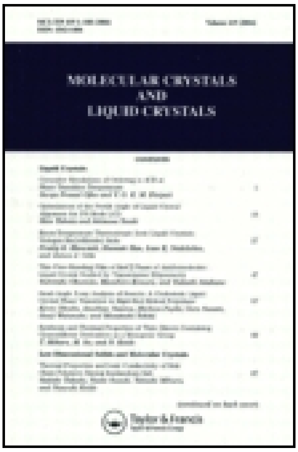

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Organic Solid State Reactivity: Reaction between 8-Hydroxyquinoline and Nitrophenols

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Organic Solid State Reactivity: Reaction between 8-Hydroxyquinoline and Nitrophenols

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8-Hydroxyquinoline reacts with 2,4-dinitro- and 2,4,6-trinitro phenols in solid state and the reactivity increased with the increase of number of nitro groups in the phenols. Phenol and m-nitro phenol formed only eutectic mixtures with 8-hydroxyquinoline. The reactivity is related with the symmetry and size of the diffusing molecules. The products obtained from solution and solid state reaction are found to be chemically identical.

INTRODUCTION

8-Hydroxyquinoline is a well known chelating agent and forms metal complexes in solution. However such reactions in solid state are limited (1). Molecular packing and geometrical considerations play an important role (2). Singh et al (3) studied the reaction between 8-hydroxyquinoline and 1,2,3-trihydroxybenzene in the solid state in detail in order to understand the mechanism of reaction. However many more such systems should be studied so that a clear picture of these type of reactions can be obtained.

In this communication we report the study of solid state reactions between 8-hydroxyquinoline and nitro phenols with a view to understand the reactivities of different nitro phenols.

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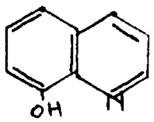
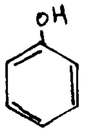
* Correspondence Author.



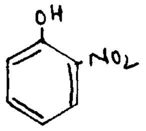
8-Hydroxy-quinoline

(8-HQ)
1



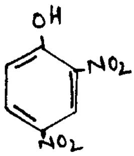
Phenol

(P)
2



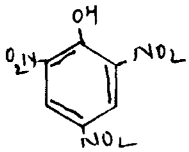
m-Nitrophenol

(NP)
3



2,4-dinitro phenol

(DNP)
4



2,4,6-trinitro phenol

(TNP)
5

MATERIALS AND METHODS

Materials

8-HQ (AR, Merck) was purified by repeated distillation under reduced pressure. The purified sample melts at 75° C. TNP and DNP were purified by successive recrystallisation from ethyl alcohol. The melting points of pure samples of TNP and DNP are 122° C and 113° C respectively, P and NP (AR, BDH) were used without further purification.

Methods

Reaction between nitrophenols and 8-hydroxyquinoline

a. In Solution

Solutions of 8-HQ and TNP in methyl alcohol were mixed in 1:1 molar ratio where an yellow coloured reaction product precipitated. Precipitate was dried and stored in desiccator (M.P. 201° C).

1.45g of 8-HQ and 1.84g of DNP were dissolved in benzene separately. Both the solutions were warmed and mixed. After 48 hours yellow coloured crystals were obtained (M.P. 100° C).

Solutions of 8-HQ and NP in chloroform were mixed in 1:1 molar ratio but no reaction product was obtained. Mixture of 8-HQ and P in chloroform also did not give any reaction product.

b. In Solid State

Solid powders of 8-HQ and TNP in equimolar amounts were ground together in an agate mortar with pestle. The entire mass was then kept in an incubator at 60°

C for a week with occasional grinding. The reaction product was dark yellow in colour and melted with decomposition (MP. 199 °C). Similarly solid powders of 8-HQ and DNP in equimolar amounts were ground together in agate mortar with pestle. The reaction product was yellow in colour and melted sharply at 98 °C. In 8-HQ – NP system, slight change in colour occurred without any reaction and 8-HQ – P system melted without any reaction.

Spectroscopic and other studies

The electronic spectra of nitrophenols, 8-HQ and their mixture in 1:1 molar ratio in methanol were recorded with Hitachi U-2000 spectrophotometer at 30° C. I.R. spectra of the products, 8-HQ and nitrophenols were recorded with the help of Perkin – Elmer spectrophotometer in nujol mull at USIC Delhi. The powder X-ray diffraction patterns of the components and reaction products obtained from solution and solid state reaction were recorded with the help of a Rigaku, Rotaflex diffractometer using CuK_α radiation at USIC Delhi. DTA studies of the components and reaction product obtained from solution and solid state reaction were recorded with the help of Rigaku thermal analyser, at U.S.I.C. Delhi, India. Phase diagram studies of 8-HQ – DNP and 8-HQ – NP were made by using the thaw melt method (4). TG studies of $(8\text{-HQ})_1(\text{DNP})_1$were also made between 30 to 320° C.

Microstructural Study

A glass slide was kept at 125 °C in an oven and a small amount of TNP was placed over the slide. TNP immediately melted. The temperature of the oven was lowered to 122° C and the molten TNP was allowed to crystallise in one direction with the help of a coverslip. This was examined under microscope and photographed. In a similar fashion the slides of 8-HQ were made at 80°C and the microstructure photographed. In a small beaker (25 ml capacity) 8-HQ was taken and heated so that beaker was filled with the vapours of 8-HQ. The slide of TNP was kept on the top of the beaker so that TNP reacted with vapours of 8-HQ and the change in microstructure was photographed.

Kinetic studies of reaction between nitrophenols & 8-HQ in solid state

a. *Capillary technique*

The detailed method for studying the kinetics of reaction is described elsewhere (5). The solid state reaction of 8-HQ with TNP was studied by capillary technique. A glass capillary sealed at one end was half filled with TNP (particle size below 100 mesh). For uniform packing of TNP each capillary was tapped for 5 minutes. The surface was made smooth by a glass rod. The remaining half of the capillaries were filled with 8-HQ (particle size below 100 mesh). At the junction of the two reactants, the reaction started with a colour change. The kinetics was followed by measuring the thickness of the reaction product at different intervals of time with the help of a travelling microscope. The experiment was performed at different temperature for fixed particle size. The reaction occurred at the surface of the TNP showing that 8-HQ is the diffusing species. Such studies could not be made in the system 8-HQ – DNP because only a thin layer of the product was formed, thickness of which did not show measurable change.

RESULTS

When P, NP, DNP and TNP were mixed individually with 8-HQ in 1:1 molar ratios in solid state, following changes were observed:

i. DNP and TNP when mixed with 8-HQ separately, a colour change from white to yellow was observed, indicating some sort of interaction and the colour change in the system 8HQ + TNP was much faster than in the system 8HQ + DNP.

ii. No change in colour was observed when NP was mixed with 8-HQ, this indicated that probably there is no interaction between the components.

iii. When 8-HQ and P were mixed in solid state at 20° C, there was a slight colour change (white to orange) and the entire mass melted.

Further when the reactions were allowed to occur in methanol/benzene, reaction products with definite melting points separated in 8-HQ-DNP and 8-HQ-TNP systems. However P and NP did not form any compound with 8-HQ.

Attempts were made to study the phase diagrams in the individual systems. In the case of 8-HQ – TNP system, the mixture melted with decomposition and hence homogeneous mixtures could not be made, so the study of phase diagram was not made. 8-HQ and DNP forms 1:1 addition compound melting at 99°C (Fig. 1). The maxima is flat and hence it appears that as a result of interaction a stable compound is formed in the solid state and dissociated in the molten state or in solution (6). In the case of 8-HQ – NP system, the phase diagram shows the formation of simple eutectic (Fig. 2). Phase diagram studies of 8-HQ and P system could not be made because of the formation of liquid even at room temperature (20°C). This may be due to eutectic formation.

Elemental analyses have shown that $(8\text{-HQ})_1(\text{TNP})_1$ is formed both in solid state and solution. The differential thermal analyses of the product $(8\text{-HQ})_1(\text{TNP})_1$obtained from solid state reaction and solution are represented in Fig. 3a. An endotherm at 205.6°C in the case of $(8\text{-HQ})_1(\text{TNP})_1$ obtained from

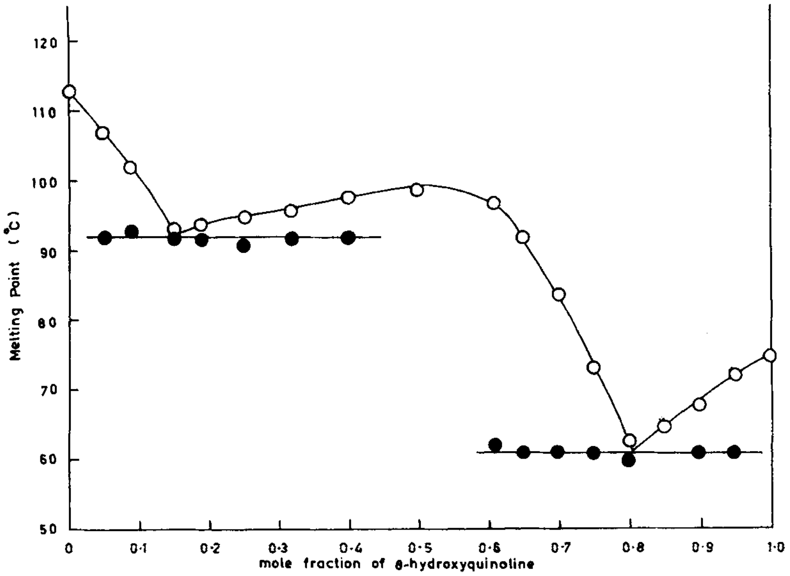


FIGURE 1 Solid liquid equilibrium data of 8-HQ – DNP system

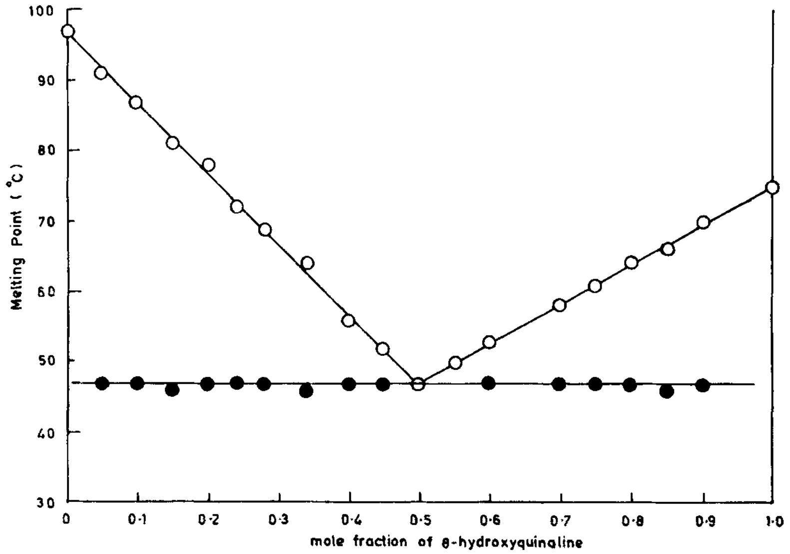


FIGURE 2 Solid liquid equilibrium data of 8-HQ – NP system

solution corresponds to its melting point. On the other hand $(8\text{-HQ})_1(\text{TNP})_1$ obtained from solid state reaction shows three endotherms at 72.9° C, 120.7 °C and 198.4 °C corresponding to the melting of unreacted 8-HQ, TNP and the product $(8\text{-HQ})_1(\text{TNP})_1$ This shows that the reaction is incomplete in solid state and the decrease in melting points is due to impurities of the unreacted components. The results show that the reaction products obtained from solution and solid state reaction are chemically identical. However, the powder X-ray diffraction patterns of the two products are not similar, indicating that the two products are structurally different.

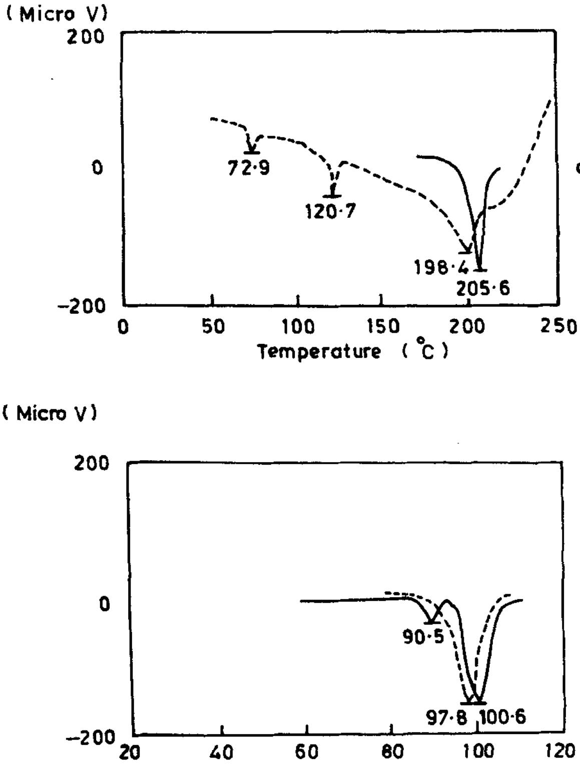


FIGURE 3 DTA curves of (a) $(8\text{-HQ})_1(\text{TNP})_1$ obtained from solid state reaction (----) and solution (--); (b) $(8\text{-HQ})_1(\text{DNP})_1$ obtained from solid state reaction (----) and solution (—)

DTA curves of the product $(8\text{-HQ})_1(\text{DNP})_1$ obtained from solid state reaction and solution are given in Fig. 3b. $(8\text{-HQ})_1(\text{DNP})_1$ obtained from solid state reaction shows an endotherm at 97.8° C corresponding to its melting point. The product may be associated with certain amount of unreacted components and hence the melting point is lower. $(8\text{-HQ})_1(\text{DNP})_1$ obtained from benzene shows two endotherms at 90.5 °C and 100.6 °C. The first peak is very small and may be due to elimination of certain entrapped benzene molecules in the crystal lattice and other is due to its melting. To confirm this point, TG studies were made. It shows no weight loss upto 100° C but between 100–150 °C there is a small weight loss which may be due to removal of entrapped benzene molecules and also due to evaporation of the product (liquid). Further to ensure that entrapped benzene molecules have been removed, the reaction product was heated at 100 °C for 10 minutes. The molten mass was then solidified and the melting point was determined. It was observed that it melted sharply at 100 °C. This confirmed that there was an entrapped benzene molecules which was removed as a result of heating.

U.V. – Visible spectroscopic studies in methanol in both the cases show that the spectra of the products are additive of the spectra of the components and no new bands are observed. This shows that either there is a very weak interaction between the components or the product is dissociated in solution. I.R. spectra of 8-HQ shows a peak at 3315 cm^{-1} due to hydrogen bonded – OH group. It is already reported that 8-HQ in the solid state exists as a dimer and the association is due to H-bonding (7). TNP does not show any stretching frequency due to OH group. It is already reported that there is intramolecular H-bonding in TNP (8). $(8\text{-HQ})_1(\text{TNP})_1$ does not show any ν_{OH} band. This shows that OH group of 8-HQ is hydrogen bonded with some of the oxygen atom of TNP.

TABLE I Parameter of Eq. (1) for reaction between 8-HQ and TNP

S. No.	*Temperature (± 1 °C)*	*k × 10^2 (cm/h)*	*n*	*E (kJ/mole)*
1	40	5.9	0.09	
2	50	6.6	0.09	13
3	55	7.5	0.08	
4	60	8.0	0.08	

When powders of 8-HQ were kept in contact to the powders of DNP in glass capillaries, yellow coloured boundary of the reaction product was formed at the surface of DNP, but the increase in thickness of the product layer with time and temperature was not appreciable and hence kinetics could not be studied. On the otherhand in the system 8-HQ – TNP, the increase in the thickness of the product layer was quite appreciable and the kinetics was studied at different temperatures. The kinetic data when the reactants were in contact obeyed eq.(1)

$$\xi = \mathbf{k}\mathbf{t}^{n} \qquad (1)$$

where ξ is the thickness of the reaction product at any time t, n is constant and k is related to rate constant. When log ξ was plotted against log t, straight lines (Fig. 4) were obtained. The values of k and n calculated from the lines are given in Table I. From Arrhenius plot, the energy of activation was found to be 13 kJ/mole.

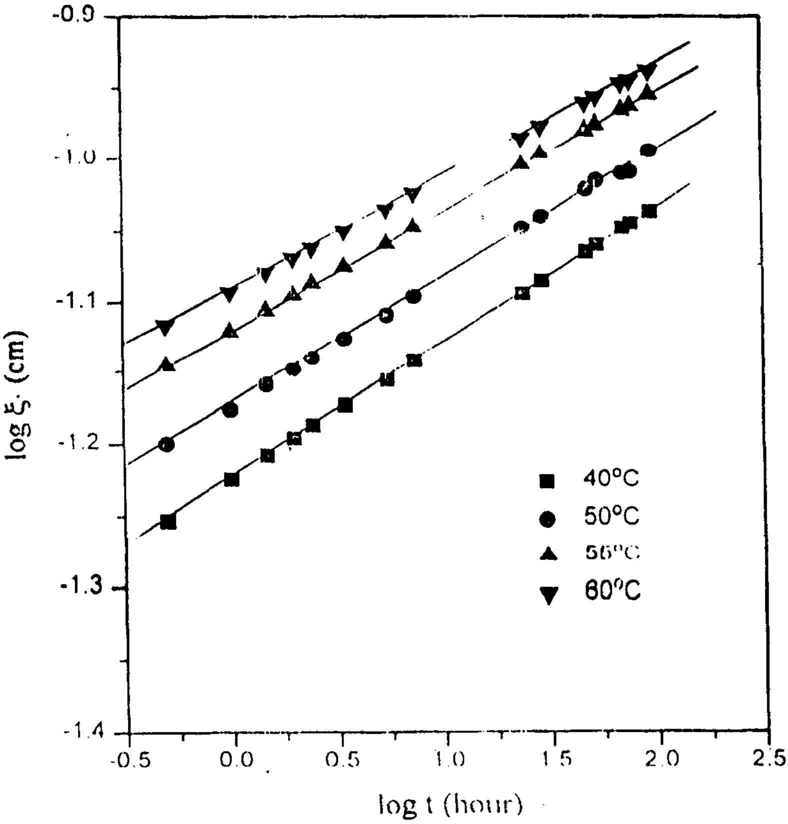


FIGURE 4 Verification of validity of eq. (1)

DISCUSSIONS

From the results it is obvious that P and NP form only eutectic mixtures with 8-HQ in the solid state whereas DNP and TNP form 1:1 molecular complexes with 8-HQ. The extent of interaction between nitrophenols and 8-HQ increases with the increase of NO_2 group in the phenol. 8-HQ may be considered as electron donor and P, NP, DNP and TNP as electron acceptors or base – acid type systems. The acid dissociation constants of P, NP, DNP and TNP are respectively 1.28×10^{-10}, 5.3×10^{-9}, 1.1×10^{-4} and 4.2×10^{-1}. The values indicate that the acidic power increase from P to TNP in the series. The reactivity of the compounds may be associated with the acidic (acceptor) power of the phenols.

In order to understand the reaction between nitrophenols and 8-HQ in solid state, kinetic studies between 8-HQ and TNP were made. The kinetic parameters were determined (Table I). 8-HQ molecule was found to diffuse towards TNP in the solid state. Diffusion may occur through number of ways: (I) vapour phase, (ii) bulk diffusion, (iii) grain boundary diffusion, (iv) surface migration. The energy of activation was found to be much less than the enthalpy of sublimation of 8-HQ (108.7 kJ/mole) (9). This shows that diffusion of 8-HQ molecules towards TNP is not a vapour phase dominated process. Also since the value is very low, bulk diffusion and grain boundary diffusions are ruled out. Diffusion may occur through surface migration. Earlier studies (10) have shown that surface migration of 8-HQ on the surfaces of glass capillaries is not uncommon. The possibility of vapour phase diffusion can further be ruled out by considering the reaction in the 8-HQ-DNP system. The enthalpies of sublimation of both 8-HQ and DNP are nearly equal (108.7 kJ/mole and 104.5 kJ/mole) and it was expected that the reaction should have occurred in the vapour phase at a much faster rate but it was not so.

For a reaction to occur in solid state, pre alignment of molecules must occur in the crystal lattice. Therefore the differences in the rate of diffusion of 8-HQ towards TNP and DNP may be due to differences in the alignment of molecules, packing geometry and symmetry of TNP and DNP molecules. Since this experiment gives information only about surface migration, surface geometries of the two molecules are more important. The dipole moment of TNP is 1.54 D whereas that of DNP is 3.0 D and 5.51 D for cis and trans form respectively. This shows that DNP is less symmetrical and offers larger hindrance during the surface migration of 8-HQ molecules. As a result the rate of surface migration in 8-HQ-DNP system will be smaller than that in the other system (11).

TABLE II Dimensions of the reactants

S. No.	*Reactants*	*Dimensions ($A^{\circ 2}$)*
1	8-HQ	6.4×5.5
2	TNP	6.4×6.2
3	DNP	4.2×6.2

The reactions can be considered as the interaction between guest (8-HQ) and host (TNP & DNP) molecules. There should be a size matching between the host and the guest. The guest molecule should fit into the cavities or channels created by the packing of the host molecules. For this reason the approximate dimensions of the reactants were calculated from the bond lengths and bond angles and are given in table II. The dimension of 8-HQ is comparable with that of TNP and hence the surface migration is faster in this system. On the other hand the dimension of DNP is of much lower value than that of 8-HQ and as a result the process of surface migration in this system is very slow.

From table I, the values of n are in the range 0.08 – 0.09. Such values may indicate the formation of fractals. However microstructural studies do not give any idea for fractal growth. Microstructural studies have shown that TNP has lamellar structure and when this is exposed with the vapours of 8-HQ, the lamellaes become thick and lamellar spacing become wider. This shows that due to reaction the basic geometry and the microstructure of TNP (host) molecule is not affected much. It can be inferred that probably very little structural change occurs during solid state reaction. However this can be confirmed only by structure determinations.

When there is a weak interaction between the two components very little structural changes are expected during solid state reaction. U.V-visible spectroscopy confirms that there is a weak interaction between the components 8-HQ and TNP. From I.R. spectral studies one may speculate that during reaction the dimeric structure of 8-HQ is broken and the hydrogen atom of -OH group is strongly hydrogen bonded with one of the oxygen atoms of NO_2 group in TNP. The overall results show a weak molecular interaction between the components during solid state reaction.

CONCLUSIONS

Results have shown that nitrophenols interact with 8-HQ in the solid state. Extent of interaction increases with the increase of NO_2 groups i.e. with the increase of the acidic powers of the nitrophenols. In the systems DNP + 8-HQ and TNP + 8-HQ, 1:1 molecular complexes are formed. In the other systems with lesser number of NO_2 groups, only eutectic mixtures are formed. Reaction products obtained from solid state reaction and solution are chemically identical. During solid state reactions 8-HQ molecule diffuses towards nitrophenols through surface migration. In the case of TNP – 8-HQ system the size of the guest molecule (8-HQ) is comparable with the size of cavities and channels in the host molecule (TNP) created as a result of crystal packing whereas in the system DNP – 8-HQ, this is not the situation. As a result of this the reaction between TNP and 8-HQ is much faster as compared to that in the system DNP – 8-HQ.

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