JOURNAL OF SOLID STATE CHEMISTRY **71**, 530–539 (1987)

Solid State Reaction between α-Naphthol and *p*-Benzoquinone

N. B. SINGH AND N. N. SINGH

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

AND R. K. LAIDLAW[1]

Department of Chemistry, University of Mississippi,
University, Mississippi 38677

Received April 2, 1984; in revised form February 20, 1987

The solid state reaction between α-naphthol and *p*-benzoquinone yields a red crystalline 1 : 1 adduct; in very concentrated solutions the red color can be seen, but it may be due either to Mulliken charge transfer or hydrogen bonding interactions. Kinetic studies of the solid state reaction by a capillary technique indicate that *p*-benzoquinone is the diffusing species, and that either surface migration or vaporphase diffusion plays an important role in the rate of complex formation. Microscopic examination of a single crystal of α-naphthol in the presence of *p*-benzoquinone vapor suggests that the reaction occurs only at defect centers on the α-naphthol surface. Since the reaction in the solid state goes to completion, it is suggested that cracks and crevices are formed, through which *p*-benzoquinone can diffuse easily into the lattice of the complex. © 1987 Academic Press, Inc.

Introduction

The reaction between quinones (as electron acceptors) and other organic molecules (as donors) was first described by Woehler in 1844 (*1*) and has been studied extensively (*2–5*). Crystal structures have been determined for quinhydrone (QH), the greenish-black 1 : 1 complex between hydroquinone (HQ) and *p*-benzoquinone (BQ), HQ_1BQ_1, in a monoclinic polymorph (*6*) and a very similar triclinic polymorph (*7*), and for phenoquinone, the 2 : 1 complex HQ_2BQ_1 (*8*). The solid state reaction between HQ and BQ has been shown to be diffusion-controlled and to occur through cracks and crevices (*9*). The crystalline optical spectrum of QH has also been measured (*10–12*). The crystal structures have been obtained for the following 1 : 1 complexes: *o*-phenyl-*p*-hydroquinone with *o*-phenyl-*p*-benzoquinone (*13*), *o*-(*p*-chlorophenyl)-*p*-hydroquinone with *o*-(*p*-chlorophenyl)-*p*-benzoquinone (*13*), HQ with naphthoquinone (NQ) (*14*), and of the 2 : 1 complexes between *p*-chlorophenol and *p*-bromophenol with BQ (*15*).

In these complexes in the solid state two effects are presumed to be operative: (1)

---

[1] On leave at Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487-9671. Permanent address: Science Department, Laramie County Community College, Cheyenne WY 82007-3299.

0022-4596/87 $3.00

the in-plane O–H . . . O hydrogen bonding between coplanar or nearly coplanar molecules, and (2) the out-of-plane π–π Mulliken charge-transfer (CT) interaction between the donor molecule (HQ or its analog) and the acceptor molecule (BQ or its analog). In CT complexes the donor is sandwiched above the acceptor within a van der Waals distance or less (this donor–acceptor distance is 3.16 Å in QH); there is either eclipsed or slipped overlap between the aromatic rings (*16, 17*). The CT complexes show almost unchanged visible and ultraviolet absorption spectra of the neutral donor and neutral acceptor molecules, plus a new, broad, and intense band, with no vibronic structure, which in the solid state is polarized with the electric vector pointing between the donor and the acceptor molecules (*11*): this is the Mulliken charge-transfer band (*18*), which occurs at 571 nm for QH (*19*). In solution the CT band is observed, blue-shifted, at 416 nm for QH in acetonitrile (*19*), and it is presumed to receive "no contribution from hydrogen bonding (*19*)."

In the solid state the reaction between hydroquinones and benzoquinones seems to be controlled by the diffusion of vapors of the more volatile component across the surface of the crystal of the other component, followed by penetration into cracks and crevices (*9, 12, 20*): this is consistent with similar studies by Rastogi and coworkers (*21–23*) for the reactions of picric acid with naphthols (*21*), aromatic hydrocarbons (*22*), and 2-naphthylamine (*23*). Whereas previous studies concentrated on QH-type structures, where there are two hydroxyl groups on the donor molecule, and two carbonyl groups on the acceptor (*9, 12, 20*), it is of some interest to study the reaction between a donor with a single hydroxyl group and an acceptor with two carbonyl groups, and to ask anew the following questions for the solid state reaction (*24–27*): (1) how is the reaction propagated in the solid state, (2) how does it go to completion, (3) does the diffusion of the more volatile component occur (3a) through surface migration, (3b) across grain boundaries, (3c) through other types of defects, or (3d) by vapor phase diffusion?

In the present paper we report on the solid state reaction between α-naphthol (AN) and BQ. In 1909 Meyer isolated from benzene solution two complexes formed between AN and BQ, the dark-red 1 : 1 complex AN_1BQ_1 (decomposition temperature 100°C), and the dark brown 2 : 1 complex AN_2BQ_1 (decomposition temperature 120°C) (*28*). Tronov and Sokolovich reacted vapors of BQ in CO_2-free air with solid AN to obtain the 2 : 1 complex AN_2BQ_1 with melting temperature 120°C (*29*). The infrared spectrum of the 1 : 1 complex was studied by Lutskii *et al.* (*30*), but otherwise the complex has not been studied.

Experimental Methods and Results

Materials purification. AN (Merck) was purified by several recrystallizations from water, giving colorless needles, melting temperature 95°C (lit. 94°C). It was also purified by sublimation from Baker and Adamson reagent-grade AN by repeated sublimation, melting temperature 93.5–94.5°C. BQ was synthesized by oxidizing hydroquinone with sodium chlorate in 2 mass% sulfuric acid (*31*): the product was crystallized from petroleum ether (80–100°C fraction), and purified several times by sublimation, yellow needles, melting temperature 116°C (lit. 110–117°C). BQ was also purified by repeated sublimation from Eastman Organic Chemicals practical grade BQ, melting temperature 109–111°C.

Preparation of the reaction product. The complex was obtained by both solid state reaction and from solution. In the solid state reaction 0.2 g of AN was allowed to react with BQ vapor at 60°C until constant mass was obtained after 240 h: mass in-

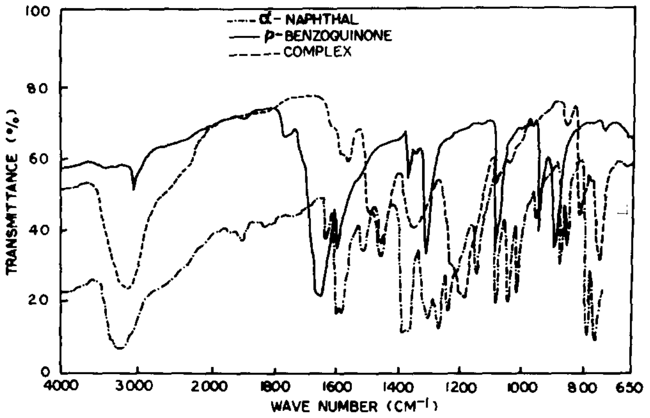

FIG. 1. Infrared transmittance spectra of KBr pellets of AN, BQ, and AN$_1$BQ$_1$ complex.

crease 0.1535 g: this indicates a 1 : 1 stoichiometry AN$_1$BQ$_1$. In a separate experiment, equimolar amounts of AN and BQ were mixed in an agate mortar and pestle; the resulting solid was recrystallized as long needles from acetone, melting temperature 80°C (in disagreement with (*28*)). As discussed below, the powder X-ray diffraction pattern of the complexes obtained by these two methods were identical. The elemental analysis was performed at the Chemistry Department, Banaras Hindu University, Varanasi: for $C_{16}H_{12}O_3$ = AN$_1$BQ$_1$. Calc: C, 76.2%; H, 4.79%. Found: C, 75.9%; H, 4.90%.

The complex is dark red in color, but for very small crystals, upon 60 min standing in air its surface turns brown; on prolonged standing the needles look whitish, presumably because the BQ diffuses out of the lattice.

In spite of our best efforts we could not isolate the 2 : 1 complex AN$_2$BQ$_1$ reported by Meyer (*28*) and by Tronov and Sokolovich (*29*).

Spectroscopic Identification. The infrared spectra were measured on a Perkin-Elmer 157 spectrophotometer at CDRI, Lucknow. The solid AN, BQ, and AN$_1$BQ$_1$ were measured in KBr pellets; the spectra are given in Fig. 1. The solution spectrum was measured in CCl_4 in a cell with LiF windows: the spectrum is displayed in Fig. 2. Whereas one expects an O–H stretching band around 3610 cm^{-1} for a compound exhibiting no hydrogen bonding (e.g., phenol, or benzyl alcohol in CCl_4) (*30*), the observed band for AN in CCl_4 solution is at 3615 cm^{-1}, but is shifted to 3250 cm^{-1} (KBr pellet), which indicates some hydrogen bonding in the solid AN; in the complex, in CCl_4 solution, the 3615 cm^{-1} band is reduced in intensity, and a broad absorption band in the region 3400–3500 cm^{-1} appears; in KBr pellets, the band is shifted to 3150 cm^{-1}: this suggests that the complex is mostly dissociated in carbon tetrachloride, but has pronounced hydrogen bonding in the solid state. The C=O stretching frequency of BQ (KBr pellet) (1650 cm^{-1}) is

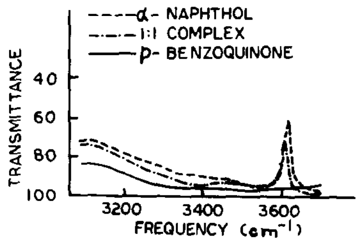

FIG. 2. Infrared transmittance spectra of 0.03 *M* CCl_4 solutions of AN, BQ, and the AN$_1$BQ$_1$ complex.

shifted to 1610 cm^{-1} in the complex, again indicating hydrogen bonding in the solid complex. These data agree with the findings of Lutskii *et al.*, who resolve a doublet C=O band absorption for BQ (1660 and 1670 cm^{-1} in mineral oil suspension and 1656 and 1670 cm^{-1} in 0.015 *M* CCl_4 solution) and find the absorption shifted to 1637 cm^{-1} for the complex in mineral oil suspension (*30*). However, Lutskii *et al.* failed to observe the O–H band in the complex (*30*).

The nuclear magnetic resonance spectra were measured in $CDCl_3$ solution using the Perkin–Elmer R-32 spectrometer at CDRI, Lucknow. The spectra are shown in Fig. 3. The phenolic proton at $\delta = 4.7$ ppm in AN is shifted to 6.6 ppm in the 1 : 1 complex; this downfield shift may be due to H-bonding (*32*).

The ultraviolet and visible spectra were first measured on a Perkin–Elmer 202 double-beam spectrophotometer at CDRI, Lucknow, and later on a Perkin–Elmer Lambda-4B double-beam spectrophotometer (190–900 nm) and on a Hewlett–Packard 8451A single-beam diode array spectrometer (350–600 nm), both at the University of Alabama. The spectra are given in Figs. 4 and 5.

In acetone solution the donor (AN) has an absorption maximum at 330 nm ($\log_{10}\varepsilon$ 1.94); the acceptor (BQ) has three absorption maxima in *n*-hexane solution: a very intense band (BQ1) at 242 nm ($\log_{10}\varepsilon$ 4.39), a medium peak (BQ2) at 281 nm (1.60) and a partially resolved multiplet (BQ3) at 434 (1.30), 457 (1.29), and 479 nm (1.08) (*33*); the BQ3 multiplet is assigned to a forbidden $^1A_g \rightarrow (^3B_{1g}, {}^3A_u)$ transition (*34, 35*). We have observed the BQ3 multiplet in *n*-heptane, with partially resolved peaks at 412, 434, 457, and 478 nm (Fig. 4).

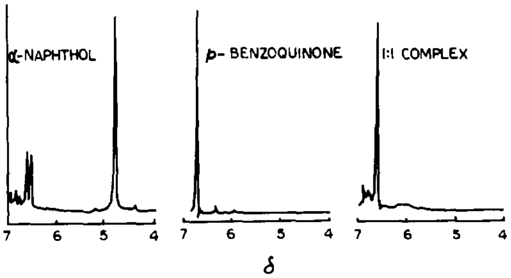

FIG. 3. Nuclear magnetic resonance spectra of AN in $CDCl_3$, BQ in $CDCl_3$, and of the 1 : 1 complex in acetone.

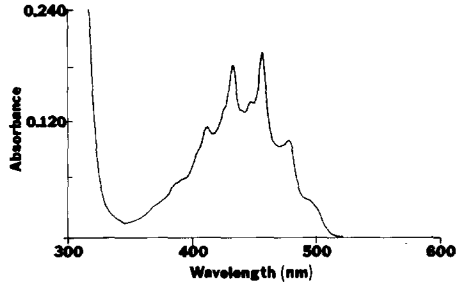

FIG. 4. Visible absorbance spectrum of BQ in heptane (8.9 × 10^{-3} *M*).

The difficulty with observing the spectrum of the red complex, is that the complex stability in solution is very limited (it must readily dissociate into the separately solvated donor and acceptor). In methanol or cyclohexane only a yellow solution is observed. The red complex was seen in 0.05 *M* HCl solution, in heptane, acetone, and in acetonitrile, but only in extremely concentrated solutions. In heptane the red complex forms a reddish insoluble "oil,"

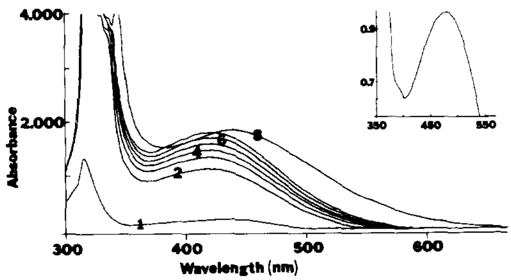

FIG. 5. Visible absorbance spectra in acetone of BQ (0.10 mole/liter) with varying concentrations (mole/liter) of AN: (1) 0.0, (2) 1.68, (3) 2.04, (4) 2.32, (5) 2.57, (6) 2.89, (7) 3.07, (8) 4.67; *insert:* spectrum of acetone solution of BQ and an extremely high concentration of AN.

which can be redissolved by adding acetone. In acetone solution the complex shows the unchanged absorptions of AN and BQ, except that the vibrationally resolved BQ3 multiplet is replaced by a much broader, unresolved peak, under which one can infer the BQ3 peak at 430 nm plus a broad peak which at lower concentrations (BQ: 0.1 M, AN: 0.02–0.38 M) also occurs at 430 nm, but at extremely high concentrations (BQ: 0.5 M, AN: above 4 M) shifts to 478 nm (Fig. 5). A Benesi–Hildebrand (*36*) plot of the data of Fig. 5 (except for curves 1 and 8) yields an equilibrium constant $K_{eq} = 0.052$, and an extinction coefficient for the 1 : 1 complex $\log_{10}\varepsilon = 3.10$, assuming the reaction

$$\mathrm{AN(acetone) + BQ(acetone) = AN_1BQ_1(acetone).} \quad (1)$$

It should be realized, however, that in cells of 1-mm path length, the absorbance maxima are still at 430 nm (the same place as BQ_3), and that an isosbestic point could not be observed because the solutions were too dilute (!).

Three explanations are possible for the red color (RC) in solution: (1) RC could be a Mulliken π–π charge-transfer complex, with $h\nu_{CT}$ somewhere in the neighborhood of 480 nm, and with the low stability of the complex indicated by K_{eq} above; (2) RC could be the forbidden intramolecular BQ3 band enhanced by some intermolecular association (hydrogen bonding); (3) RC could be due to a reaction intermediate: upon heating the acetone solution above 50°C, or after storing the solution in air (but sealed) for 12–14 h, both RC and BQ3 disappear, yielding a light yellow solution: obviously a chemical reaction has occurred, which could be the formation of an adduct such as 2-(1-naphthoxy)-1,4,-benzoquinone; similar reactions have been studied for BQ and phenol (*37, 38*).

X-ray diffraction, density, and solution conductivity. Powder X-ray diffraction data for the complex grown both from solution and from solid state reaction were obtained on a General Electric XDR-5 2-circle diffractograph at Indian Institute of Technology, Kanpur. Eighteen lines were measured, and are listed in Table I. The lines were indexed by the Hesse–Lipson method, and were determined to have orthorhombic symmetry, with a primitive unit cell. The calculated unit cell constants for the complex are compared with the unit cells of the crystals of the components (*39, 40*) in Table II.

The density of the complex was measured in a pycnometer at 30°C, using water as a displacing liquid.

The conductivity of 1 *M* nitrobenzene solutions of the components and the complex were measured at 30°C with a conductivity bridge. The results are given in Table III.

Kinetics of the solid state reaction in a

TABLE I

COMPARISON OF OBSERVED AND CALCULATED INTERPLANAR DISTANCES FOR THE 1 : 1 AN_1BQ_1 COMPLEX, FROM POWDER X-RAY DIFFRACTION DATA

h k l	d_{obs} (Å)	d_{calc} (Å)	*h k l*	d_{obs} (Å)	d_{calc} (Å)	*h k l*	d_{obs} (Å)	d_{calc} (Å)
0 0 1	13.392	13.430	0 0 4	4.374	4.358	0 5 0	2.429	2.438
1 0 1	9.935	9.958	2 2 2	3.850	3.856	1 5 1	2.368	2.368
0 1 1	9.118	9.026	4 1 0	3.547	3.549	7 0 0	2.118	2.120
1 1 1	7.694	7.712	4 1 1	3.427	3.432	7 1 0	2.103	2.089
0 2 1	5.539	5.550	1 1 4	3.220	3.163	9 0 0	1.637	1.649
3 1 0	4.575	4.584	4 2 1	3.079	3.084	5 5 5	1.556	1.552

TABLE II

LATTICE PARAMETERS FOR THE COMPONENTS AND THE COMPLEX

	AN (39)	BQ (40)	AN_1BQ_1 (this study)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
a (Å)	13.00	7.005	14.84
b (Å)	4.80	6.795	12.19
c (Å)	13.40	5.767	13.43
β	117.16	101.47	—
Z (molecules/cell)	4	2	8
Volume/molecule (Å^3)	185.98	134.51	303.69
Observed density (g/cm^3)	1.224	1.318	1.41
Calculated (X-ray) density	1.287	1.335	1.38

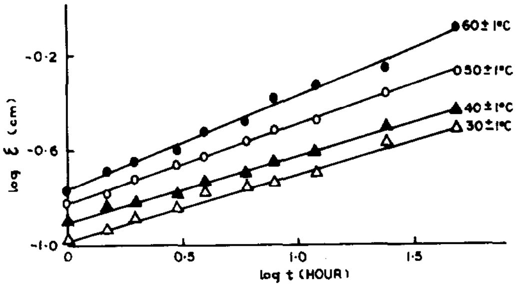

FIG. 6. Kinetic data for the reaction between AN and BQ in the solid state as a function of temperature (capillary experiment, no air gap).

capillary (with and without air gaps between reactants). For the study of the solid state reaction a method similar to that described by Rastogi *et al.* (*22*) was used. Half of a glass capillary was filled with 40 mg powdered AN (particle size 100–140 mesh), and the tube was tapped for 5 min in order to achieve a reproducible packing density. The surface of AN was made smooth with a glass rod. The remaining half of the capillary tube was filled with powdered p-benzoquinone (particle size 100–140 mesh); the capillary was sealed, and was placed horizontally into a constant-temperature incubator. The kinetics of the reaction were followed by measuring the thickness of the colored product layer formed at the junction of the two components at different time intervals, and measurements were performed at several temperatures. The reaction occurred only on the AN side of the capillary. The results were analyzed by

$$\varepsilon = k_1 t^n \qquad (2)$$

where ε is the thickness of the product layer at time t, and n is a constant associated with the diffusion coefficient. The validity of Eq. (2) is verified by plotting log ε vs log t (Fig. 6).

TABLE III

ELECTRICAL CONDUCTIVITIES OF THE COMPONENTS AND THE COMPLEX IN 1 M NITROBENZENE SOLUTIONS AT 30°C

Substance	Conductivity (Siemens)
α-Naphthol	0.059×10^{-5}
p-Benzoquinone	0.070×10^{-5}
1 : 1 Complex	0.380×10^{-5}

The parameters for Eq. (1) were refined by a least-squares procedure. The results are given in Table IV for the case of no air gap. The validity of an Arrhenius-type law for k_1 is shown by plotting log k_1 $1/T$ (Fig. 7). From the slope of the straight line, the energy of activation for interdiffusion is calculated to be E_d = 13.1 kJ/mole.

Kinetic studies of the reaction in the capillary tube were also performed at a constant temperature when the two reactants were separated by air gaps of different length. When the reactants in the capillary tube are separated by air gaps of different lengths, Eq. (2) is obeyed, but the rate constant (now called k_1') depends on the air

TABLE IV

LEAST-SQUARES PARAMETERS OF EQ. (2) FOR SOLID STATE REACTION BETWEEN 100–140 MESH POWDER LAYERS OF AN AND BQ IN A GLASS CAPILLARY WITH NO AIR GAP BETWEEN LAYERS

Run	Temperature (°C)	k_1 (cm/h)	n
1	30	0.106	0.27
2	40	0.125	0.27
3	50	0.150	0.33
4	60	0.175	0.38

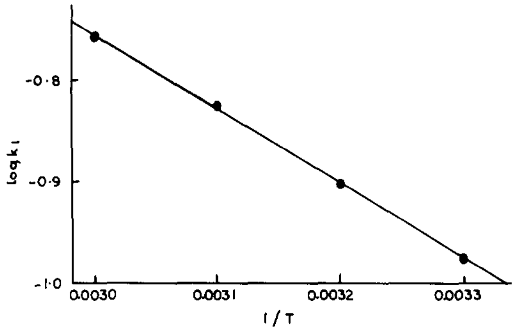

FIG. 7. Arrhenius plot of the effect of temperature on the reaction rate (capillary experiment, no air gap).

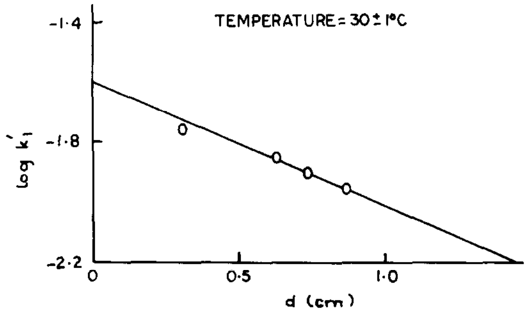

FIG. 8. Dependence of the rate constant k_1' on the size of the air gap, d at 30 ± 1°C (capillary experiment).

gap length d as follows:

$$k_1' = Be^{-pd} \tag{3}$$

where B and p are constants. The least-squares fits to Eq. (3) are shown in Table V, and the data are plotted in Fig. 8.

Kinetics of interdiffusion by the inverted U-tube technique (gravimetric technique). The reaction was also studied by placing known amounts of AN (0.2 g) and of BQ into two arms of an inverted U-tube connected by standard-taper joints, and kept in a incubator at a constant temperature, as described before (*22*). Since the reaction occurred always in the arm (tube) containing AN, the kinetics were followed by weighing the AN arm periodically. The data are given in Table VI and are displayed in Fig. 9: the data follow the law

$$W = k_2t \tag{4}$$

where W is the increase in weight of AN at the time t, and k_2 is a rate constant for interdiffusion, i.e., diffusion of BQ vapor into the AN lattice. An Arrhenius plot of log k_2 reciprocal temperature (Fig. 10) is linear, and yields an activation energy E_i = 56.5 kJ/mol.

Reaction with single crystal of AN. A single crystal of AN was obtained by slow crystallization of AN from hot water. In spite of our best efforts, we could not obtain a single crystal which was free from cracks and crevices; however, a single crystal with a minimum number of cracks and defects was chosen and examined under a microscope (magnification 15 × 10). The crystal was then exposed to the vapors of BQ at 60°C for 5 min. It was observed that the reaction started only at those points where cracks and crevices were

TABLE V

LEAST-SQUARES PARAMETERS OF EQ. (3) FOR SOLID STATE REACTION BETWEEN 100–140 MESH POWDER LAYERS OF AN AND BQ WITH AN AIR GAP OF THICKNESS d BETWEEN THEM, AT 30 ± 1°C

Run	d (cm)	$k_1' \times 10^{-2}$ (cm/h)	n'
1	0.309	1.74	0.53
2	0.627	1.39	0.53
3	0.740	1.22	0.50
4	0.968	1.09	0.49

TABLE VI

PARAMETERS FOR THE INTERDIFFUSION OF BQ INTO BULK AN CRYSTAL, AS MEASURED BY THE INVERTED U-TUBE TECHNIQUE, FOLLOWING EQ. (4)

Run	Temperature (°C)	$k_2 \times 10^{-4}$ (g/hr)
1	30	1.54
2	40	4.09
3	50	5.47
4	60	11.43

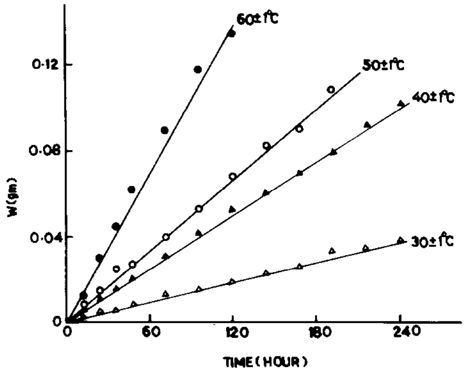

FIG. 9. Kinetic data for the reaction between AN and BQ (inverted U-tube experiment) at various temperatures.

present at the surface of the crystal. On further exposure the reaction product increased in size only at those points.

Discussion

It has been shown here that a 1 : 1 red solid state complex is formed when AN and BQ are allowed to react either in solution or in the vapor phase, or when BQ vapor meets an AN crystal. In solution the NMR and IR evidence suggests the presence of hydrogen bonding. The red color in solution (peak at 480 nm) can be interpreted either as a very weak Muliken CT complex (π–π stacking) or as an intermolecular hydrogen-bonded complex (which enhances a forbidden BQ transition) or as a reaction intermediate prior to covalent bonding of AN to BQ.

The electrical conductivities of donor and acceptor in nitrobenzene are very close to that of the pure solvent; the conductivity of the complex in the same solvent is much higher; one is tempted to ascribe this to a partial ionic character of the complex, but, given the weak charge transfer forces expected, the explanation does not seem convincing.

The molecular volume of the complex in the solid state (Table II) is 5.53% smaller than the sum of the volumes of AN and BQ separately: this volume contraction is quite typical for a weak charge-transfer complex (*41, 42*). Although we can only speculate about the packing geometry of the AN_1BQ_1 crystal, it is tempting to guess that it should be similar to those of the 1 : 1 complexes of p-chlorophenol with BQ (*15*) and p-bromophenol with BQ (*15*), namely, with pancake stacks DADADA of phenol over quinone (with some staggering of the intermolecular overlap), and with hydrogen-bonding network in the plane perpendicular to the stacking direction. Since the crystals seem to be susceptible to efflorescence of the more volatile BQ component, a full structure determination may not be easy.

The kinetics of reaction of BQ with AN exhibit two activation energies, E_d = 13.1 kJ/mol for the reaction between solid phases in contact within the capillary tube, and E_i = 56.5 kJ/mol for the interdiffusion of BQ into solid AN. The enthalpies of sublimation of AN and BQ are 91.5 and 62.8 kJ/mol, respectively (*43*). It is clear that BQ is the more volatile component (its ΔH_{subl} is two-thirds that of AN), which explains why the complex grows on the solid and less volatile AN surface. It is also clear that the activation energy of interdiffusion is much larger than that of diffusion,

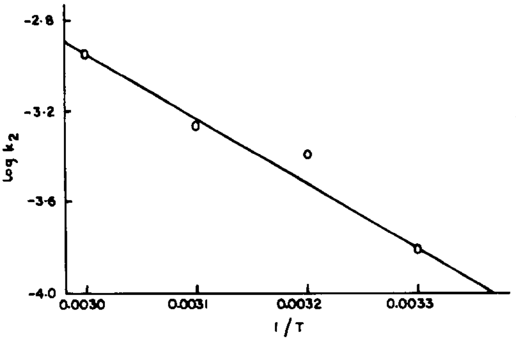

FIG. 10. Arrhenius plot of the effect of temperature on the rate of solid-vapor reaction (inverted U-tube experiment).

since migration into the solid AN lattice is implied by the interdiffusion experiment, with much greater resistance to reaction.

What is less clear is why the E_d value should be so much smaller than the enthalpy of sublimation of BQ. It may be that a surface diffusion process dominates, with a much smaller activation contribution than if the growth of the complex were limited by the vapor-phase diffusion of BQ toward AN. In fact, the analysis of Eq. (4) shows that when $d = 0$, the extrapolated value of k_1' is 2.51×10^{-2} cm/h, and not zero: this suggests that the diffusion between the separated layers occurs not only by vapor transport, but also by a surface migration process, as has been shown elsewhere (*9*).

The growth of the complex on cracks and crevices of the AN crystal can be explained by the initial requirements for free volume in which the complex can grow. Since the molecular volume per molecule of the complex crystal is 5.53% smaller than the volumes per molecule of the component crystals, strain energy will build up during crystal growth, so that formation of further cracks and crevices will be favored during the growth of the complex, as observed.

In conclusion, the following picture emerges for the kinetics of growth of the AN_1BQ_1 crystal: vapor-phase diffusion of the more volatile component (BQ) and surface migration both can start crystal growth; since the growth ultimately goes to completion, one can surmise that at first a small nucleus is formed at the surface of AN, wherever surface defects (dislocations, grain boundaries, cracks, and crevices) are present. Once the nuclei of the complex reach a critical size, further growth occurs, and the reaction ultimately becomes diffusion-controlled. Given the strain energy involved in the growth of the complex crystal, more cracks and crevices are produced, thus facilitating further growth, and allowing the reaction to go to completion.

Acknowledgments

The authors are grateful to Prof. R. P. Rastogi, Head, Chemistry Department, Gorakhpur University, for providing the necessary facilities, and to the authorities at CDRI (Lucknow) and IIT (Kanpur) for their assistance, and to Prof. R. M. Metzger (University of Alabama) for helpful suggestions.

References

1. F. Woehler, *Ann.* **51,** 145 (1844).
2. G. Briegleb, "Elektronen Donator-Acceptor-Komplexe," Springer-Verlag, Berlin (1961).
3. L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco (1964).
4. R. S. Mulliken and W. B. Person, "Molecular Complexes—A Lecture and Reprint Volume," Wiley–Interscience, New York (1969).
5. R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York (1969).
6. H. Matsuda, K. Osaki, and J. Nitta, *Bull. Chem. Soc. Japan* **31,** 611 (1958).
7. T. Sakurai, *Acta Crystallogr.* **19,** 320 (1965).
8. T. T. Harding and S. C. Wallwork, *Acta Crystallogr.* **6,** 791 (1953).
9. N. B. Singh and H. C. Singh, *J. Solid State Chem.* **38,** 211 (1981).
10. K. Nakamoto, *J. Amer. Chem. Soc.* **74,** 1739 (1952).
11. B. G. Anex and L. J. Parkhurst, *J. Amer. Chem. Soc.* **85,** 3301 (1963).
12. A. O. Patil, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.* **106,** 348 (1984).
13. G. R. Desiraju, D. Y. Curtin, and I. C. Paul, *Mol. Cryst. Liq. Cryst.* **52,** 259 (1979).
14. A. Thozet and J. Gaultier, *Acta Crystallogr.* **B33,** 1052 (1977).
15. G. G. Shipley and S. C. Wallwork, *Acta Crystallogr.* **22,** 585 (1967).
16. F. H. Herbstein, *in* "Perspectives in Structural Chemistry," Vol. IV (J. D. Dunitz and J. A. Ibers, Eds.), pp. 151–208, Wiley, New York (1971).
17. Z. G. Soos and D. J. Klein, *in* "Molecular Association," Vol. I (R. Foster, Ed.), pp. 1–109, Academic Press, New York (1975).
18. R. S. Mulliken, *J. Amer. Chem. Soc.* **72,** 600 (1950).
19. K. H. Kalninsh, *J. Chem. Soc. Faraday Trans. 2* **78,** 327 (1982).
20. R. P. Rastogi, *J. Sci. Indian Res.* **29,** 177 (1970).
21. R. P. Rastogi and N. B. Singh, *J. Phys. Chem.* **70,** 3315 (1966).

22. R. P. Rastogi, P. S. Bassi, and S. L. Chaddha, *J. Phys. Chem.* **67,** 2569 (1963).
23. R. P. Rastogi and N. B. Singh, *J. Phys. Chem.* **72,** 4446 (1968).
24. M. D. Cohen and B. S. Green, *Chem. Brit.* 490 (1973).
25. S. R. Byrn, *J. Pharmacol. Sci.* **65,** 1 (1976).
26. A. Gavezzotti and M. Simonetta, *Chem. Rev.* **82,** 1 (1982).
27. S. Byrn, "Solid State Chemistry of Drugs," Academic Press, New York (1982).
28. K. H. Meyer, *Ber.* **42,** 1149 (1909).
29. B. V. Tronov and V. B. Sokolovich, *Izvest. Tomsk. Politekh. Inst.* **83,** 91 (1956); *Chem. Abstr.* **53,** 6169h (1959).
30. A. E. Lutskii, S. V. Semenenko, P. A. Chernyavskii, and V. P. Rubtsova, *Russ. J. Gen. Chem.* **38,** 1327 (1968).
31. A. I. Vogel, "A Textbook of Practical Organic Chemistry," 4th ed., p. 788, EDBS and Longman, London (1978).
32. G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," p. 77, Freeman, San Francisco (1960).
33. E. A. Braude, *J. Chem. Soc.* 490 (1945).
34. J. W. Sidman, *J. Amer. Chem. Soc.* **78,** 2363 (1956).
35. R. M. Hochstrasser, L. W. Johnson, and H. P. Trommsdorff, *Chem. Phys. Lett.* **21,** 251 (1973).
36. H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.* **71,** 2703 (1949).
37. H. Musso, U. V. Gizycki, U. I. Zahorszky, and D. Bormann, *Ann.* **676,** 10 (1964).
38. R. Pummerer and G. Huppman, *Ber.* **60,** 1442 (1927).
39. B. Robinson and A. Hargreaves, *Acta Crystallogr.* **17,** 944 (1964).
40. J. Trotter, *Acta Crystallogr.* **13,** 86 (1960).
41. A. I. Kitaigorodsky, "Molecular Crystals and Molecules," Academic Press, New York (1973).
42. F. M. Wiygul, R. M. Metzger, and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.* **107,** 115 (1984).
43. J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York (1970).