

Study of the Reaction Between 1,2,3-Trihydroxybenzene and 8-Hydroxyquinoline in the Solid State

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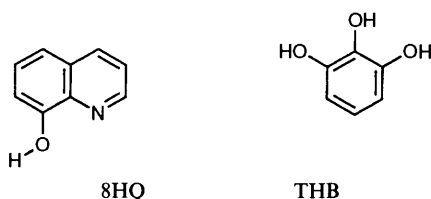
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1,2,3-Trihydroxybenzene (THB) reacts with 8-hydroxyquinoline (8HQ) in the solid state forming an orange-coloured charge transfer complex THB⁺ (8HQ)₂⁻. When the reaction was carried out in a petri dish, or when the vapours of 8HQ were allowed to react with solid THB (gravimetric study), the reaction product separated out as good quality, shiny single crystals. X-Ray diffraction studies on single crystals showed that they belong to the orthorhombic system with $a = 15.408(1)$, $b = 16.276(1)$, $c = 7.825(1)$ Å, $Z = 4$, $D_x = 1.413$ g cm⁻³ and space group $Pnaa$. From the crystallographic evidence it has been found that the proton of the middle OH group of THB is transferred to the N atom of 8HQ. This accounts for the observed colour change.

Kinetic studies on the solid state reaction showed that the 8HQ molecules diffuse towards THB, and the lateral diffusion occurs through surface migration, grain boundary diffusion and vapour phase diffusion. Gravimetric studies of the reaction between solid THB and 8HQ vapour showed that the diffusion of 8HQ molecules into the crystal lattice of THB has a higher energy of activation than that observed when the reactants are in contact. The nature of the crystal packing in the reaction product indicates diffusion of 8HQ molecules into the crystal lattice of THB along the c -axis, to occupy the cavities present between the THB molecules in the unit cell.

8-Hydroxyquinoline (8HQ) is a familiar complexing agent. However, the chelation of 8HQ with metal ions in the solid state is rare.^{1,2} Recently, some solid state reactions of 8HQ with anhydrides³ and with metal salts⁴ have been studied, with a view to understanding the mechanism of diffusion of 8HQ molecules into the crystal lattice of the other reactant. However, due to the failure in obtaining crystal structures of the reaction products, the exact mechanism could not be determined.

Our preliminary results showed that when 8HQ was allowed to react with 1,2,3-trihydroxybenzene (THB) in the solid state, the reaction products separate out as orange coloured, single crystals. This was an unusual observation. Therefore, it was thought worthwhile to study the solid state reactivity of this system and to determine the detailed crystal structure of the reaction product (the single crystal that formed during the solid state reaction), so that the mechanism of the diffusion can be understood.



Experimental

Materials and Purification.—THB (AR Merck) and 8HQ (AR Merck) were purified by repeated distillation under reduced pressure. The m.p.s of the purified samples were 133.5 and 74.5 °C, respectively.

Reaction Between THB and 8HQ.—(a) *From solution.* Saturated solutions of THB and 8HQ in methanol were mixed. Orange-coloured crystalline material precipitated. The compound thus formed had a sharp m.p. (105 °C).

(b) *By solid state reaction.* Solid powders of THB and 8HQ were mixed thoroughly in a 1:2 molar ratio in an agate mortar

for 1 h and then placed in an incubator at 50 °C for 24 h. During this period, the material was occasionally crushed. As soon as the two components had been mixed, an orange colour developed. The orange-coloured reaction product so formed could not be washed with any solvent to remove unreacted components because the product itself was soluble in all the solvents employed.

Spectroscopy and Analysis.—The reaction product obtained from solution, as well as the single crystals obtained by solid state reaction of THB and 8HQ (described later), were analysed for C, H and N [Found C, 69.0; H, 5.15; N, 6.7%. THB⁺ (8HQ)₂⁻ requires C, 69.23; H, 4.84; N, 6.73%]. Differential scanning calorimetry (DSC) studies of THB, 8HQ and reaction products obtained by solid state and solution reactions were made with a General Du Pont 910 at IIT, Kanpur (India). Powder X-ray diffraction studies of the components and reaction products were made with a General Electric XDR-52-Circle diffractometer using CuK α radiation at IIT, Kanpur (India). UV-VIS spectra of THB, 8HQ and their mixture in a 1:2 molar ratio at the same concentration in methanol were recorded over 200–800 nm with a Bausch and Lomb Spectronic 2000 spectrophotometer. IR spectra of the components and the reaction product obtained from solution as well as single crystals obtained by the solid state reaction of THB and 8HQ were recorded on a Perkin Elmer 157 spectrophotometer at CDRI, Lucknow (India). Diffuse reflectance spectra of the components and the solid state reaction product were recorded over 200–800 nm at Guru Nanak Dev University, Amritsar (India). Phase diagram studies were made by using the thaw-melt method.⁵ Homogeneous mixtures of the two components in different proportions were prepared and their m.p.s (± 0.1 °C) determined using a digital thermometer (Century CT 802, India).

Kinetic Studies of Reaction Between THB and 8HQ.—(a) *Capillary technique.* The orange reaction product is easily distinguished from the reactants, enabling the kinetics to be studied by measuring the thickness of the coloured product

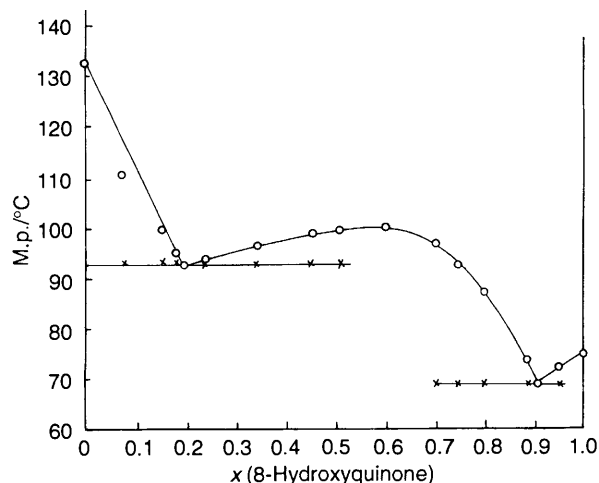


Fig. 1 Phase diagram for the THB-8HQ system

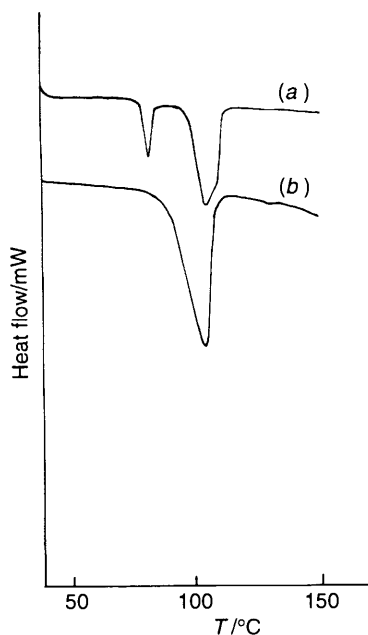


Fig. 2 DSC traces of (a) solid state reaction mixture of THB-8HQ; (b) reaction product (single crystals)

layer as a function of time by the capillary technique first used by Rastogi *et al.*^{6,7} Half of the glass capillary tube was filled with powdered THB (particle size 100–150 mesh) and the tube was tapped for 5 min in order to achieve a reproducible packing density. The remaining half of the capillary tube was filled with powdered 8HQ (particle size 100–150 mesh), and the capillary was sealed and placed horizontally into a constant temperature incubator. The reaction occurred only in the THB end of the capillary tube. The reaction was studied at different temperatures at constant particle size, and at constant temperature with the two reactants separated by air gaps of varying length.

(b) *Gravimetric technique.* The kinetics of reaction between solid THB and vapours of 8HQ were studied gravimetrically as a function of time. The reaction was studied by placing a known amount of THB (0.2200 g) in one glass tube, and 8HQ in the other. The two tubes, fitted with standard joints, were joined together and placed in an incubator at constant temperature. The kinetics were followed by noting the increase in weight of THB as a function of time. The experiment was repeated at different temperatures.

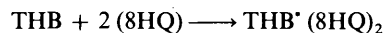
(c) *Single crystal growth technique.* Into a petri dish was

placed THB powder and from the centre of the dish a small portion of the powder was removed to leave an empty circular space of diameter ≤ 0.5 cm. Into this space was added a small amount of 8HQ, and the dish was then covered with a glass plate and placed in an incubator at constant temperature. The reaction started at the surface of THB, indicated by a change of colour to orange. After 24 h, shiny crystals of the reaction product appeared which grew further with time. The position of one single crystal of the reaction product was fixed and the kinetics (at 55 °C) were monitored by measuring the length of the crystal as a function of time. Only qualitative information could be derived from this experiment since the crystal is a three-dimensional object and the kinetic measurements are made in one dimension.

X-ray Crystallographic Analyses of the Reaction Product.— Good quality, orange-coloured single crystals of the reaction product THB' (8HQ)₂ were obtained when the solid state reaction was carried out in a petri dish. The crystal chosen for the data collection was sealed in a Lindeman capillary tube so as to avoid any aerial oxidation on the crystal surface. Crystal data: C₂₄H₂₀O₅N₂, *M* = 417.44. Orthorhombic, *a* = 15.408(1), *b* = 16.276(1), *c* = 7.825(1) Å, *V* = 1962.4(3) Å³, space group *Pnaa*, *Z* = 4, *D_x* = 1.413 g cm⁻³, *F*(000) = 876, $\mu(\text{Mo-K}\alpha)$ = 0.93 cm⁻¹, *S* = 2.1839, *T* = 295 K, crystal dimensions = 0.275 × 0.15 × 0.1 mm³. The three-dimensional intensity data were collected on an ENRAF-NONIUS CAD-4 diffractometer with graphite monochromated Mo-K α (λ = 0.7107 Å) radiation. The cell dimensions were refined using 25 well centred reflections in the range 5.7 < θ < 21.6°. The data were collected in ω -2 θ scan mode in the range 1 ≤ θ ≤ 25° with 0 ≤ *h* ≤ 18, 0 ≤ *k* ≤ 19, 0 ≤ *l* ≤ 9. A total of 2089 reflections were measured, of which 1796 were unique and 956 observed with *F_o* ≥ 3 σ (*F_o*). The data were corrected for Lorentz and polarization corrections but not for absorption. The structure was solved by direct methods using the SHELXS86 program⁸ and refined using |*F*|*s* in a full matrix least squares refinement with the SHELX76 program.⁹ H-Atoms were assigned by a $\Delta\rho$ map. The non-H-atoms were refined anisotropically and the H-atoms isotropically, to final values *R* = 0.072 and *wR* = 0.076. The individual weighting scheme was based on counting statistics, where $w = 1/[\sigma^2|F_o| + 0.000189|F_o|^2]$.

Results and Discussion

Elemental analyses of the reaction product indicated that the reaction between THB and 8HQ occurred in 1:2 molar ratio. The stoichiometry of the reaction can be represented as



When vapours of 8HQ were allowed to react with solid THB at 65 °C, the final increase in weight of product corresponded to the reaction product THB'(8HQ)₂. The phase diagram (Fig. 1) clearly shows that the reaction occurs in 1:2 molar ratio. Since the maximum is broad, this suggests that the molecular compound formed is stable in the solid state and dissociates in solution or the fused state.⁵

Powder X-ray diffraction studies of the products obtained from methanol, and from the solid state reaction (single crystals) indicated that the two products were identical. However, the solid state reaction product obtained by mixing the two reactants showed some additional lines in its diffraction pattern, due to unreacted components. DSC studies also confirmed that the solution and solid state reaction products were identical (Fig. 2). DSC traces of THB' (8HQ)₂ obtained from solution and of single crystals obtained by solid state reaction gave

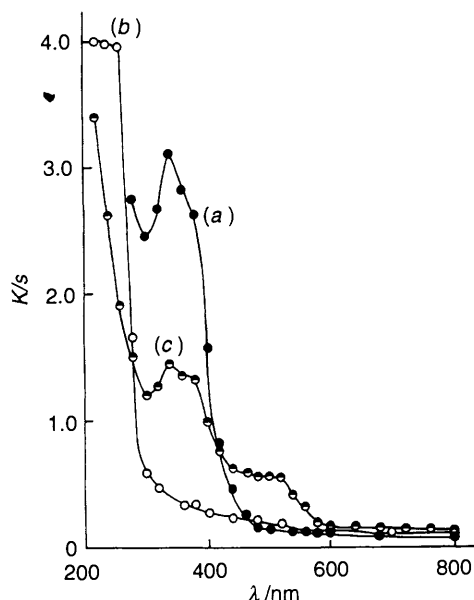
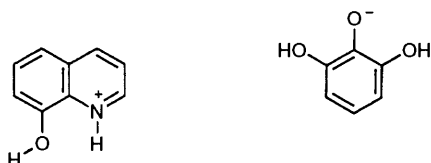


Fig. 3 Diffuse reflectance spectra in terms of Kubelka-Munk function of (a) 8HQ, (b) THB and (c) THB·(8HQ)₂

one endotherm at 105 °C, whereas THB·(8HQ)₂ obtained by mixing the two components in a 1:2 molar ratio in the solid state gave two endotherms, one at 105 and the other at 75 °C. This second endotherm is due to the melting of 8HQ. It appears that during the solid state reaction, some unreacted 8HQ molecules were contaminated with the reaction product.

IR spectral studies showed the presence of a sharp peak at 2362 cm⁻¹ confirming the presence of NH⁺ in the reaction product. X-Ray diffraction studies also showed that the proton of the middle OH group of THB is transferred to the N atom of 8HQ. The colour of the reaction product may be due to this effect. Formation of the following ions is proposed.



Since THB·(8HQ)₂ is an orange-coloured reaction product, this suggests that it is a charge transfer (CT) complex. However, spectroscopic studies in solution do not give any CT band. This suggests that either THB·(8HQ)₂ is dissociated in solution or it is not a CT complex. In order to avoid dissociation, diffuse reflectance spectra of the reactants and the product in the solid state were recorded. The spectra were plotted in terms of the Kubelka-Munk function K/S (Fig. 3) which is given as;

$$K/S = (1 - R)^2/2R \quad (1)$$

where K is the absorption coefficient, S the scattering coefficient and R the reflectance. The spectrum contains a new band at $\lambda = 520$ nm in the case of THB·(8HQ)₂, indicating the possibility of a CT interaction between the components, in which 8HQ⁺ might be acting as acceptor and the phenolate ion as donor.¹⁰

Detailed information regarding the structure of the reaction product THB·(8HQ)₂ has been obtained from X-ray diffraction studies on single crystals. The atom labelling is shown in Fig. 4. The packing diagram¹¹ down the c -axis of the unit cell is shown in Fig. 5. The THB molecule is on a crystallographic

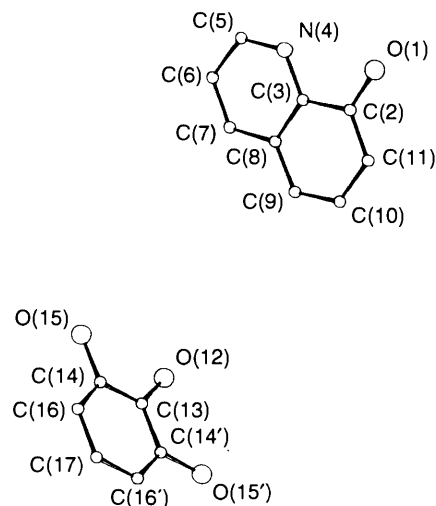


Fig. 4 Juxtapositions of the closed neighbours of THB and 8HQ in the unit cell of the reaction product

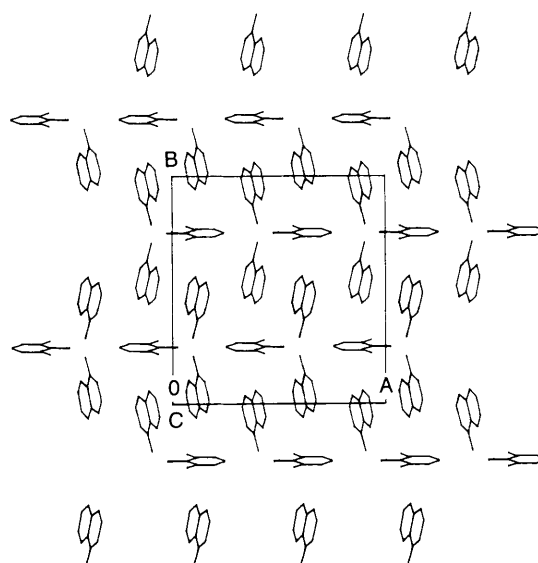


Fig. 5 Packing of molecules in the unit cell of THB·(8HQ)₂ viewed down c -axis

two-fold axis making an angle of 83.95° with the 8HQ molecule. The oxygen atom O(12) of THB is involved in a bifurcated hydrogen bond with the nitrogen N(4) of 8HQ. The oxygen O(1) of 8HQ is involved in a bifurcated hydrogen bond with C(11) and O(15).

The presence of a peak of height $ca. 1 \text{ e } \text{Å}^{-3}$ at a stereochemically reasonable position for a hydrogen atom close to N(4) clearly shows that proton transfer has taken place from O(12) and there is an intermolecular hydrogen bond between N(4) and O(12). In the unit cell, the molecules are stabilized by N-H...O and O-H...O types of hydrogen bonds as well as by C-H...O interactions.

Kinetic studies were made by the capillary technique. When $\log \xi$ is plotted against $\log t$, straight lines (Fig. 6) showing the validity of eqn. (2) are obtained; where ξ is the thickness of

$$\xi = k_1 t^{n_1} \quad (2)$$

the product layer at time t , n_1 is a constant and k_1 is an apparent rate constant. From an Arrhenius plot, the energy of activation for lateral diffusion was found to be $E = 28.7 \text{ kJ mol}^{-1}$. The parameters of eqn. (2) were refined by a least squares procedure.

Table 1 Least-squares parameters of eqn. (2) for solid state reaction between 100–150 mesh powder layers of THB and 8HQ in a glass capillary with no air gap between layers. Each observation is an average of four measurements

$T/^\circ\text{C}$	$k_1/10^{-2} \text{ cm h}^{-1}$	n_1
50 ± 1	2.29 ± 0.02	0.18 ± 0.01
55 ± 1	2.69 ± 0.02	0.17 ± 0.01
60 ± 1	3.13 ± 0.11	0.15 ± 0.01
65 ± 1	3.72 ± 0.12	0.15 ± 0.01

Table 2 Least squares parameters of eqn. (2) for solid state reaction ($60 \pm 1^\circ\text{C}$) of 100–150 mesh powder layers of THB and 8HQ separated by an air gap of thickness d

d/cm	$k'_1/10^{-2} \text{ cm h}^{-1}$	n'_1
0.218	11.22	0.25
0.451	8.51	0.25
0.702	7.08	0.26
0.873	6.31	0.25
1.360	3.89	0.26

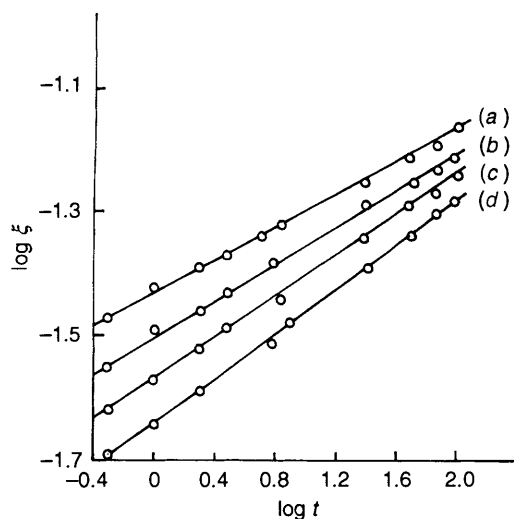


Fig. 6 Test of eqn. (2) for reaction of THB and 8HQ by capillary technique

The results are given in Table 1 for the case of no air gap. The energy of activation is much less than the heat of sublimation of 8HQ indicating that surface migration plays an important role in the diffusion process. It has been pointed out by Patil *et al.* that volatility is not the only factor affecting solid state reactivity.¹²

The surface migration of 8HQ over a glass surface is not uncommon.³ It has been shown that when 8HQ is allowed to sublime in open glass tubes, the rate of sublimation k depends on the diameter of the tube [eqn. (3)]; where $\alpha = \pi C_e D_v / l$,

$$k/r = \alpha r + \beta \quad (3)$$

$\beta = 2\pi C_e D_s$, r is the radius of the tube, l is the distance of the 8HQ surface from the open end of the tube, C_e is the equilibrium concentration of 8HQ just above the surface, D_v is the vapour phase diffusion coefficient and D_s is the diffusion coefficient for surface migration. The values of α and β at 60°C were found to be 4.047×10^{-5} and $3.75 \times 10^{-5} \text{ g h}^{-1} \text{ cm}^{-1}$, respectively, indicating that during sublimation of 8HQ, surface migration has a significant contribution.

Table 3 Parameters for the diffusion of 8HQ into solid THB, as measured by the gravimetric technique following eqn. (6). Each observation is an average of four measurements

$T/^\circ\text{C}$	$k_2/10^{-5} \text{ g h}^{-1}$
45 ± 1	2.50 ± 0.11
55 ± 1	4.55 ± 0.09
60 ± 1	7.33 ± 0.04
65 ± 1	10.61 ± 0.12

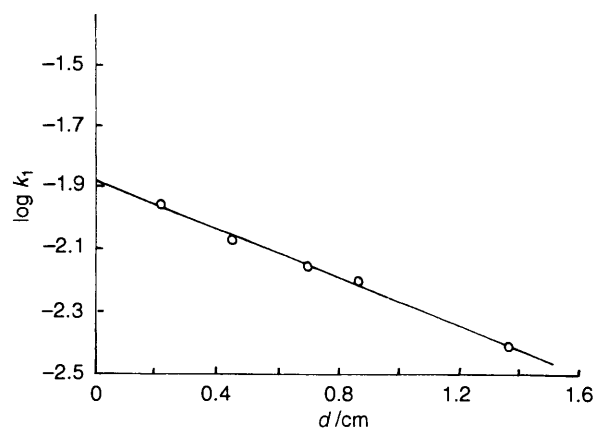


Fig. 7 Test of eqn. (4) for reaction of THB and 8HQ separated by an air gap

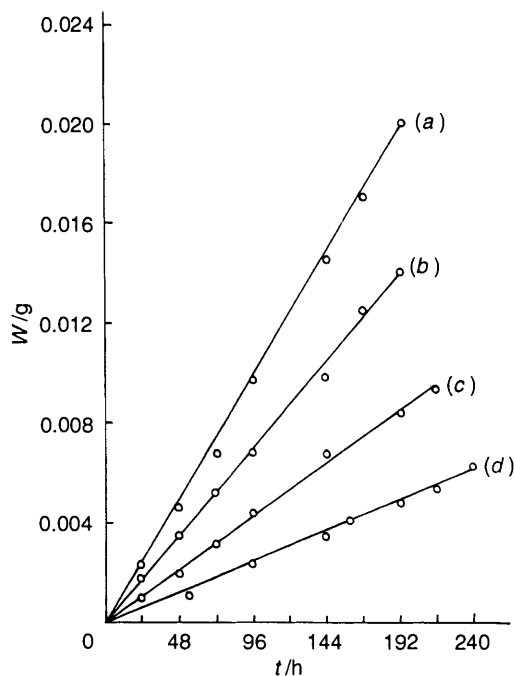


Fig. 8 Test for eqn. (6) for reaction of THB and 8HQ monitored by gravimetry.

When the kinetics were studied with air gaps of different length, kinetic data were again fitted by eqn. (2). For this case, k_1 and n_1 are referred as k'_1 and n'_1 . The values of k'_1 decreased with increase of length of air gap (d). This variation is described by eqn. (4); where A and p are constants.

$$k'_1 = A e^{-pd} \quad (4)$$

When $\log k'_1$ is plotted against d , a straight line is obtained (Fig. 7). The kinetic parameters are given in Table 2. The rate

constant on extrapolation to zero air gap is $1.32 \times 10^{-2} \text{ cm h}^{-1}$, much less than the rate constant when the reactants are in contact ($3.12 \times 10^{-2} \text{ cm h}^{-1}$) at $60 \pm 1^\circ \text{C}$. This simply shows that, apart from vapour phase diffusion, the migration of 8HQ towards THB involves some easier mode of migration. The following modes of diffusion may contribute towards lateral diffusion of 8HQ molecules over the surface of THB: (a) surface migration; (b) grain boundary diffusion; (c) vapour phase diffusion; (d) bulk diffusion. Hence the rate constant k_1 can be represented as k_1 [eqn. (5)]; where k_s , k_g , k_b and k_v

$$k_1 = A k_s + B k_g + C k_b + D k_v \quad (5)$$

are the rate constants related to surface migration, grain boundary diffusion, bulk diffusion and vapour phase diffusion,

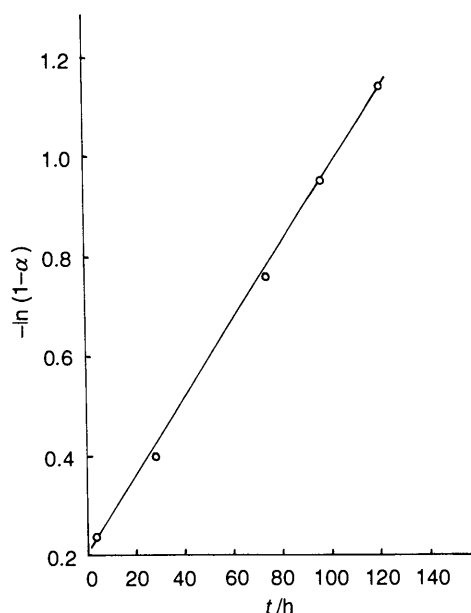


Fig. 9 Test of eqn. (7) for reaction of THB and 8HQ monitored by increase in length of single crystal of product

respectively, and A , B , C and D are constants denoting the relative contributions for each process. Rastogi *et al.* have tried to estimate the contribution of each process using an approximate method.¹³

In order to understand the mechanism of penetration of 8HQ molecules into the crystal lattice of THB, gravimetric studies were made. The kinetic data obeyed eqn. (6); where W

$$W = k_2 t \quad (6)$$

is the increase in mass of THB at any time t and k_2 is the rate of reaction. A plot of W against t gave straight lines (Fig. 8) indicating the validity of eqn. (6). An Arrhenius plot gave an apparent activation energy of 74.5 kJ mol^{-1} . The kinetic parameters are given in Table 3. The energy of activation value is much higher than the value obtained for lateral diffusion. This shows that the diffusion of 8HQ molecule is taking place into the crystal lattice of THB. From the nature of the crystal packing, it also appears that 8HQ molecules have diffused into the crystal lattice of THB along the c -axes occupying the cavity present between THB molecules in the

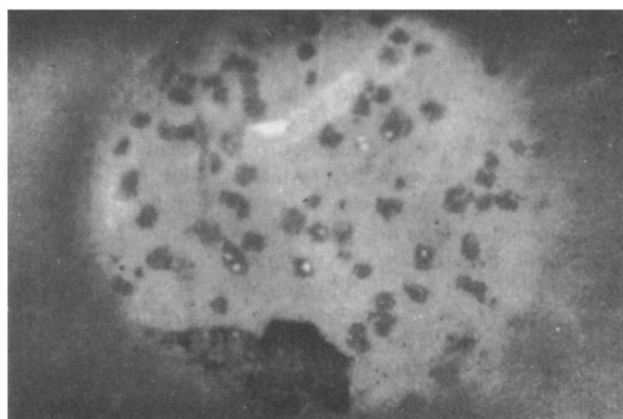


Fig. 10 Photographs for the initiation of reaction at the surface of THB during the gravimetric experiment

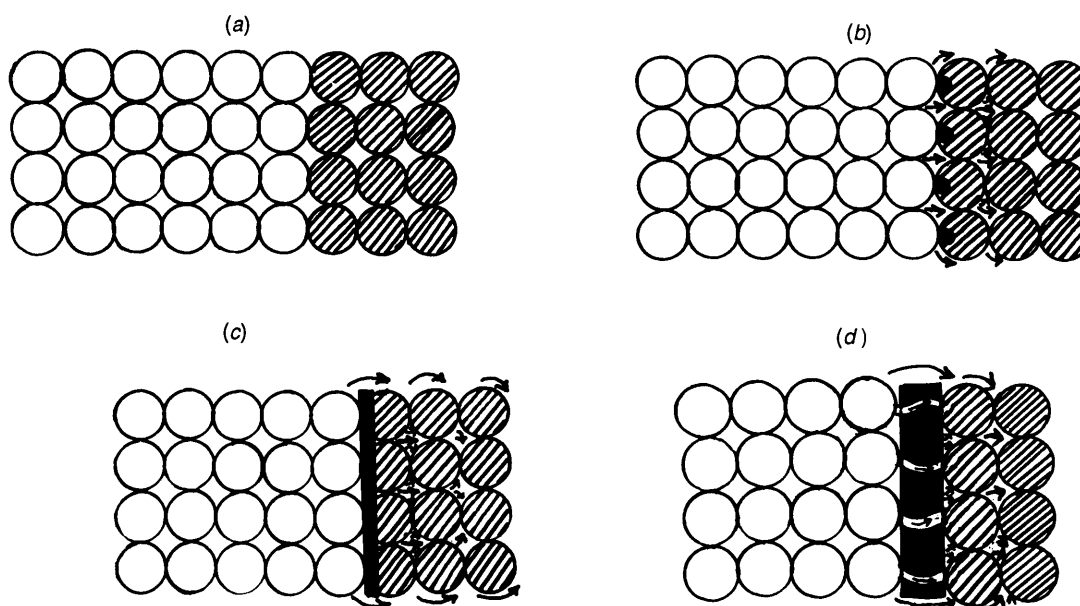


Fig. 11 Stages of solid state reaction between 8HQ (○) and THB (●) (two molecules of 8HQ react with one of THB): (a) reactants in contact; (b) start of reaction at surface of THB; (c) layer of product formed at surface of THB and diffusion of 8HQ; (d) increase in thickness of product layer, formation of cracks and channels in this layer, lateral diffusion of 8HQ and inner penetration of 8HQ into the grains of THB

unit cell. Although the crystal structure of THB is reported in the literature,¹⁴ the atomic coordinates from that study are not available for comparison with our work. Further, since the increase in mass is linear with time, it appears that there is no hindrance to the diffusion of 8HQ molecules. This is possible only when the reaction product formed is incoherent and porous. It is possible that during reaction, the lattice of THB slowly breaks, giving fresh surface for further reaction. Expansion or contraction of the unit cell of THB' (8HQ)₂ then occurs and as a result of this, cracks and channels are created in the reaction product through which the diffusing molecules may pass to come into contact with a fresh surface of THB.

Kinetics of reactions were also studied by measuring the length of a single crystal forming as a function of time. The kinetic data obeyed the Avrami-Erofeev eqn. (7);¹⁵ where

$$-\ln(1 - \alpha)^n = kt \quad (7)$$

α is the fraction reacted at any time t . The value of α cannot be determined directly but can be related to the length of a single crystal by $\alpha = L_t/L_\infty$, where L_t and L_∞ are the lengths of the single crystal at time t and when growth has ceased, respectively. When $-\ln(1 - \alpha)$ is plotted against t , a straight line is obtained (Fig. 9). This simply shows that the growth of a single crystal in the solid state reaction is a nucleation controlled process.

In order to see how the reaction between single crystals of THB and 8HQ starts, single crystals of each were placed in contact for 10 min then the surfaces of the individual crystals were examined under a microscope. It was found that reaction started only at certain points, probably defect sites, on the surface of the THB crystal. Some etching also occurred on the surface of the 8HQ crystals. Thus, one can say that during the solid state reaction, a small nucleus of product is first formed at the surface of the THB crystal where some type of defect is present. When the reactions proceed further, these nuclei grow in size and the reaction at a later stage becomes diffusion controlled. Attempts were made to obtain photographs at different stages of reaction but good quality examples could not be obtained.

During the kinetic studies by the gravimetric method, a photograph of the surface of THB after reaction for 24 h was taken (Fig. 10). The photograph showed that the reaction did not occur uniformly all over the surface but started only at

certain points where some type of strain or defect was present in the crystal lattice. At these defects, less energy would be required to initiate the reaction.

The overall process of diffusion during the solid state reaction is represented in Fig. 11.

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