

Solid state reaction between *o*-toluidine and *p*-benzoquinone

N B Singh*, N P Singh†, (Km) Renu & (Km) Kalpana Singh

Department of Chemistry, University of Gorakhpur, Gorakhpur 273 009, India

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o-Toluidine reacts with *p*-benzoquinone both in the solid state and solution giving 1 : 1 molecular complex. During the course of solid state reaction, *p*-benzoquinone diffuses towards *o*-toluidine and surface migration plays a dominant role.

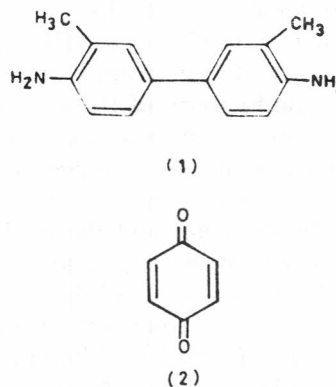
Phenols or amines react with quinones in solid state forming molecular complexes¹⁻⁷. Symmetrical phenols or amines react with a much faster speed as compared to bulky and unsymmetrical molecules^{2,5}. It has also been reported that higher the degree of substitution of the components, lesser is the reactivity⁸. The crystal packing and the geometry of the molecules play an important role during solid state reactivity⁹. The above complexes are formed as a result of weak interactions such as charge transfer, H-bonding/vander Waals, etc. between the component molecules.

Recently Rastogi *et al.*¹⁰ have studied the solid state reaction between benzidine and *p*-benzoquinone. When methyl group is introduced at the *ortho*-position in the benzidine molecule, the symmetry, size and other properties change. As a result when *p*-benzoquinone is allowed to react, the mode of diffusion, and the nature of reaction product may change. In the present paper, the solid state reaction between *o*-toluidine **1** and *p*-benzoquinone **2** has been studied with a view to understand the process of diffusion and its correlation with crystal structures of the components. Nature of interaction involved in the formation of the reaction product has also been discussed.

Materials and Methods

Materials. *p*-Benzoquinone was prepared as described in the literature¹¹. Its melting point was found to be 116°. *o*-Toluidine (Sigma) was used without further purification. Its melting point was 132° (reported m.p. 129-31°).

p-Benzoquinone and *o*-toluidine are referred as *p*-BQ and *o*-Td, respectively.



Methods

Preparation of reaction product: (i) From solid state reaction. Solid powders of *o*-Td and *p*-BQ in equimolar amounts were ground together in an agate mortar with pestle. The colour of the mixture, initially light brown, darkened quickly as reaction progressed and then black coloured complex appeared. Liquid phase did not appear during the course of reaction. Grinding was continued until no further colour change was observed (nearly 1 hr). The entire mass was then kept in an incubator at 60°C for a week with occasional grinding. This was then washed with methyl alcohol to remove traces of unreacted components if any. The reaction product was black in colour and melted with decomposition.

(ii) From solution. Solutions of *o*-Td and *p*-BQ in methyl alcohol were mixed in 1 : 1 molar ratio and as a result of this, black coloured reaction product precipitated. This was washed with methyl alcohol, dried at 100°C and stored in a desiccator.

Spectrometric studies of the reaction product. The electronic spectra of compounds *o*-Td, *p*-BQ and their mixture in 1 : 1 molar ratio in methanol were recorded on a Hitachi U-2000 spectrophoto-

*Department of Chemistry, U.P. College, Varanasi, India.

tometer at 25°C. The spectra of the reaction product obtained from methanol and solid state reactions were also recorded in DMF.

IR spectra of the product and the reactants were recorded in KBr on a 577, Perkin-Elmer spectrophotometer at CDRI, Lucknow.

The NMR spectra of the reactants and the product were recorded using NMR spectrometer R-32 (Perkin Elmer) in DMSO- d_6 at CDRI, Lucknow.

Elemental analysis. The reaction products obtained from solution and solid state reaction were analysed for C, H and N using an element analyser at CDRI, Lucknow.

X-ray diffraction studies. The powder X-ray diffraction patterns of the reaction products obtained from solution and also from solid state reaction were recorded on an XRD-52 circle diffractograph at IIT, Kanpur using CuK_α radiation.

Electrical conductivity of the reaction product in the solid-state. In order to measure the electrical conductivity of the reaction product in the solid-state, a pellet was prepared at a pressure of five tones. The diameter and the thickness of the pellet were respectively 1.30 and 0.09 cm. The surface of the pellet was polished with a silver paint. The electrical conductivity at different temperatures (30-130°C) and at different frequencies (60 KHz to 65 Hz) was measured by determining the complex impedance with computer-controlled Schlumberger Solatron (1286) electrochemical interface using platinum electrodes at BHU, Varanasi. Both capacitance and the impedance were measured and the electrical conductivities were calculated from the equation, $\sigma = G/lA$ (G = capacitance, l = thickness of the pellet and A = area of the pellet).

In order to know the ionic and electronic contributions towards conductivity, polarisation measurements were made. The pellet was placed between the platinum electrodes and current was passed at a fixed voltage (2 V). The decrease in current was noted as a function of time with the help of a multimeter. After 2 hr further decrease in current did not take place. By measuring the initial current and that after 2 hr, values of electronic and ionic conductivities were calculated.

DTA studies. DTA studies of the reaction product obtained from methanol were made on a Rigaku Thermal Analyser at Delhi University.

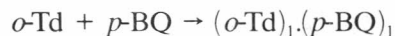
Kinetics of solid-state reaction between *o*-toluidine and *p*-benzoquinone in capillary. The detailed method for studying the kinetics of reaction is described elsewhere¹². Half of a glass capillary was filled with *o*-toluidine (particle size 150-

200 mesh) and the other half was filled with *p*-benzoquinone (particle size 150-200 mesh) in such a way that *o*-Td and *p*-BQ came in close contact. The kinetics was followed by measuring the thickness of the reaction product (black in colour) at different intervals of time and at different temperatures. Attempts were made to study the kinetics by creating air gap but very little reaction occurred and hence could not be studied.

Microstructural study. Microstructural studies were also made¹³. A glass slide was kept at 135°C in an oven and a small amount of *o*-Td was placed over the slide, which immediately melted. The temperature of the oven was lowered down up to 130°C and the melt was allowed to crystallise in one direction with the help of a coverslip in such a way that a very thin layer of *o*-Td is obtained. This was examined under microscope and photographed. One small beaker containing *p*-BQ was taken and heated so that the beaker was filled with the vapours of *p*-BQ. The *o*-Td slide was put at the top of the beaker filled with the vapours and covered with bigger beaker and kept at 60°C. The exposure was made at different time intervals and the changes in micro-structures recorded.

Results and Discussion

When *o*-Td and *p*-BQ were ground in solid-state, a black colour developed, indicating that reaction occurs in solid-state. When solutions of *o*-Td and *p*-BQ in methyl alcohol were mixed in 1 : 1 molar ratio, a black coloured compound precipitated. The filtrate when evaporated to dryness, only a trace amount of black coloured product was obtained. The X-ray diffraction patterns of the reaction products obtained from solution and solid-state reactions were identical indicating that both the products are same. The UV-visible spectra of the reaction product obtained from solution and solid-state reactions in DMF were superimposable indicating the products to be identical. Elemental analysis showed $C_{\text{Theo}} = 73.80\%$, $H_{\text{Theo}} = 5.81\%$, $N_{\text{Theo}} = 8.66\%$, $C_{\text{Obs}} = 74.08 \pm 0.2\%$, $H_{\text{Obs}} = 5.88 \pm 0.14\%$, $N_{\text{Obs}} = 8.74 \pm 0.3\%$. Thus, *o*-Td reacts with *p*-BQ in 1 : 1 molar ratio in the following manner:



The reaction product is feebly soluble in almost all the common solvents but fairly soluble in DMF. DTA studies show that it starts decomposing above 130°C but with a very slow rate; be-

yond 280°C the decomposition rate increases considerably and reaches a maximum value at 330°C.

There is a little increase in the electrical conductivity of the product in solid state up to 130°C. However, the value increases with the increase in frequency. This shows that carrier generation upto 130°C is almost complete. The average value of energy of activation for conduction at all frequencies (60 kHz - 65 Hz) is 0.14 eV and roughly equals of kT . When a constant potential difference (2 volts) is applied across the sample and the current is measured as a function of time, the current decreases considerably. This simply shows that the electrical conduction of the reaction product in solid state might be due to ionic as well as electronic.

In order to understand the nature of interaction between the reactants, spectroscopic studies were made. The UV spectrum of the product in methyl alcohol does not give any new band indicating that either the charge-transfer interaction is absent or the complex is dissociated in solution.

The IR spectrum of *o*-Td shows four peaks at 3340, 3370, 3410 and 3470 cm^{-1} which are assigned to the stretching modes of the NH_2 group, the bands in the regions 3210 and 2825-3010 cm^{-1} are assigned to $\nu_{\text{C-H}}$ of the phenyl and CH_3 group respectively. The bands due to δ_{NH_2} appear in the range of 1550-1625 cm^{-1} . Rest of the peaks are due to the phenyl moiety of *o*-Td and τ_{NH_2} frequencies. Spectral investigation¹⁴ of *p*-BQ has shown that it has D_{2h} symmetry with 21 in-plane fundamentals ($6a_g, 5b_{3g}, 5b_{1u}$ and $5b_{2u}$) and 9 out-of-plane fundamentals ($1b_{1g}, 3b_{2g}, 2a_u$ and $3b_{3u}$). The IR bands^{15,16} in the region 1575-1700 cm^{-1} arise due to normal coordinates having contribution from $\nu_{\text{C=C}}$ and $\nu_{\text{C=O}}$ with the band at 1610 cm^{-1} (br) having relatively more contribution due to $\nu_{\text{C=O}}$. In the spectra of the complex the bands appear in the regions 3100-3200 and 1450-1650 cm^{-1} . It appears that due to complex formation the position of the bands arising due to NH_2 group shifts to lower wave-numbers suggesting some sort of weak interaction possibly H-bonding between the two components in the complex.

In the ^1H NMR spectra of the complex, NH_2 group resonates around δ 6.8 ppm and the band is broad which may be due to quadrupole moment of the N atom of NH_2 group. The broadening may also be due to intermolecular H-bonding of the NH_2 and C=O groups respectively of *o*-Td and *p*-BQ. The same band in the ^1H NMR spectra of *o*-Td appears at δ 6.6 ppm which splits the

signal of methyl protons into three bands at δ 2.15, 2.25 and 2.5 ppm. This shows that due to some sort of intermolecular interactions the CH_3 protons become nonequivalent resulting in the splitting of CH_3 protons. These results show that there is some weak interaction possibly intermolecular H-bonding between the components in the product.

Reaction in glass capillaries indicate that when the two reactants are kept in contact, starting of the reaction is indicated by a change in colour at the point of contact. The kinetics were followed by measuring the thickness of the product layer as a function of time. It is found that *p*-benzoquinone diffuses towards *o*-toluidine. This may be due to:

(i) Vapour pressure of *p*-benzoquinone is much higher than that of *o*-toluidine.

(ii) *p*-Benzoquinone molecules being symmetrical and smaller in size can migrate easily over the surface of *o*-Td molecules.

The kinetic data (reactants in contact in capillaries) obeyed equation (1).

$$\xi = k \exp.(-C/\sqrt{t}) \quad \dots (1)$$

where ξ is the thickness of the product layer at any time t , k is an apparent rate constant and C is some constant. The validity of Eq. (1) was tested by plotting $\log \xi$ vs $1/\sqrt{t}$, where straight lines were obtained (Figure 1). The parameters of Eq. (1) are given in Table I. The Arrhenius plot gave the energy of activation equal to 20.0 kJ/mol which is much lower than the heat of sublimation of *p*-benzoquinone (62.8 kJ/mol)¹⁷. This indicates that during lateral diffusion of *p*-benzoquinone towards *o*-toluidine, surface migration plays a dominant role.

The product formed in the capillary by the reaction of *p*-BQ and *o*-Td was cut, taken out and observed under magnifying glass. The reaction product was found to be randomly distributed on

Table I—Parameters of Eq. (1), particle size = 150-200 mesh

Sl No.	Temperature (°C)	k cm/h	C	E kJ/mole
1	55	1.23×10^{-1}	1.69	
2	45	0.99×10^{-1}	1.68	20.0
3	35	0.71×10^{-1}	1.46	
4	25	0.58×10^{-1}	1.28	

Table II — Crystal data of the reactants

Reactants	End-to-end distance (Å)	Breadth of the molecules (Å)	Interlayer spacing in the crystal lattice (Å)	Unit cell volume (Å) ³	Planar character
<i>p</i> -Benzoquinone ¹⁷	O—O 5.3	3.2	2.3	260	Planar
<i>o</i> -Tolidine ¹⁸	H ₂ N—NH ₂ 9.2	4.4 or 5.9 depending on the position of methyl group	3.5	1141	The two phenyl rings are not coplanar but twisted around the linkage between C—C bond so that mutually inclined at an angle of 41°.

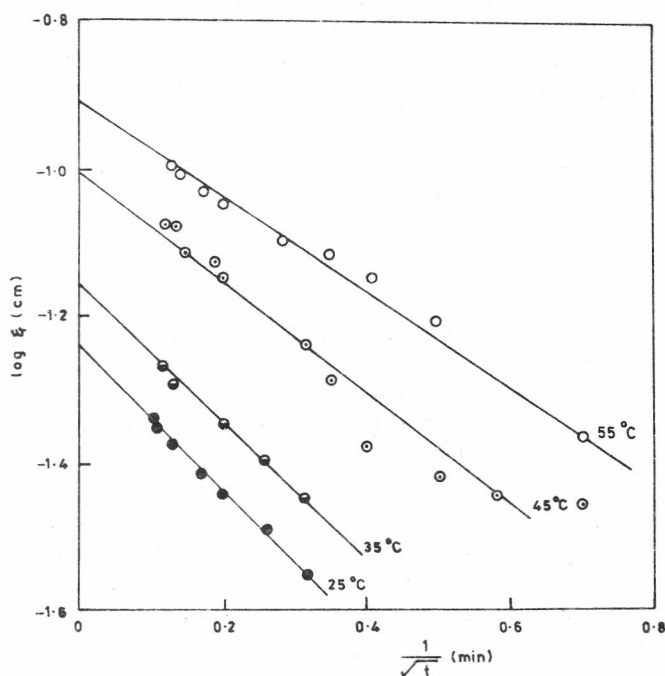


Figure 1 — Plot of kinetic data obtained at different temperatures

the surface of microcrystallites of *o*-Td but penetration of *p*-BQ into the interior of *o*-Td crystallites was apparently incomplete. This shows that at least two kinds of diffusion processes with different reaction rates are involved in the reactions of this type. One, the diffusion of one reactant through the space between or on the surface of microcrystallites of the other, is relatively rapid and the second, the penetration of the molecules of one reactant into the interior of the crystallite of the other, slower. In order to understand the mechanism of inner penetration into the crystal lattices, the crystal structure of the two reactants

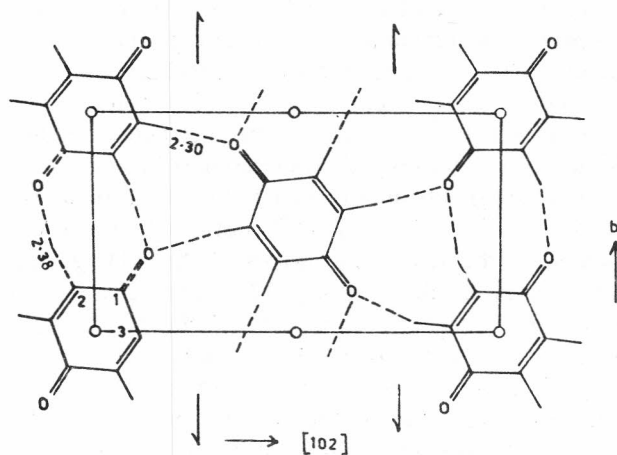


Figure 2 — Crystal structure of *p*-BQ around the (201) plane with the numbering scheme and those intermolecular distance shorter than the sum of the relevant vander Walls radii $r(c) = 1.7$, $r(o) = 1.4$, $r(II) = 1.1$ Å : Pauling 1960¹⁹

were examined^{18,19} (Figures 2 and 3). The end to end distances and other crystal parameters are given in Table II. From Table II, it is obvious that *p*-BQ molecules can easily enter into the interlayer spacing of *o*-Td but because the *o*-Td molecule is not planar (the two phenyl rings are at an angle of 41°) and bulky, it will not be possible for it to enter into the crystal lattice of *p*-BQ. It is therefore inferred that *p*-benzoquinone molecules penetrate into the crystal lattice of *o*-Td. However, this interpretation is not valid when the reaction occurs between the vapours of the two components.

In order to examine further the reactivities of the components, microstructural studies were made. The microstructure of *o*-Td is given in Figure 4a which shows a hair like structure. When

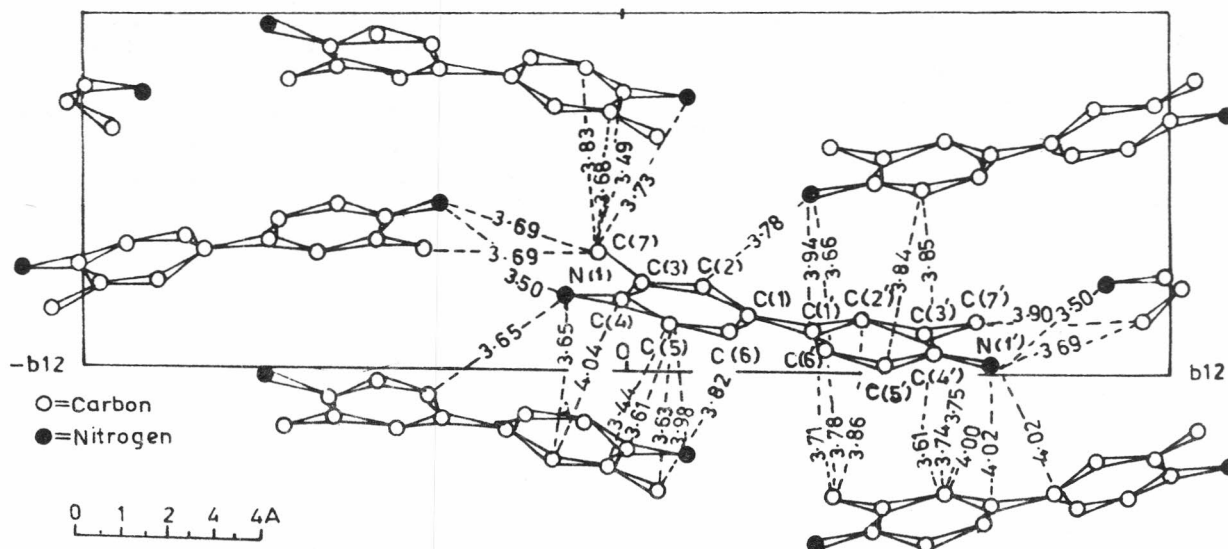


Figure 3 — Crystal structure of *o*-Td viewed along (001) showing all intermolecular distances (excluding hydrogen atoms) of less than 4.1 Å

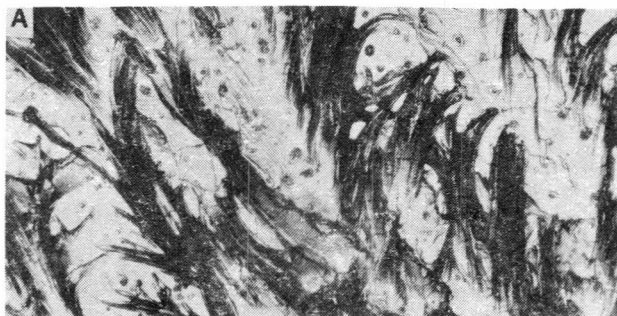


Figure 4 — (a) Microstructure of *o*-Td. (b) Change in microstructure of *o*-Td after exposure of the vapour of *p*-BQ for 5 min. (c) Change in microstructure of *o*-Td after exposure of the vapour of *p*-BQ for 30 min

this is exposed to the vapours of *p*-BQ (Figures 4b, 4c), the microstructure is changed completely and it is covered with reaction product. These studies clearly indicate that *p*-BQ reacts at the surface of *o*-toluidine at a much faster rate penetrating inside the grains, as a result of which the microstructure of *o*-toluidine is completely changed.

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