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Organic Solid State Reactions: Part II—Kinetics of 8-Hydroxyquinoline with Maleic Anhydride, Succinic Anhydride, Phthalic Anhydride, Catechol & Resorcinol

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Kinetics and mechanism of the reactions between 8-hydroxyquinoline as one component and maleic anhydride, succinic anhydride, phthalic anhydride, catechol and resorcinol as the other components have been studied in the solid state employing capillary and dilatometric techniques. Kinetic studies by capillary technique show that 8-hydroxyquinoline diffuses by surface migration. Dilatometric study shows that the reaction is propagated through cracks, voids and channels produced in the reaction system. Elemental analyses show that the complexes obtained from solutions are of 1 : 1 type. From X-ray diffraction studies it follows that these are identical to the complexes obtained by solid state reactions. Reflectance spectra of solid complexes indicate the possibility of charge transfer interaction between the reactants.

REACTIONS between powders in solid state are of practical interest specially in the preparation of catalysts, spinels, ceramics, refractory materials and pharmaceutical materials[1-4]. Studies have been made from time to time in order to understand the mechanism of such reactions. Mechanism of the reaction is complicated by the fact that (i) when two solids A and B are kept side by side, initially a surface reaction takes place, which is then propagated by surface migration, (ii) in the second stage, the molecules of A diffuse either inside the grains of B through grain boundaries or through cracks and channels created in the crystal on account of shrinkage or expansion and (iii) in the third stage, the penetration of A into the crystal lattice occurs.

Stage (i) can be studied by capillary technique while stage (ii) can be investigated by dilatometric technique described in a recent communication[5]. The stage (ii) is difficult to study since the best way would be to follow the kinetics with single crystals.

In a previous paper[5] solid state reaction between 8-hydroxyquinoline and phthalic anhydride has been studied and comprehensive picture of stages (i) and (ii) has been obtained including information about the mode of diffusion. In order to have more information about the mechanism of reactions, additional experimental data are needed and in the present paper we have studied the reaction between 8-hydroxyquinoline as one component and maleic anhydride, succinic anhydride, phthalic anhydride, catechol and resorcinol as the other components in the solid state.

Materials and Methods

All the reactants were of BDH quality and purified either by distillation or by recrystallization.

The reactants were mixed in equimolar ratios in acetone and the complexes formed crystallized twice and then analysed. The UV spectra of 1:1 complexes in acetone ($0{\cdot}01M$) were recorded on a Cary-14 spectrophotometer whereas the reflectance spectra of the components and the complexes were recorded on a Hilger-Watts spectrophotometer using $MgCO_3$ as reference.

Electrical conductivities of $0{\cdot}2M$ solutions of components and the complexes in acetone were determined at 37° using the conventional conductivity bridge.

X-ray diffraction patterns of solid complexes of anhydrides with 8-hydroxyquinoline were obtained from a X-ray diffractograph using CuK_α radiations.

X-ray diffraction patterns of 8-hydroxyquinoline, phthalic anhydride and their solid state reaction product were also taken. The solid state reaction product was obtained by mixing 8-hydroxyquinoline and phthalic anhydride in 1:1 molar ratio in a polythene bag. The mixture was then pressed in the form of a pellet by applying a pressure of 10 tons/sq in. and kept in an oven maintained at 50° overnight. The pellet was crushed into a fine powder and the powder again pressed in the form of a pellet by applying the same pressure and kept for 24 hr at 50°. This pellet was finally crushed into fine powder.

The density of anhydride complexes were determined at 35° by pyknometric method using cyclohexane as the displacing liquid.

Phase diagram of 8-hydroxyquinoline and catechol system was studied by thaw melt method[6].

Kinetic study: Capillary technique — The kinetics of the reaction between 8-hydroxyquinoline as one component and maleic anhydride or phthalic anhydride or catechol as the other component were studied by capillary technique in a similar way as described by Rastogi and coworkers[7,8]. The reactants were kept side by side in glass capillaries at constant temperatures and the thickness of the product layers were measured with the help of a travelling microscope. The experiments were per-

formed at different temperatures for a fixed particle size.

Kinetics of the reaction in capillary when the reactants are separated by air-gap — The two components were kept in glass capillaries with air-gaps of different lengths. It was observed that reaction occurred only towards the side of reactants other than 8-hydroxyquinoline. The thickness of the product layer was measured at different intervals of time and for various lengths of air-gap. This study could be performed for 8-hydroxyquinoline-maleic anhydride and 8-hydroxyquinoline-phthalic anhydride systems.

Gravimetric study — The gravimetric study was performed for phthalic anhydride and 8-hydroxyquinoline system in a similar way as described earlier[5].

Dilatometric technique — Kinetics of the reactions by this technique were studied in a similar way as described previously[5]. The reactants in 1:1 molar ratios were mixed in the solid state and made in the form of pellets. The pellets were kept in a mercury dilatometer. The kinetics were followed by noting the change in mercury level in the mercury manometer. The experiments were performed at different temperatures and different particle sizes. Blank runs were also made for individual components but no change in volume was observed.

Surface migration study of 8-hydroxyquinoline — Surface migration study was made in a similar way as described by Rastogi and Dubey[9]. Five glass tubes of equal lengths and different diameters were taken, in which 8-hydroxyquinoline of known weights were taken in such a way as the length of the open end of the tubes from the surface of the 8-hydroxyquinoline were same in all the tubes. These were then kept at $60° \pm 1°$ and the loss in weight were noted at different intervals of time.

Results and Discussion

Complex from solution — When solutions of 8-hydroxyquinoline as one component and maleic anhydride, succinic anhydride, phthalic anhydride, catechol and or resorcinol as the other component were mixed in 1:1 molar ratios in acetone, coloured molecular complexes were found to separate. The elemental analyses (Table 1) show that the complexes have 1:1 stoichiometry. X-ray diffraction studies prove that the complexes are definite chemical species. The diffraction patterns were indexed for orthorhombic symmetry for maleic anhydride-8-hydroxyquinoline complex and tetragonal symmetry for succinic anhydride-8-hydroxyquinoline and phthalic anhydride-8-hydroxyquinoline complexes. The lattice parameters are given in Table 2.

One may guess that the complexes are CT complexes[10]. In order to examine this point, UV spectra of anhydride complexes with 8-hydroxyquinoline in CCl_4 were taken. The absence of any new band in the spectra indicates that probably CT interactions are not involved. It is also likely that the complexes are dissociated in solution. In order to confirm this point, phase diagram of 8-hydroxyquinoline-catechol system was studied. The solid-liquid equilibrium data, recorded in Fig. 1, indicate that 1:1 complex is formed in the solid state, but since the maxima is flat, it appears that the complex is dissociated in the liquid state. If this is so and the complexes are CT complexes, the electrical conductivity of the complexes in solution would be more than that of the solutions of the parent components. The results given in Table 3 show that the electrical conductivities of the complexes in acetone are higher than the sum of the parent components, suggesting that the

TABLE 1 — ELEMENTAL ANALYSIS OF 1:1 COMPLEXES OF 8-HYDROXYQUINOLINE WITH OTHER COMPONENTS

Other component	Found (%)			Calc. (%)		
	C	H	N	C	H	N
Maleic anhydride	64·30	3·70	5·70	64·44	3·72	5·76
Succinic anhydride	63·61	4·44	5·68	63·66	4·48	5·71
Phthalic anhydride	69·40	3·80	4·80	69·60	3·75	4·77
Catechol	70·51	5·10	5·50	70·58	5·09	5·49
Resorcinol	70·60	5·12	5·46	70·58	5·09	5·49

TABLE 2 — CRYSTAL DATA OF THE COMPONENTS AND THE COMPLEXES

Compound	System	a	b	c	V	z	$d_{obs.}$	$d_{calc.}$	Fig. of merit
Maleic anhydride	Orthorhombic	5·37	11·20	7·17	431·0	2			
1:1 Complex	do	7·345	8·076	9·947	590·0	2	1·320	1·366	12
Succinic anhydride	Orthorhombic	5·414	11·71	6·99	443·2	4			
1:1 Complex	Tetragonal	5·92	5·92	17·36	608·2	2	1·377	1·337	16
Phthalic anhydride	Orthorhombic	7·9	14·16	5·95	666·0	4			
8-Hydroxyquinoline	Tetragonal	13·12	13·12	14·18	2441·0	12			
1:1 Complex	do	11·61	11·61	15·42	2079.0	6	1·40	1·33	14

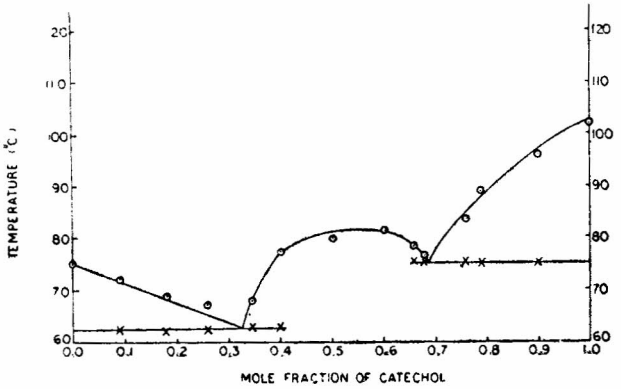

Fig. 1 — Phase diagram of catechol and 8-hydroxyquinoline

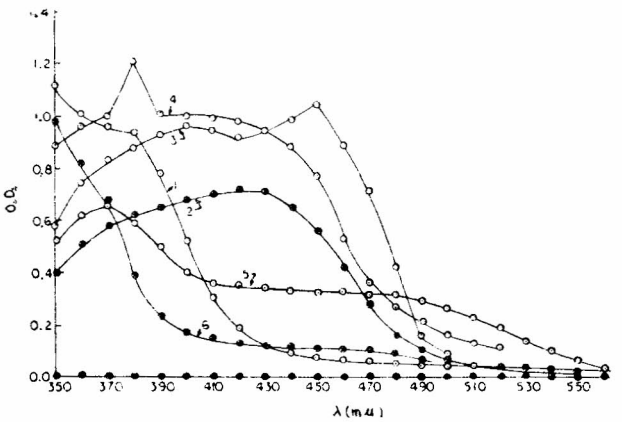

Fig. 2 — Reflectance spectra of (1) 8-hydroxyquinoline, (2) maleic anhydride-8-hydroxyquinoline complex, (3) succinic anhydride-8-hydroxyquinoline complex, (4) phthalic anhydride-8-hydroxyquinoline complex, (5) catechol-8-hydroxyquinoline complex and (6) resorcinol-8-hydroxyquinoline complex

complexes have polar character and undergo dissociation in solution.

In order to avoid the complication due to dissociation of the complexes, reflectance spectra of the solids were taken (Fig. 2). The presence of new bands except in the case of 8-hydroxyquinoline-catechol complex show the formation of new compounds. This clearly indicates that probably CT interaction is involved in the formation of complexes.

Complex obtained from solid state reaction — In the case of phthalic anhydride-8-hydroxyquinoline system, X-ray diffraction patterns of the complex prepared from the solution and obtained by solid-state reaction were compared and found to contain similar stronger lines. In addition, the diffraction pattern of solid state reaction product contains some of the lines of the components, showing that the reaction does not go to completion in solid state. These results clearly show that 1:1 complex is formed both in solid state as well as in solution.

Kinetic studies — We shall first examine the kinetic data in order to understand the mechanism of surface migration. The kinetic data for the solid state reaction obtained from capillary experiments are found to fit the following equation:

TABLE 3 — ELECTRICAL CONDUCTIVITIES OF COMPONENTS AND OF 1:1 COMPLEXES OF 8-HYDROXYQUINOLINE IN ACETONE (0·2*M*)

(Temp. = 37°)

Compounds	Conductivity (mhos)
8-Hydroxyquinoline	$0{\cdot}080\times10^{-4}$
Maleic anhydride	$0{\cdot}135\times10^{-4}$
8-Hydroxyquinoline-maleic anhydride	$0{\cdot}180\times10^{-3}$
Succinic anhydride	$0{\cdot}150\times10^{-4}$
8-Hydroxyquinoline-succinic anhydride	$0{\cdot}195\times10^{-3}$
Phthalic anhydride	$0{\cdot}115\times10^{-4}$
8-Hydroxyquinoline-phthalic anhydride	$0{\cdot}165\times10^{-3}$
Catechol	$0{\cdot}220\times10^{-4}$
8-Hydroxyquinoline-catechol	$0{\cdot}250\times10^{-3}$
Resorcinol	$0{\cdot}225\times10^{-4}$
8-Hydroxyquinoline-resorcinol	$0{\cdot}250\times10^{-4}$

TABLE 4 — EFFECT OF TEMPERATURE ON RATE CONSTANTS (CAPILLARY TECHNIQUE)

(Particle size = 300-350 mesh)

System	Temp. (°C)	$k_1\times10^{-2}$ (cm/hr)	n
8-Hydroxyquinoline-maleic anhydride	25±1	2·49±0·02	0·40±0·03
	30±1	2·73±0·02	0·39±0·02
	35±1	3·25±0·02	0·40±0·04
	40±1	3·67±0·04	0·46±0·01
8-Hydroxyquinoline-phthalic anhydride	30±1	1·24±0·01	0·51±0·03
	35±1	1·33±0·01	0·52±0·01
	40±1	1·56±0·02	0·52±0·04
	45±1	1·69±0·03	0·59±0·04
8-Hydroxyquinoline-catechol	34±1	0·63±0·03	0·28±0·03
	40±1	1·10±0·04	0·26±0·01
	45±1	1·29±0·02	0·27±0·02
	50±1	1·91±0·03	0·26±0·04

$$\xi = k_1 t^n \qquad \ldots(1)$$

where ξ is the thickness of the product layer at any time t and k_1 and n are constants. The linear plots of log ξ against t (Fig. 3) confirm the validity of Eq. (1). The kinetic data could not be obtained for succinic anhydride-8-hydroxyquinoline and resorcinol-8-hydroxyquinoline systems. In the former case only a surface reaction occurred and the thickness of the product layer could not be measured as a function of time, whereas in the latter, a colourless product was formed. The kinetic parameters are given in Table 4.

The plots of log k_1 against $1/T$ were linear, showing the validity of Arrhenius equation. The values of energy of activation are given in Table 5. The low values of energy of activation indicate that diffusion of 8-hydroxyquinoline in the solid state is occurring via surface migration. Since 8-hydroxyquinoline is the diffusing species, the question arises why the reaction is not propagated in the case of succinic anhydride. It appears that in this case blocking of the reaction paths takes place as a result of the product formation[11].

The rates of diffusion when two reactants are kept in contact and when they are separated by air-gap are not the same. As the length of the

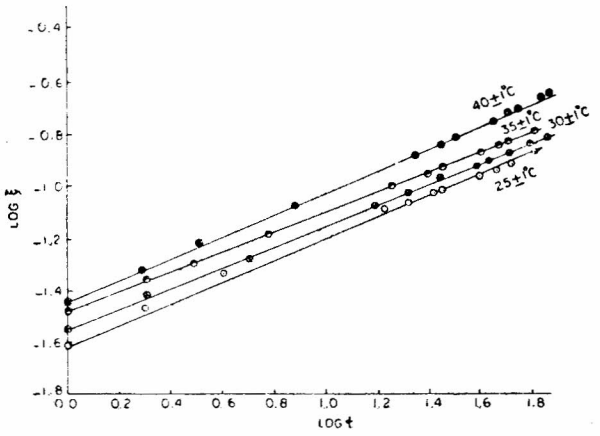

Fig. 3 — Kinetic data for the reaction between maleic anhydride and 8-hydroxyquinoline at different temperatures (capillary technique)

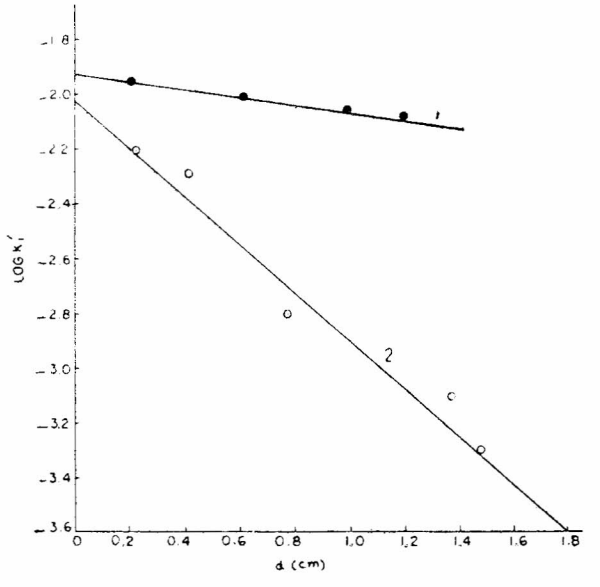

Fig. 4 — Dependence of rate constant on the length of air-gap for the reaction of (1) 8-hydroxyquinoline-maleic anhydride and (2) 8-hydroxyquinoline-phthalic anhydride

air-gap increases, the rate decreases and is given by relationship (2)

$$k_1' = Ae^{-pd} \qquad \ldots(2)$$

where k_1' is the rate at different lengths of air-gap; d, A and p are constants. The plots of log k_1' against d are linear (Fig. 4), indicating that vapour phase diffusion is certainly not taking place and diffusion is occurring via surface migration.

The experiment on diffusion of 8-hydroxyquinoline in air supports the above facts. The data fit Eq. (3)

$$S = kt \qquad \ldots(3)$$

where S is the amount of 8-hydroxyquinoline diffused in air at any time t and k is constant. The value of k depends on the diameter of the tube according to Eq (4)

$$k/r = \alpha r + \beta \qquad \ldots(4)$$

α and β in Eq. (4) are given by $\alpha = \pi\ C_e D_v/l$ and $\beta = 2\pi C_e D_S$, where r is the radius of the tube, l is the distance of 8-hydroxyquinoline surface from open end of the tube, C_e is the equilibrium concentration of 8-hydroxyquinoline just above the surface, D_v is the vapour phase diffusion coefficient and D_S is the diffusion coefficient for surface migration. The test of Eq. (4) has been made by plotting k/r against r in Fig. 5. The values of α and β are found to be 0·05 and 0·327 respectively at $60° \pm 1°$. This clearly shows that the diffusion of 8-hydroxyquinoline via surface migration is not uncommon.

The data in Table 4 clearly show that the values of k_1 for different systems follow the decreasing order: maleic anhydride > phthalic anhydride > catechol. The data in Table 5 show that the values of energy of activation are in the sequence: maleic anhydride ≃ phthalic anhydride > catechol. These observations clearly indicate that as the molecules become non-planar, it becomes difficult for 8-hydroxyquinoline to migrate over the surfaces of the reactants during diffusion.

TABLE 5 — VALUES OF ENERGY OF ACTIVATION FOR THE REACTIONS OF 8-HYDROXYQUINOLINE WITH OTHER COMPONENTS

Other component	E(dilatometry) (kcal/mole)	E(capillary) (kcal/mole)
Maleic anhydride	21·4	4·6
Succinic anhydride	35·1	—
Phthalic anhydride	10·8	4·5
Catechol	37·5	13·0
Resorcinol	13·1	—

The diffusion of 8-hydroxyquinoline inside the grains can be followed by a study of gas-solid reaction. In gravimetric experiment, the vapours of 8-hydroxyquinoline were allowed to react with phthalic anhydride (solid) and the kinetics was followed by noting the change in weight of the phthalic anhydride. The kinetic data obeyed Eq. (5)

$$W = k_2 t \qquad \ldots(5)$$

where W is the change in weight at any time t and k_2 is constant. The energy of activation calculated from Arrhenius plot is found to be 23·0 kcal. This value is similar to heat of vaporization of 8-hydroxyquinoline, which indicates that probably vapour

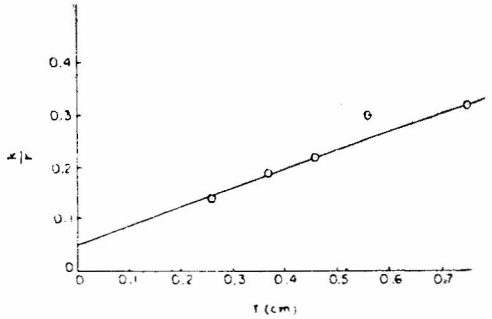

Fig. 5 — Estimation of the diffusion coefficient of 8-hydroxyquinoline in air and the coefficient for surface migration

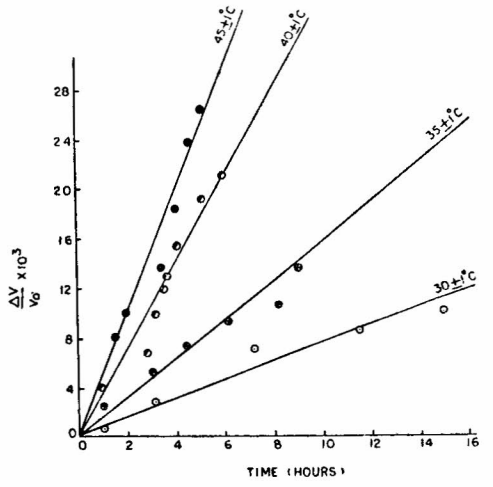

Fig. 6 — Kinetic data for the reaction between maleic anhydride and 8-hydroxyquinoline at different temperatures (dilatometric technique)

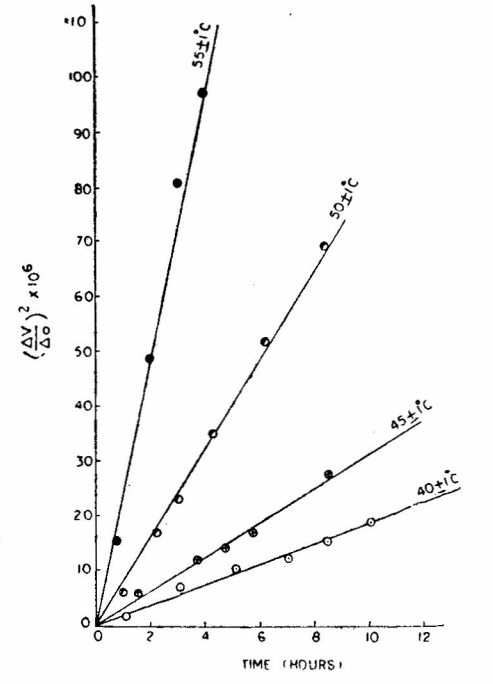

Fig. 7 — Kinetic data for the reaction between catechol and 8-hydroxyquinoline at different temperatures (dilatometric technique)

phase diffusion is taking place. From Eq. (5), it follows that cracks are developed in the product layer which permit continued access of vapour to the fresh surface of the reactants and consequently the weight of the product is directly proportional to the time during which the reactant is exposed with the vapours of 8-hydroxyquinoline.

The kinetic data for the reaction between 8-hydroxyquinoline and anhydrides obtained from dilatometric study are found to fit Eq. (6).

$$\frac{\Delta V}{V_0} = k_3 t \qquad \ldots(6)$$

However, in the reaction of 8-hydroxyquinoline and catechol or resorcinol, Eq. (7) fits the kinetic data.

$$\left(\frac{\Delta V}{V_0}\right)^2 = k_3 t \qquad \ldots(7)$$

where ΔV is the decrease in volume at any time t, V_0 is the initial volume and k_3 is a constant. The validity of Eqs. (6) and (7) were tested by plotting $(\Delta V/V_0)$ vs t and $(\Delta V/V_0)^2$ vs t respectively (typical Figs. 6 and 7). The parameters of the two equations at different temperatures and for particles of different sizes at constant temperatures are given in Tables 6 and 7 respectively.

The plots of log k_3 against $1/T$ were linear and the values of energy of activation were calculated from the slopes of the linear plots and are given in Table 5.

After the reaction was over, the pellet was taken out from the dilatometer in every experiment and it was noticed that the surface of the pellets became rough and when the pellets were broken, mercury drops were found to be randomly distributed inside the pellets. It appears that cracks are produced during the reaction and mercury enters through the voids and channels produced. This is supported when the cell volumes of the reactants and the products were compared (Table 2). It is obvious that the cell volumes of the complexes are less than the sum of the cell volumes of the components. Further, when the cell volumes per molecule (Table 8) of the complexes were compared with those of components, it is found that the cell volumes per molecule of the complexes contracted approximately by 5%. On account of volume contraction, cracks and voids are created in the pellets. Also since the crystal shapes of the components are different than those

TABLE 6 — EFFECT OF TEMPERATURE ON RATE CONSTANTS (DILATOMETRY TECHNIQUE)

(Particle size = 300-350 mesh)

System	Temp. (°C)	k_3 (hr^{-1})
8-Hydroxyquinoline-maleic anhydride	30±1	$(0{\cdot}8\pm0{\cdot}2)\times10^{-3}$
	35±1	$(1{\cdot}6\pm0{\cdot}1)\times10^{-3}$
	40±1	$(3{\cdot}5\pm0{\cdot}4)\times10^{-3}$
	45±1	$(5{\cdot}0\pm0{\cdot}1)\times10^{-3}$
8-Hydroxyquinoline-succinic anhydride	45±1	$(1{\cdot}7\pm0{\cdot}1)\times10^{-4}$
	50±1	$(3{\cdot}0\pm0{\cdot}1)\times10^{-4}$
	55±1	$(9{\cdot}0\pm0{\cdot}4)\times10^{-4}$
	60±1	$(25{\cdot}4\pm0{\cdot}5)\times10^{-4}$
8-Hydroxyquinoline-phthalic anhydride	40±1	$(2{\cdot}2\pm0{\cdot}1)\times10^{-4}$
	45±1	$(3{\cdot}2\pm0{\cdot}1)\times10^{-4}$
	50±1	$(4{\cdot}4\pm0{\cdot}1)\times10^{-4}$
	55±1	$(5{\cdot}4\pm0{\cdot}3)\times10^{-4}$
8-Hydroxyquinoline-catechol	40±1	$(1{\cdot}9\pm0{\cdot}3)\times10^{-6}$
	45±1	$(3{\cdot}2\pm0{\cdot}2)\times10^{-6}$
	50±1	$(8{\cdot}1\pm0{\cdot}4)\times10^{-6}$
	55±1	$(24{\cdot}0\pm0{\cdot}1)\times10^{-6}$
8-Hydroxyquinoline-resorcinol	40±1	$(2{\cdot}0\pm0{\cdot}1)\times10^{-6}$
	45±1	$(2{\cdot}8\pm0{\cdot}2)\times10^{-6}$
	50±1	$(3{\cdot}6\pm0{\cdot}1)\times10^{-6}$
	55±1	$(5{\cdot}0\pm0{\cdot}2)\times10^{-6}$

TABLE 7 — EFFECT OF PARTICLE SIZE ON RATE CONSTANTS (DILATOMETRIC STUDY)

System	Temp. (°C)	Particle size (mesh)	k_3 (hr^{-1})
8-Hydroxy-quinoline-maleic anhydride	40±1	300-350	$(3{\cdot}5\pm0{\cdot}4)\times10^{-3}$
		240-300	$(2{\cdot}3\pm0{\cdot}1)\times10^{-3}$
		200-240	$(1{\cdot}8\pm0{\cdot}2)\times10^{-3}$
		150-200	$(1{\cdot}5\pm0{\cdot}1)\times10^{-3}$
8-Hydroxyquino-line-succinic anhydride	60±1	300-350	$(25{\cdot}4\pm0{\cdot}5)\times10^{-4}$
		240-300	$(20{\cdot}0\pm0{\cdot}3)\times10^{-4}$
		200-240	$(14{\cdot}1\pm0{\cdot}2)\times10^{-4}$
		150-200	$(8{\cdot}3\pm0{\cdot}2)\times10^{-4}$
8-Hydroxyquino-line-phthalic anhydride	50±1	300-350	$(4{\cdot}4\pm0{\cdot}1)\times10^{-4}$
		240-300	$(2{\cdot}3\pm0{\cdot}1)\times10^{-4}$
		200-240	$(1{\cdot}7\pm0{\cdot}3)\times10^{-4}$
		150-200	$(1{\cdot}5\pm0{\cdot}2)\times10^{-4}$
Catechol	50±1	300-350	$(8{\cdot}1\pm0{\cdot}4)\times10^{-6}$
		240-300	$(4{\cdot}6\pm0{\cdot}17)\times1^{-6}$
		200-240	$(3{\cdot}3\pm0{\cdot}3)\times10^{-6}$
		150-200	$(2{\cdot}5\pm0{\cdot}2)\times10^{-6}$
Resorcinol	40±1	300-350	$(2{\cdot}0\pm0{\cdot}1)\times10^{-6}$
		240-300	$(1{\cdot}5\pm0{\cdot}3)\times10^{-6}$
		200-240	$(1{\cdot}1\pm0{\cdot}1)\times10^{-6}$
		150-200	$(0{\cdot}9\pm0{\cdot}2)\times10^{-6}$

TABLE 8 — CELL VOLUME PER MOLECULE

System	Cell volume/ molecule	Contraction (%)
8-Hydroxyquinoline	203·4	—
Maleic anhydride	107·7	—
Succinic anhydride	110·8	—
Phthalic anhydride	166·5	—
8-Hydroxyquinoline-maleic anhydride	295·0	5·14
8-Hydroxyquinoline-succinic anhydride	304·0	3·18
8-Hydroxyquinoline-phthalic anhydride	346·5	6·65

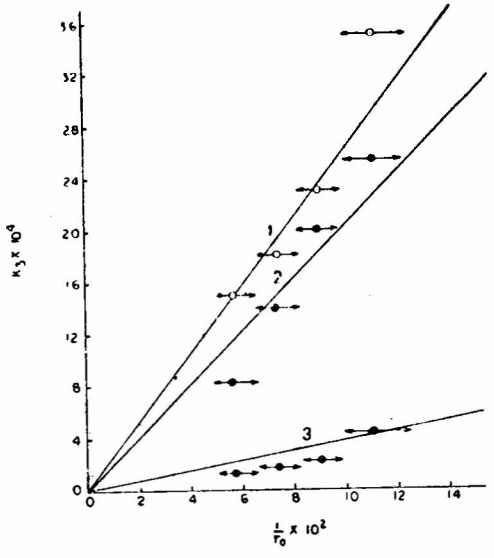

Fig. 8 — Effect of particle size on rate constant (dilatometric technique) of the reaction between (1) 8-hydroxyquinoline and maleic anhydride at 40°±1°, (2) 8-hydroxyquinoline and succinic anhydride at 60°±1° and (3) 8-hydroxyquinoline and phthalic anhydride at 50°±1°

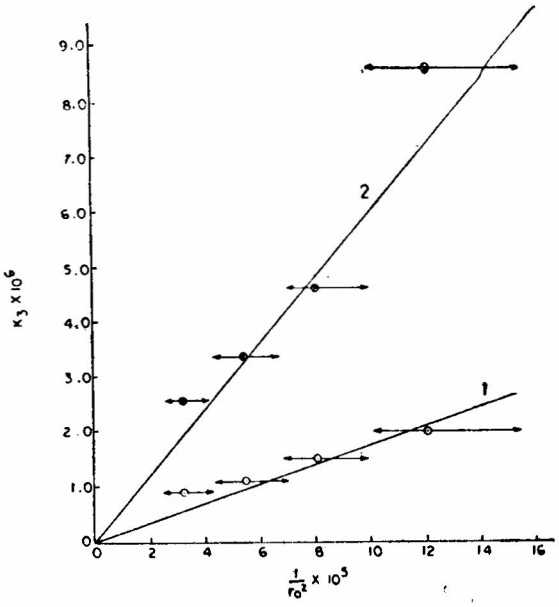

Fig. 9 — Effect of particle size on rate constant (dilatometry) of the reaction between (1) 8-hydroxyquinoline and resorcinol at 40°±1° and (2) 8-hydroxyquinoline and catechol at 50°±1°

of the complexes, strains are expected. It has been shown in an earlier paper[5] that $\Delta V/V_0 = 3\delta/r_0$, where ΔV = decrease in volume, V_0 = total initial volume of the reactants, δ = thickness of the product layer, and r_0 = radius of the reacting grains.

When $\delta = k't$, we have $\Delta V/V_0 = 3k't/r_0$ and when $\delta^2 = k't$, we have $(\Delta V/V_0)^2 = 9k't/r_0^2$.

This shows that in the first case a plot of $\Delta V/V_0$ versus t would be linear and the value of k_3 in Eq. (6) would vary linearly as the reciprocal of the radius of the grains, whereas for the second case a plot of $(\Delta V/V_0)^2$ vs t would be linear and the value of k_3 in Eq. (7) would vary linearly as the reciprocal of the square of the radius of the grains. Actually it is found to be so. The plots of k_3 against $1/r_0$ and that of k_3 against $1/r_0^2$ for the reactions of an hydrides with 8-hydroxyquinoline and of catechol and resorcinol with 8-hydroxyquinoline respectively are linear (Figs. 8 and 9).

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