

Solid state reaction between 8-hydroxyquinoline and *p*-nitrobenzoic acid

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8-Hydroxyquinoline reacts with *p*-nitrobenzoic acid in solid state forming 1:1 molecular complex. In solid state the diffusion of 8-hydroxyquinoline occurs towards *p*-nitrobenzoic acid and the process of diffusion is not vapour phase dominated process. Micro structural studies have indicated that reaction during solid state may be nucleation controlled process. Reaction products obtained from solution and solid state reaction are identical and there is a hydrogen bonding between the components in the reaction product.

In recent years considerable interest has developed in the study of organic reactions in the crystalline state.¹⁻⁹ Many such reactions have been studied from the synthetic and mechanistic point of view. Recently a few solid state reactions of 8-hydroxyquinoline with anhydrides¹⁰ and also with metal salts¹¹ have been studied with a view to understand the mechanism of diffusion of 8-hydroxyquinoline molecules into the crystal lattice of the other reacting components. However due to non availability of the crystal structures of the reaction products, the exact mechanism could not be understood. In this paper solid state reaction between *p*-nitrobenzoic acid and 8-hydroxyquinoline has been studied with a view to understand the mechanism of reaction and the nature of reaction product.

Materials and Purification

8-hydroxyquinoline (A.R. Merck) was purified by repeated distillation under reduced pressure. The purified sample melts at 75°C.

p-Nitrobenzoic acid (A.R. CDH) was used without further purification. The melting point was found to be 242°C. 8-Hydroxyquinoline and *p*-nitrobenzoic acid are abbreviated as 8-HQ and *p*-NBA respectively.

Preparation of reaction product from solution—*p*-nitrobenzoic acid (*p*-NBA) (0.5566 g) and of 8-hydroxyquinoline (8-HQ) (0.4833 g) were dissolved in methanol separately. Both the solutions were warmed and mixed. After 24h very

thin yellow colour crystals were obtained, m.p. 180°C.

Preparation of reaction product from solid-state reaction—Solid powders of 8-HQ and *p*-NBA were mixed thoroughly in 1:1 molar ratio in an agate mortar and kept in an incubator at 50°C for a week with occasional mixing and crushing. The reaction product was yellow in colour and melted sharply at 171°C.

Methods

The electronic spectra of 8-HQ, *p*-NBA and mixture of the two in 1:1 molar ratio were recorded in DMF (0.02M). The I.R. spectra of 8-HQ, *p*-NBA and the reaction products obtained from solution and solid-state reaction were recorded in Nujol mull.

The powder X-ray diffraction patterns and DTA data of the 8-HQ, *p*-NBA and the reaction products obtained from solution and solid-state reactions were recorded.

Microstructural studies were also made¹². A clean slide was kept at 245°C in an oven and a small amount of *p*-NBA was placed over the slide which immediately melted. The temperature of the oven was lowered down up to 242°C and crystallised in one direction with the help of a cover slip in such a way that a very thin layer of *p*-NBA crystallised. This was examined under microscope and photographed.

The slide of *p*-NBA was kept on the top of the beaker filled with vapours of 8-HQ and covered

with big beaker and kept at 70°C for different time intervals. *p*-NBA reacted with vapours of 8-HQ and change in microstructure was photographed.

Kinetics of solid -state reaction between *p*-nitrobenzoic acid and 8-hydroxyquinoline in capillary (reactions in contact)—The detailed method for studying the reaction is described elsewhere¹³. A pyrex glass capillary was used for the purpose. One end of the capillary was sealed with the help of sealing wax. Half of the capillary was filled with *p*-nitrobenzoic acid (particle size <100 mesh) and the remaining half of the capillary was filled with 8-hydroxyquinoline (particle size < 100 mesh) in such a way that *p*-nitrobenzoic acid and 8-hydroxyquinoline came in close contact. At the junction of the two components, the reaction started with a colour change (intense yellow). The kinetics was followed by measuring the thickness of the reaction product at different intervals of time with the help of a travelling microscope at different temperatures (40, 50, 55 and 60°C). The kinetics was also studied when the reactants were separated by air gaps. Reaction occurred at the surface of *p*-nitrobenzoic acid

Kinetic studies between *p*-nitrobenzoic acid (solid) and 8-hydroxyquinoline (vapour)—In order to understand the inner penetration of 8-hydroxyquinoline into the crystal lattice of *p*-nitrobenzoic acid, the reaction of *p*-nitrobenzoic acid (solid) was carried out with 8-hydroxyquinoline (vapours) gravimetrically. The detailed method for studying out the reaction is described elsewhere¹⁴. The kinetics was followed by noting the increase in weight of *p*-nitrobenzoic acid at different intervals of time at different temperatures 50, 55, 60 and 65°C.

Results and Discussion

Before we speculate on the mechanism of diffusion and solid-state reactivity, it is desirable to characterise the reaction product. When *p*-nitrobenzoic acid and 8-hydroxyquinoline were mixed in solid-state in 1:1 molar ratio, immediately an yellow colour developed, indicating that reaction occurred in solid state. When solutions of *p*-nitrobenzoic acid and 8-hydroxyquinoline in methyl alcohol were mixed in 1:1 molar ratio, thin yellow coloured crystals were obtained.

The X-ray diffraction patterns of the

components and the reaction products obtained by solid-state reaction and from methanol were recorded. The reaction product obtained from methanol showed sharp intense and new peaks indicating that there is a formation of new compound with a definite crystal lattice. The diffraction patterns of the reaction product obtained by solid-state reaction is almost identical to that of the product obtained from methanol except that the intensities of the peaks are very low. The results show that the reaction products obtained from solution and solid-state reactions are identical but the reaction in solid-state is slow.

When vapours of 8-hydroxyquinoline were allowed to react with solid *p*-nitrobenzoic acid at 65°C, the final increase in weight of *p*-nitrobenzoic acid corresponded to reaction product (8-HQ)₁.(*p*-NBA)₁. The differential thermal analyses of the product (8-HQ)₁.(*p*-NBA)₁ obtained from solid state reactions and solution were recorded. An endotherm at 179.6°C in the case of (8-HQ)₁.(*p*-NBA)₁ obtained from solution corresponds to its melting point. On the other hand DTA of (8-HQ)₁.(*p*-NBA)₁ obtained from solid-state reactions shows 3 endotherms at 75.9°C, 170.0°C and 240.8°C corresponding to the melting of unreacted 8-hydroxyquinoline, product (8-HQ)₁.(*p*-NBA)₁ and unreacted *p*-nitrobenzoic acid. This shows that reaction is incomplete in solid-state and decrease in melting points is due to impurities of the components. The results show that the reaction product obtained from solution and solid-state reaction are identical.

Since the reaction product is coloured, one can expect a CT interaction between the two components. The UV spectra of the reaction product in DMF does not give any new band indicating that either the charge transfer interaction is absent or very weak interaction is present. However the IR spectral studies of the reactants and the product gave some information regarding the nature of interactions. It is already reported that 8-hydroxyquinoline in the solid state exists as dimer and the association is due to hydrogen bonding¹⁵. Due to reaction the dimeric structure of 8-hydroxyquinoline is broken and the W = O group of *p*-nitrobenzoic acid is hydrogen bonded with the hydrogen atom of -OH group of 8-hydroxyquinoline and at the same time nitrogen atom of 8-hydroxyquinoline is hydrogen bonded

with hydrogen atom of -COOH group of *p*-nitrobenzoic acid.

When powders of 8-hydroxyquinoline and *p*-nitrobenzoic acid were kept in glass capillary in contact, the start of the reaction was indicated by the formation of an yellow coloured boundary at the point of contact. As the reaction proceeded, boundary moved towards *p*-nitrobenzoic acid, indicating that 8-hydroxyquinoline is the diffusing species. The kinetics was followed by measuring the thickness of the product layer as a function of time and the kinetic data obeyed the Eq. (1)

$$\xi = k_1 t^n \quad \dots (1)$$

where ξ is the thickness of the product layer at time t , k_1 and n are constants. k_1 is temperature dependent and hence an apparent rate constant related to diffusion coefficient. The validity of Eq. 1 is tested by plotting $\log \xi$ vs. $\log t$ where straight lines are obtained. The values of k_1 and n are given in Table 1. The energy of activation was calculated from Arrhenius plot and was found to be 30.1 kJ mol⁻¹. The energy of activation value is much lower than the heat of sublimation of 8-hydroxyquinoline (108.7 kJ mol⁻¹)¹⁶. This shows that the diffusion of 8-hydroxyquinoline molecules towards *p*-nitrobenzoic acid is not a vapour phase diffusion dominated process. Diffusion may occur through surface migration. It has been pointed out by Patil *et al.*¹⁷ that volatility is not the only factor affecting the solid-state reactivity. For example, methyl quinone reacted relatively rapidly with the unsubstituted hydroquinone and also the unsubstituted quinone reacted readily with methyl hydroquinone.

When the kinetics were studied by creating air-gaps of different length, kinetic data were again fitted by Eq. 1. For this case k_1 and n are referred to as k_1' and n' . The values of k_1' is decreased with the increase of the length of air-gap. The variation of rate constant (k_1') with length of air-gap (d) is given by Eq. 2.

$$k_1' = A e^{-pd} \quad \dots (2)$$

where A and p are constants. When $\log k_1'$ is plotted against d , a straight line is obtained. The kinetic parameters are given in Table II. The rate constant on extrapolation to zero air-gap comes out to be 3.63×10^{-2} cm h⁻¹ which is much less than

Table I—Effect of temperature on the kinetic parameters of Eq. (1)
Particle size < 100 mesh

Temperature (°C)	$k_1 \times 10^2$ (cm/h)	n	E (kJ. mol ⁻¹)
40	2.5	0.24	30.1
50	3.6	0.24	
60	4.1	0.24	
70	4.7	0.24	

Table II—Effect of air - gaps on the kinetic parameters of Eq. (3.1)
Temperature = 60 ± 1°C; Particle size < 100 mesh

d (cm)	$k_1' \times 10^2$ (cm/h)	n'
1.190	2.0	0.37
0.800	2.5	0.41
0.500	3.0	0.40
0.194	3.3	0.41

When $d=0$ on extrapolation $k_1' = 3.6 \times 10^{-2}$ cm/h;
 $k_1(\text{contact}) = 4.7 \times 10^{-2}$ cm/h

the rate of reaction when the reactants are in contact (4.67×10^{-2} cm h⁻¹) at 60 ± 1°C. This simply shows that during migration of 8-hydroxyquinoline towards *p*-nitrobenzoic acid apart from vapour phase diffusion some easier mode of migration such as surface migration is also involved. The surface migration of 8-HQ over the glass surface is not uncommon.¹⁸

The process of inner penetration of 8-hydroxyquinoline into the crystal lattice of *p*-nitrobenzoic acid can be understood by gravimetric studies. The kinetic data obeyed the Eq. (3)

$$\Delta W/W_0 = k_2 t \quad \dots (3)$$

where ΔW is the increase in weight of *p*-nitrobenzoic acid at any time t , W_0 is the initial weight of *p*-nitrobenzoic acid and k_2 is the rate constant. The validity of Eq. (3) is tested by plotting $\Delta W/W_0$ vs t . when straight lines are obtained. The values of k_2 calculated from these plots are listed in Table III. The energy of activation calculated from Arrhenius plot is found to be 78.7 kJ. mol⁻¹. During the course of diffusion of 8-hydroxyquinoline towards *p*-nitrobenzoic acid, the following two processes will occur simultaneously: (i) Migration of 8-hydroxyquinoline over the surface of *p*-nitrobenzoic acid, and (ii) Inner penetration into crystal lattice of *p*-nitrobenzoic acid.

Table III—Inner-diffusion of 8-hydroxyquinoline (vapour) in *p*-nitrobenzoic acid (solid) increase in weight, gravimetric technique following Eq. (3)

Temperature (°C)	$k_2 \times 10^3$ (g/h)	E (kJ. mol ⁻¹)
50	0.63	78.7
55	0.85	
60	1.05	
65	1.42	

Out of the above two processes, the first is much faster and easier as compared to the second one. Microscopic studies give informations only for the first process whereas gravimetric studies account for both processes. Since inner penetration in organic solids is difficult, it will require higher energy of activation as shown by gravimetric studies.

During solid-state reactions, very little structural changes occur. This can be confirmed by complete structural determinations. In the absence of structural data some idea can be made from microstructural changes. The microstructure of *p*-nitrobenzoic acid shows that small crystallites are joined together indicating that structure is probably globular in nature. When *p*-nitrobenzoic acid was exposed to the vapours of 8-hydroxyquinoline for 30 minutes, long and thin crystals of the product were observed. This indicated that the growth of the product is mainly in one direction which shows that the solid-state reaction is a nucleation controlled process.

The overall results show that 8-HQ reacts with *p*-NBA both in solid state and solution forming 1:1 hydrogen bonded molecular crystalline complex. During solid state reaction, 8-HQ diffuses towards

p-NBA and the process of diffusion is not vapour phase dominated process. Microstructural studies have shown that the solid state reaction might be nucleation controlled process.

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