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Solid State Reaction between *p*-Benzoquinone and Dihydroxybenzene

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Reaction kinetics of *p*-benzoquinone–*p*-dihydroxybenzene; *p*-benzoquinone–*m*-dihydroxybenzene and *p*-benzoquinone–*o*-dihydroxybenzene systems have been studied in the solid state using capillary, gravimetric, and dilatometric techniques. It is found that *p*-benzoquinone is the diffusing species. The diffusion occurs through surface migration and depends very much on the symmetry of the dihydroxybenzene molecules. Gravimetric studies indicate that cracks are formed in the product during reaction and that the reaction reaches completion. Dilatometric studies indicate that the reaction products are more compact and contraction in volume takes place during the course of reaction.

Introduction

Solid state reactions involving inorganic solids have been studied extensively (*1*). However, only a few studies have been made regarding the mechanism of reactions between organic solids (*2, 3*). The basic difference between the two types of reactions is that most of the inorganic solid state reactions involve metal atoms or small ions and hence the diffusion is easier. On the other hand because of the bigger size and complex nature of the molecules, the diffusion in the case of organic solid state reactions is difficult and requires higher activation energy.

Recently Rastogi and co-workers (*3*) have studied the reaction between 8-hydroxyquinoline and anhydrides. They have found that the reactions are diffusion-controlled and cracks and voids are formed in the product during the reaction. However, more research data are needed in order to understand the mechanism of such reactions. The present paper describes the reaction between *p*-benzoquinone as one component and other components such as *p*-dihydroxybenzene, *m*-dihydroxybenzene, and *o*-dihydroxybenzene in the solid state. The mechanism of diffusion is discussed.

Experimental

Materials

p-Benzoquinone (AR BDH) was purified by steam sublimation, and *o*-, *m*-, and *p*-dihydroxybenzenes (all AR BDH) were purified by repeated distillation under reduced pressure. The purity of the samples was checked by determining the melting points. The melting points of purified *p*-benzoquinone, *o*-, *m*-, and *p*-dihydroxybenzenes were respectively 115.0, 104.0, 110.0, and 170.2°C.

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Methods

Kinetics in the capillary. Glass capillaries sealed at one end were half filled with hydroxybenzenes and the other half filled with *p*-benzoquinone and then sealed and kept in an incubator at constant temperature. The starting points of the reactions were indicated by the change in color because the reaction products formed were colored. The kinetics were followed by measuring the thickness of the product layer formed at the junction of two reactants at different intervals of time. The experiment was performed at different temperatures. The details of the method are given elsewhere (*4*).

Gravimetric studies. The details of the method are described in Ref. (*4*). Two glass tubes fitted with standard joints were used. *p*-Benzoquinone placed in one tube and 0.4 g of the other component in the other. The two tubes were joined together and kept in an incubator at constant temperature. The kinetics were followed by noting the increase in weight of hydroxybenzenes at different intervals of time. The experiments were performed at different temperatures.

Dilatometric studies. A mercury dilatometer as described earlier (*3*) was used with slight modification. The reactants were mixed in 1 : 1 molar ratio in a glass mortar and immediately pressed into the form of a pellet (1 cm high and 1 cm in diameter) and kept in the dilatometer. The fall in mercury level in the manometer was noted as a function of time at a constant temperature. The experiments were done at different temperatures.

Surface migration studies. Glass capillaries differing in diameter but of the same length closed at one end were used. The tubes were half filled with *p*-benzoquinone and kept in an incubator maintained at constant temperature. The loss in weight of *p*-benzoquinone was noted at different intervals of time.

X-Ray diffraction studies. p-Benzoquinone and *p*-dihydroxybenzene were mixed in 1 : 1 molar ratio in acetone, crystallized and dried. The product formed is a dark-colored crystalline compound, quinhydrone. The two reactants were again mixed in a similar fashion in the solid state. They were ground in a glass mortar, made into a pellet, and kept at 50°C for 24 hr. The pellet was crushed and the powder obtained again made into the form of a pellet and kept at 50°C for 1 day. The pellet was crushed into powder, and powder X-ray diffraction patterns for both products, i.e., the one obtained from acetone and the other obtained by solid state reaction, were taken using Cu$K\alpha$ radiations at I.I.T. Kanpur.

Elemental analysis: The reactants were mixed in 1 : 1 molar ratios in acetone and then crystallized. The C and H estimations in the crystallized products were made by a microanalytical technique at the Chemistry Department, Banases Hindu University, Varanasi (India).

Infrared spectral studies. Infrared spectra of the crystallized products were obtained in KBr with Perkin–Elmer 621 Spectrophotometer at Banaras Hindu University, Varanasi (India).

Results and Discussion

Carbon and hydrogen estimations in the reaction products, obtained after crystallization from acetone, indicate that *p*-benzoquinone reacts with dihydroxybenzenes in 1 : 1 molar ratios. Infrared spectral studies show that the OH groups of the dihydroxybenzene molecules are involved in hydrogen bonding with the oxygen of *p*-benzoquinone. Further, since the reaction products have intense color, there is a possibility of charge-transfer interaction also. In these systems, *p*-benzoquinone will act as an acceptor and the dihydroxybenzene molecules as donor.

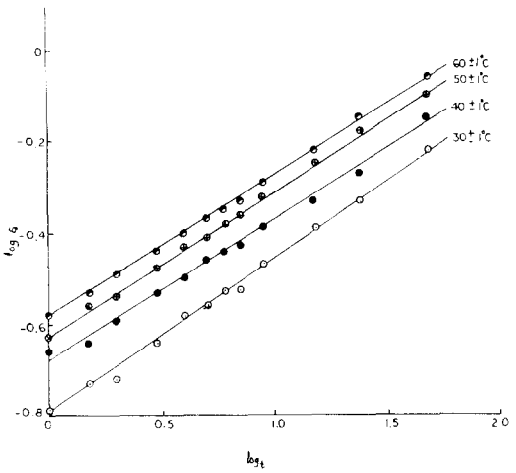

FIG. 1. Kinetic data for the reaction between *p*-benzoquinone and *p*-dihydroxybenzene in solid state at different temperatures (capillary technique).

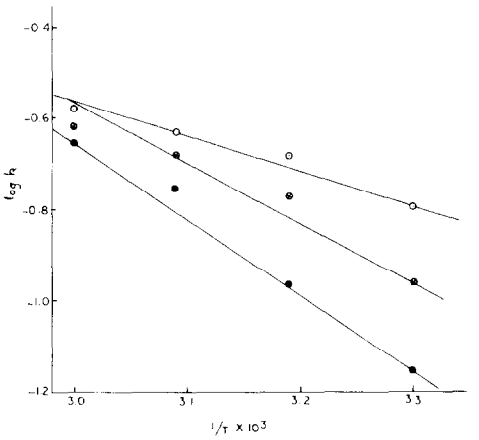

FIG. 2. Effect of temperature on the rate of reaction (capillary technique): ⊙, *p*-Benzoquinone–*p*-dihydroxybenzene system; ⊗, *p*-Benzoquinone–*m*-dihydroxybenzene system; ●, *p*-Benzoquinone–*o*-dihydroxybenzene system.

In order to know whether the reaction products obtained from solution are the same as those obtained from solid state reaction, powder X-ray diffraction patterns of *p*-benzoquinone–*p*-dihydroxybenzene were taken. The X-ray diffraction patterns indicate that the two products are identical.

Capillary experiments show that the kinetic data follow Eq. (1):

$$\zeta = k_1 t^n, \tag{1}$$

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

TABLE I

KINETIC PARAMETERS OF EQ. (1) AND ENERGY OF ACTIVATION[a]

Reaction system	Temperature (°C)	k_1 (cm/hr)	n	E (kcal/mole)
p-benzoquinone–*p*-dihydroxybenzene	30 ± 1	0.16 ± 0.02	0.33	3.5
	40 ± 1	0.21 ± 0.02	0.31	
	50 ± 1	0.23 ± 0.01	0.32	
	60 ± 1	0.26 ± 0.01	0.31	
p-benzoquinone–*m*-dihydroxybenzene	30 ± 1	0.11 ± 0.01	0.30	6.1
	40 ± 1	0.17 ± 0.01	0.28	
	50 ± 1	0.21 ± 0.02	0.32	
	60 ± 1	0.24 ± 0.01	0.31	
p-benzoquinone–*o*-dihydrobenzene	30 ± 1	0.07 ± 0.01	0.30	7.6
	40 ± 1	0.11 ± 0.02	0.32	
	50 ± 1	0.18 ± 0.02	0.29	
	60 ± 1	0.22 ± 0.01	0.35	

[a] Particle size = 100–140 mesh.

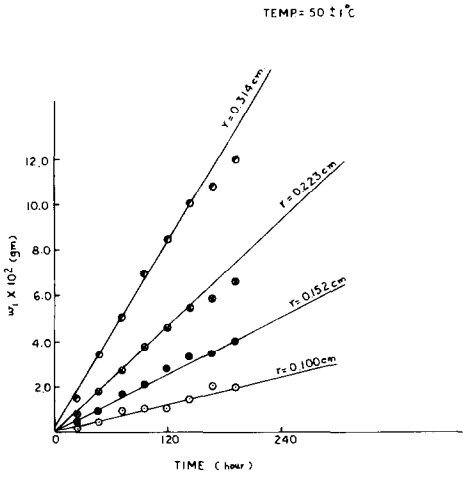

FIG. 3. Kinetic data for rate of sublimation of *p*-benzoquinone kept in glass tubes of different radius (*r*).

of log k_1 vs $1/T$ also gave straight lines, showing that the Arrhenius equation is obeyed (Fig. 2). From the slope of the curves, the energy of activations were calculated; they are given in Table I. Inspection of Table I indicates that the rate of reaction and the energy of activation (E) varies in the following sequence:

$$k_{1\,p\text{-dihydroxybenzene}} > k_{1\,m\text{-dihydroxybenzene}} > k_{1\,o\text{-dihydroxybenzene}},$$

$$E_{p\text{-dihydroxybenzene}} < E_{m\text{-dihydroxybenzene}} < E_{o\text{-dihydroxybenzene}}.$$

Further, the magnitudes of the energy of activation indicate that probably the diffusion of *p*-benzoquinone is taking place via surface migration. In order to have an idea regarding the surface migration of *p*-benzoquinone, a separate experiment was performed. The weight loss of *p*-benzoquione in glass capillaries of different diameters obeys Eq. (2)

$$W_1 = k_2 t \qquad (2)$$

where W_1 is the weight loss of *p*-benzoquinone at any time t and k_2 is the rate of weight loss. The validity of Eq. (2) is tested by plotting W_1 vs t, where straight lines are obtained (Fig. 3). When k_2/r is plotted against r, a straight line is obtained (Fig. 4), indicating that Eq. (3) is obeyed (*3*).

$$k_2/r = \alpha r + \beta, \qquad (3)$$

where α and β 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 capillary, l is the distance of the *p*-benzoquinone surface from the open end of the capillary, C_e is the equilibrium concentration of *p*-benzoquinone just above the surface, D_v is the vapor phase diffusion coefficient, and D_s is the diffusion coefficient for surface migration. It is likely that in the sublimation of *p*-benzoquinone, most of the material goes as vapor but solid molecules also glide on the surface of the glass capillary and contribute to the total weight loss. The value of D_s is obtained from the intercept of the line (Fig. 4) and this intercept is appreciable, hence it is likely that some of the weight loss in *p*-benzoquinone is due to surface migration of the molecules. From this experiment, it can be inferred that when *p*-benzoquinone molecules migrate on the glass surface, it is more likely that they will migrate on the surface of the dihydroxybenzene molecules. Surface mi-

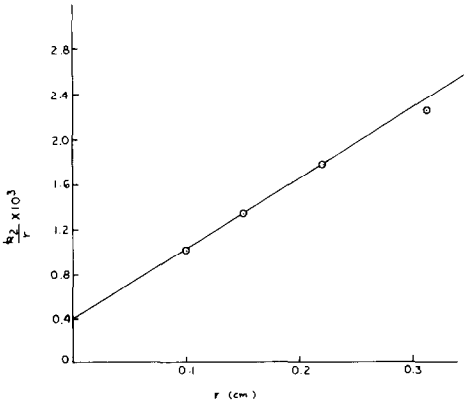

FIG. 4. Test of Eq. (3).

gration will be easier if the surface of the molecule on which the surface migration is to take place is planar and symmetrical. In the present investigation, *p*-dihydroxybenzene molecules have maximum symmetry and hence the rate of reaction with *p*-benzoquinone is a maximum and the energy of activation for diffusion is a minimum. On the other hand, the *o*-dihydroxybenzene molecules have minimum symmetry and hence minimum rate of reaction and maximum energy of activation for diffusion. The symmetry of *m*-dihydroxybenzene is between that of *o*- and *p*-dihydroxybenzene, hence the rate of reaction and energy of activation are also in between. The surface migration of *p*-benzoquinone on the surfaces of dihydroxybenzene molecules can be visualized as given in Fig. 5.

From Fig. 5, it is clear that *o*-dihydroxybenzene molecules offer maximum hindrance to the surface migration of *p*-benzoquinone molecules, molecules of *p*-dihydroxybenzene offer minimum hindrance. From this it may also be postulated that in the reaction products, an alternate stacking of reactant molecules will take place and the force of interaction, which is mostly charge transfer and hydrogen bonding, will probably be a maximum in the *p*-benzoquinone–*p*-dihydroxybenzene system and a minimum in the *p*-benzoquinone–*o*-dihydroxybenzene system.

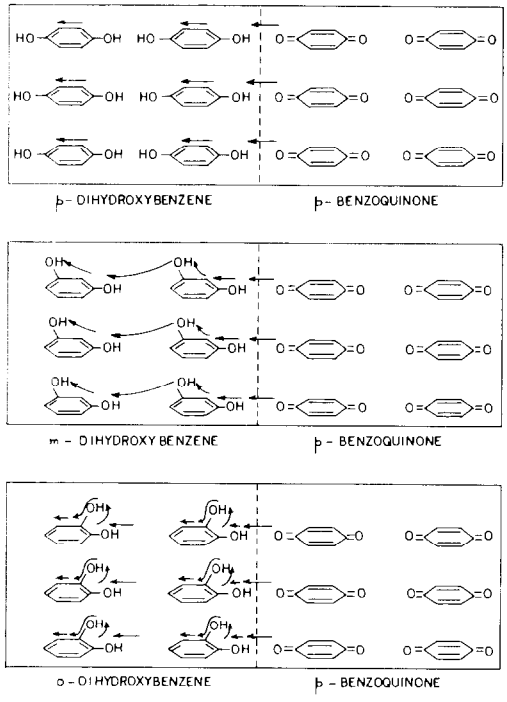

FIG. 5. Surface migration of *p*-benzoquinone.

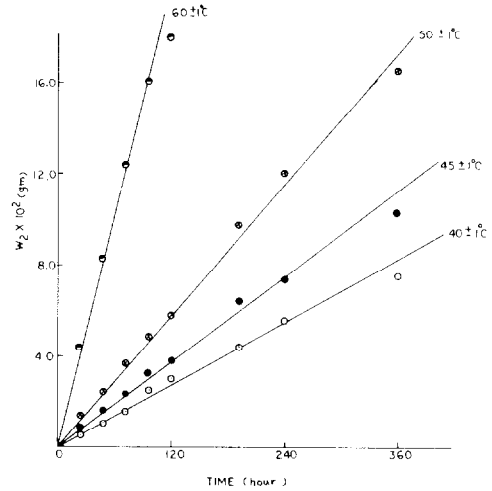

FIG. 6. Kinetic data for the reaction between *p*-benzoquinone (vapor) and *p*-dihydroxybenzene (solid) at different temperatures (gravimetric study).

In order to understand the mechanism of penetration inside the grains of dihydroxybenzene, gravimetric studies were made. The kinetic data obeyed Eq. (4).

$$W_2 = k_3 t, \tag{4}$$

where W_2 is the increase in weight of dihydroxybenzene at any time t and k_3 is the rate of reaction. A plot of W_2 vs t gave straight lines (Fig. 6) indicating the validity of Eq. (4). From the curves, the values of k_3 were calculated and are given in Table II. When log k_3 is plotted against $1/T$, straight lines are obtained (Fig. 7), indicating that the Arrhenius equation is obeyed. The en-

TABLE II

KINETIC PARAMETERS OF EQ. (4) AND ENERGY OF ACTIVATION

Reaction system	Temperature (°C)	$k_3 \times 10^4$ (g/hr)	E (kcal/mole)
p-benzoquinone–*p*-dihydroxybenzene	40 ± 1	2.3 ± 0.1	24
	45 ± 1	3.1 ± 0.2	
	50 ± 1	4.8 ± 0.1	
	60 ± 1	16.7 ± 0.3	
p-benzoquinone–*m*-dihydroxybenzene	40 ± 1	1.5 ± 0.2	28
	45 ± 1	2.2 ± 0.1	
	50 ± 1	4.3 ± 0.1	
	60 ± 1	15.4 ± 0.4	
p-benzoquinone–*o*-hydroxybenzene	40 ± 1	1.0 ± 0.1	28
	45 ± 1	1.9 ± 0.3	
	50 ± 1	4.0 ± 0.2	
	60 ± 1	14.8 ± 0.4	

[a] Particle size = 100–140 mesh.

ergy of activation calculated from the lines is also given in Table II. Here again the trend in the values of k_3 and E is similar to that obtained in the capillary experiments. The only difference is that the corresponding values of k_3 are much smaller and the corresponding values of E are much higher. These results are expected because the diffusion of *p*-benzoquinone molecules inside the grains of dihydroxybenzene will be a relatively difficult process.

At 60°C, in each system, the reactions were allowed to continue to completion, i.e., until there was no further increase in

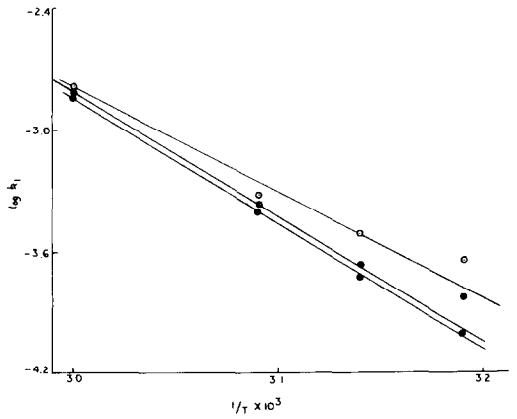

FIG. 7. Effect of temperature on the rate of vapor–solid reaction (gravimetric study): ⊙, *p*-Benzoquinone–*p*-dihydroxybenzene system; ⊗, *p*-Benzoquinone–*m*-dihydroxybenzene system; ●, *p*-Benzoquinone–*o*-dihydroxybenzene system.

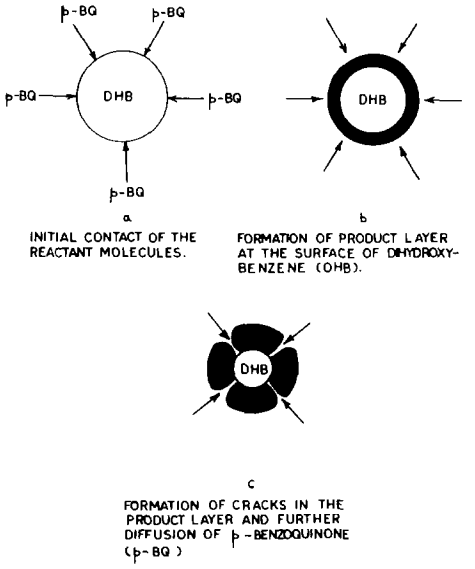

FIG. 8. Penetration of *p*-benzoquinone in the grains of dihydroxybenzene.

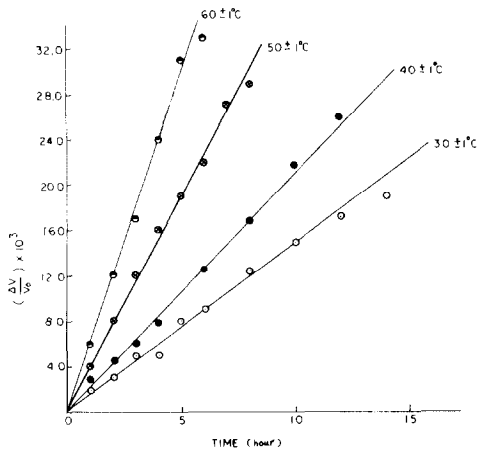

FIG. 9. Kinetic data for the reaction between *p*-benzoquinone and *p*-dihydroxybenzene (dilatometry).

weight of the dihydroxybenzene molecules. From the stoichiometry of the reactions, it was found that in all the systems, the reactions took place in 1 : 1 molar ratio. Since the reaction proceeds to completion, it is likely that first a coating of product layer is formed at the surface of the dihydroxybenzene molecules and, due to internal pressure of the system, cracks are formed in the product layer which allows further continued reaction of *p*-benzoquinone molecules with dihydroxybenzene. The diffusion inside the grains may take place through grain boundaries and other imperfections. The overall reaction sequence can be visualized as shown in Fig. 8.

The kinetics of the reactions were also followed by noting the change in volume of the reaction mixtures in the form of pellets at different temperatures. It was found that during the course of reactions, the volume of the pellets decreased and the kinetic data obeyed Eq (5).

$$\Delta V/V_0 = k_4 t, \qquad (5)$$

where V_0 is the initial volume of the pellets (reaction mixtures), ΔV is the decrease in volume at any time t, and k_4 is the apparent rate of reaction. A plot of $\Delta V/V_0$ vs t gave straight lines (Fig. 9); a plot of log k_4 vs $1/T$ also gave straight lines (Fig. 10), showing that the Arrhenius equation is obeyed. From the slope of the lines, the energy of activation is calculated and is given in Table III. In the same table, the values of k_4 are also given. Here again the trend in the values of k_4 is the same as before. Also the energy of activation increases from *p*- to *o*-dihydroxybenzene and the values are more than those for surface migration. Since the values of the energy of activation are higher, it is likely that interpenetration inside the grains of dihydroxybenzene is taking place. Further, after the reaction was over, the pellets were removed from the dilatometer and examined under a microscope. It was found that the pellets were more compact and the surfaces were rough. This observation simply indicates that due to reaction, the reactant molecules come closer to each other forming a compact species resulting in a decrease in volume. Further, since the surfaces of the pellets are rough, this indicates that cracks and voids are formed in the product.

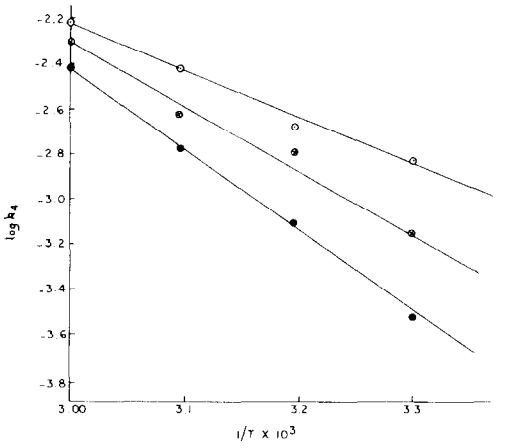

FIG. 10. Effect of temperature on the rate of reaction (dilatometry): ⊙, *p*- Benzoquinone–*p*-dihydroxybenzene; ⊗, *p*-Benzoquinone–*m*-dihydroxybenzene; ●, *p*-Benzoquinone–*o*-dihydroxybenzene.

TABLE III

KINETIC PARAMETER OF EQ. (5)[a]

Reaction system	Temperature (°C)	k_4 (hr^{-1}) × 10^3	E (kcal/mole)
p-benzoquinone–*p*-dihydroxybenzene	30 ± 1	1.5 ± 0.2	9.4
	40 ± 1	2.1 ± 0.1	
	50 ± 1	3.8 ± 0.2	
	60 ± 1	6.0 ± 0.2	
p-benzoquinone–*m*-dihydroxybenzene	30 ± 1	0.7 ± 0.1	13.0
	40 ± 1	1.6 ± 0.2	
	50 ± 1	2.4 ± 0.1	
	60 ± 1	5.0 ± 0.1	
p-benzoquinone–*o*-dihydroxybenzene	30 ± 1	0.3 ± 0.1	16.4
	40 ± 1	0.8 ± 0.1	
	50 ± 1	1.7 ± 0.2	
	60 ± 1	3.9 ± 0.2	

[a] Particle size = 100–140 mesh.

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