of diffusion decreases. In both cases the kinetic data obeyed Eq. (2). When log k_1' (where k_1' is the rate constant for air-gap experiments) is plotted against the length of the air gap, a straight line is obtained (Fig. 7), showing that Eq. (3) is obeyed.

$$k_1' = A\,e^{-pd}, \qquad (3)$$

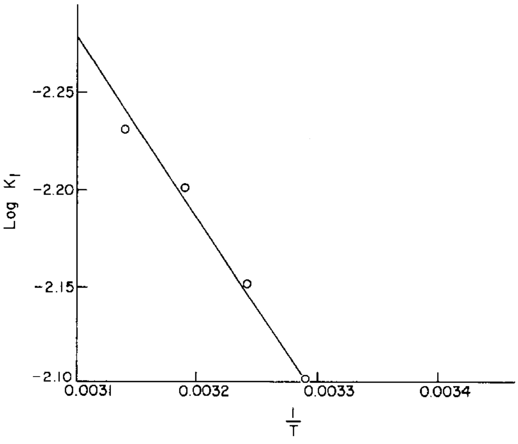

FIG. 6. Dependence of rate constant on temperature (capillary technique).

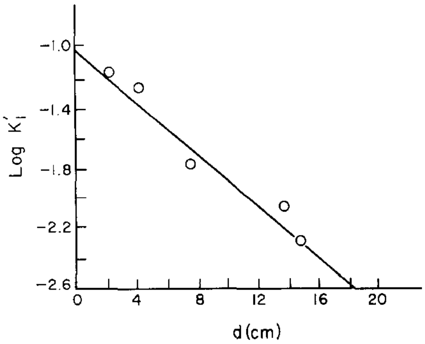

FIG. 7. Dependence of rate constant on the length of the air gap.

where d is the length of the air gap and A and p are constants. This shows that vapor-phase diffusion is certainly not taking place and diffusion is occurring via surface migration as in process I.

Process II can be understood by the study of gas–solid reactions. In gravimetric experiments, the vapors of 8-hydroxyquinoline were allowed to react with phthalic anhydride and the kinetics were followed by noting the change in weight of phthalic anhydride. The kinetic data obey the following equation,

$$W = k_2 t, \tag{4}$$

where w is the change in weight at any time t and k_2 is constant. The plot of W vs t is a straight line (Fig. 8). The energy of activation for this reaction was found to be 23 kcal/mole. The value is nearly equal to the heat of sublimation of 8-hydroxyquinoline, which suggests that only vapor-phase diffusion is taking place in this experiment. It appears that cracks are developed (as in process II) in the product layer which permits the continued access of vapors to the fresh surface of phthalic anhydride and consequently the weight of the product is directly proportional to the time during which the anhydride was exposed.

We now examine the results of a dilatometric study to investigate the role of cracks and voids in reactivity. The kinetic data for the solid-state reaction obtained from the dilatometric study are found to fit the following equation,

$$\frac{\Delta V}{V_0} = k_3 t \tag{5}$$

where V_0 is the total initial volume of the reactants, ΔV is the decrease in volume at any time t, and k_3 is constant. The validity of Eq. (5) was tested by plotting $\Delta V/V_0$ against t (Fig. 9). The parameters of (5) at different temperatures and for particles of different sizes are given in Tables IV and V, respectively.

The plot of log k_3 against $1/T$ gave a straight line (Fig. 10). From the slope of the

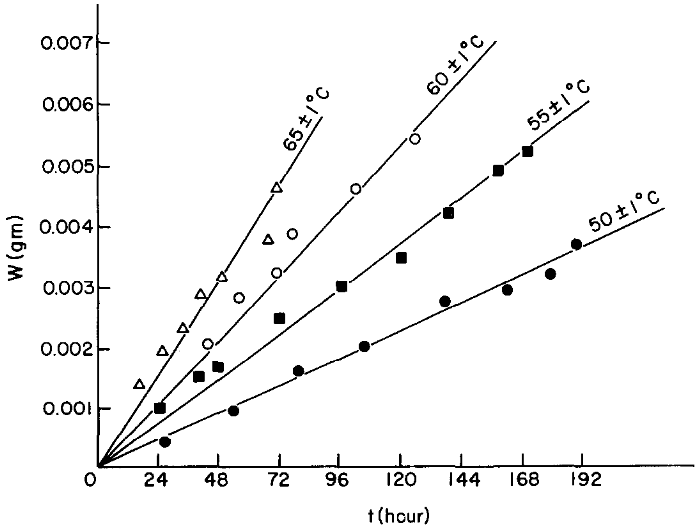

FIG. 8. Kinetic data for the reaction between phthalic anhydride (solid) and 8-hydroxyquinoline (vapors).

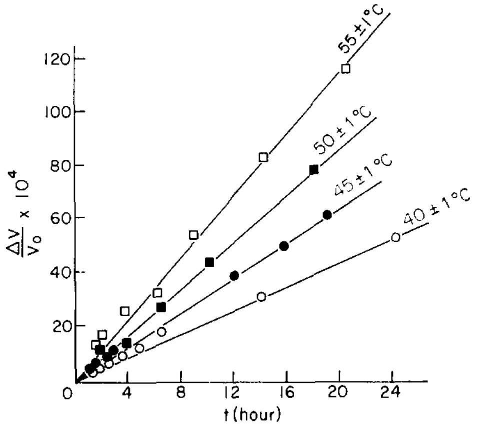

FIG. 9. Kinetic data for the reaction between phthalic anhydride and 8-hydroxyquinoline at different temperatures studied by dilatometric technique.

TABLE IV

EFFECT OF TEMPERATURE ON k_3 WHERE PARTICLE SIZE = 300–350 MESH

Temperature (°C)	k_3 (h^{-1})
40 ± 1	$(2.2 \pm 0.1) \times 10^{-4}$
45 ± 1	$(3.2 \pm 0.2) \times 10^{-4}$
50 ± 1	$(4.4 \pm 0.1) \times 10^{-4}$
55 ± 1	$(5.4 \pm 0.3) \times 10^{-4}$

TABLE V

EFFECT OF PARTICLE SIZE ON k_3 WHERE TEMPERATURE = 50 ± 1°C

Particle size (mesh)	k_3 (h^{-1})
150–200	$(1.5 \pm 0.2) \times 10^{-4}$
200–240	$(1.7 \pm 0.3) \times 10^{-4}$
240–300	$(2.3 \pm 0.1) \times 10^{-4}$
300–350	$(4.4 \pm 0.1) \times 10^{-4}$

line, the energy of activation came to 10.8 kcal/mole.

After the reaction was over, the pellet was taken out of the dilatometer in every experiment and the surface of the pellet became rough; when the pellet was broken, mercury drops were found to be randomly distributed inside the pellet. The presence of the mercury inside the pellet may be due to any of the following reasons. (1) Mercury might be acting as a transporting agent as follows: During solid-state reactions, mercury reacts with one of the reactants and the reaction product subsequently reacts with the other component liberating mercury again and producing the complex.

$$\mathrm{Hg} + R_1 \rightarrow \mathrm{Hg}R_1$$
$$\mathrm{Hg}R_1 + R_2 \rightarrow \mathrm{Hg} + R_1 R_2$$

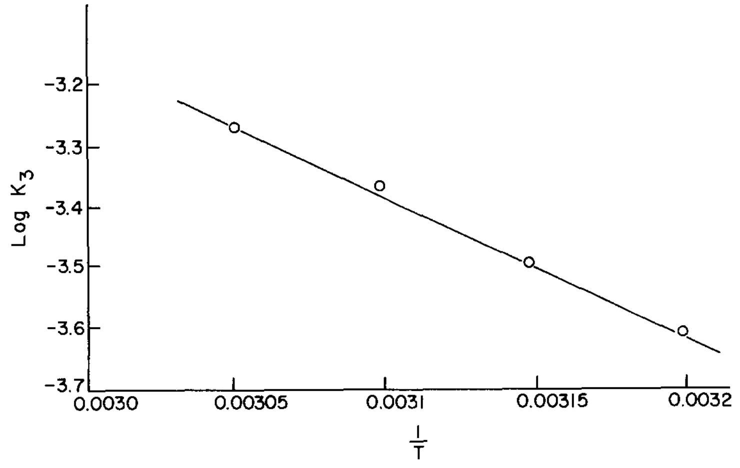

FIG. 10. Dependence of rate constant on temperature (dilatometric technique).

where R_1 and R_2 are the components of the reaction. Experiments were performed to test whether Hg reacts with either of the components. No reactivity could be detected, hence the above explanation is not a correct one. (2) Cracks are produced during the reaction and mercury enters the voids and channels produced. This appears to be a sensible explanation when we compare the cell volumes. The values of the cell volumes for the complex and the components are given in Table VI. It is obvious that the cell volume of the complex is much less than the cell volumes of the components.

Since the cell volume decreases as a result of complexation, it is expected that the total volume of the reaction mixture (pellet) will decrease during the course of the reaction. Because of volume contraction, cracks and voids are created in the pellet. As a result mercury would pass through the cracks. Since the development of the cracks will be random, the distribution of mercury globules would also be random, as is actually found to be the case.

In order to have a quantitative idea about the presence of mercury inside the pellet, a weighed pellet was kept inside the dilatometer (45°C) and after the reaction was over (nearly 20 hr), the weight of the pellet was again taken. The total increase in weight was 0.023 ± 0.001 g. This weight corresponds to 0.0016 c.c. of mercury, whereas the total volume change of the pellet during this period corresponds to 0.009 c.c.

The above experiment confirms the hypothesis that, during the reaction, cracks are formed and the diffusion of the reactants occurs through these cracks.

TABLE VI

CELL VOLUMES OF REACTANTS AND PRODUCTS

Compounds	Cell volume (Å³)
8-Hydroxyquinoline	2441
Phthalic anhydride	666
Complex	2079

In order to have a quantitative correlation we assume that A and B are the two reactant molecules which react in solid state forming the product AB. During reaction the total volume decreases. Let v_A', m_A', ρ_A, and v_B', m_B', ρ_B be the initial volume, mass, and density of the reactants A and B, respectively. After time t, the mass and the volume of A and B becomes equal to m_A'', v_A'', m_B'', v_B'', respectively. We further assume that the densities of the reactants before and after the start of the reaction remain constant. Let r_0 be the initial radius of the particle of one of the components (Fig. 11) and δ be the thickness of the product layer formed at any time t.

Since the reaction is an addition type of reaction, the total weight before and after the start of the reaction remains constant. Therefore,

$$m_A' + m_B' = m_A'' + m_B'' = \text{constant} \quad (6)$$

The volume change

$$\Delta V = (v_A' - v_A'') + (v_B'' - v_B'), \quad (7)$$

$$= (1 + (\rho_A/\rho_B)(v_A' - v_A'')). \quad (8)$$

Since the density of the two components is roughly equal, we have

$$\Delta V = 2(v_A' - v_A''). \quad (9)$$

Since the particle size of both the components A and B are the same, we can write,

$$v_A' = v_B' = v,$$

and

$$v_A' + v_B' = 2v = V_0.$$

Dividing Eq. (9) by $2v$, we get

$$\Delta V/2v = (1 - v_A''/v), \quad (10)$$

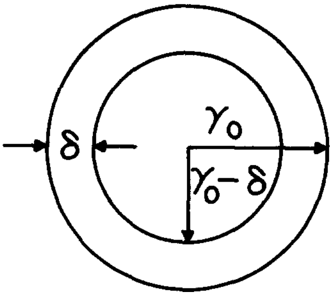

FIG. 11. Model of a reacting grain,

or

$$\Delta V/V_0 = \left[1 - \frac{\frac{4}{3}\pi(r_0-\delta)^3}{\frac{4}{3}\pi r_0^3}\right]. \tag{11}$$

Neglecting the higher powers of δ, we get,

$$\frac{\Delta V}{V_0} = \frac{3\delta}{r_0} \tag{12}$$

For noncoherent films (*10*), we can write

$$\delta = k't \tag{13}$$

Combining (12) and (13) we get Eq. (5). This result is expected in view of the fact that the reaction is propagated through cracks and voids. From (5), it follows that k_3 would be inversely proportional to r_0. However, this would be true when the particle size of both the components is the same.

In Figure 12 k_3 has been plotted against $1/r_0$. Although k_3 increases with increasing values of $1/r_0$, the curve is not a truly straight line as expected. This may be due to the fact that uncertainty in k_3 is, in general, large, since the particle size of the reactants can not be taken exactly the same and particles can only be chosen within a certain size range.

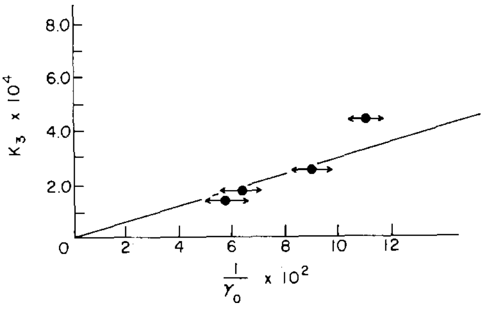

FIG. 12. Effect of particle size on the rate constant (dilatometric technique).

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