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Solid-State Reaction between *p*-Phenylenediamine and *p*-Benzoquinone

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p-Phenylenediamine reacts with *p*-benzoquinone in solution as well as in the solid state forming a 1 : 1 molecular complex which may be polymeric or agglomeric in nature. When the two components are mixed in the solid state in an agate mortar first a blue color develops which ultimately (after a few minutes) changes to dark brown. Differential scanning calorimetric studies show that the reaction products obtained from solution and by solid-state reactions are the same. Spectroscopic studies reveal that charge transfer stabilized by hydrogen bonding is involved in the formation of the complex. UV and visible spectroscopic studies in solution show that the complex either is unstable in solution or requires some time for stabilization. Magnetic measurements and ESR spectroscopy show the presence of an unpaired electron in the complex. Electrical conductivity measurements in the solid state show that the complex is a semiconductor. Kinetic studies of reaction in the solid state by different techniques reveal different energies of activation. The energy of activation determined by gravimetric studies is higher than the energy of activation determined by capillary techniques when the reactants are in contact with each other. The reaction is propagated through surface migration and inner penetration of *p*-benzoquinone molecules into the crystal lattice of *p*-phenylenediamine occurs. Microscopic studies show that the reaction in the solid state is initiated first at the edges and the points where *p*-phenylenediamine crystal is strained. © 1988 Academic Press, Inc.

Introduction

Quinhydrone is a well-known aromatic molecular complex consisting of *p*-benzoquinone and hydroquinone in a 1 : 1 molar ratio. Apart from this complex, *p*-benzoquinone and its substituted compounds form a number of complexes with substituted *p*-phenylenediamine (*1*). These complexes in general are said to be charge-transfer (CT) complexes and the principal binding forces between the molecules are the charge-transfer interactions stabilized by hydrogen bonding (*2–3*). X-ray diffraction studies have confirmed that the complexes consist of alternately superposed quinone and another molecule (*4–5*).

Recently Singh *et al.* (*6*) in the reaction of α-naphthol with *p*-benzoquinone did not find a new CT band although the absorption of the complex increased in the UV and visible region. There was definite evidence for the presence of hydrogen bonding between the –OH group of α-naphthol and C=O group of *p*-benzoquinone.

Crystal structures of complexes between *p*-benzoquinone and π-electron donors, which are also potential hydrogen donors in hydrogen-bond complex formation, have

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been studied particularly by Wallwork and his co-workers (*7, 8*). In the normal monoclinic form of quinhydrone both constituent molecules may be deformed to some extent (*9*). The quinone and hydroquinone molecules are linked alternately through O–H. . .O hydrogen bonds to form a zigzag chain which extends through the crystal. These chains are stacked side by side to form a molecular sheet. In the 2 : 1 complex of phenol and *p*-benzoquinone, each quinone molecule is sandwiched between two phenol molecules which are parallel to the quinone (*7*). Groups of three such molecules are stacked discontinuously in columns. Hydrogen bonds link the phenolic hydroxyl groups with quinone–oxygen atoms in adjacent columns. The stoichiometry on the one hand and the parallel arrangement of neighboring electron donor and acceptor molecules on the other suggest a compromise between hydrogen bonding and charge-transfer bonding, respectively.

Formation of complexes of *p*-benzoquinone with other aromatic molecules are well studied in solution. However, studies of such complexes are very limited in the solid state (*6, 10, 11*). Singh and Singh (*10*) studied the reaction between *p*-benzoquinone and hydroquinone and Singh *et al.* (*6*) also studied the reaction of α-naphthol with *p*-benzoquinone in the solid state. The results indicate that in the solid state *p*-benzoquinone is the diffusing species and that either surface migration or vapor phase diffusion plays an important role in the process of complex formation. However, a thorough investigation is needed in order to understand the nature of interaction and mechanism of solid-state reactions in these systems. In order to investigate these points, reaction between *p*-benzoquinone and *p*-phenylenediamine in the solid state has been studied and the nature of interaction established. The results are discussed in this paper.

Experimental Methods

Materials and Purification

p-Benzoquinone. *p*-Benzoquinone (BQ) was synthesized by oxidizing hydroquinone with sodium chlorate in 2 mass% sulfuric acid (*12*). The product was crystallized from petroleum ether (80–100°C fraction) and purified several times by sublimation; yellow needles, melting temperature 116°C, were obtained.

p-Phenylenediamine. *p*-Phenylenediamine (PDA, BDH) was purified by repeated distillation under reduced pressure. The purified sample melts at 140°C.

Methods

Preparation of reaction product from solution. Saturated solutions of BQ and PDA in water were mixed and a dark-brown-colored solid complex precipitated. This solid product was washed several times with water and finally with acetone to remove even a trace amount of either of the components. A dark brown reaction product was also precipitated when saturated solutions of components in methanol were mixed. Solutions of the two components in ether on mixing gave a blue-colored product which immediately changed to dark brown. All three reaction products obtained from solution were the same color, stable, and had the same melting point range. The complex did not have a sharp melting point. It melted at approximately 237°C.

Preparation of reaction product by grinding. An agate mortar and pestle was used to grind an equimolar amount of BQ and PDA in solid state. It was found that simple grinding of BQ and PDA in 1 : 1 molar proportion for 2 min gave a blue color and on further grinding it became dark brown. It was observed that simple grinding of the components together in equimolar proportion in an agate mortar for 10 min was sufficient to bring about a change to a dark brown color.

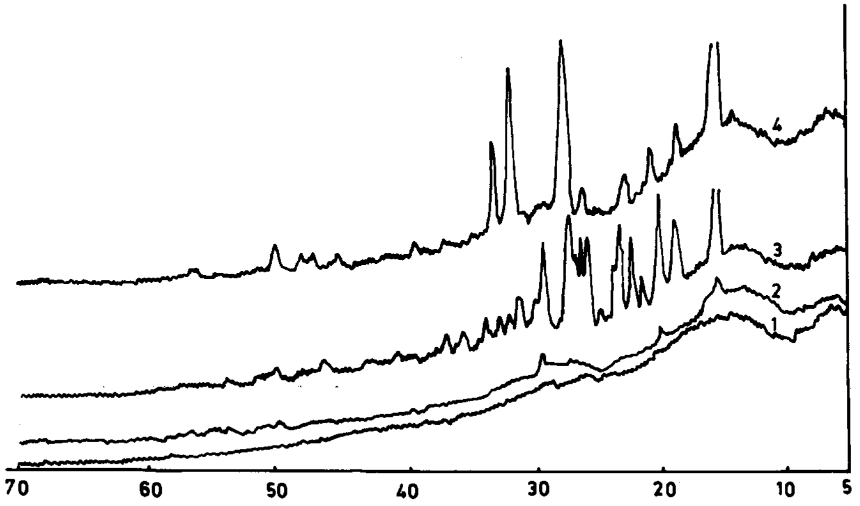

FIG. 1. Powder X-ray diffraction pattern of (1) PDA_1BQ_1 (obtained from solution), (2) PDA_1BQ_1 (obtained from solid-state reaction), (3) PDA, (4) BQ.

Elemental analysis. The reaction products obtained by solid-state reactions and from solutions were analyzed for C, H, and N at CDRI Lucknow.

Stoichiometry of the Reaction

A known amount of PDA (0.1860 g) was taken in a glass tube and allowed to react with the vapors of BQ at 70°C for about 312 hr. The increase in weight was found to be 0.1858 g, which corresponded to that for the reaction in 1 : 1 molar ratio.

X-ray diffraction studies. Powder X-ray diffraction patterns were obtained for BQ, PDA, and the complex obtained from solution. X-ray diffraction of the reaction product obtained by the reaction between solid PDA and vapors of BQ at 70°C for about 312 hr (reaction goes to completion giving 1 : 1 complex) was also recorded. The diffraction patterns were taken with a General Electric XDR-52-circle diffractograph at the Indian Institute of Technology, Kanpur (India), and are given in Fig. 1.

Differential scanning calorimetric measurements. Differential scanning calorimetric (DSC) studies were made for the following samples with a General V2.2A DuPont 9900 instrument and are given in Fig. 2.

(1) Solid-state reaction product after washing with water.

(2) Reaction product obtained from water.

(3) Reaction product obtained from water and then heating at 100°C for 1 hr.

IR spectral studies. The infrared spectra of BQ, PDA, and PDA_1BQ_1 (obtained from solution) were recorded with a Perkin–Elmer 157 spectrophotometer at CDRI Lucknow in KBr pellets and in nujol. The spectra in nujol are recorded in Fig. 3. The stretching frequencies due to NH_2 and C=O groups were found at lower wave numbers in KBr than in nujol.

UV and visible spectra. The UV and visible spectra of PDA, BQ, and their complex were recorded with a Bausch and Lomb Spectronic 2000 spectrophotometer in methanol between 300 and 800 nm and are recorded in Fig. 4.

ESR spectral measurements. Electron spin resonance spectra of PDA_1BQ_1 obtained by solid-state reaction as well as from solution were recorded at IIT Kanpur.

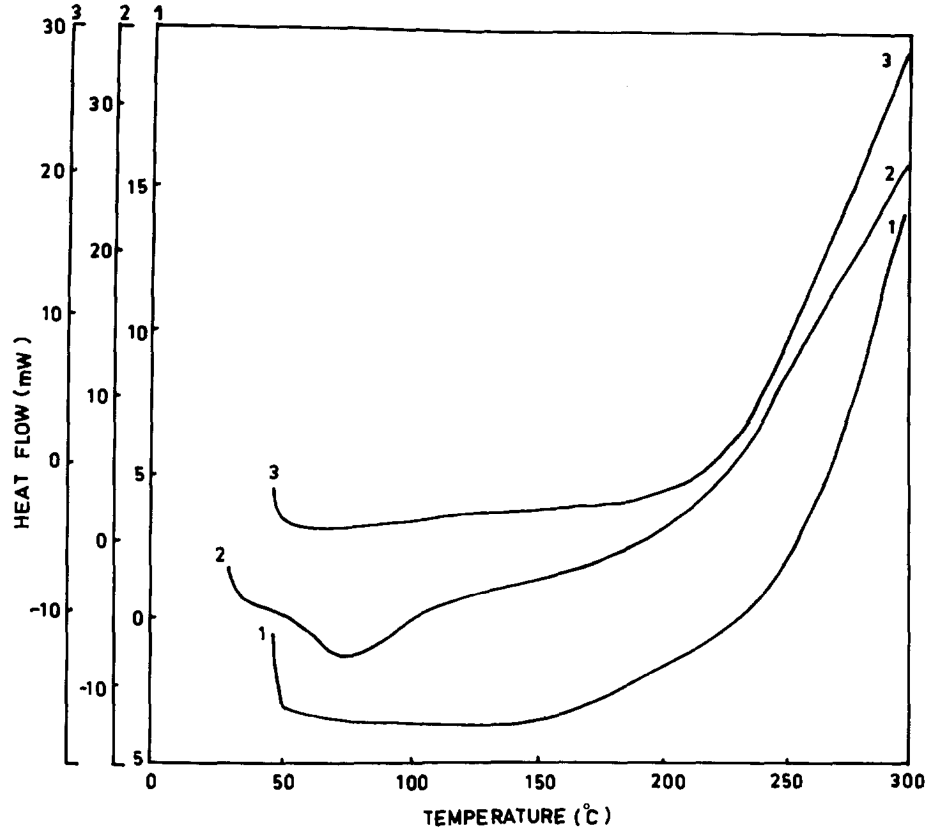

FIG. 2. Differential scanning calorimetric traces of (1) solid-state reaction product (PDA_1BQ_1) after washing with water. (2) Reaction product (PDA_1BQ_1) obtained from water. (3) Reaction product (PDA_1BQ_1) obtained from water and heated at 100°C for 1 hr.

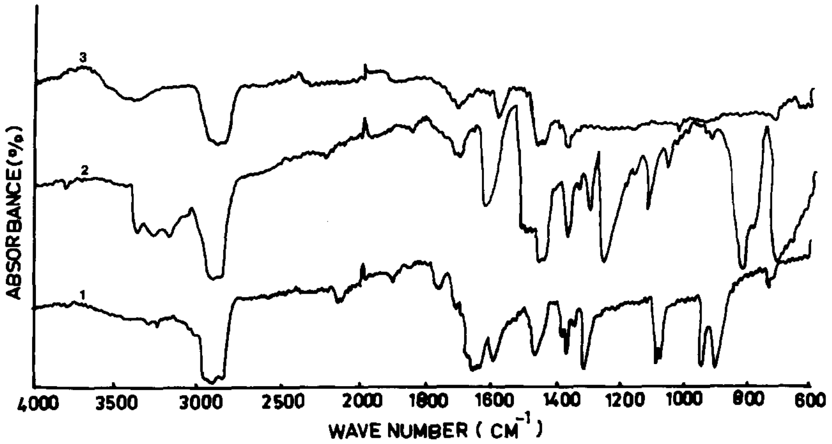

FIG. 3. Infrared spectra of (1) PDA_1BQ_1, (2) PDA, (3) BQ in nujol.

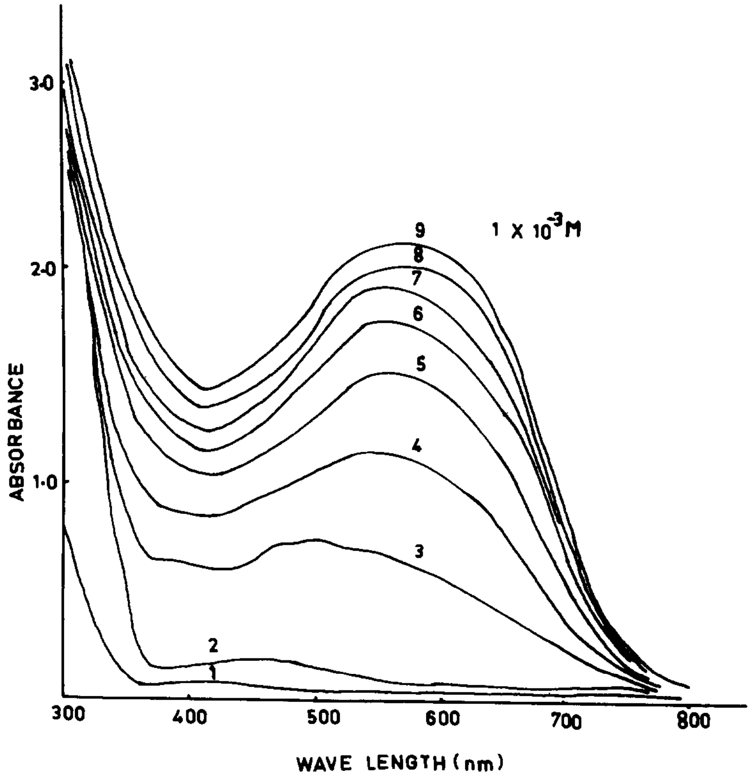

FIG. 4. UV and visible absorbance spectra 1 × 10^{-3} M solutions in methanol (1) BQ, (2) PDA. Mixture of solutions of PDA and BQ in 1 : 1 molar ratio of concentration 1 × 10^{-3} M: (3) after 5 min, (4) after 10 min, (5) after 15 min, (6) after 20 min, (7) after 25 min, (8) after 30 min, (9) after 35 min.

Magnetic measurements. A known weight (0.06290 g) of PDA_1BQ_1 was placed in a magnetic field and due to this field the weight was increased by 2.68%. The increase was the same in both products, i.e., the one obtained by solid-state reaction and other obtained by solution.

Electrical conductivity of the reaction product in solid state. Electrical conductivity of PDA_1BQ_1 obtained from solution in the form of a cylindrical pellet (diameter = 1.075 cm, thickness = 0.50 cm) applying a pressure of 50 kN was measured with the help of a PM 2522/90 Philips (India) digital multimeter with an accuracy better than ±0.25%. Platinum electrodes were used for the measurement.

Kinetics of the solid-state reaction in capillaries. Kinetics of solid-state reaction in capillaries were studied by a technique as described earlier by Rastogi *et al.* (*13*). Pyrex glass capillaries were used for the purpose. One end of the capillary was sealed with a sealing wax and half of it was filled with PDA (particle size 100–150 mesh), the capillary tube was tapped for 5 min in order to have uniform packing density and the surface was smoothened with a glass rod. The remaining half of the capillary was filled with BQ of same particle size in such a way that it touched the surface of PDA. The other end of the capillary was sealed with sealing wax and it was then kept horizontally in an incubator at constant temperature. The start of the reaction was indicated by a change in color at the interface of the reactants. The kinetics of the reaction was followed by measuring the thickness of the colored product layer as a function of time with the help of a traveling microscope. The reaction occurred only at the side of PDA, i.e., BQ is the diffusing species.

The experiments were performed at 30, 40, 50, and 60°C for one particle size (100–150 mesh). The experiments were also performed at 40 ± 1°C for particles of different sizes (100–150, 150–200, 200–240, and 240–300 mesh).

Kinetics of solid-state reaction in capillaries when the reactants are separated by an air gap. Kinetic studies of the reaction in capillary tubes were also performed at constant temperature 50 ± 1°C when the reactants were separated by an air gap of different lengths. In this experiment the glass capillaries were filled with the reactants in such a way that air gaps of different lengths were created between the reactants. The kinetics of the reaction was followed by measuring the thickness of product layer formed (dark brown color) at the PDA side.

Kinetic studies between PDA (solid) and BQ (vapor). The kinetics of reaction between solid PDA and vapors of BQ was studied gravimetrically as a function of time. For this purpose two glass tubes fitted with B_{19} male and female joints closed at the other end were used. In one glass tube a known amount of PDA (0.1860 g) was taken and its surface was made smooth with the help of a glass rod; the other tube was filled with BQ. The two tubes were connected with each other and kept in an incubator maintained at a constant temperature. The distance of separation between PDA and BQ was 5.3 cm in each experiment. The vapors of BQ started reacting with solid PDA and the kinetics was followed as a function of time by noting the change in weight in solid PDA. The experiment was performed at 40, 50, and 60°C with particle size 100–150 mesh.

Results and Discussion

When PDA is mixed with BQ in the solid state in an agate mortar, a color change occurs. First a blue coloration develops which ultimately becomes dark brown. The formation of blue color in the initial states of reaction suggests the formation of an intermediate complex with one or more molecules of PDA per molecule of BQ. However, this could not be confirmed since the intermediate was short lived. Also, when solutions of the two components in water or methanol were mixed, a dark-brown-colored complex was obtained. When an ether solution of the two components was mixed, a blue-colored compound precipitated which immediately changed to dark brown. Parini *et al.* (*14*) also reported the formation of dark brown polymer by the reaction of *p*-benzoquinone to *p*-phenylenediamine and they found that this complex is a paramagnetic and strongly aggregate in solution.

Now the question arises as to whether the reaction product obtained from solid state and solution are identical or different. X-ray diffraction studies (Fig. 1) of the two products were made. The diffraction patterns for both reaction products show only a broad line between $2\theta = 10°$ to $2\theta = 20°$. Apart from this some lines of very low intensities were also seen in the diffraction pattern of the solid-state reaction product which are due to unreacted PDA. Since only a broad line is observed this shows that the products are amorphous or polymeric in nature or the crystal sizes are below a certain optimum limit. The reaction product obtained from solution was crystallized several times to have crystals of appreciable size but no success was obtained. Such diffraction patterns can be obtained for any amorphous or polymeric material. So from these results it is difficult to say that the two products are identical. Complexes obtained by the reaction of substituted PDA and substituted BQ have been reported to be polymeric in nature. Since the complex in the present system is feebly soluble in common solvents, and the X-ray diffraction patterns do not give any line, it may be polymeric in nature or an agglomerate.

In order to determine the stoichiometry of the reaction products, elemental analyses for C, H, and N were made for products obtained by solid-state reaction and from solutions. The results are given in Table I. The results in Table I clearly show that solid-state reaction occurs in 1 : 1 molar ratio. The reaction products obtained from solutions did not correspond to PDA_1BQ_1. However, when the reaction products were analyzed after heating for 1 hr at 100°C, it corresponded to a stoichiometry of 1 : 1. It can be inferred that during precipitation, some solvent molecules get trapped with PDA_1BQ_1, which results in the change in percentages of C, H, and N. However, after heating at 100°C the solvent molecules are detached and the analytical results correspond to a stoichiometry of 1 : 1. Similar results were reported by Ottenberg *et al.* (*16*) in determining the stoichiometry of the charge-transfer complexes formed between *p*-chloranil and *p*-phenylenediamine.

Schlenk (*15*) reported that PDA reacts with BQ ether in 2 : 5 molar ratio but our results do not confirm this observation.

The elemental analyses clearly indicate that both in solution and in solid state the reaction occurred in a 1 : 1 molar ratio as follows:

$$PDA + BQ \rightarrow PDA_1BQ_1.$$

In order to know whether the reaction products obtained from solution and solid-state reaction are identical, DSC studies were made. The results are given in Fig. 2.

TABLE I

CHEMICAL ANALYSIS OF *p*-PHENYLENEDIAMINE : *p*-BENZOQUINONE COMPLEX[a]

	Theoretical values (%)	Experimental values (%)
Sample I	For 1 : 1 complex C = 66.67 H = 5.56 N = 12.95	C = 66.30 H = 6.05 N = 13.72
Sample II	For 1 : 1 complex + ½ mole water C = 64.0 H = 5.7 N = 12.4	C = 63.50 H = 5.60 N = 12.26
Sample III	For 1 : 1 complex C = 66.67 H = 5.56 N = 12.95	C = 66.63 H = 5.60 N = 12.60
Sample IV	For 1 : 1 complex + 1 mole methanol C = 62.9 H = 6.4 N = 11.29	C = 63.00 H = 5.90 N = 10.70
Sample V	For 1 : 1 complex + 1 mole ether C = 65.2 H = 7.5 N = 9.6	C = 66.00 H = 6.8 N = 8.73

[a] Sample I was prepared by direct reaction between the solid constituents. Sample II was precipitated by mixing saturated solutions of the constituents in water at room temperature. The samples were washed with acetone and then dried. Sample III is the same sample as sample II but was heated for 1 hr at 100°C. Sample IV was precipitated by mixing saturated solutions of the constituents in methanol at room temperature. The samples were washed with benzene and dried. Sample V was precipitated by mixing saturated solutions of the constituents in ether at room temperature. The samples were washed with benzene and then dried.

Curves 1, 2, and 3 are almost identical except there is an endotherm in curve 2 at 74.54°C. This is due to an entrapped water molecule in the complex which gets eliminated at this temperature. When this sample was heated at 100°C for 1 hr the entrapped water molecule goes off and the DSC run (curve 3) is the same as in curve 1. The results clearly confirm that the reaction products obtained from solution and solid-state reaction are identical.

In order to understand the nature of interaction involved in the complex PDA_1BQ_1, UV and visible spectroscopic studies of the components and the complex were made in methanol between 300 and 800 nm. The spectra of the complex was also recorded as a function of time. BQ has a peak at 429.1 nm and PDA at 430 nm. The complex has an absorption maxima at 558 nm; this is a new CT band which confirms that it is a Mulliken π–π charge-transfer complex. The absorption spectra of the complex shows that PDA_1BQ_1 is unstable in solution or the CT complex requires some time for stabilization because the intensity of visible absorption changes markedly with time (Fig. 4). However, the complex seems to be stable in solid state. This is indicated by the fact that (a) the resistivity does not change on storage and (b) MP also does not change with storage.

Interaction of BQ and its derivatives have been extensively studied by Slifkin and Walmsely (*17*) by using infrared spectroscopy. Infrared spectral studies of BQ, PDA, and PDA_1BQ_1 were made between 4000 and 600 cm^{-1} in nujol and are recorded in Fig. 3. BQ shows a strong peak in between 1660 and 1640 cm^{-1} with slight splitting due to C=O absorption. This type of splitting is quite common in solid state spectra and is probably due to intermolecular attraction in unit cell (*18*). PDA shows three peaks at 3190, 3290, 3370 cm^{-1} due to NH_2 absorption. The peak at 3190 cm^{-1} is an overtone of the NH_2 peak appearing at 1620 cm^{-1}. The spectra of the complex are not a superimposition of the spectra of BQ and PDA. The C=O stretching frequency (1640–1660 cm^{-1}) and NH_2 bending frequency (1620 cm^{-1}) are shifted toward a lower frequency region (1590 cm^{-1}) indicating that the carbonyl group of BQ and the NH_2 group of PDA are involved in some sort of interaction. Furthermore, the sharp $-NH_2$ stretching frequencies of PDA appearing at (3190, 3290, 3370 cm^{-1}) become broader and shift toward a lower frequency region in the complex. This also shows that the $-NH_2$ group of PDA is involved in certain interaction with BQ. It appears that the oxygen of the C=O group of BQ is hydrogen bonded with the hydrogen of the $-NH_2$ group in PDA. The spectroscopic studies reveal that PDA_1BQ_1 is a charge transfer stabilized by a hydrogen-bonding-type complex.

Magnetic measurements of reaction products indicate a paramagnetic character. A complex between diamine and quinone has already been reported to be paramagnetic in nature (*19, 20*). ESR gives a signal characteristic of a free radical. The *g* factor for the powdered samples (obtained both from solid state and from solution) were found to be 2.0023. This confirms the existence of unpaired electron in PDA_1BQ_1 complex. The explanation for paramagnetism and free radical in the complex is based on considerations of the ionic state of an adduct derived from components with filled electron shells. The free ions $[BQ^{\cdot-}]$ and $[PDA^{\cdot+}]$ each have an unpaired electron formed by the transfer of an electron from PDA to BQ. In this state the compound is bound both by ionic and weak covalent forces. Mulliken considers the resonance between these two singlet states which is essential for the stability of the compound.

The electrical conductivity of solid PDA_1BQ_1 has been measured in the temperature range 300 to 475°K and a plot of logarithms of electrical conductivity (log σ) against inverse of temperature ($10^3/T$) is shown in Fig. 5. As seen from Fig. 5 the electrical conductivity of PDA_1BQ_1 increases with temperature in the entire temperature range studied with a change in the slope of the curve at 337°K. This behavior of electrical conductivity with temperature shows the semiconducting nature of the

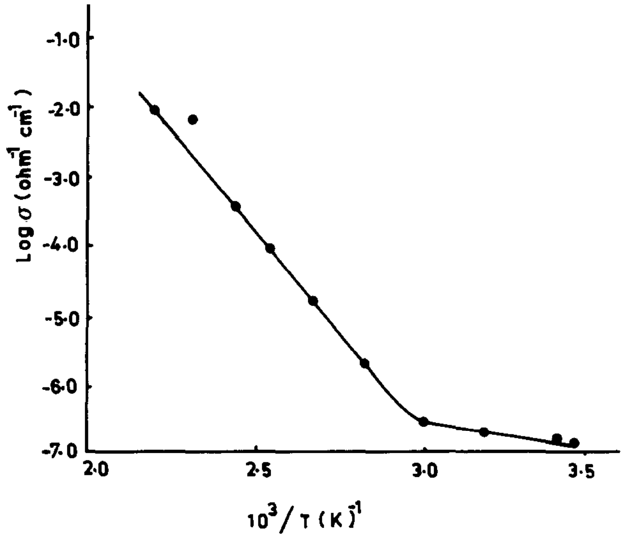

FIG. 5. Electrical conductivity of PDA_1BQ_1 complex in solid state as a function of inverse of temperature $10^3/T$.

material and follows the typical exponential relation for semiconductors

$$\sigma = \sigma_0 \exp(-E_a/kT), \qquad (1)$$

where σ_0 is constant and E_a is the activation energy.

We have estimated an activation energy below and above 337°K. The values are 0.178 and 1.33 eV in the lower and higher temperature ranges, respectively. Similar results have been reported by Darish *et al.* (*21*) on some CT complexes. The low value of the activation energy below 337°K seems to be impurity dominated because at lower temperature even the presence of a small amount of impurity lowers the activation energy to a greater extent. Impurity conduction in this complex may be either band-type conduction of ionized impurity centers in terms of donor or acceptor levels or hopping of the impurity charge carrier.

Band-type conduction of ionized impurity charge carriers takes place according to the relation (*22*)

$$\sigma_d = A \exp(-E_i/kT), \qquad (2)$$

where A is constant and E_i is the ionization energy and is usually ≈0.1 eV. The activation energy (0.178 eV) calculated below 337°K is larger than the ionization energy E_i (0.1 eV), so this type of conduction mechanism may not be possible in this complex. At lower temperature in any imperfect semiconductor or insulator, charge carriers are always bound to donors or acceptors and thus in localized state (*23, 24*). Since this complex is amorphous in nature as evidenced by the X-ray analysis, it seems that impurity conduction is due to hopping and occurs via phonon-assisted hopping of the impurity charge carriers.

The activation energy of 1.33 eV estimated above 337°K seems to be an intrinsic activation energy. Since the complex is amorphous in nature and log δ is a linear function of T^{-1}, electrical conduction may be either due to band-like motion of the charge carriers or via phonon-assisted hopping near the Fermi level (*25*). Phonon-assisted hopping takes place at low temperature, so this mechanism is ruled out above 337°K. Therefore, band-type conduction in

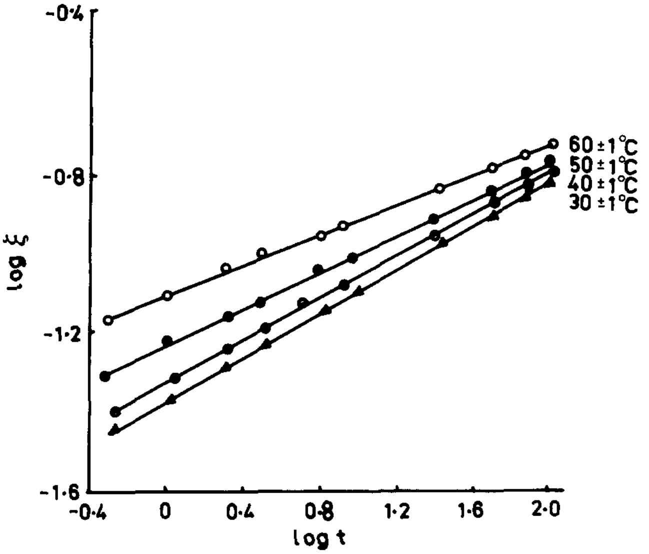

FIG. 6. Kinetic data for the reaction between PDA and BQ in the solid state as a function of temperature (capillary experiment with no air gap).

terms of donors and acceptor levels is taking place at higher temperature.

Once the nature of the complex is established it is necessary to understand how BQ diffuses in the crystal lattice of PDA in the solid state. For this purpose kinetic studies of the reactions in capillaries reveal that the kinetic data obey the following equation

$$\xi = kt^n, \qquad (3)$$

where ξ is the thickness of the product layer formed at the surface of PDA (BQ is the diffusing species) at any time t, n is a constant, and k is also a constant associated with the rate of the reaction. The validity of Eq. (3) is tested by plotting a graph of log ξ against log t where straight lines are obtained (Fig. 6). From the intercepts of the lines the values of k were calculated and are given in Table II along with the values of n. When log k is plotted against $1/T$, the Arrhenius equation is obeyed (Fig. 7). From the slope of the curve the energy of activation is calculated and is found to be 18.2 kJ/mole. This value of energy of activation is much lower than the enthalpy of sublimation of BQ (62.8 kJ/mole). This suggests that probably BQ diffuses toward PDA via surface migration.

When the kinetics was studied for different particle sizes at 40 ± 1°C, the kinetic data were again fitted by Eq. (3) and plotted in Fig. 8. The values of k_1 and n_1 are given in Table III. The variation of k_1 against 1/2 is a straight line (Fig. 9) indicating the effect of particle size on the rate of reaction.

When the reactants are separated by an air gap, the kinetic data are again obeyed by

TABLE II

LEAST-SQUARES PARAMETERS OF EQ. (3) FOR SOLID-STATE REACTION BETWEEN 100- TO 150-MESH POWDER LAYER OF PDA AND BQ IN A GLASS CAPILLARY WITH NO AIR GAP BETWEEN LAYERS

Sample no.	Temp. (°C)	k (cm/hr)	n
1	30	$(3.95 \pm 0.18) \times 10^{-2}$	0.30 ± 0.011
2	40	$(4.54 \pm 0.14) \times 10^{-2}$	0.28 ± 0.011
3	50	$(6.20 \pm 0.23) \times 10^{-2}$	0.22 ± 0.006
4	60	$(7.54 \pm 0.15) \times 10^{-2}$	0.19 ± 0.016

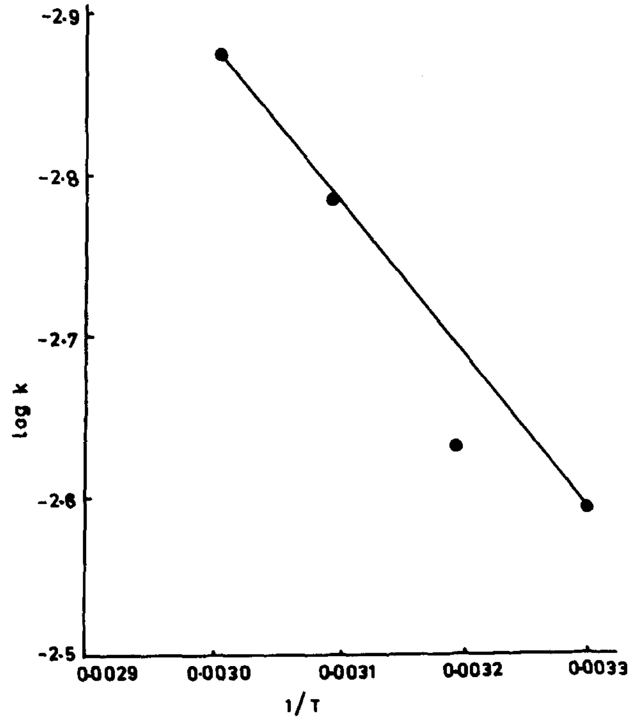

FIG. 7. Arrhenius plot of the effect of temperature on the reaction rate (capillary experiment with no air gap).

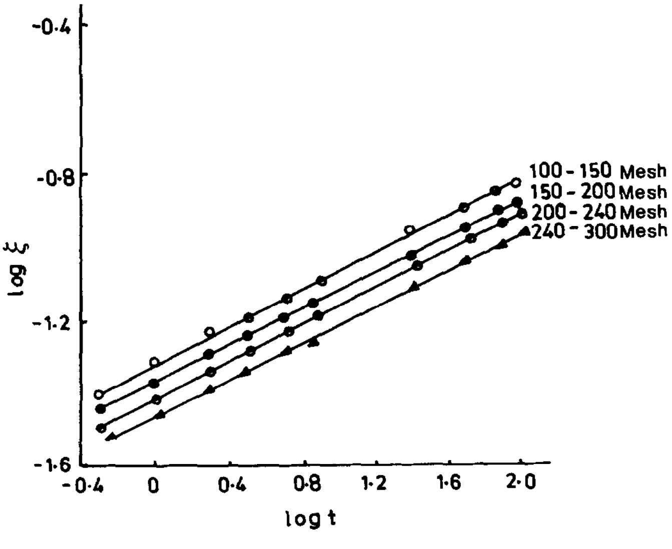

FIG. 8. Kinetic data for the reaction between PDA and BQ in the solid state for different particle sizes (100–150 mesh, 150–200 mesh, 200–240 mesh, and 240–300 mesh) at 40 ± 1°C.

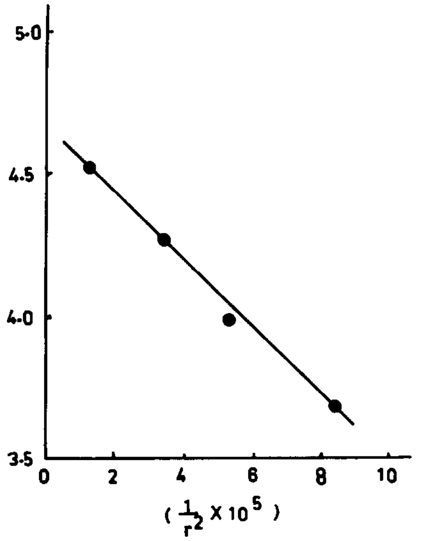

FIG. 9. Plot of k_1 versus $1/r^2$ showing the effect of particle size on k_1 for the reaction between PDA and BQ.

TABLE III

LEAST-SQUARES PARAMETERS FOR REACTION BETWEEN PDA AND BQ OF DIFFERENT PARTICLE SIZES (100–150, 150–200, 200–240, AND 240–300 MESH) IN A GLASS CAPILLARY WITH NO AIR GAP BETWEEN LAYERS

Sample no.	Particle size in mesh	k_1 (cm/hr)	n_1
1	100–150	$(4.54 \pm 0.14) \times 10^{-2}$	0.29 ± 0.001
2	150–200	$(4.27 \pm 0.05) \times 10^{-2}$	0.28 ± 0.009
3	200–240	$(4.00 \pm 0.11) \times 10^{-2}$	0.27 ± 0.006
4	240–300	$(3.69 \pm 0.06) \times 10^{-2}$	0.26 ± 0.007

Eq. (3) (Fig. 10) and the values of k_2 and n_2 at different air gaps are given in Table IV. The variation of k_2 with length of the air gaps is given in Fig. 11. This figure simply indicates that as the length of the air gap is increased the rate of the reaction is decreased. When the curve in Fig. 11 is extrapolated to zero air gap the value of k_2 does not become equal to the value of k. The value of rate constant at 50°C when the reactants are in contact in capillaries is 6.20×10^{-2} cm/hr, whereas, when the reactants are separated by an air gap, on extrapolation the value comes out to be 3.45×10^{-2} cm/hr. This means that when the reactants

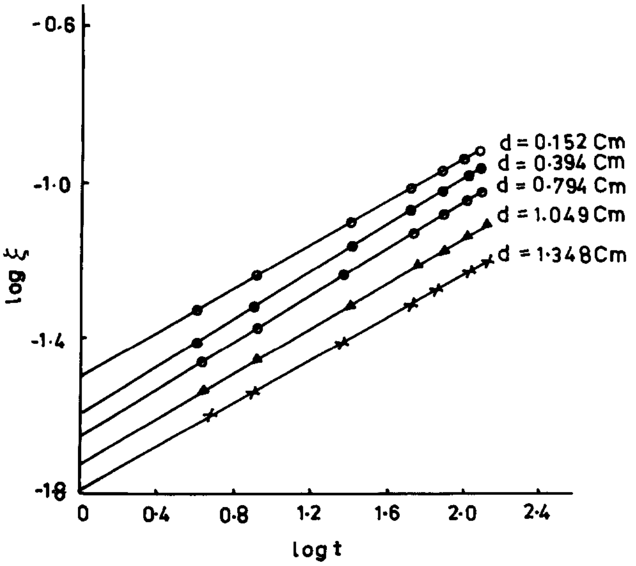

FIG. 10. Kinetic data for the reaction between PDA and BQ, when the reactants are separated by an air gap of different length at 50 ± 1°C (capillary experiment).

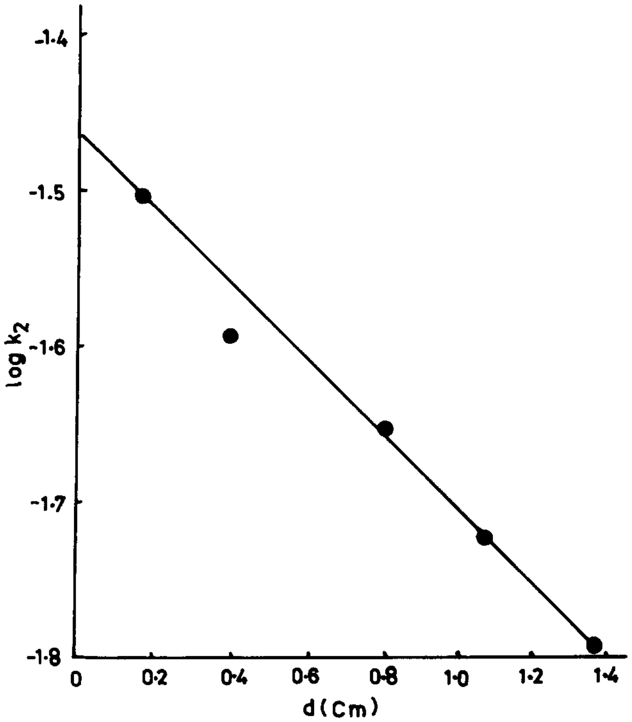

FIG. 11. Dependence of the rate constant k_2 on the length of the air gap d at 50 ± 1°C (capillary experiment).

are in contact it is faster and diffusion of both solid BQ and BQ vapor takes place, whereas when they are separated by air gaps mostly it is a vapor phase diffusion. The higher rate of reaction may be related to surface migration.

TABLE IV

LEAST-SQUARES PARAMETERS FOR THE REACTION BETWEEN PDA AND BQ (100–150 MESH) IN A GLASS CAPILLARY WITH AN AIR GAP OF THICKNESS d BETWEEN THEM AT 50 ± 1°C

Sample no.	d (cm)	k_2 (cm/hr)	n_2
1	0.152	3.16×10^{-2}	0.29
2	0.394	2.57×10^{-2}	0.31
3	0.794	2.24×10^{-2}	0.30
4	1.049	1.90×10^{-2}	0.30
5	1.348	1.62×10^{-2}	0.29

In order to understand the mechanism of diffusion of BQ vapors into the crystal lattice of PDA, gravimetric studies were made at different temperatures. The kinetic data obeyed the following equation

$$W^2 = k_3t, \tag{4}$$

where W is the change in weight of PDA at any time t and k_3 is the rate of reaction. A plot of W^2 against t gives a straight line (Fig. 12). From the slope of the curves the values of k_3 are calculated and the energy of activation is calculated by an Arrhenius plot (Fig. 13) and found to be 28.7 kJ/mol. This value of energy of activation is higher than the energy of activation of the reaction, when the reactants are in contact in the capillaries. This difference obviously indicates that the two methods account for two different processes. Reaction kinetics

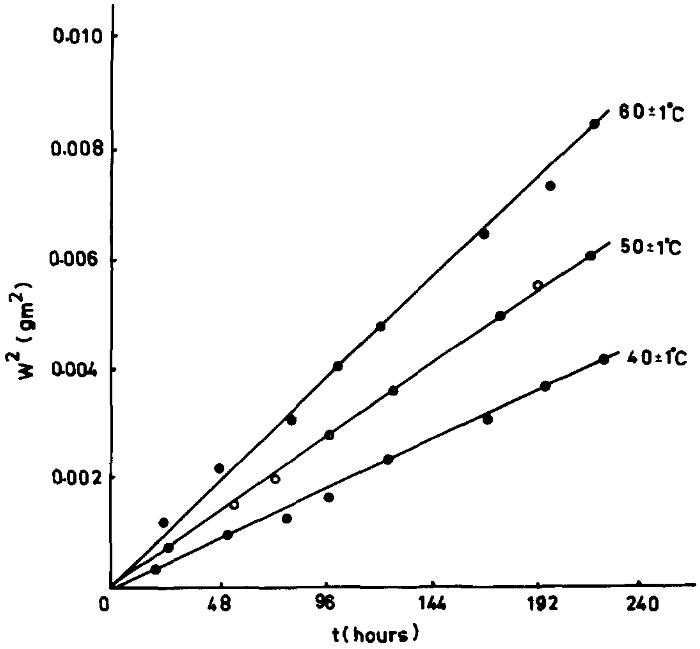

FIG. 12. Kinetic data for the reaction between PDA (solid) and BQ (Vapor) at various temperatures (gravimetric experiment).

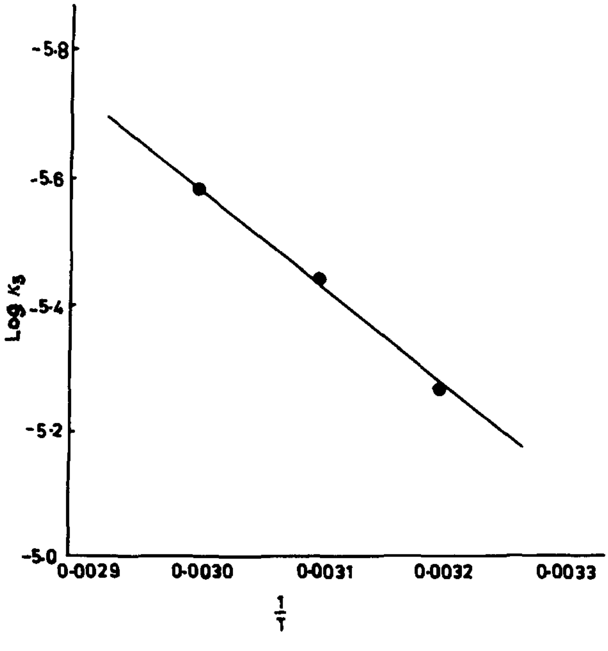

FIG. 13. Arrhenius plot of the effect of temperature on the rate of solid–vapor reaction (gravimetric experiment).

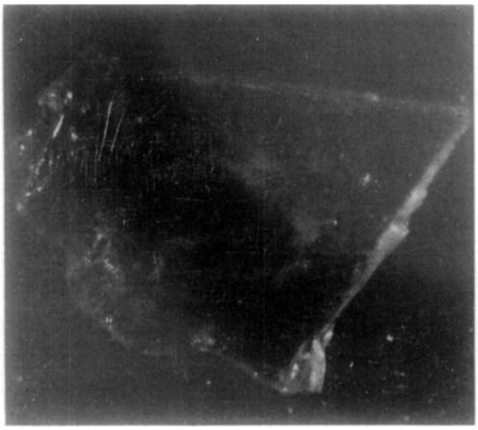

FIG. 14. Microphotograph of crystal of PDA (magnification 10 × 2).

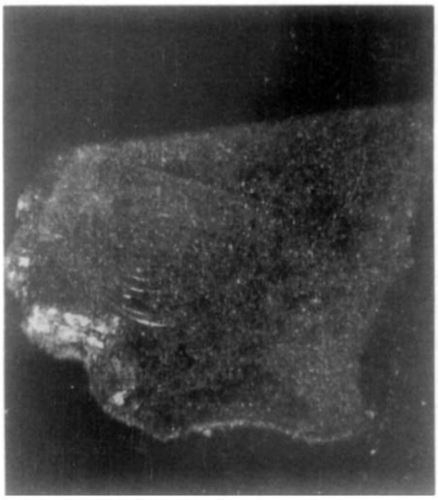

FIG. 16. Microphotograph of PDA crystal exposed with the vapor of BQ for half an hour (magnification 10 × 2).

in the capillaries are studied by measuring the thickness of colored product formed at the surface of PDA. It does not take into account the inner penetration of BQ in the crystal lattice of PDA, whereas gravimetric studies do take into account the process of inner penetration. The latter process will be difficult and hence will require higher activation energies.

In order to find the reaction sites, attempts were made to study the reaction on a single crystal of PDA. Despite our best efforts we could not develop a single crystal of well-formed faces as observed under a microscope (Fig. 14). Without disturbing the crystal of PDA it was exposed for 5 min to the vapors of BQ and the change in morphology of crystal was photographed (Fig. 15). The results indicate that first the reaction started at the edges and at the joints of the polycrystalline material. This means that the reaction originates at those points where less energy is required. Once the reaction nucleus is formed, it grows with time

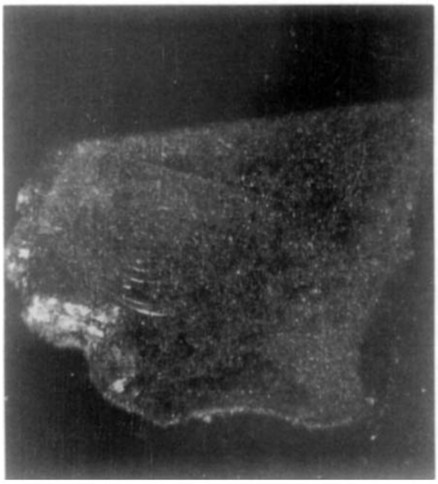

FIG. 15. Microphotograph of PDA crystal exposed with the vapors of BQ for 5 min (magnification 10 × 2).

TABLE V

PARAMETERS OF THE INTERDIFFUSION OF BQ (VAPORS) IN SOLID PDA AS MEASURED BY GRAVIMETRIC TECHNIQUE

Sample no.	Temperature (°C)	k_3 (g/hr)
1	40	1.89×10^{-5}
2	50	2.86×10^{-5}
3	60	3.85×10^{-5}

and ultimately covers the whole of the crystal surface (Fig. 16).

We can supply little insight into the details of the process whereby solid BQ can interpenetrate into the crystal lattice of PDA to form amorphous PDA_1BQ_1. The mechanism is undoubtedly complicated. BQ molecules attack the crystal lattice of PDA at those points where the lattice is strained and contains a certain amount of defects. Since the BQ molecules are the diffusing species and the PDA crystal is the host lattice, some rearrangement in this lattice occurs. An alternate stacking of PDA and BQ molecules with weak molecular forces probably charge-transfer-interaction stabilized by hydrogen bonding is expected. Probably this arrangement is random and hence the PDA_1BQ_1 solid is amorphous in nature.

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